

1980

# Aliphatic semidiones

Christopher Erion Osuch  
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**Aliphatic semidiones**

**by**

**Christopher Erion Osuch**

**A Dissertation Submitted to the  
Graduate Faculty in Partial Fulfillment of the  
Requirements for the Degree of  
DOCTOR OF PHILOSOPHY**

**Department: Chemistry  
Major: Organic Chemistry**

**Approved:**

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**In Charge of Major Work**

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**1980**

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## I. INTRODUCTION

### A. Ion Pairs

Ion pairs are extremely important in organic chemistry. Most reactions are run in the liquid state, and of these reactions ones involving ionic mechanisms make up a large class. Many "solvent" effects noted in various reactions can be rationalized as being due to the change of solvation of an ion pair. This change is then reflected as a change in the apparent reactivity of the substrate. As a consequence of this importance, a great deal of effort has gone into understanding the various aspects of ion pairs in solution. A number of reviews exist which will permit the interested reader to gain a general appreciation for this field.<sup>1-6</sup> Areas specifically related to the study of ion pairs via electron spin resonance (esr) have also been reviewed.<sup>4,7</sup>

For the purpose of this discussion, it will suffice to consider ion pairs in a rather qualitative way. This is not meant to imply that mathematical models of ion pairing are nonexistent. One of the earliest models of ion pairing, that of Bjerrum, is treated by Szwarc in Chapter V of reference 6. This model considers a radial distribution function describing the concentration of counter ions around a reference ion. A distance  $r_c$  is determined at which the radial distribution function has a maximum. It is then assumed that ions more distant than  $r_c$  are free while those closer together are paired. The physical meaning of this, in terms of interaction between the ions (other than coulombic interactions) is not clear.

Models more satisfactory to the organic chemist are also discussed in reference 6. The essence of a "satisfactory" model is that it invoke discrete parameters describing the ion pair and the free ions and that it allow calculation of conventional thermodynamic properties.<sup>8</sup> (The thermodynamic properties reported in this work are phenomenological values. No attempt was made to calculate values of thermodynamic functions from a model, although the values obtained by experiment will be rationalized in a qualitative way using this type of model.)

The model which I find most pleasing is that of Brus and Bondybey.<sup>9</sup> They consider two types of ionic pairing. The first is called coulombic and consists of a state where the two oppositely charged particles are held together by electrostatic attraction. There is zero overlap of wavefunctions between the anion and cation. Typically, the spacing of the two ions is greater than about ten Angstroms. The second type of pair they call a chemically bonded ion pair. In this pair, overlap occurs between the cation and the anion wavefunctions. However, there is essentially complete transfer of charge from the cation to the anion, i.e., the charge density integrated over the anion (cation) is -1 (+1). The inter-ion distance characteristic for this type of ion pair is less than ten Angstroms. The so-called contact ion pair falls under the classification of chemically bonded, whereas the solvent separated ion pair might be either a chemically bonded pair, or a coulombic pair.

A pair defined as having overlapping cation and anion wavefunctions is required by the experimental observation of metal hyperfine coupling in the esr spectrum of some radical ions in solution. (Recall that

dipolar effects are averaged to zero in solution by rapid tumbling.) One way to explain the transfer of spin from the radical anion to the cation is by configuration interaction, also known as spin polarization. Direct overlap between an  $s$  orbital of the alkali metal and the orbital of the radical ion which contains the unpaired electron may also cause spin density to appear at the metal, although the sign of this coupling is opposite to that generated by the former mechanism.<sup>10</sup>

It is not certain that an ion pair which exhibits metal hyperfine splitting is a contact ion pair, since the presence of intercalated solvent does not preclude the observation of metal ion splitting.<sup>11</sup> Nor is it the case that the absence of hyperfine interaction implies the lack of ion pairing. The coulombic type of ion pair described above would be expected to show no hyperfine from the metal cation, at least in solution. Rapid exchange of the paired cation will "wash out" counter ion hyperfine, even for a contact ion pair. Finally, hyperfine splitting may be present, yet be unresolved, due to excessive linewidth.

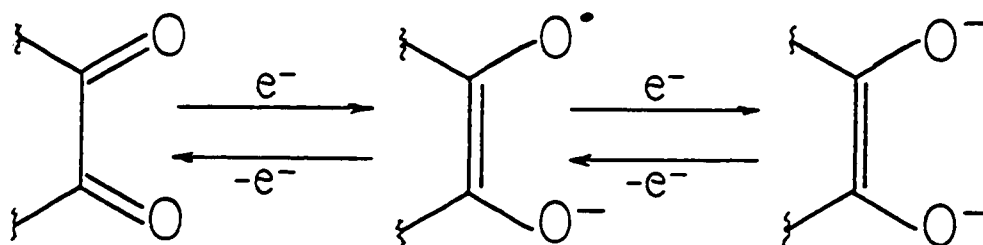
In short, it appears that: a) ion pairs may be either molecular, involving overlap of wave functions, or simply coulombic; b) ion pairs can be visualized as discrete entities, possessing characteristic heats of formation, etc.; and c) hyperfine interaction between the radical center and the metal nucleus is proof of some type of ion pair, but need not necessarily be seen when invoking ion pairing.

#### B. Semidiones

Semidiones have been reviewed.<sup>12-15</sup> Readers interested in semidiones in general are encouraged to investigate these references. The

characteristic of semidiones most important for this work is simply the fact that they are radical anions. For the most part, only the esr parameters are of interest, although in section IV the discussion of conformational effects in large rings will require that some consideration be given to other aspects of the molecules containing the semidione moiety.

Put most simply, a semidione is a one electron oxidation product of an enediol dianion, or a one electron reduction product of a diketone.



The semidione may be either E or Z in configuration depending upon the various circumstances. The fact that spin density is delocalized from the  $\pi$  system into other parts of the molecule results in the observation of splitting by protons, or other nuclei with nonzero magnetic moment, remote from the  $\pi$  system. The splitting constant is symbolized by  $\underline{a}^x$ , where  $x$  represents the atom which caused the observed splitting. In this work the most important splittings are those due to the protons alpha to the semidione group.

Semidiones, as well as all other paramagnetic species, have another characteristic esr parameter known as the  $g$ -value, which is derived from the expression for resonance, equation 1.

$$\underline{h\nu} = \underline{g}\beta H_0 \quad (1)$$

This simple formula, where  $\beta$  is the Bohr magneton,  $H_0$  is the strength of the static field,  $h$  is Plank's constant and  $\nu$  is the frequency of the microwave radiation at resonance, relates the energy of the RF field, ( $h\nu$ ), to the static field strength.<sup>16</sup> The value of  $g$ , which is close to two for the free electron and most organic radicals, varies slightly with changes in the chemical nature of the radical. It is analogous to the chemical shift observed in nuclear magnetic resonance.

These two numbers,  $a^H$  and  $g$ , will be the principal means of probing the ion pairing of semidione radical ions.

### C. General Considerations

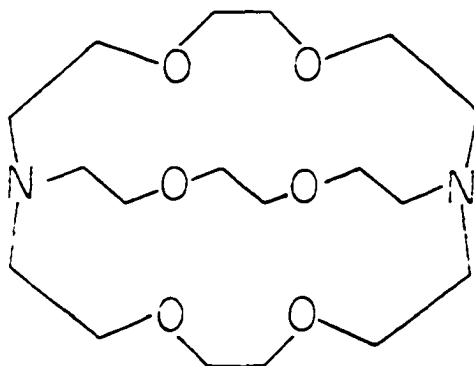
The semidiones were usually generated by treating the appropriate 1,2-bis-trimethylsilyloxy alkene with potassium dimsylate in dimethyl sulfoxide (DMSO). A few low temperature experiments were done which required a solvent other than DMSO (m.p. = 18°C). Either tetrahydrofuran or N,N-dimethylformamide were used under those conditions. Occasionally, a base other than potassium dimsylate, such as an alkoxide, was more suitable for generating the radical anions.

The semidione solutions were observed via esr in the presence of various alkali metal cations. The concentration of the alkali metal iodide salts was varied and the  $g$ -value and  $a^H$  were recorded as a function of salt concentration. The concentration of salt was varied by two different methods, depending on the nature of the experiment. Most often the samples were diluted with solvent between spectra. A few experiments were performed by adding aliquots of concentrated salt



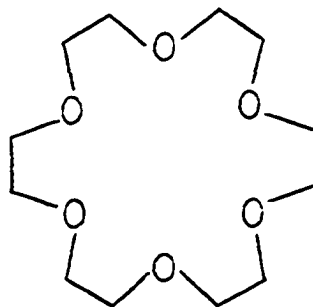
solution (or solid salt) to the radicals under a blanket of argon.

To obtain the esr parameters of the "free" radical ions, a complexing agent, [2.2.2]-cryptand, was used to "remove" the potassium ions from solution. The [2.2.2]-cryptand works by



trapping the potassium inside the "crypt" formed by the six oxygens and two nitrogens. This greatly increases the apparent size of the cation, which prevents the cation from ion pairing with the radical anion.

The cyclic polyether 18-C-6 (pronounced, eighteen crown six) represents a second type of complexing agent which was used.



This also traps potassium ions but, unlike the [2.2.2]-cryptate, the trapped cation is still free to ion pair with an anion.

Data were gathered for various semidiones, with a number of different cations, at various concentrations and temperatures. Depending on the part of the work being discussed, one or another of these independent variables will be most important.

## II. ION PAIRING IN SMALL RINGS

### A. Introduction

On numerous occasions, spectra of semidiones prepared in dimethylsulfoxide (DMSO) have shown asymmetric line broadening, where the high field part of the spectrum is poorly resolved in comparison to the low field part. For example, see Figure 1. This phenomenon did not appear consistently, being sometimes more noticeable than at other times. However, a given formula for sample preparation would yield reproducible spectra. Further, all semidiones did not seem to be affected. The spectra where the high field broadening was most noticeable were those of cyclic molecules which had relatively narrow line widths.

Several explanations for this effect which can be rejected are: a) decay of the radicals; b) instrument error; and c) slow tumbling of the radicals in solution, which results in the incomplete averaging of anisotropies. The first idea is easily rejected by observing that repetitive scans give exactly the same spectrum. The second may be rejected by noting that no obvious malfunction of the instrument could be found and that the same type of spectra are produced on two different instruments. Indeed, spectra run many years ago may show the same effects. The spectrometers would also give normal spectra of other species, such as perylene radical cation, immediately before and after recording a semidione spectra which showed asymmetric line broadening.

Suggestion "c" above is somewhat more difficult to rule out.<sup>17</sup> If  $g$  and  $a^H$  of the semidione are anisotropic, a likely situation, then in

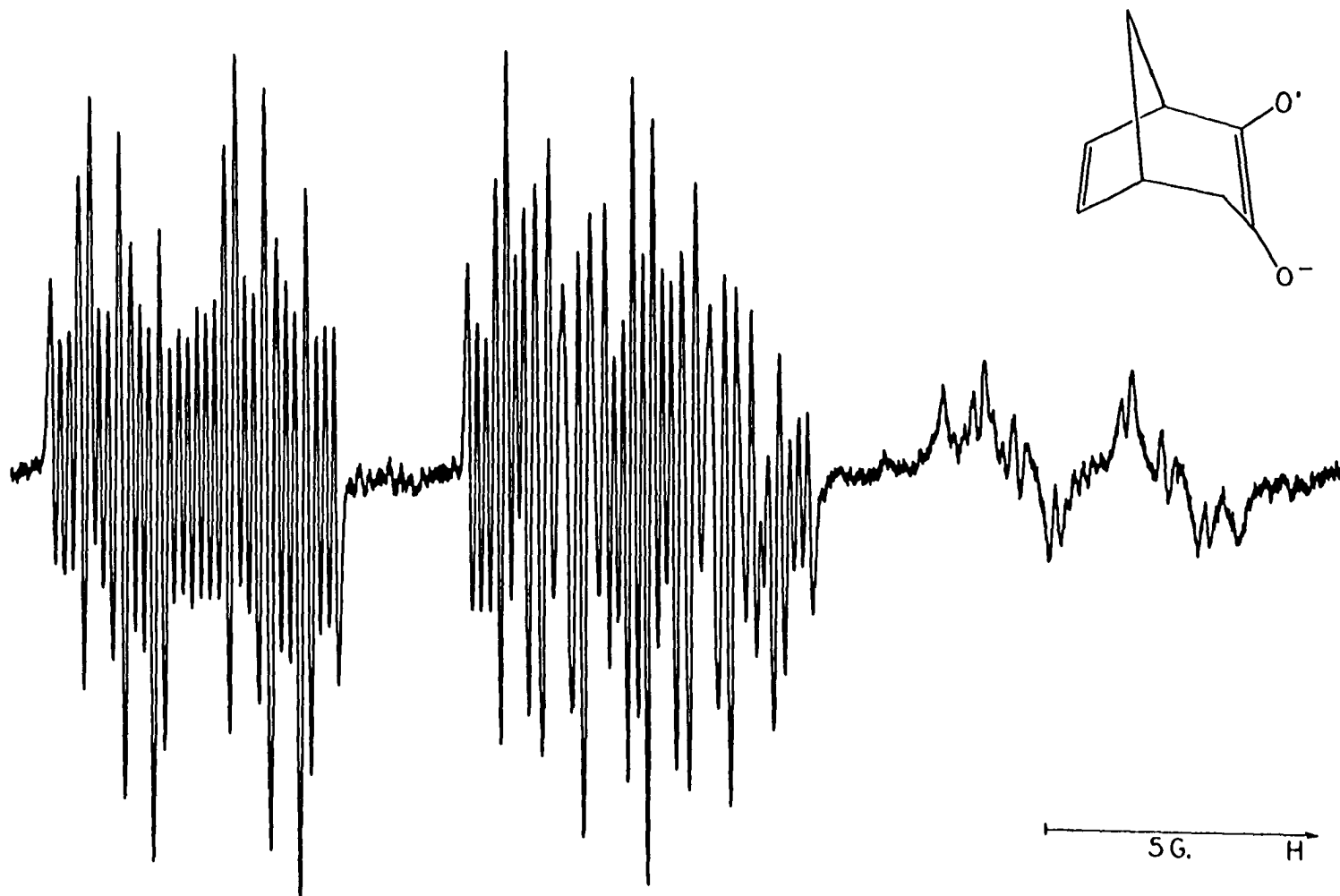


Figure 1. ESR spectrum of bicyclo-[3.2.1]-oct-6-ene-2,3-semidione, showing asymmetric line broadening

solvents where molecular rotation is not fast on the esr time scale asymmetric broadening of the lines will be observed. Either the high or the low field lines might be affected. One way to test this type of hypothesis is to vary the viscosity of the solvent in order to effect a change in the rate of molecular rotation. It is true that semidiones generated in solvents other than DMSO often appear to have normal line shapes. Heating the DMSO solution in the esr cavity also improved the symmetry of the spectrum. Thus, at first it appears that slow rotation of the radicals is responsible for the observed line broadening. It turns out this is not correct. The proof is that an alternate explanation, that of ion pairing, will account for both the line broadening as well as a number of other observations.

This part of the dissertation will establish the existence of ion pairing in cyclic semidiones and will attempt to discern some of the properties of alkali metal-semidione ion pairs.

## B. Results

### 1. Cyclobutane-1,2-semidione

This semidione was observed via esr in the presence of various concentrations of the following cations:  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ , and  $\text{K}^+$ (18-C-6). These were added to the DMSO solution as the iodide salts. The values for  $\underline{a}^{\text{H}}$  and  $\underline{g}$  which were obtained are presented in Figure 2. Note the typical increase in  $\underline{a}^{\text{H}}$  with a concomitant decrease in  $\underline{g}$  as the cation concentration increases. When lithium was used as the counter ion, a relatively small change in the  $\underline{g}$ -value and in  $\underline{a}^{\text{H}}$  was noted. In the

Cyclobutanesemidione

[NaI] (molar)	<u>g</u>	<u>a<sup>H</sup></u> (G)	[CsI] (molar)	<u>g</u>	<u>a<sup>H</sup></u> (G)
0.43	2.004981	14.21	0.64	2.005047	14.03
0.21	2.005008	14.13	0.32	2.005050	14.01
0.11	2.005030	14.06	0.16	2.005058	13.97
0.053	2.005044	14.01	0.081	2.005062	13.95
0.027	2.005061	13.96	0.040	2.005065	13.93
0.013	2.005071	13.93			
[KI] (molar)	<u>g</u>	<u>a<sup>H</sup></u> (G)	[K(18-C-6)I] (molar)	<u>g</u>	<u>a<sup>H</sup></u> (G)
1.05	2.004993	14.17	0.43	2.005071	13.91
0.53	2.005013	14.11	0.22	2.005075	13.90
0.26	2.005034	14.05	0.11	2.005079	13.89
0.23	---	---	0.054	2.005082	13.88
0.13	2.005052	13.99			
0.12	2.005051	13.99	[RbI] (molar)	<u>g</u>	<u>a<sup>H</sup></u> (G)
0.066	2.005068	13.95	1.17	2.005003	14.11
0.058	2.005065	13.95	0.59	2.005010	14.06
0.029	2.005076	13.92	0.29	2.005041	13.98
0.015	2.005083	13.90		2.005032	14.01
0.0073	2.005087	13.89	0.15	2.005053	13.96
				2.005039	13.97
			0.073	2.005064	13.93
				2.005052	13.95
			0.037	2.005075	13.91
				2.005063	13.92
			0.018	2.005079	13.90
			0.009	2.005092	13.89
				<u>g</u>	<u>a<sup>H</sup></u> (G)
			Free Ion: K <sup>+</sup> DMSO <sup>-</sup> /[2.2.2]-cryptand		
				2.005102	13.85

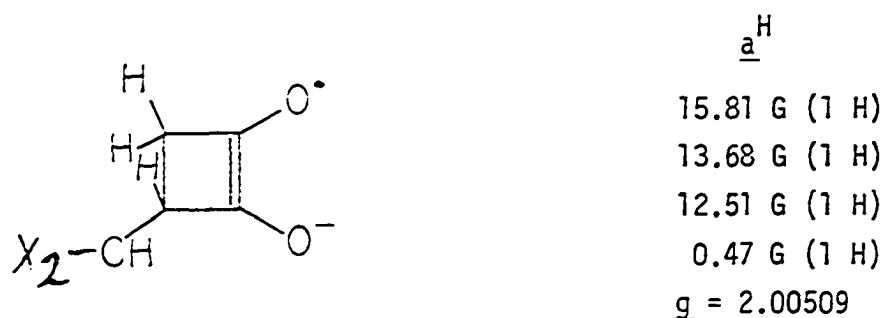
Figure 2. The values for g and a<sup>H</sup> obtained from cyclobutanesemidione in the presence of various counter ions

presence of 0.3 M lithium iodide, the esr parameters changed from the free ion values of  $\underline{a}^H = 13.85$  G,  $\underline{g} = 2.00510$  to  $\underline{a}^H = 13.86$  G,  $\underline{g} = 2.00509$ . In a saturated solution of lithium iodide in DMSO, the semidione has a  $\underline{g}$ -value of 2.00509 and an  $\underline{a}^H$  of 13.92 G.

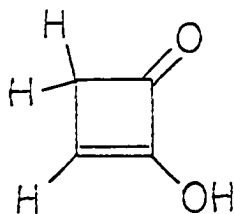
In all cases, except when M was potassium, [2.2.2]-cryptand was added to the solution before the experiment was started, for the purpose of removing potassium ions which were the counter ions of the base used (potassium dimsylate). This is generally true throughout this section.

In general, the spectra observed with this system had narrow line widths, although at high salt concentrations the lines broadened slightly. At certain concentrations asymmetric line broadening could be observed as well.

Occasionally spectra due to a species felt to be



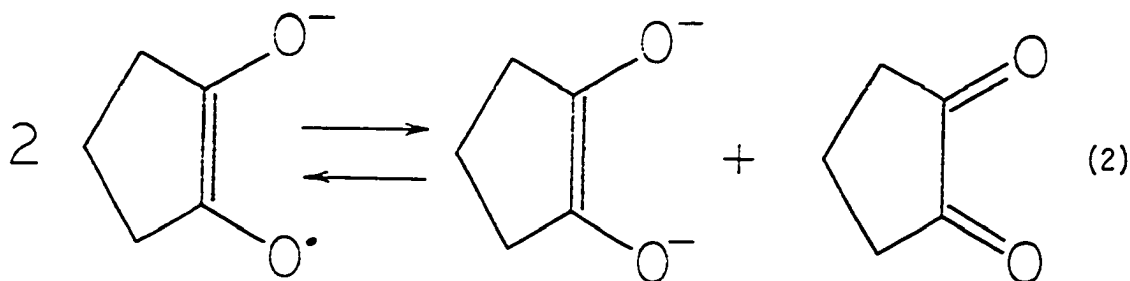
were obtained. The nature of the X group is not known. Presumably, this radical arises from addition of dimsyl anion to molecules of the type



This has been seen with  $\text{K}^+\text{DMSO}^-/\text{DMSO}$  (0.1 M), with cesium tert-butoxide/DMSO, and with  $\text{K}^+\text{DMSO}^-/\text{DMSO}/[2.2.2]\text{-cryptand/LiI}$ .

## 2. Cyclopentane-1,2-semidione

This semidione was also observed by esr in the presence of varying concentrations of  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ , and  $\text{K}^+(18\text{-C-6})$ . The numerical data are presented as Figure 3. The changes in  $\underline{a}^{\text{H}}$  and  $\underline{g}$  observed here are greater than in the case of cyclobutyl, but the trends are in the same direction. When lithium was the counter ion, two superimposed spectra, one of them with lithium hyperfine couplings, could be seen if the concentration of lithium iodide was about 0.05 M (see Figure 4). Addition of excess lithium salt to the previously generated semidione resulted in the complete loss of signal intensity, presumably due to the formation of dianion and diketone by disproportionation of the semidione, as in equation 2 below.



Alternatively, the lithium iodide may simply destroy the radical ions via some other chemical reaction. No attempt was made to regenerate the spectrum after it had been lost.

When sodium was the counter ion, two species could be seen if the conditions were chosen properly. However, in this case further



Figure 3. The values for  $\underline{g}$  and  $\underline{a}^H$  obtained from cyclopentanesemidione in the presence of various counter ions

Cyclopentanesemidione

[LiI] (molar)	<u>g</u>	<u>a<sup>H</sup></u> (G)	[RbI] (molar)	<u>g</u>	<u>a<sup>H</sup></u> (G)
0.024	2.005077	13.05	0.85	2.004851	13.56
0.045	2.005068	13.06	0.42	2.004860	13.48
0.065	2.005071	13.08	0.21	2.004576	13.42
0.074	2.005082	13.11	0.11	2.004892	13.37
0.15	2.004713	14.48	0.052	2.004913	13.32
			0.027	2.004932	13.27
[NaI] (molar)	<u>g</u>	<u>a<sup>H</sup></u> (G)	[CsI] (molar)	<u>g</u>	<u>a<sup>H</sup></u> (G)
0.05	2.004884	13.88	0.71	2.004733	13.43
0.10	2.004884	13.93	0.36	2.004731	13.36
0.21	2.004872	13.99	0.18	2.004742	13.32
0.41	2.004852	14.07	0.12	2.004811	13.26
[KI] (molar)	<u>g</u>	<u>a<sup>H</sup></u> (G)	0.089	2.004776	13.26
1.06	2.004919	13.72	0.058	2.004854	13.21
0.53	2.004933	13.64	0.044	2.004812	13.22
0.26	2.004949	13.56	0.029	2.004891	13.17
0.23	2.004946	13.56	0.022	2.004853	13.18
0.13	2.004958	13.51	0.014	2.004938	13.13
0.11	2.004960	13.50	0.0072	2.004976	13.10
0.085	2.004959	13.47	[K(18-C-6)I]		
0.066	2.004973	13.45	(molar)	<u>g</u>	<u>a<sup>H</sup></u> (G)
0.057	2.004971	13.44	0.40	2.004998	13.33
0.042	2.004971	13.41	0.20	2.005005	13.30
0.033	2.004984	13.40	0.10	2.005015	13.26
0.028	2.004989	13.38	0.05	2.005026	13.22
0.021	2.004988	13.35	0.025	2.005037	13.18
0.014	2.005002	13.31	0.0125	2.005049	13.14
0.011	2.005012	13.28			
0.0071	2.005028	13.22			
				<u>g</u>	<u>a<sup>H</sup></u> (G)
			Free ion: K <sup>+</sup> DMSO <sup>-</sup> /[2.2.2]-cryptand		
				2.005100	12.93

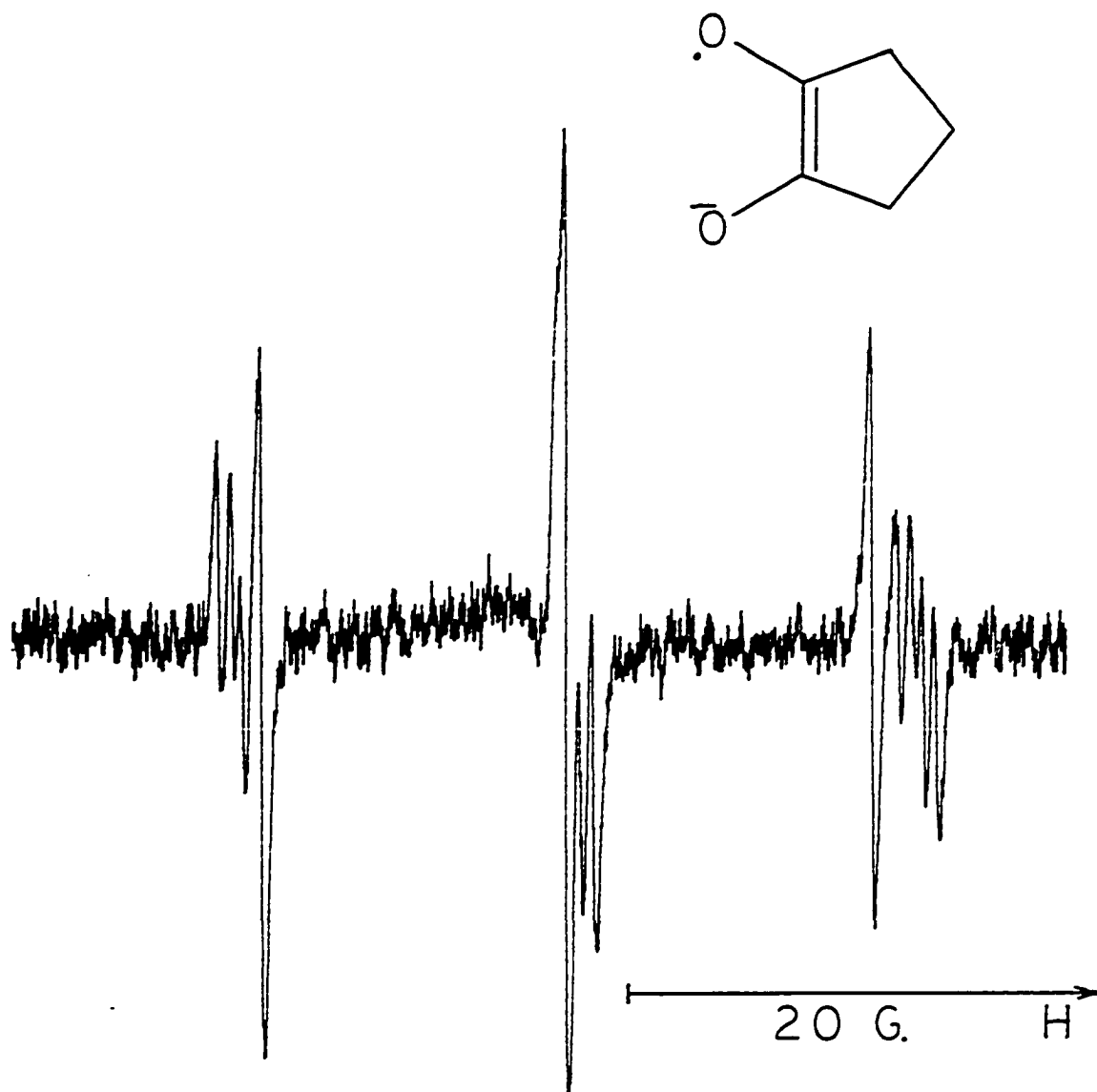


Figure 4. ESR spectrum of cyclopentane-1,2-semidione in the presence of lithium iodide with only the inner three lines shown

addition of sodium iodide caused the sodium hyperfine to vanish, while the spectrum remained relatively strong in intensity. At more dilute concentrations of sodium iodide the spectrum consists of five lines (see Figure 5).

Hyperfine interaction could never be seen for potassium, as is usually the case for semidiones. At appropriate concentrations of potassium iodide the spectrum shows asymmetric line broadening. See Figure 6 for a typical example of this.

The spectra run with rubidium or cesium present appeared similar in nature to those run in the presence of potassium.

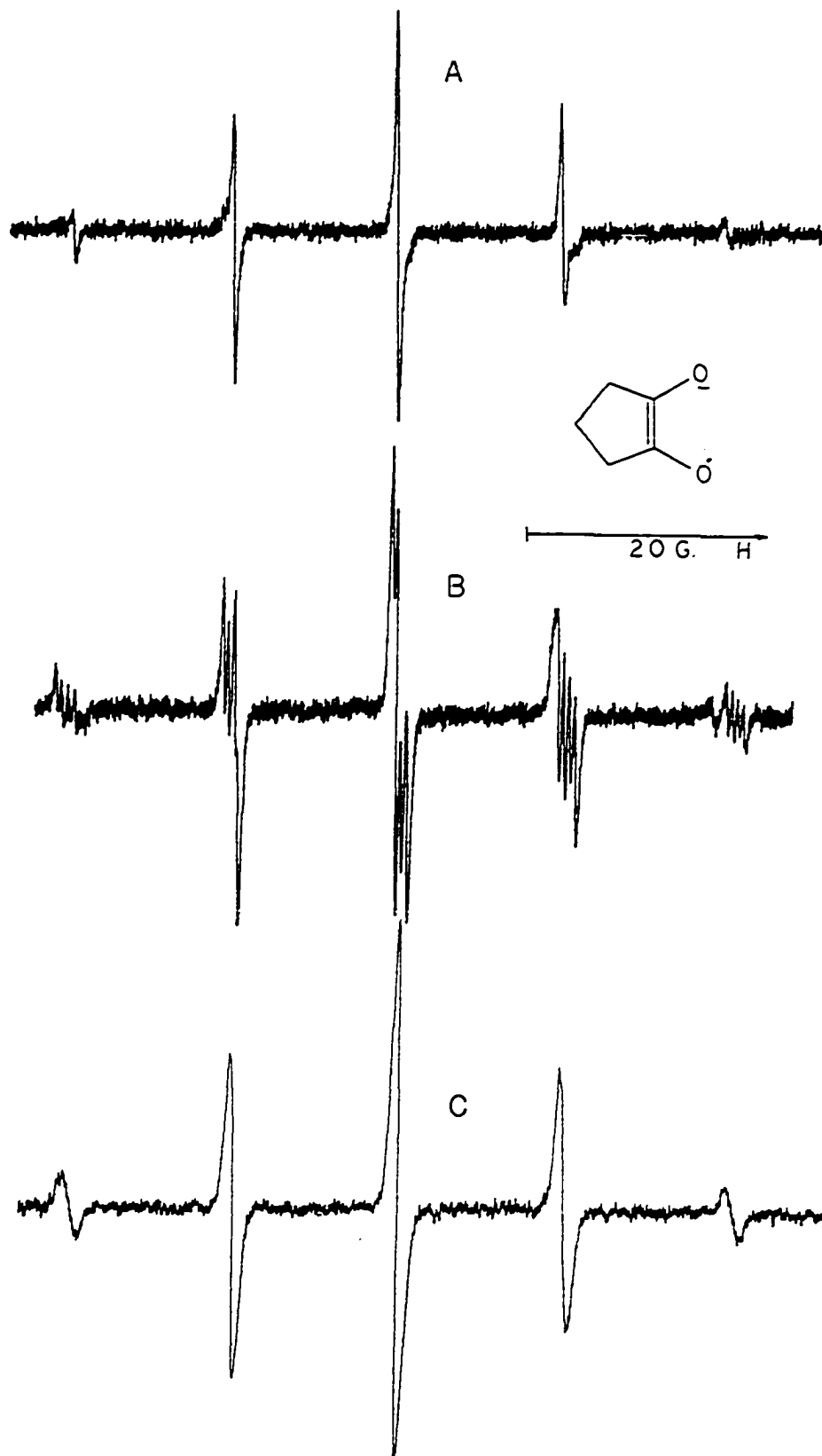
### 3. Cyclohexane-1,2-semidione

Again,  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ , and  $\text{K}^+$ (18-C-6) were used as counter ions for the radical anion in DMSO solutions. The esr spectra were observed at various concentrations, and the numerical data obtained are presented as Figure 7. When lithium was the counter ion and the lithium concentration was less than about 0.1 M, two species could be observed. One of these showed metal hyperfine. Addition of excess lithium iodide caused the spectra without the hyperfine interaction to vanish. The esr parameters of the second set of lines did not change appreciably as lithium iodide was added (see Figure 8).

When sodium was the counter ion, only one species could be seen except at very low sodium iodide concentrations. Some line broadening could be observed at certain concentrations of sodium iodide. (See Figure 9.) Note that the esr parameters for this radical change only

Figure 5. ESR spectra of cyclopentane-1,2-semidione in the presence of sodium iodide

- A. Low sodium iodide concentration
- B. Approximately 0.05 M sodium iodide concentration
- C. High sodium iodide concentration



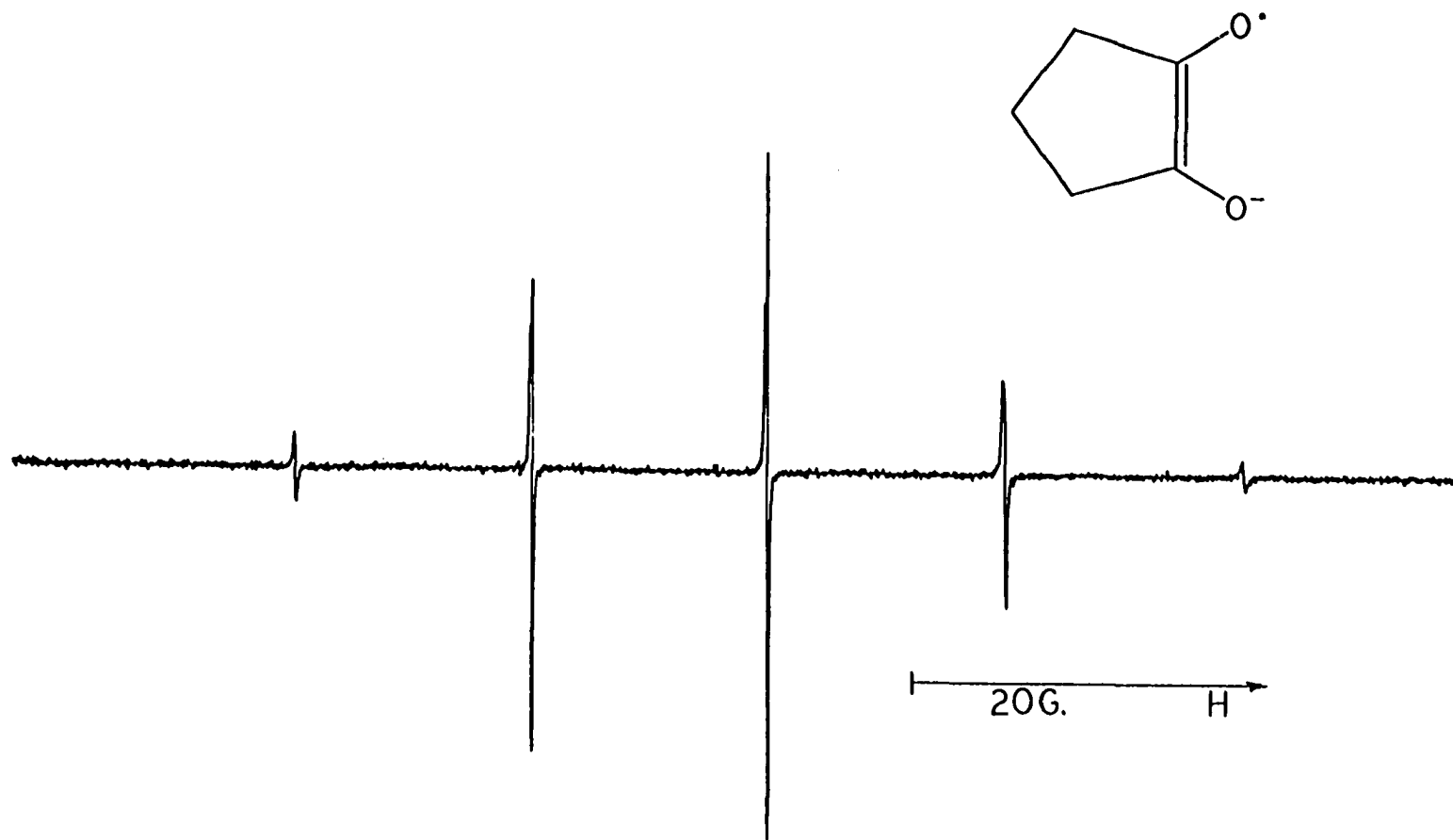


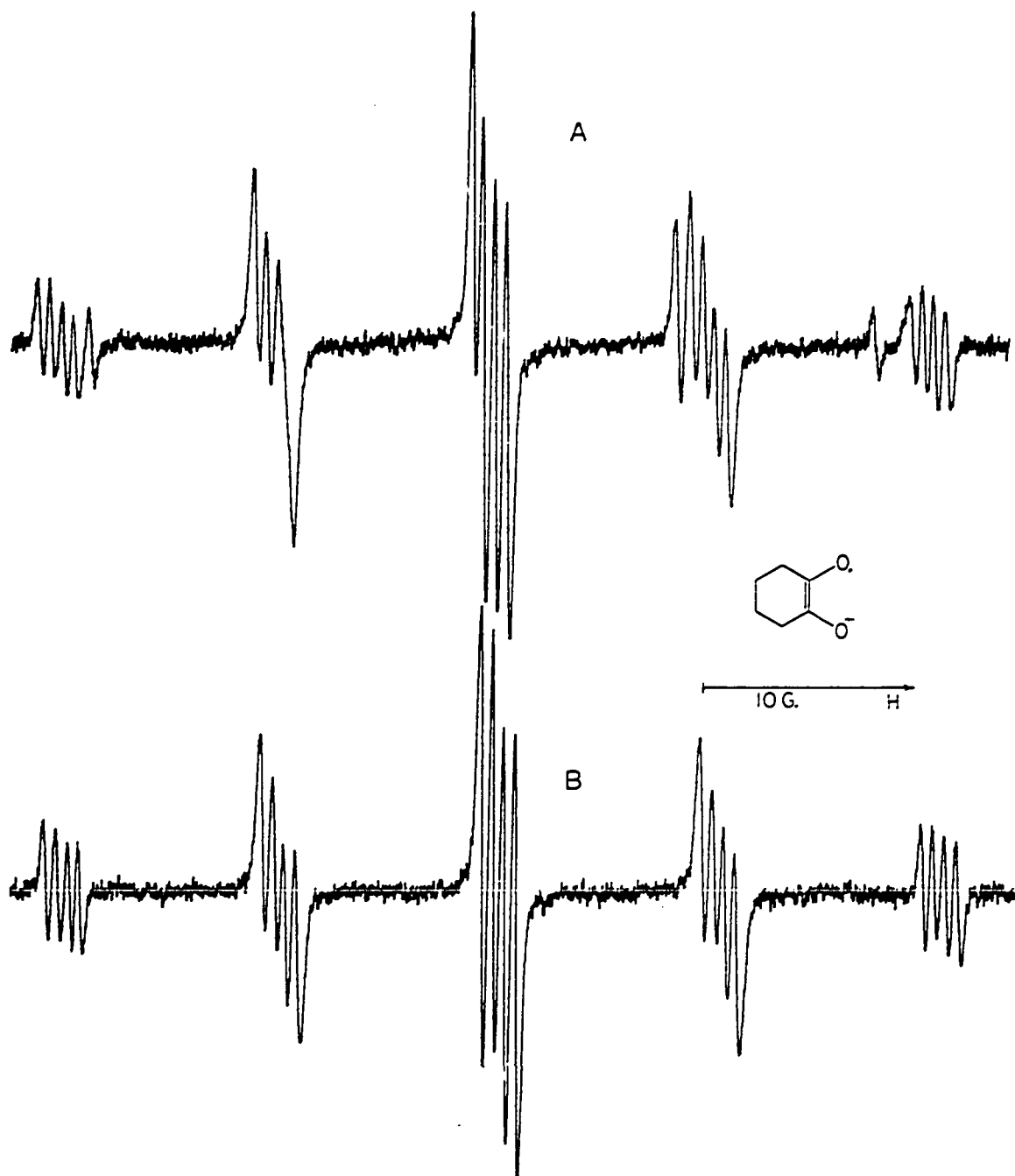
Figure 6. ESR spectrum of cyclopentane-1,2-semidione in the presence of potassium iodide

Cyclohexanesemidione

[KI] (molar)	<u>g</u>	<u>a<sup>H</sup></u> (G)	[CsI] (molar)	<u>g</u>	<u>a<sup>H</sup></u> (G)
0.69	2.004908	10.02	0.72	2.004607	9.84
0.34	2.004925	9.97	0.36	2.004594	9.81
0.17	2.004931	9.93	0.18	2.004602	9.77
0.16	2.004929	9.93	0.12	2.004712	9.76
0.086	2.004936	9.89	0.059	2.004767	9.70
0.084	2.004939	9.90	0.030	2.004835	9.66
0.043	2.004947	9.87	0.015	2.004909	9.61
0.042	2.004946	9.86	0.0074	2.004932	9.59
0.022	2.004956	9.85	0.0037	2.004967	9.58
0.021	2.004954	9.84			
0.011	2.004966	9.83	[K(18-C-6)I]		
0.010	2.004963	9.81	(molar)	<u>g</u>	<u>a<sup>H</sup></u> (G)
0.0052	2.004975	9.79	0.85	2.004993	9.76
0.0026	2.004989	9.75	0.42	2.004992	9.74
			0.21	2.004995	9.73
			0.11	2.005000	9.72
[RbI] (molar)	<u>g</u>	<u>a<sup>H</sup></u> (G)	0.053	2.005006	9.70
0.87	2.004801	9.93	0.026	2.005007	9.69
0.43	2.004803	9.88	0.013	2.005017	9.67
0.22	2.004811	9.84			
0.11	2.004831	9.82		<u>g</u>	<u>a<sup>H</sup></u> (G)
0.054	2.004841	9.79	NaI	2.004880	10.13
0.027	2.004867	9.77	LiI	2.004800	10.58
0.014	2.004890	9.74	Free ion: . K <sup>+</sup> DMSO <sup>-</sup> /[2.2.2]-cryptand		
0.0068	2.004922	9.69		2.005100	9.48

Figure 7. The values for g and a<sup>H</sup> obtained from cyclohexanesemidione in the presence of various counter ions



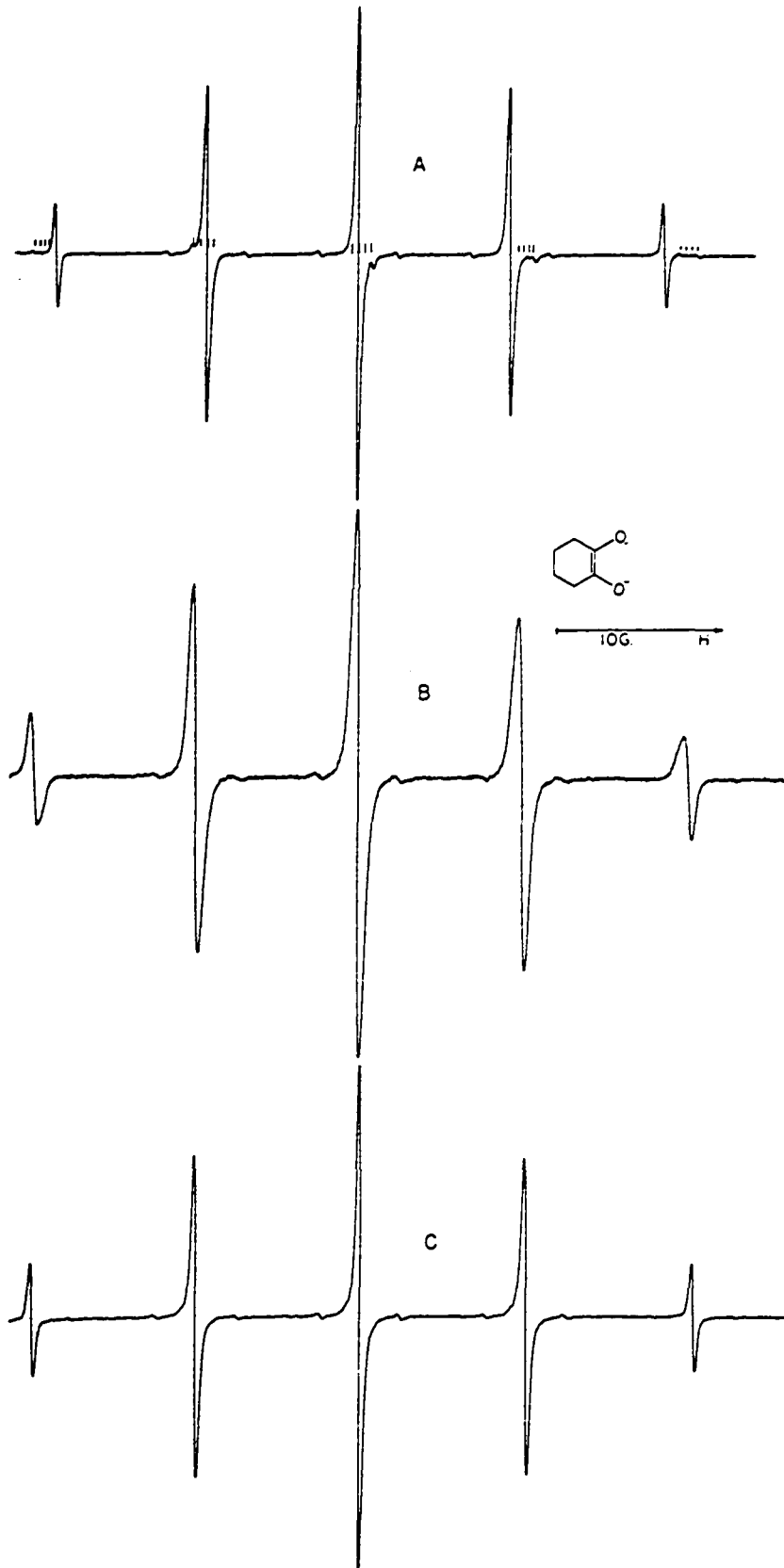


- A. Less than one equivalent of lithium iodide
- B. Slightly more than one equivalent of lithium iodide

Figure 8. ESR spectra of cyclohexane-1,2-semidione in the presence of lithium iodide

Figure 9. ESR spectra of cyclohexane-1,2-semidione in the presence of sodium iodide

- A. Low sodium iodide concentration, marked lines are due to the ion pair
- B. One equivalent of sodium iodide
- C. High sodium iodide concentration



slightly after one equivalent of sodium iodide has been added. The  $g$ -value and  $\underline{a}^H$  value recorded at very high ( $\sim 0.6$  M) sodium iodide concentration ( $g = 2.00484$ ,  $\underline{a}^H = 10.27$  G) are slightly different than those taken from the lines showing metal hyperfine at more dilute concentrations. The high concentration values of  $\underline{a}^H$  and  $g$  are much different from  $\underline{a}^H$  and  $g$  measured at low concentrations for the species without metal hyperfine. It should be pointed out that at low concentrations of sodium iodide the signal from the species showing sodium hyperfine is rather small, which makes accurate determination of  $g$  and  $\underline{a}^H$  somewhat difficult.

When potassium was the counter ion, a spectrum could be obtained where two species appear to be present, but neither of them shows potassium hyperfine. (See Figure 10.) Usually these two species could not be resolved, however.

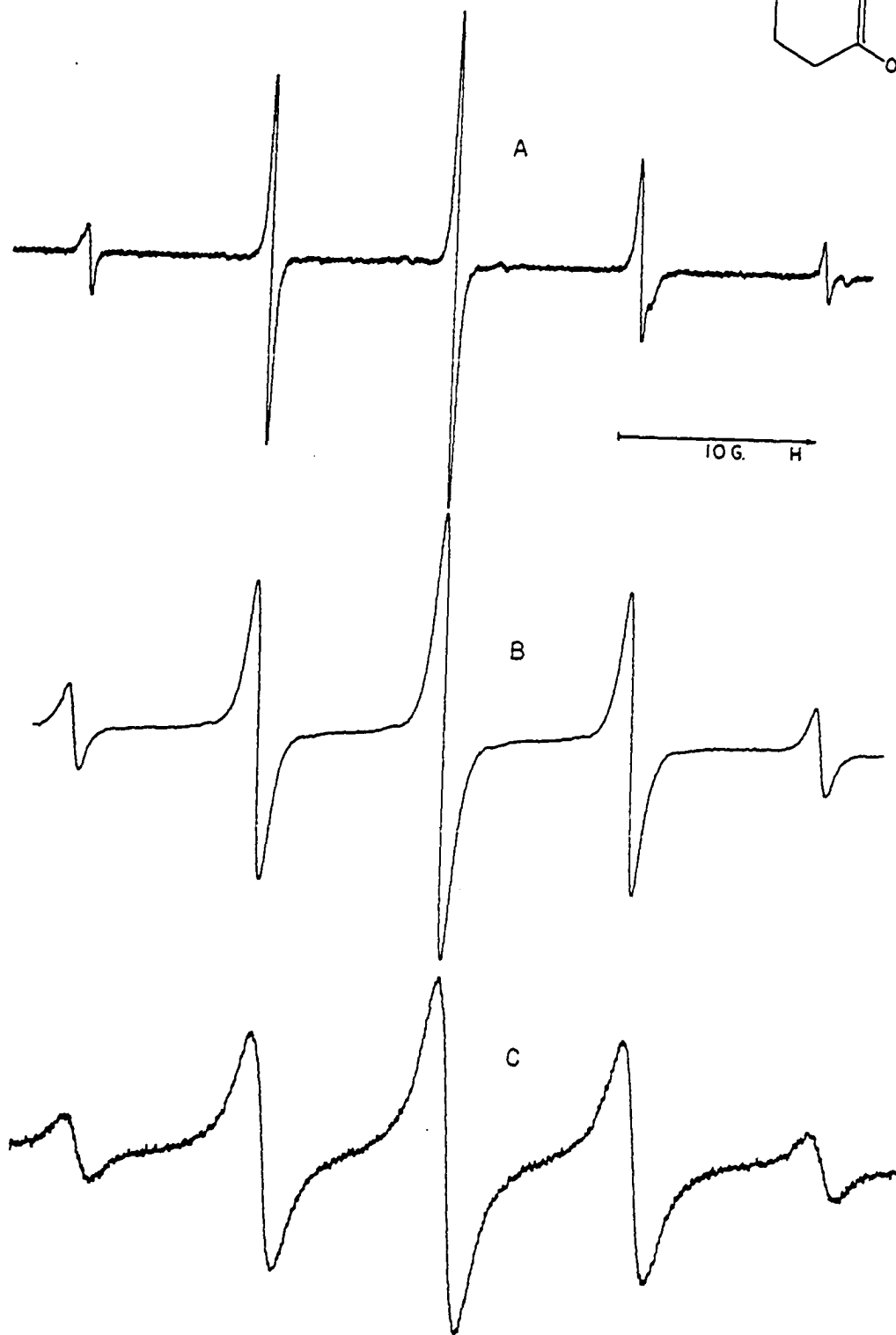
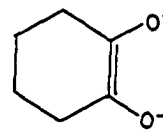
The spectral line width was larger when rubidium and cesium were the counter ions, compared to the potassium case. (See Figure 10.) Furthermore, the width of the lines decreased as the concentration of rubidium or cesium decreased. This effect was also present when potassium was the counter ion, but to a lesser extent.

#### 4. Cycloheptane-1,2-semidione

This radical anion was observed in the presence of  $K^+$ . There was no overriding reason to limit the study to this counter ion. However, since the information that would be obtained by expanding the investigation is not likely to contribute further to the understanding of ion pairing, the work was restricted to potassium. The data obtained are

Figure 10. ESR spectra of cyclohexane-1,2-semidione in the presence of various counter ions

- A. 0.1 M  $K^+DMSO^-$ /DMSO plus 0.5 equivalents of [2.2.2]-cryptand, at 12°C
- B. Saturated rubidium iodide solution
- C. Saturated cesium iodide solution



presented in Figure 11. Note that this system has an anomalously low  $g$ -value, relative to the other cyclic semidiones. (For example, compare  $g_f$  in Figure 11 to  $g_f$  in Figures 2, 3, or 7.) In general, the signal intensities were lower with cycloheptyl than with the other small rings. The existence of extensive long range hyperfine splittings also contributed to the problem of obtaining satisfactory data in this case.<sup>18</sup>

#### 5. Cyclooctane-1,2-semidione

No attempts were made to measure the esr parameters of the  $C_8$  cyclic semidione at various metal ion concentrations. This is because of the complex spectra observed for this radical. Although good signal intensity was seen, both when [2.2.2]-cryptand was present and when excess potassium iodide was added, the spectra were uninterpretable.<sup>19</sup>

#### 6. Cyclononane-1,2-semidione

Like cycloheptane semidione, this radical anion was observed only in the presence of  $K^+$ . This system provided a strong signal which lent itself to the dilution method used to obtain data, but the existence of long range hyperfine interactions made accurate determination of the esr parameters difficult. The data which were obtained are given in Figure 12. Again, it was felt that additional work with other counter ions was not required.

Strictly speaking, seven-, eight-, and nine-membered rings are not usually classed as "small" rings. Since these semidiones are known to be of Z configuration, they are included here with the four-, five-, and

Cycloheptanesemidione

[KI] (molar)	$\underline{g}$	$\underline{a}^H$ (G)
1.89	2.004808	6.97
1.47	2.004802	6.95
1.26	2.004808	6.97
0.95	2.004813	6.87
0.92	2.004807	6.86
0.75	2.004811	6.87
0.47	2.004824	6.79
0.46	2.004821	6.79
0.37	2.004823	6.79
0.23	2.004823	6.74
0.19	2.004830	6.74
0.18	2.004827	6.76
0.12	2.004838	6.70
0.090	2.004837	6.69
0.045	2.004845	6.67
0.023	2.004850	6.61
0.011	2.004856	6.19

$\underline{g}$                        $\underline{a}^H$  (G)

Free Ion:  $K^+DMSO^-/222$ -cryptand

2.004975      6.19

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$\underline{a}^H$  is for the largest splitting, which is a triplet.

---

Figure 11. The values for  $\underline{g}$  and  $\underline{a}^H$  obtained from cycloheptanesemidione in the presence of various concentrations of potassium iodide and potassium dimethylate/[2.2.2]-cryptand



Cyclononanesemidione

[KI] (molar)	$\underline{g}$	$\underline{a}^H$ (G)
1.92	2.004905	5.29
1.28	2.004915	5.28
1.08	2.004914	5.29
0.96	2.004916	5.28
0.54	2.004923	5.28
0.48	2.004925	5.29
0.32	2.004928	5.29
0.27	2.004931	5.27
0.24	2.004936	5.28
0.16	2.004935	5.28
0.13	---	5.30
0.12	2.004938	5.28
0.080	2.004940	5.28
0.067	2.004947	5.27
0.040	2.004948	5.27
0.034	2.004954	5.27
0.020	2.004957	5.27
0.010	2.004962	5.26

	$\underline{g}$	$\underline{a}^H$
Free Ion: $K^+DMSO^-/[2.2.2]$ -cryptand	2.005095	5.10

---

<sup>a</sup>The  $\underline{a}^H$  values are for the largest splitting, which is a triplet.

---

Figure 12. The values for  $\underline{g}$  and  $\underline{a}^H$  obtained from cyclononanesemidione in the presence of potassium iodide and potassium dimsylate/[2.2.2]-cryptand

six-membered rings as a matter of convenience. Cyclopropane-1,2-semidione does not appear to have been prepared yet.

### C. Discussion

#### 1. General observations

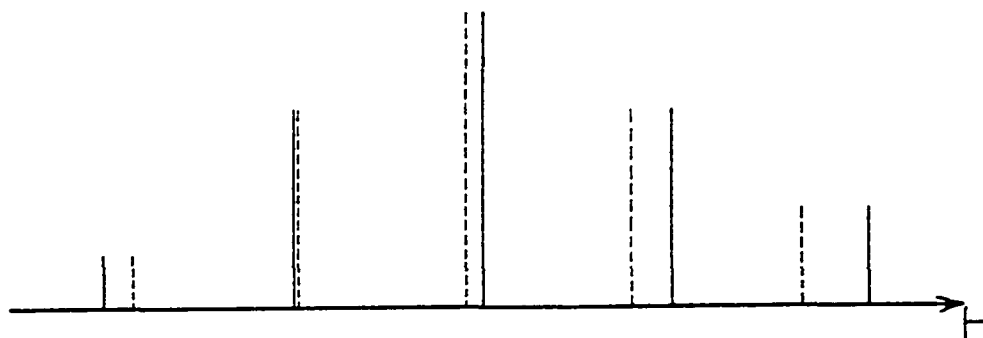
It seems clear from the data that under certain conditions two sets of lines, corresponding to different species, can be obtained in the esr spectra of semidiones. The existence of metal hyperfine coupling in one of these sets of lines, and the correspondence of the measured esr parameters for the other set of lines with those of the "free" radical ion generated with excess [2.2.2]-cryptand present implies that one set of lines is derived from an ion pair, the other from a free ion. The spectra shown in Figure 8 are an example of this situation.

It has also been observed that under different conditions two sets of lines may be obtained where neither set has observable metal hyperfine. Figure 10 shows a case where this is true. It seems reasonable to say that this situation also arises from the coexistence of free ion and ion pair, except that now the ion pair does not exhibit metal hyperfine for some reason. Possible explanations for this include:

- a) rapid exchange of the metal, which removes the splitting;
- b) unresolved splitting present (potassium has a small magnetic moment, relative to sodium or lithium); and c) change in the structure of the ion pair from a tight ion pair to a solvent separated ion pair. An attempt to ascertain which of these reasons is the correct one will be made at a later point.

The most common situation is one similar to Figures 1 and 6. The observed spectrum consists of only one set of lines, but the lines have an asymmetry to them, where the higher field lines have greater width than the low field ones. The situation here is explained by invoking two species, an ion pair and a free ion, and requiring that they be exchanging with one another at a rate intermediate between fast and slow exchange on the esr time scale. To clarify this situation, consider the stick spectra shown below. This is a simplified representation of the spectra of two species, one having larger  $a^H$  and lower  $g$  than the other.

There are three situations to consider: a) "slow" exchange between species (In this case two discrete spectra are resolved.); b) "rapid" exchange between species (Now one set of lines is seen. The position of the observed lines is dependent upon the relative concentrations of the two species.); and c) "intermediate" exchange. (The position of the



observed lines is shifted toward the position they would have in case "b" but the lines are broadened. The extent of broadening depends upon the spacing between the frozen lines (case "a"). Hence, in our example, the high field lines are of greater width than the low field lines.)<sup>20</sup>

This situation is not unique to semidione spectra. Cases involving ion pairing of aromatic radical ions, ketyl radical ions, and semiquinone radical ions, as well as other types of radical ions have been reported and each of the three situations described above has been seen.<sup>5,11,21-42</sup> Ion pairs between thallium and 1,2-semidiones have been reported, in which case the metal cation appears to be tightly complexed with the radical anion.<sup>43,44</sup> Work with perfluorobiacetyl semidione has also been published, where a number of solvents and alkali metals were studied, and again ion pairing is seen to occur, as evidenced by metal hyperfine interaction or line broadening.<sup>45a</sup>

In short, there can be no doubt that cyclic-1,2-semidiones ion pair even in DMSO, a relatively polar solvent.

## 2. Determining ion pairing constants

The essence of my argument concerning the behavior of semidiones in DMSO has been that two species, an ion pair and a free ion, coexist in solution. If this is true, it should be possible to determine ion pairing constants for pairing between semidiones and alkali metal cations.

If the observed  $g$  value, with fast exchange between species, is a weighted average then equation 3 is true, where  $g_0$  represents the observed  $g$  value,  $g_f$  and  $g_p$  are the  $g$  values for the free ion and ion pair respectively, and  $p_f$  and  $p_p$  are the probabilities of a given radical being a free ion or an ion pair. This is generally held to be correct when the "two jump" model describes the system under

consideration. In effect, this means that all the paramagnetic molecules must exist as either pairs or free ions, with exchange between the two being essentially instantaneous, i.e., there are no intermediates.

$$g_o = g_f p_f + g_p p_p \quad (3)$$

It is possible to derive a simple formula from this which allows graphical analysis of the data. Rewriting 3 as 4 and rearranging gives 6.

$$g_o = g_p p_p + g_f (1 - p_p) \quad (4)$$

$$g_o = (g_p - g_f) p_p + g_f \quad (5)$$

$$g_f - g_o = (g_f - g_p) p_p \quad (6)$$

Inverting gives

$$\frac{1}{(g_f - g_o)} = \frac{1}{(g_f - g_p)} \cdot \frac{1}{p_p} \quad (7)$$

But

$$p_p = \frac{[P]}{[F] + [P]} = \frac{1}{\frac{[F]}{[P]} + 1} \quad (8)$$

Where [P] is the concentration of the pair and [F] is the concentration of the free radical anion. So

$$\frac{1}{(g_f - g_o)} = \frac{1}{(g_f - g_p)} \cdot \left( \frac{[F]}{[P]} + 1 \right) = \frac{\frac{[F]}{[P]}}{(g_f - g_p)} + \frac{1}{(g_f - g_p)} \quad (9)$$

And since

$$\frac{[F]}{[P]} = \frac{1}{K[M^+]} \quad (10)$$

Finally

$$\frac{1}{(g_f - g_o)} = \frac{1}{(g_f - g_p)K[M^+]} + \frac{1}{(g_f - g_p)} \quad (11)$$

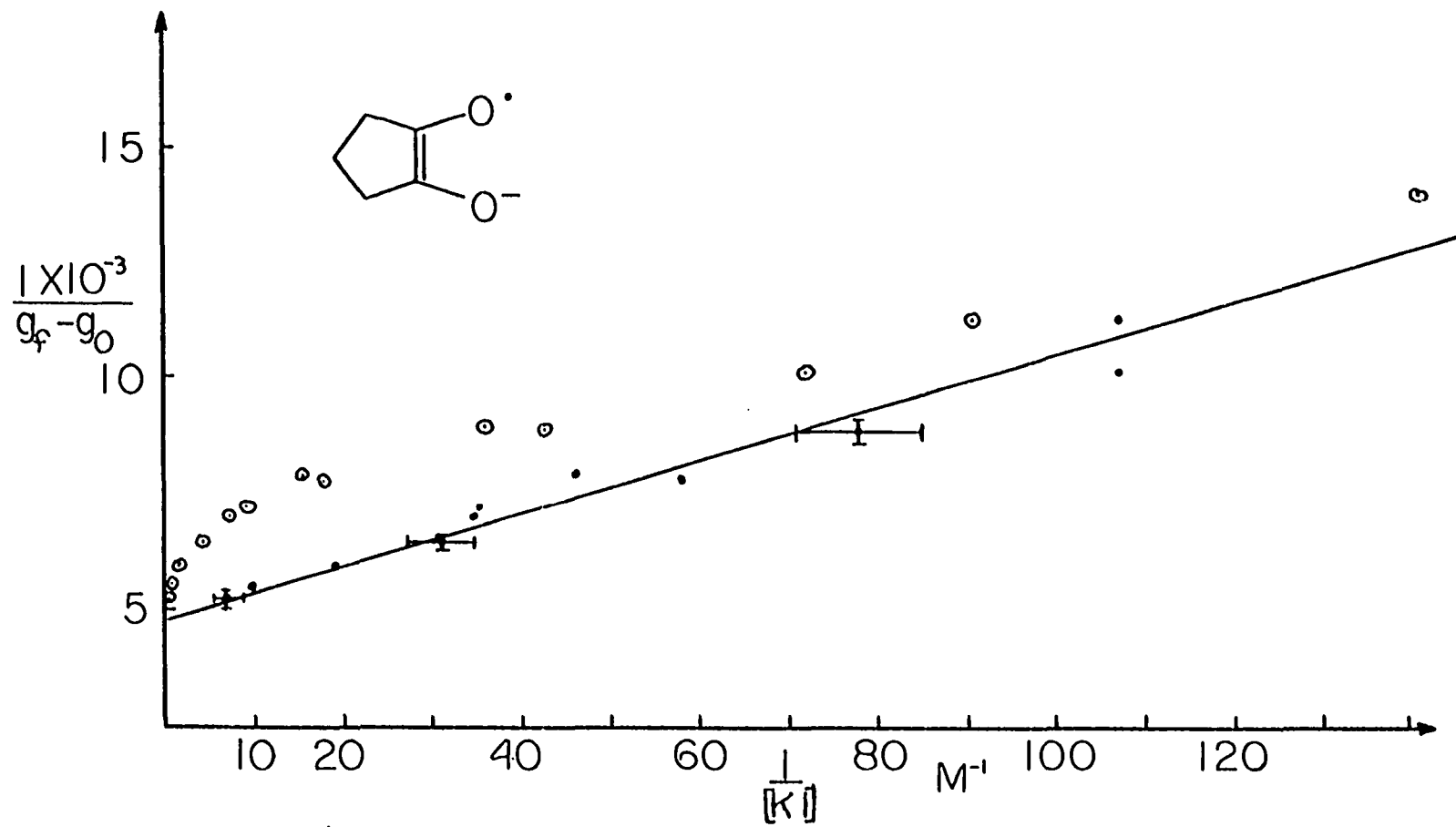
Note that the equilibrium constant  $K$  introduced in equation 10 is for the reaction



It is apparent from equation 11 that a plot of  $1/(g_f - g_o)$  vs  $1/[M^+]$  should yield a straight line with a slope of  $1/(g_f - g_p)K$  and an intercept of  $1/(g_f - g_p)$ . Since the value of  $g_f$  may be obtained from a solution containing excess [2.2.2]-cryptand, the term on the left side of equation 11 is an observable. Initially, the value of the independent variable  $1/[M^+]$  was obtained by assuming that  $[M^+]$  was equal to  $[MI]$ . When plots were made of the data, results similar to the circled points in Figure 13A were obtained. (Figure 13B shows a plot of  $g$  and  $\bar{a}^H$  vs  $[KI]$ .)

It is apparent from Figure 13A that the circled points do not fall on a straight line. The situation is the same in all the cases studied. One way to understand this curvature is to consider that  $[M^+]$  may not necessarily be equal to  $[MI]$ . What this would mean is that the salts undergo less than 100% dissociation in solution. At concentrations

Figure 13. A. Plot of  $1/(g_f - g_0)$  vs  $1/[KI]$  for cyclopentane-1,2-semidione, the circled points are raw data, the solid points are plotted after taking  $\gamma_{app}$  into account





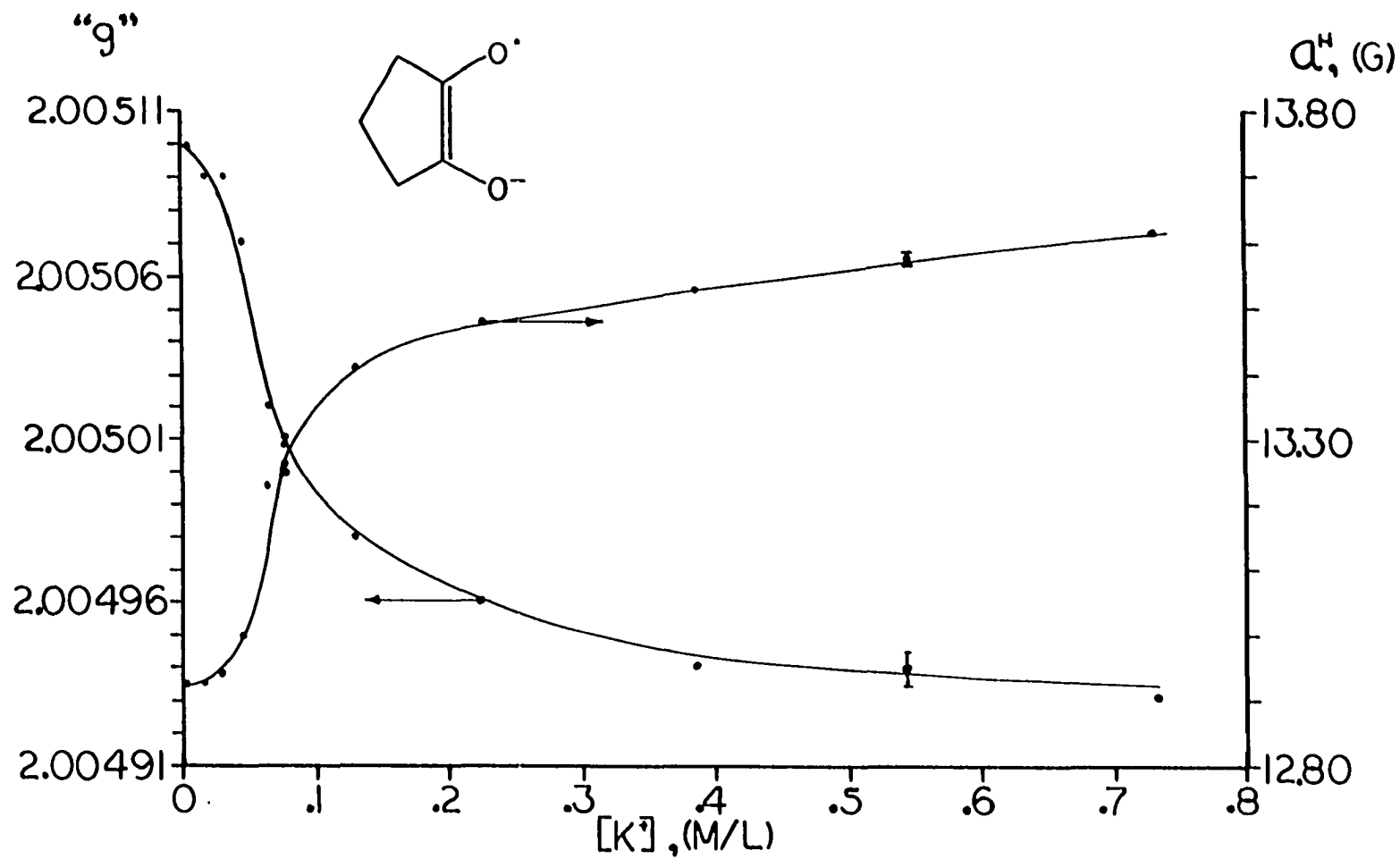


Figure 13. B. Observed values of  $a^H$  and  $g$  plotted against  $[KI]$

of 0.1  $M$  and higher this seems to be a reasonable possibility. In order to take this pairing of the alkali metal salts into consideration, the following curve fitting procedure was adopted. The discussion will illustrate the case where  $M$  equals potassium.

Upon examination of all the data plotted as shown in Figure 13A, it appears as if the graph converges to an intercept with the  $Y$  axis which is fairly easy to estimate by extrapolation. Also, when  $[K^+]$  is small the assumption that  $[K^+]$  is equal to  $[KI]$  should be a good one. Therefore, a line was drawn from the extrapolated intercept to the most distant (dilute) point available on the graph. Then each of the (circled) points was moved over horizontally to the line. From this an apparent value of  $[K^+]$  was obtained for each of the data points. A coefficient,  $\gamma_{app}$ , was defined as being equal to  $[K^+]_{app}/[KI]$ , and the calculated values of  $\gamma_{app}$  were plotted against  $[KI]$ . All the data for each of the semidiones studied by dilution experiments with potassium as the counter ion were treated in this way. All the values for  $\gamma_{app}$  were plotted upon the same graph. After this was completed, a line was drawn through the points to give an empirical function relating  $\gamma_{app}$  and  $[KI]$  (see Figure 14).

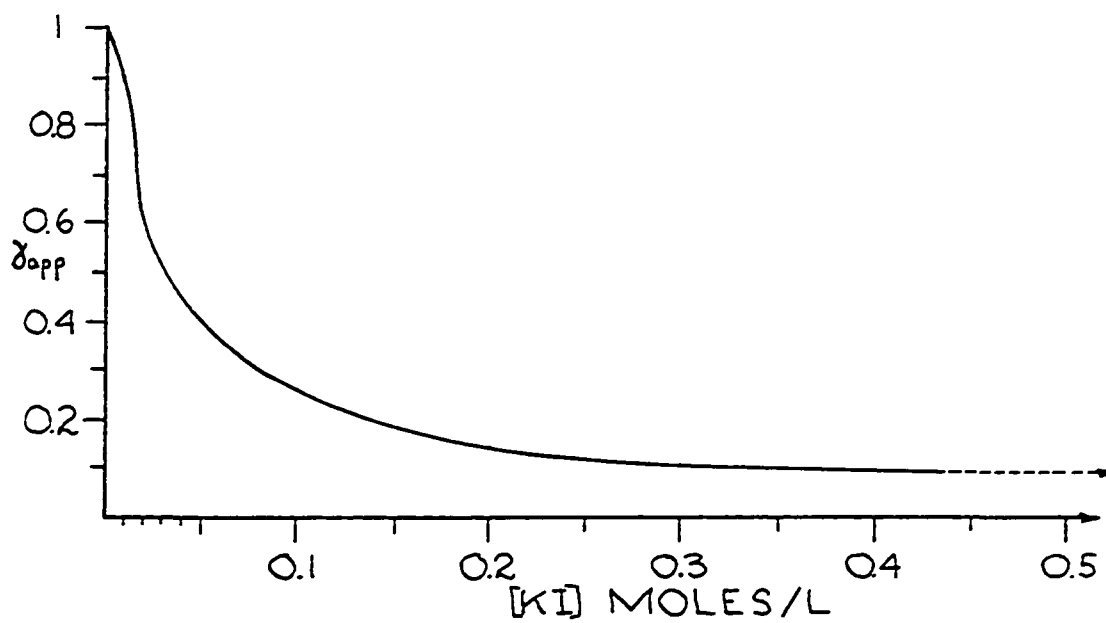
At this stage all the data relating  $1/(g_f - g_o)$  to  $1/[K^+]$  were replotted, this time substituting for  $[K^+]$  the value  $[KI]\gamma_{app}$ . The best straight line, determined by eye, was drawn through the resulting points and this line was used to obtain  $g_p$  and  $K$ . A typical result is shown in Figure 13A as the uncircled points, through which the line is drawn. (A linear regression cannot be used on this type of plot since the

Figure 14. Plots of  $\gamma_{\text{app}}$

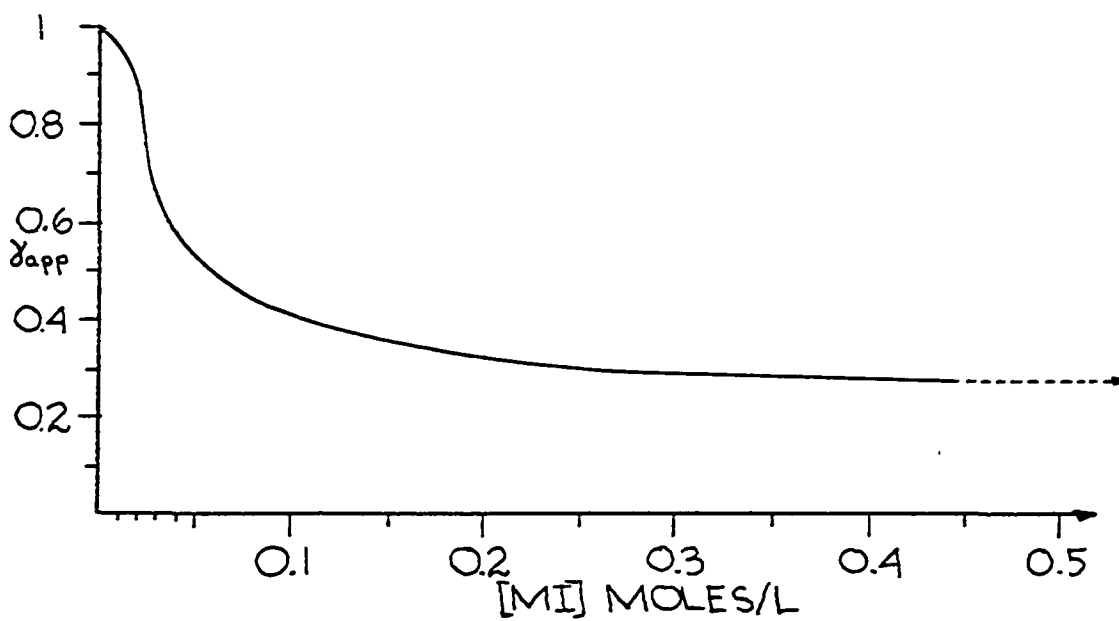
A. The plot used for potassium iodide

B. The plot used for all other alkali metal salts

A



B



experimental error is a given fraction of the value observed, not a constant. To see this effect illustrated, observe the three sets of error bars in Figure 13A.) The meaning of  $\gamma_{app}$ , if any, will be discussed in a later section.

Exactly the same procedure was followed for M equal to rubidium, cesium, and  $K^+$ (18-C-6). A second plot of  $\gamma_{app}$  vs [MI] was used for all three of these cations, since experimentally there appeared to be no significant difference in  $\gamma_{app}$  between the three.

The values for the ion pairing constants obtained by the preceding method, as well as the values of  $\underline{g}$  and  $\underline{a}^H$  and  $[(g_p - g_f)/g_f] \cdot 100$ , which will be discussed below, are displayed as Figure 15. All of the ion pairing constants reported herein were obtained by the preceding approach. For brevity only one example, cyclopentane-1,2-semidione, was shown. The plots for this case are neither much better nor much worse than the others insofar as fit to a line is concerned. The reason all the original graphs are not simply photo-reproduced here is that the procedure used to fit the data leads to very messy looking results. All the graphs would have had to have been redrawn for inclusion in the dissertation, an odious task for the benefit received. The numerical data presented in section II-B are sufficient to generate these plots.

### 3. Determining the esr parameters of the ion pairs

The  $\underline{g}$  value for the ion pair may be obtained from the intercept of a plot similar to Figure 13A where

$$\text{intercept} = \frac{1}{(g_f - g_p)} \quad (13)$$

The method used to plot the data was described in part 2 above.

In principle, similar plots might be made using splitting constants,  $\underline{a}^H$ , rather than  $g$ -values. From these additional plots the value of  $\underline{a}^H$  for the ion pair could be obtained. The original decision to use  $g$  values was based on the fact that the error in the field measurement used to find  $g$  is half the error in  $\underline{a}^H$ . Rather than re-plot all the data with  $\underline{a}^H$  as the dependent variable, the observation that for these systems  $\underline{a}^H$  is a linear function of  $g$  was utilized. Available data for each radical anion-alkali metal counter ion system were fit to a linear equation,

$$\underline{a}^H = b_0 + b_1 g \quad (14)$$

The correlation between  $g$  and  $\underline{a}^H$  is quite linear. The worst case gave a correlation coefficient of -0.94 (12 data points). The numbers for  $\underline{a}^H$  in Figure 15 are derived by this method when necessary. When both the free ion and the ion pair are observed simultaneously in solution, the values of  $\underline{a}^H$  and  $g$  can be measured directly. Such values are marked with an asterisk in Figure 15.

#### 4. The significance of $K$ and $[(\underline{a}_p^H - \underline{a}_f^H)/\underline{a}_f^H] \cdot 100$

The ion pairing constants obtained had values ranging from 4 to 280. To help fit these values into perspective, Figure 16 shows a few ion pairing constants for various ions which are available from the existing literature. It is interesting to note that the ion pairing

Radical	Cation <sup>a</sup>	$g^b$	$a^H$ (G)	K (l/mole)	$[(a_p^H - a_f^H)/a_f^H] \cdot 100$
C <sub>4</sub>	"free"	2.00510*	13.85*	---	---
	Li	---	---	small <sup>c</sup>	---
	Na	2.00493	14.37	16	3.8
	K	2.00498	14.20	14	2.5
	Rb	2.00497	14.16	14	2.2
	Cs	2.00504	14.07	59	1.6
	K(18-C-6)	2.00506	13.93	33	0.6
C <sub>5</sub>	"free"	2.00510*	12.91*	---	---
	Li	2.00471*	14.48* <sup>d</sup>	large <sup>c</sup>	12.2
	Na	2.00488*	13.88* <sup>e</sup>	large <sup>c</sup>	7.5
	K	2.00489	13.85	87	7.1
	Rb	2.00484	13.56	100	5.0
	Cs	2.00472	13.36	70	3.5
	K(18-C-6)	2.00499	13.36	69	3.5

<sup>a</sup>"Free" refers to a solution containing excess [2.2.2]-cryptand.

<sup>b</sup>Numbers marked with an \* were measured directly from a single spectrum.

<sup>c</sup>The value of  $K$  made the use of the dilution technique impossible.

<sup>d</sup>Lithium splitting seen, 0.50 gauss.

<sup>e</sup>Sodium splitting seen, 0.55 gauss.

Figure 15. Summary of  $g$ ,  $a^H$ , ion pairing constant and  $[\Delta a^H/a_f^H] \cdot 100$  for various cyclosemidione ion pairs

Radical	Cation <sup>a</sup>	$g^b$	$a^H^b$ (G)	K (l/mole)	$[(a_p^H - a_f^H)/a_f^H] \cdot 100$
C <sub>6</sub>	"free"	2.00510*	9.47*	---	---
	Li	2.00480*	10.50* <sup>f</sup>	large <sup>c</sup>	11.7
	Na	2.00488*	10.13* <sup>g</sup>	large <sup>c</sup>	7.0
	K	2.00490	10.04	220	6.0
	Rb	2.00479	9.90	200	4.5
	Cs	2.00454	9.84	46	3.9
	K(18-C-6)	2.00499	9.75	250	3.0
C <sub>7</sub>	"free"	2.00498*	6.19* <sup>h</sup>	---	---
	K	2.00480	6.95 <sup>h</sup>	190	12.3
C <sub>8</sub>	"free"	2.00511*	---	---	---
	.1 M K <sup>+</sup> DMSO <sup>-</sup>	2.00494*	---	---	---
C <sub>9</sub>	"free"	2.00510*	5.10* <sup>h</sup>	---	---
	K	2.00491	5.30 <sup>h</sup>	280	3.9

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<sup>f</sup>Lithium splitting seen, 0.60 gauss.

<sup>g</sup>Sodium splitting seen, 0.40 gauss.

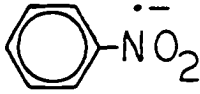
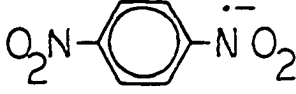
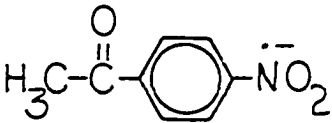
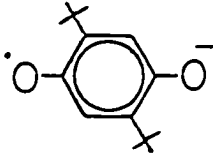
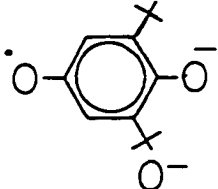
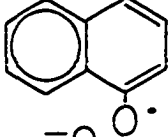
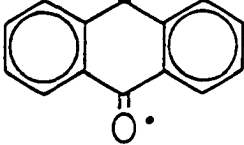

<sup>h</sup>Largest splitting.

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Figure 15. (Continued)



Figure 16. Some representative ion pairing constants taken from the literature

Anion	Counter-ion	Solvent	K	Reference
	Li <sup>+</sup>	HMPA	0.21	27
	Na <sup>+</sup>	HMPA	0.39	27
	K <sup>+</sup>	HMPA	2.8	27
	Na <sup>+</sup>	HMPA	1.4 or 2.9	23 or 28
	K <sup>+</sup>	HMPA	17	45b
	K <sup>+</sup>	HMPA	12	32
	K <sup>+</sup>	HMPA	11 or 9.1	34 or 37
	K <sup>+</sup>	HMPA	36	37
	K <sup>+</sup>	HMPA	7.1	37
	Na <sup>+</sup>	HMPA	6.7	35
	K <sup>+</sup>	HMPA	28.0	35
Cyclooctatetraene <sup>•-</sup>	K <sup>+</sup>	HMPA	45.0	45c
Tetraphenylethylene <sup>•-</sup>	Na <sup>+</sup>	THF	$2.5 \times 10^{-3}$	5
Tetraphenylethylene <sup>2-</sup>	Na <sup>+</sup>	THF	0.33	5

constants increase for the series lithium, sodium, potassium in hexamethylphosphoramide (HMPA). This is contrary to my results in DMSO, which show a trend toward larger ion pairing constants as the alkali metal becomes smaller. This order in ion pairing constants is not strictly observed, however, and several reversals can be noted. For example, in the case of cyclobutane-1,2-semidione the values of  $K$  are all fairly similar, increasing slightly for cesium and  $K^+$ (18-C-6). At first the lack of a consistent order to the ion pairing constants of the semidiones as the counter ion was varied caused some alarm. This behavior is not inexplicable and may be understood by considering the nature of the radical anions (see below).

In order to obtain a measure of the relative perturbation which a given cation causes when pairing with a particular semidione, a parameter was defined as equal to  $[(\underline{a}_p^H - \underline{a}_f^H)/\underline{a}_f^H] \cdot 100$ . This is just the percent change in  $\underline{a}^H$  caused by the formation of an ion pair from the free ion. For a given size ring it is observed that the value of this number becomes smaller as the size of the counter ion increases. It is reasonable to assume that this number, in some sense, shows the effect that a given cation has upon the molecular orbitals of the radical anion. Thus, the small lithium cation, which has a high potential gradient surrounding it, has a greater effect on the anion than does the cesium ion, a large ion surrounded by a smaller potential gradient.

The small values observed for  $[\Delta \underline{a}^H/\underline{a}_f^H] \cdot 100$  with the  $K^+$ (18-C-6) ion pairs may arise from two effects. The first is that the macrocyclic ether may add enough steric bulk to prevent the close approach of the

anion to the cation. The second is the fact that the presence of the macrocyclic ether "solvates" the cation to some extent and lowers the cation's electronegativity. Although there are no data available to allow an immediate distinction to be drawn between these two influences, I feel the latter is more important than the former. The reasons for this are: A) Obviously the presence of the crown ether stabilizes the potassium ion, relative to its "free" state in solution. If this was not true, the  $K^+(18-C-6)$  complex would not form. Part of this stabilization comes from the fact that in an entropic sense it costs less to solvate the cation with the crown ether than with solvent molecules. An interaction between the nonbonding electrons of the crown ether and the cation provides the rest of the stability of the complex. (When di-benzo-18-crown-6-ether complexes with potassium ions in DMSO,  $\Delta S = -6.9$  e.u. and  $\Delta H = -5.5$  kcal mol<sup>-1</sup>.)<sup>46</sup> This second contribution must in some way decrease the charge density at the cationic center, i.e., make the positive charge more diffuse, by electron donation to the cation. This is the same as saying that the electronegativity of the potassium is lowered. B) There is experimental evidence that, at least with some radical ions, a  $K^+(18-C-6)$  counter ion paired to a radical is close enough to allow splitting by the methylene protons of the crown ether to be observed.<sup>47</sup> C) There is evidence for metal hyperfine splitting by  $M^+(18-C-6)$  cations in some systems.<sup>40,48</sup> D) In one instance, a fluorenone ketyl radical anion, the addition of crown ether increased the metal hyperfine splitting relative to that observed in the absence of crown.<sup>40</sup> This may be interpreted as a change

from a solvent separated ion pair to a tight ion pair upon complexation of the cation by the crown ether. It must be admitted that this last observation is open to another interpretation, namely that the change is due to a change in the position of the cation relative to the radical anion upon complexation. This would be expected to cause a change in  $\underline{a}^M$  because of the change in orbital overlap between alternate positions.

Another interesting trend is seen by comparing the values of  $\underline{K}$  for potassium and the four-, five-, and six-membered rings. (The values are 14, 87 and 220  $\ell$ /mole, respectively.) This can be rationalized by noticing that the oxygen-oxygen distance decreases upon going from cyclobutyl to cyclopentyl and then to cyclohexyl (see Figure 17). Presumably, the spacing between oxygens in cyclobutyl is greater than optimum in regard to the potassium chelating ability of the semidiones. As this space closes up, the ability to chelate potassium goes up and, consequently, the ion pairing constant increases. It should be recognized that this argument assumes that the solvation of all three free semidiones is similar, a reasonable assumption under the conditions.

Now it is easier to understand the apparently odd behavior of the cyclobutyl semidione ion pairing constants. The larger oxygen-oxygen spacing in cyclobutyl causes lithium to fail to ion pair. The lithium cation remains solvated by DMSO. The larger cesium and  $K^+(18-C-6)$  cations which are less solvated in DMSO show slightly higher ion pairing constants than the smaller sodium, potassium and rubidium. In other words, more energy is expended by removing solvent from around

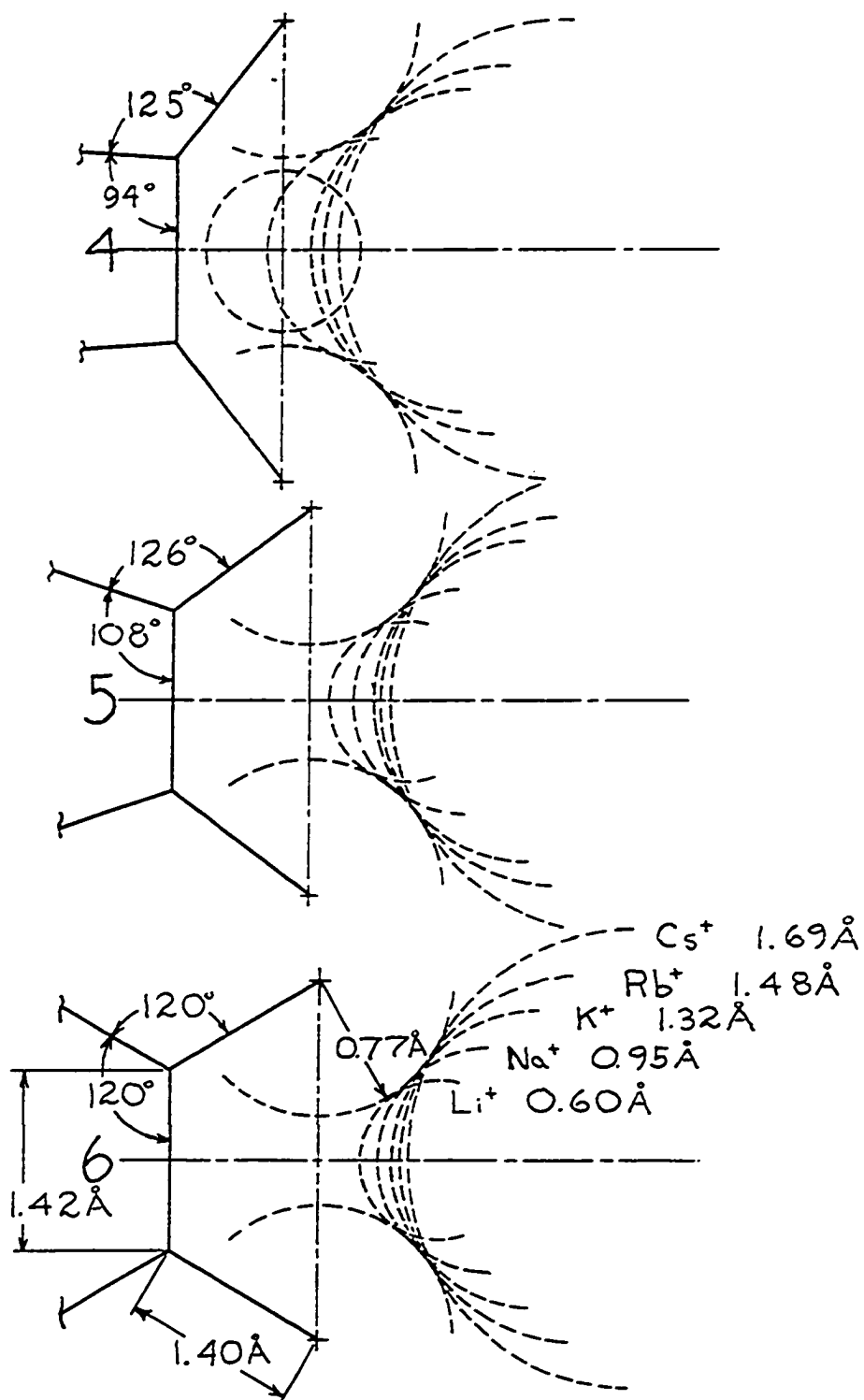


Figure 17. Schematic drawing showing the relative geometries of cyclobutane, cyclopentane and cyclohexane semidiones with dimensions taken from Dreiding models

the lithium cation than can be gained by ion pairing between the cation and radical anion. Consequently, no ion pairing occurs. As the oxygen-oxygen distance decreases this situation no longer prevails and the values of  $K$  for lithium and sodium increase markedly.

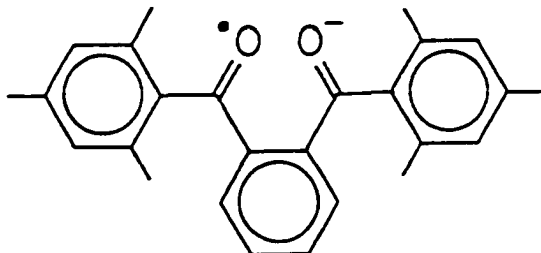
In summary, the size of the cation which is pairing with a given semidione radical anion determines the relative effect of that cation on the molecular orbitals of the radical. The equilibrium constant reflects the stability of the ion pair relative to that of the unpaired solvated ions. The effects of solvation on the free ions are important and must not be ignored if the observed results are to be understood.

#### 5. The ion pairs: Tight or solvent separated?

In principle, the ion pair may be either a tight, or contact, ion pair or a solvent separated pair. The observation of alkali metal hyperfine splitting is occasionally invoked as proof of the existence of tight ion pairs. That this is not sufficient evidence may be seen in the work reported in reference 11. Sodium naphthalenide, where two species with metal hyperfine splitting are seen simultaneously, has been extensively investigated. One of these species is attributed to the tight ion pair, the other to a solvent separated pair.

The magnitude of the metal splitting is not a reliable measure of the ion pair's nature. The value of  $a^{\text{Na}}$  reported for sodium naphthalenide tight ion pair in THF is 0.39 G.<sup>11</sup> Much larger metal hyperfine splittings have been observed. For instance, the radical anion shown on the following page pairs with alkali metal cations, with the

pairs exhibiting large metal splittings. For example,  $\underline{a}^{\text{Na}}$  was found to be 6.9 G.<sup>42</sup> Clearly, the magnitude of the alkali metal splitting is



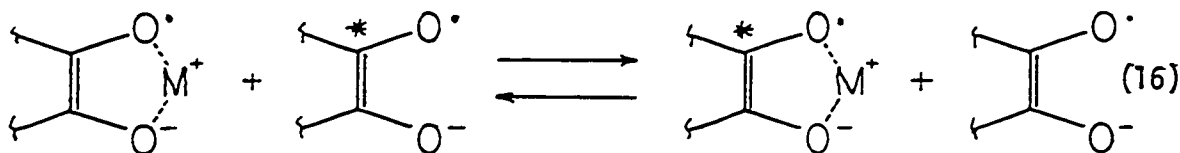
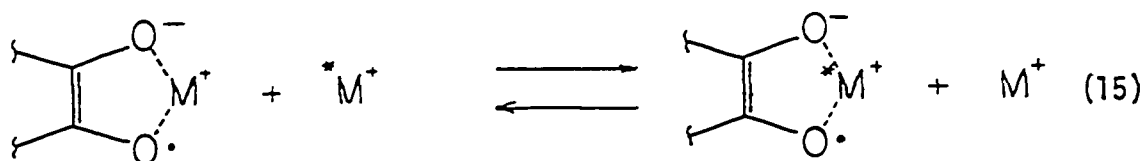
dependent on the spin density at the metal nucleus, which is a function of variables other than whether or not the pair is tight or solvent separated.<sup>49</sup>

The simultaneous observation of both tight and solvent separated ion pairs is the most satisfactory method of distinction between them. When this is the case, it is usually assumed that the spectrum with the larger value of  $\underline{a}^{\text{M}}$  is due to the contact ion pair. This is not completely satisfactory. Conclusive distinction may be made if a mixed solvent system can be found where one of the solvents will form a solvated ion pair, but not the other. Then the ratios of the two species may be measured in various mixtures of the solvents, and the tight ion pair identified as the species which decreases upon addition of the solvent expected to form the separated ion pair. This still requires the assumption that certain solvents (usually glymes) are more prone to form solvated ion pairs. In any event, no evidence has been observed for the semidiones studied which would indicate the existence of two ion pairs with different metal hyperfine coupling



constants. In fact, most of the systems discussed in this work show no metal hyperfine coupling at all.

This lack of observed metal hyperfine in semidione radical ion pairs is probably due, at least in part, to an exchange process such as 15 or 16. The observation of a concentration "window", above or below which



$\underline{a}^{\text{Na}}$  is washed out, is support for this rationale. This is shown for cyclopentenesemidione in Figure 5.

One observation which can be interpreted to argue in favor of tight ion pairs is the apparent perturbation of the radical anion by  $\text{K}^+$  (18-C-6). Recall that this cation causes less of a change in  $\underline{a}^{\text{H}}$  than potassium itself does. In reference 50, it was claimed that an increase in  $\underline{a}^{\text{Na}}$  occurred upon addition of crown ether to a ketyl radical anion-sodium pair. As was mentioned previously, this may be caused by the collapse of a solvent separated ion pair to a tight ion pair. The contrast of this behavior with that of semidione radicals may reflect

the fact that the semidione ion pairs are already tight ion pairs before the addition of the crown ether. However, the solvents are different, the substrates are different, and the values of  $a^M$  have not been shown to be directly proportional to the perturbation of the radical anion caused by the metal cation. These points weaken the argument somewhat.

#### 6. The rate of exchange between ion pair and free ion

The broadening of the esr lines may be used to determine the lifetimes of the species under observation.<sup>20</sup> Consider a pair of lines belonging to two interconverting species in the fast exchange mode, i.e., when the mean lifetime  $\tau$  is less than  $\Delta t$  determined by the uncertainty principle,  $\Delta\nu\Delta t \approx h$ , where  $\Delta\nu$  is the separation of the two lines in frequency units. It is known that under these conditions,

$$\langle \underline{H} \rangle = \frac{p_a \underline{H}_a + p_b \underline{H}_b}{p_a + p_b} \quad (17)$$

and that

$$\Gamma = \Gamma_0 + \gamma_e \tau p_a p_b \langle (\delta \underline{H}_0)^2 \rangle \quad (18)$$

where  $\underline{H}$  is the field position of the observed line,  $p_a$  and  $p_b$  are the probabilities of the observed molecule being in form a or b, respectively,  $\Gamma$  is the observed line width,  $\Gamma_0$  is the intrinsic line width in the absence of exchange (or in the limit of very rapid exchange),  $\gamma_e$  is the magnetogyric ratio of the free electron ( $1.7608 \times 10^7$  rad/sec G), and  $\delta \underline{H}_0$  is the difference between the lines

in gauss. Obviously,  $\tau$  may be determined by means of equation 18.

Since  $\tau$  may be defined in terms of the mean lifetimes of the two species,

$$\tau = \frac{\bar{\tau}_a \tau_b}{\tau_a + \tau_b} \quad (19)$$

it is possible to obtain the individual lifetimes of the ion pairs and the free ion.

One spectrum, taken of cyclopentane-1,2-semidione in the presence of potassium counter ion, was analyzed in this manner.  $\Gamma$  was determined by the equation

$$\Gamma = \frac{\sqrt{3}}{2} \Delta \frac{H}{pp} \quad (20)$$

which relates  $\Gamma$  to the distance between the maximum and minimum of a Lorentzian line. The values of  $\Gamma$  determined were,  $M_I = \pm 2$ ;  $\Gamma = 0.113$ , 0.615 G,  $M_I = \pm 1$ ;  $\Gamma = 0.069$ , 0.433 G. A value of 0.066 G was used for  $\Gamma_0$ , as measured from a spectrum which was not observed to be broadened. This value is very close to the lowfield,  $M_I = \pm 1$ , value of 0.069 G. The spacings between the "frozen" lines were calculated from  $\underline{g}$  and  $\underline{a}^H$  of the ion pair and free ion. The numbers used for  $\delta H_0$  were 1.09, 0.40, 0.98 and 1.67 G for the four wing peaks, in order of increasing field strength.  $\underline{p}_a$  and  $\underline{p}_b$  were determined to be 0.25 and 0.75 where "a" represents the free ion and "b" the ion pair. These probabilities were obtained from the observed  $\underline{g}$  value of the spectrum. From this data an average value of  $5.4 \times 10^{-7}$  sec was calculated for  $\tau$ .

Now, since at equilibrium  $R_f$  and  $R_r$  must be equal,



the lifetime of species b must be three times that of species a, i.e.,  $\rho_b/\rho_a = 1/3$ . So,

$$\tau_b = 3 \tau_a \quad (22)$$

$$\tau = \frac{3\tau_a^2}{4\tau_a} = \frac{3}{4} \tau_a \quad (23)$$

$$\tau_a = 7.2 \times 10^{-7} \text{ sec} \quad (24)$$

$$\tau_b = 2.2 \times 10^{-6} \text{ sec} \quad (25)$$

Thus, it appears that the lifetime of a free ion in this solution is about  $7 \times 10^{-7}$  seconds and that of the ion pair is  $2 \times 10^{-6}$  seconds.

One may notice that the complicating effects of exchange processes such as 15 and 16 above have been neglected. This is reasonable if the sole source of broadening comes from the exchange process (21). The magnitude of  $\Gamma_0$  is very similar to  $\Gamma$  for the sharpest line of the spectra, implying that the intrinsic line width is not being affected by other line broadening processes.

#### 7. The shift of the esr parameters with formation of ion pairs

The question of the underlying cause for the shift in  $g$  and  $a^H$  has been addressed by other workers. It has not been the purpose of this work to study these effects per se. However, a few brief points will be mentioned to familiarize the reader with the concepts involved.

Undoubtedly, the effects of the counter ion on the molecular orbitals of the anion must be considered in detail. Roughly speaking, the difference in the  $g$ -value for a given radical, measured relative to  $g$  for a free electron, is a function of the coupling between the spin angular momentum and the orbital angular momentum of the electron. This being the case, a theoretical calculation of  $g$  requires explicit knowledge of the energy levels of the various molecular orbitals. The value of  $a^H$  is related to the unpaired spin density on the hydrogen nuclei in question, and may be calculated by simple methods, such as the extended Hückel approximation. These simple approaches are successful for calculation of  $a^H$  since the spin density at a given atom is not usually a strong function of the properties of unoccupied molecular orbitals. Glendell, Freed and Fraenkel have attempted to account theoretically for changes of  $a^H$  in semiquinone ion pairs by invoking changes in the electronegativity of the oxygen atoms.<sup>49</sup>

Two mechanisms to explain the (usually) observed change in  $g$  with temperature have been considered. The first is the so-called Hirota model, involving two species, the relative concentrations of which are temperature dependent. This concept should seem familiar by now. The second is the Atherton-Weissman model. In this case the change in  $g$  is caused by a temperature induced change in the population of various vibrational levels of a single species.

Occasionally, ion pair formation is observed where  $a^H$ , but not  $g$ , is seen to differ between species. For example, in one case Reddoch reported a lithium azulene pair where he claimed the change in  $g$  was

less than 0.000006 upon ion pair formation.<sup>24</sup> So far, it appears as if no cases are reported where  $\underline{g}$  changes but  $\underline{a}^H$  remains constant, although it might be expected that ion pairs involving cations with large atomic number may show a  $\underline{g}$  shift while appearing not to show a shift in  $\underline{a}^H$ . Heavy cations have large spin orbit coupling factors and this enhances the sensitivity of  $\underline{g}$  as a probe of ion pairing. (This also explains the low values reported herein for the  $\underline{g}$ -values of cesium and rubidium ion pairs.) This has been seen and discussed by others.<sup>24,25,36,39,50,51</sup>

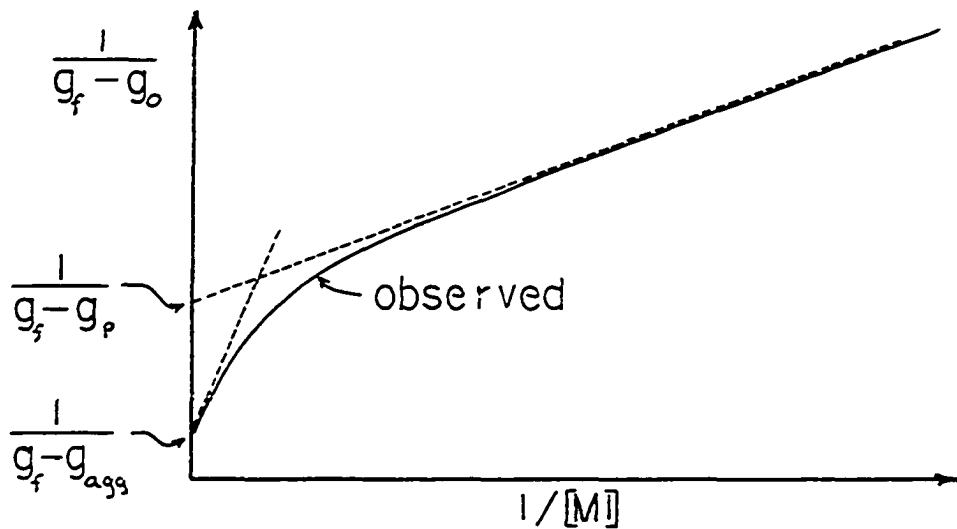
A case has also been reported where the change in  $\underline{g}$  with temperature was zero, but the change in  $\underline{a}^H$  over the same temperature range was not.<sup>36</sup> These temperature data were then used to obtain the enthalpy and entropy of formation for the ion pairs. This seems a questionable procedure since in this case the change of  $\underline{g}$  upon formation of the ion pair was not equal to zero.

The intention of this discussion is to convince the reader that the observed  $\underline{g}$  and  $\underline{a}^H$  shifts in semidione ion pairs are not unusual, but are not well understood, either.

#### 8. Apparent activity coefficients ( $\gamma_{app}$ )

The apparent activity coefficients were introduced in an ad hoc manner to "straighten out" a series of points on a plot. No one can doubt that the activity of potassium and iodide ions is something other than unity in DMSO solutions at concentrations greater than 0.01 M. However, it is a significant jump to go from this belief to the "observed" activity plotted in Figure 14. Although a complete justification of this intellectual leap may not be possible, it warrants consideration.

One alternative explanation for curvature in plots like those of Figure 13A is the existence of more than one equilibrium. The first of these would be the ion pairing equilibrium under consideration all along. A second could be an equilibrium involving the formation of an ion aggregate from the ion pair (e.g., triple ion, quadruple ion, etc.). One essential characteristic this aggregate would have to possess is a smaller  $g$  value than the ion pair. This is true because the observed  $g$  value continues to decrease with higher concentration of counter ion. To clarify this consider the following plot:



Let us assume for the moment the species at high  $M^+$  concentrations is a triple ion,  $PM^{+}$ . Now in addition to the previously considered equilibrium a second one, namely



must be accounted for. This equilibrium by itself can be treated

similarly to the simple ion pairing case, except that the two  $g$ -values of interest are  $g_p$  and  $g_{\text{aggregate}}$ . Looking at the plot, we can assume that at low  $M^+$  concentrations the triple ion is unimportant, and that the extrapolation of this portion of the curve to  $[M^+]$  equal to infinity yields an intercept, the value of which provides  $g_p$ . Now, the part of the curve at high concentration is dominated by the equilibrium for triple ion formation. Extrapolation of this portion of the curve to  $[M^+]$  equal to infinity gives an intercept which provides  $g_{\text{agg}}$ . It is clear that if this model is to reproduce the observed curve (heavy line)  $g_p$  must be larger than  $g_{\text{agg}}$ . The inclusion of other types of aggregates complicates the matter but cannot remove the fundamental requirement that  $g_p$  be larger than the (combined)  $g_{\text{agg}}$ . With this in mind, the formation of aggregates was ruled out by the following observations: A) adding excess lithium iodide to a DMSO solution of cyclohexanesemidione does not result in the change of the spectral parameters observed at ca. 0.1 M lithium iodide. This spectrum shows alkali metal splitting from one lithium nucleus. B) Adding lithium iodide to a solution of cyclopentanesemidione to which one equivalent (based on  $K^+_{\text{DMSO}^-}$ ) of [2.2.2]-cryptand has been added results in the appearance of a species split by one lithium atom and the disappearance of the signal attributed to the free ion. The spectrum due to the ion pair does not change upon further addition of lithium iodide, although the spectral intensity decreases. (Unfortunately, in this case the spectrum finally disappears when slightly more than one equivalent of iodide salt has been added.) C) Addition of sodium iodide to a DMSO solution of cyclopentanesemidione



results in a slight shift of the lines, then the appearance of two sets of lines, one the ion pair and one the free ion, followed by coalescence of the spectrum to one set of lines, the  $g$ -value of which is the same as that of the ion pair. If a very large amount (0.8 M) of sodium iodide is added, the  $g$ -value does shift to a lower value, but only slightly.

The question of formation of ion aggregates is a serious one. A number of workers have reported seeing various kinds of multiple ions. In some cases splitting from two alkali metal nuclei was seen in the esr spectrum.<sup>29,39,52-55</sup> The existence of aggregates has also been established by other means.<sup>41</sup> Despite this, I feel the correct conclusion in this case is that cyclic semidiones in DMSO solution do not form multiple ions with esr parameters differing from those of the simple ion pair, except perhaps at very high concentrations of counter ion.

It is reasonable to enquire as to the fundamental nature of  $\gamma_{app}$ . If the principal process involved in the removal of potassium from solution is ion pairing of potassium with iodide,



it is possible to derive an expression for  $\gamma_{app}$  involving  $K'$ ,  $[I^-]$ , and the thermodynamic activity coefficients of the various species.

From 27,

$$K' = \frac{[KI]}{[K^+][I^-]} \cdot \frac{\gamma_{KI}}{\gamma_{K^+}\gamma_{I^-}} \quad (28)$$

$$[\text{KI}] = \frac{K'[\text{K}^+][\text{I}^-]\gamma_{\text{K}^+}\gamma_{\text{I}^-}}{\gamma_{\text{KI}}} \quad (29)$$

where  $[\text{KI}]$  refers to the actual concentration of potassium iodide in solution.

From the equation defining ion pairing of the semidione,



we have

$$K = \frac{[\text{P}]}{[\text{F}][\text{K}^+]} \cdot \frac{\gamma_{\text{P}}}{\gamma_{\text{F}}\gamma_{\text{K}^+}} = \frac{[\text{P}]}{[\text{F}][\text{KI}]_{\text{T}}\gamma_{\text{app}}} \quad (31)$$

since we agreed that all the deviation from ideality would be absorbed by  $\gamma_{\text{app}}$ . Therefore,

$$\frac{\gamma_{\text{P}}}{\gamma_{\text{F}}\gamma_{\text{K}^+}[\text{K}^+]} = \frac{1}{[\text{KI}]_{\text{T}}\gamma_{\text{app}}} \quad (32)$$

or

$$[\text{KI}]_{\text{T}} = \frac{\gamma_{\text{F}}\gamma_{\text{K}^+}[\text{K}^+]}{\gamma_{\text{P}}\gamma_{\text{app}}} \quad (33)$$

where it should be understood that  $[\text{KI}]_{\text{T}}$  is the measured concentration of potassium iodide.

However, by definition

$$[\text{KI}]_{\text{T}} - [\text{K}^+] = [\text{KI}] \quad (34)$$

and from 29 and 34,

$$[\text{KI}]_{\text{T}} - [\text{K}^+] = \frac{K'[\text{K}^+][\text{I}^-]\gamma_{\text{K}^+\gamma_{\text{I}^-}}}{\gamma_{\text{KI}}} \quad (35)$$

and from 33 and 35,

$$\frac{\gamma_{\text{f}}\gamma_{\text{K}^+}[\text{K}^+]}{\gamma_{\text{p}}\gamma_{\text{app}}} - [\text{K}^+] = \frac{K'[\text{K}^+][\text{I}^-]\gamma_{\text{K}^+\gamma_{\text{I}^-}}}{\gamma_{\text{KI}}} \quad (36)$$

$$\frac{\gamma_{\text{f}}\gamma_{\text{K}^+}}{\gamma_{\text{p}}\gamma_{\text{app}}} - 1 = \frac{K'[\text{I}^-]\gamma_{\text{K}^+\gamma_{\text{I}^-}}}{\gamma_{\text{KI}}} \quad (37)$$

$$\frac{\gamma_{\text{p}}\gamma_{\text{app}}}{\gamma_{\text{f}}\gamma_{\text{K}^+}} = \frac{\gamma_{\text{KI}}}{K'[\text{I}^-]\gamma_{\text{K}^+\gamma_{\text{I}^-}} + \gamma_{\text{KI}}} \quad (38)$$

$$\gamma_{\text{app}} = \frac{\gamma_{\text{KI}}\gamma_{\text{f}}\gamma_{\text{K}^+}}{K'[\text{I}^-]\gamma_{\text{K}^+\gamma_{\text{I}^-}}\gamma_{\text{p}} + \gamma_{\text{KI}}\gamma_{\text{p}}} \quad (39)$$

or, eliminating single ion activities,

$$\gamma_{\text{app}} = \frac{\gamma_{\text{KI}}\gamma_{\pm}}{K'[\text{I}^-]\gamma'_{\pm}\gamma_{\text{p}} + \gamma_{\text{KI}}\gamma_{\text{p}}} \quad (40)$$

where  $\gamma_{\pm}$  is the mean activity coefficient of free semidione and potassium, and  $\gamma'_{\pm}$  is the mean activity coefficient of potassium and iodide.

It appears, then, that  $\gamma_{\text{app}}$  is actually a complex term containing a number of coefficients.

For die-hards, substituting  $\gamma_{app}$  from equation 40 back into equation 31 gives

$$K = \frac{[P]}{[F][KI]_T \gamma_{app}} = \frac{[P][K'[I^-]\gamma_{\pm}'\gamma_p + \gamma_{KI}\gamma_p]}{[F][KI]_T \gamma_{KI}\gamma_{\pm}} \quad (41)$$

Estimates for  $\underline{K}'$ , the ion pairing constant of potassium iodide in DMSO, are available. Stevenson has obtained a value for  $\underline{K}'$  of 4.3, unfortunately in the solvent HMPA.<sup>28</sup> His method was based on a comparison of  $\underline{K}'$  with that of  $\underline{K}$  for  $KNO_3$ , a value known from conductimetric studies. Ion pairing with a radical anion, monitored by esr, was his probe. One group has worked with association constants for potassium iodide, as determined by conductimetric studies.<sup>56a</sup> They have investigated a number of solvents and arrive at a value for  $\underline{K}'$  of about 5 in DMSO. Unless one or more of the activity coefficients is radically different from one by the time a concentration of 0.005  $\underline{M}$  is reached, it is hard to see how this value of  $\underline{K}'$  allows for appropriate values of  $\gamma_{app}$ . It would appear that a value for  $\underline{K}'$  between 50 and 100 would be more realistic. As there is no way to establish the behavior of the combined activity coefficients, the point is moot.

Fuoss makes an interesting point when he claims that an association constant of less than about 0.1 is meaningless, since this is the value obtained for uncharged hard spheres of appropriate radius. Yet ion pairing constants significantly less than that value have been measured.<sup>5</sup> Is it true that " $K^+$ " available for conducting current is identical to " $K^+$ " available for ion pairing? Perhaps not. One experiment to consider would be to measure a series of solutions of potassium

iodide in DMSO with  $^{39}\text{K}$  or  $^{127}\text{I}$  nuclear magnetic resonance. A treatment similar to the one used to obtain  $K$  for semidiones may be utilized, except that now the chemical shift is the parameter being measured. The difficulty involved is that to obtain the chemical shift for free potassium or iodide, a very dilute solution must be used, which creates problems in regards to spectrometer sensitivity. There is also a possibility that no change in the chemical shift will be observed. It has been reported that  $^{23}\text{Na}$  shows no variation in chemical shift with changes of sodium iodide concentration in DMSO solution.<sup>56b</sup> This has been ascribed to a lack of tight ion pair formation. Since the larger potassium ion is probably not as well solvated as is sodium, perhaps the chemical shifts of potassium could be observed to change. Nevertheless, one is bothered by the problem that some type of ion pair or ion aggregate of potassium iodide, other than a contact ion pair, which might have a significant ion pairing constant relative to the semidione may be forming in DMSO solutions.

In summary, although the use of apparent activity coefficients appears to be the most reasonable method of accounting for the curved plots (a sample of which is shown in Figure 13A) there are problems which remain to be worked out in fitting the numbers obtained to a physical model constant with all the data available.

#### 9. Conclusion of section II-C: Discussion of ion pairing in semidiones

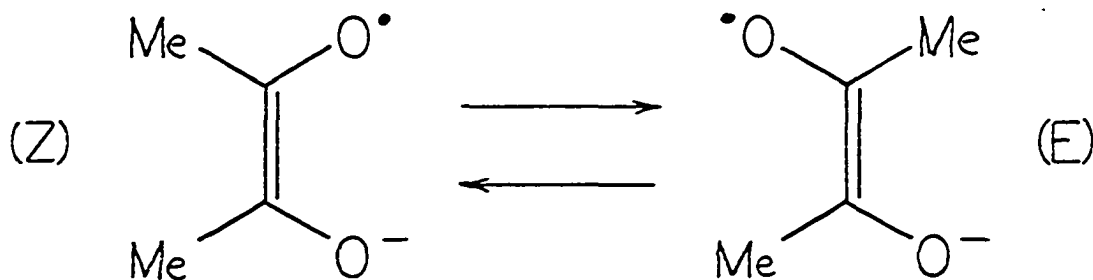
Hopefully, the reader is now convinced that: a) cyclosemidiones do ion pair in DMSO; b) the size of the cation determines the relative

perturbation which that ion has on the semidione; c) the value of the ion pairing constant which a specific semidione-cation pair exhibits depends on the comparative ability of the semidione to 'solvate' the cation, relative to DMSO. (Note that so far we have ignored solvation of the free semidione. Because all the cyclic semidiones have approximately equal geometries, because the semidiones have a diffuse charge, and because DMSO solvates cations better than anions, this is a reasonable omission.)

## III. ION PAIRING WITH BIACETYL SEMIDIONE

## A. Introduction

The biacetyl radical anion can exist in either a Z or an E configuration. An early attempt to obtain the ratio of E to Z by using a



chemical trap was made by Bauld.<sup>57</sup> The first esr work on acyclic semidione systems seems to have been reported soon after this by Luckhurst and Orgel.<sup>58</sup> These workers assigned the E configuration to di-tert-butyl semidione in the presence of both sodium and potassium counterions. They also described the diphenyl semidione radical as being of the Z configuration, again in the presence of both potassium and sodium. Since that time, a number of more extensive reports have appeared.<sup>45,59-66</sup> Among other things, these papers have indicated that perfluorobiacetyl radical anions do not ion pair in DMSO,<sup>45</sup> that ion pairing seems to be a controlling factor in  $[\text{E}]/[\text{Z}]$  ratios for the biacetyl semidione system in DMSO,<sup>59,62,65,66</sup> that other more highly substituted acyclic semidiones also form ion pairs,<sup>60,64</sup> and that biacetyl radical anions do not appear to be affected by the addition of alkali metal cations in aqueous solution.<sup>63</sup> Comments have been made regarding the different  $a^{\text{H}}$  values

for E and Z biacetyl semidione.<sup>61</sup> There has been an attempt to calculate the  $g$  values of [E]- and [Z]-glyoxyl radical anions by an ab-initio method.<sup>67</sup>

By the beginning of this work on biacetyl, the [E]/[Z] ratio had been observed to change with varying amounts of cation or with different cations. This was attributed to a change in the effective chelating ability of the Z isomer with the various cations.

It was also known that the Z configuration has a larger value of  $a^H$  than does the E, and that  $g$  for the E isomer appears to be larger than  $g$  for the species attributed to the Z radical ions.

## B. Results

### 1. Lithium counter ion

Addition of lithium iodide to a solution of biacetyl radical anions resulted in a decrease in the signal intensity. The esr parameters obtained at one concentration of lithium are reported in Figure 18. Lithium hyperfine coupling was observed. This represents essentially all the work done on solutions containing lithium counter ion, during this investigation.

### 2. Sodium counter ion

A small amount of data was obtained for the biacetyl semidione system in the presence of sodium iodide. The values of  $g$ ,  $a^H$ , and [E]/[Z] as determined in DMSO solution containing added sodium iodide are also reported in Figure 18. More information regarding the behavior of



biacetyl radicals in the presence of sodium counter ions may be obtained from references 59 and 68.

### 3. Potassium counter ion

The majority of the work with biacetyl semidione reported in this thesis deals with experiments done when potassium was the counter ion. Figure 18 contains the values of the esr parameters obtained at various concentrations of potassium iodide. As expected, the  $g$ -values increase and the  $a^H$ -values decrease as the concentration of potassium ions decreases. Simultaneously, the values for the ratio  $[E]/[Z]$  are seen to increase.

A DMSO solution of biacetyl radicals was observed at various temperatures. The solution was saturated with potassium iodide at room temperature. The data are presented in Figure 19.

A few spectra were obtained in solvents other than DMSO. For example, spectra obtained in tetrahydrofuran (THF) and dimethylformamide (DMF) are shown in Figure 20. With these solvents the solutions could be cooled to  $-90^{\circ}\text{C}$ . Two spectra, one taken in the presence of potassium ions, which were measured at  $-90^{\circ}\text{C}$  are presented in Figure 21.

### 4. Rubidium counter ion

When solutions of biacetyl semidione containing rubidium iodide are prepared, the  $[E]/[Z]$  ratio becomes rather large. This makes determination of the ratio and the  $[Z]$  species' esr parameters difficult. Data taken over a range of concentrations are presented in Figure 18. Figure 22 shows a representative spectrum.

Biacetyl semidione						
MI	$g_E$	$\underline{a}_E^H$ (G)	$g_Z$	$\underline{a}_Z^H$ (G)	$[E]/[Z]$	Notes
LiI	2.00491	6.17	2.00477	7.70	0.2 (0.7 M)	$a^{Li} = 0.5$
NaI	2.00495	5.96	2.00485	7.40	0.2 (0.8 M)	
[KI] (molar)						
1.31	2.004996	5.89	2.004913	7.21	1.1	
0.66	2.005022	5.82	2.004918	7.17	1.6	
0.35	2.005040	5.77	2.004928	7.13	3.2	
0.33	2.005041	5.77	2.004927	7.13	2.7	
0.17	2.005054	5.74	2.004935	7.10	5.3	
0.16	2.005056	5.73	2.004939	7.09	5.1	
0.088	2.005061	5.71	2.004943	7.08	9.6	
0.082	2.005061	5.71	2.004944	7.03	8.4	
0.044	2.005067	5.70	2.004951	7.06	17.3	
0.022	2.005067	5.69	2.004957	7.04	23.0	
0.011	2.005065	5.69	2.004962	7.02	30 - 35	
[RbI] (molar)						
0.61	2.005027	5.77	2.004799	7.08	19.0	
0.30	2.005041	5.74	2.004814	7.05	30.0	
0.15	2.005051	5.72	---	---	---	
0.76	2.005057	5.71	---	---	---	
0.38	2.005059	5.70	---	---	---	
[CsI] (molar)						
1.0	2.005103	5.80	---	---	40 - 50	
0.59	2.005081	5.76	---	---	---	
0.30	2.005071	5.73	---	---	---	
0.15	2.005067	5.72	---	---	---	
0.074	2.005073	5.71	---	---	---	
0.037	2.005071	5.70	---	---	---	
0.018	2.005068	5.69	---	---	---	

Figure 18. The values of  $g$ ,  $\underline{a}^H$ , and  $[E]/[Z]$  obtained from biacetyl semidione in the presence of various counter ions

MI	$g_E$	$\frac{a_E^H}{E}$	$g_Z$	$\frac{a_Z^H}{Z}$	$[E]/[Z]$	Notes
[K <sup>+</sup> (18-C-6)I] (molar)						
0.43	2.005066	5.71	2.004989	6.97	13.4	
0.41	2.005060	5.71	2.004985	6.97	13.7	
0.40	2.005059	5.70	2.004983	6.97	14.8	
0.37	2.005064	5.70	2.004988	6.97	---	
0.21	2.005065	5.70	2.004990	6.96	17.5	
0.20	2.005060	5.71	2.004986	6.97	18.6	
0.18	2.005066	5.70	2.004993	6.96	22.0	
0.10	2.005060	5.71	2.004993	7.00	24.0	
0.090	2.005066	5.70	2.005001	6.95	23.0	
0.045	2.005065	5.70	---	---	---	
0.023	2.005068	5.70	---	---	---	
K <sup>+</sup> DMSO <sup>-</sup> /[2.2.2]-cryptand						
	2.005075	5.67	2.005109	6.75	125.0	
K <sup>+</sup> DMSO <sup>-</sup> (CH <sub>3</sub> ) <sub>3</sub> N <sup>+</sup> CH <sub>2</sub> φ I <sup>-</sup>						
0.10	2.005063	5.71	2.005075	6.88	35.0	0.80
0.05	2.005070	5.70	2.005082	6.86	32.0	0.40
0.025	2.005070	5.69	2.005082	6.83	~50.0	0.20
0.012	2.005069	5.68	---	---	---	0.10
Saturated (CH <sub>3</sub> ) <sub>4</sub> N <sup>+</sup> I <sup>-</sup>						
0.10 M K <sup>+</sup> DMSO <sup>-</sup> [2.2.2]-cryptand						
	2.005075	5.67	2.005102	6.78	~100.0	

Figure 18. (Continued)

## Biacetyl semidione

Saturated potassium iodide/DMSO/0.10 M  $K^+DMSO^-$ 

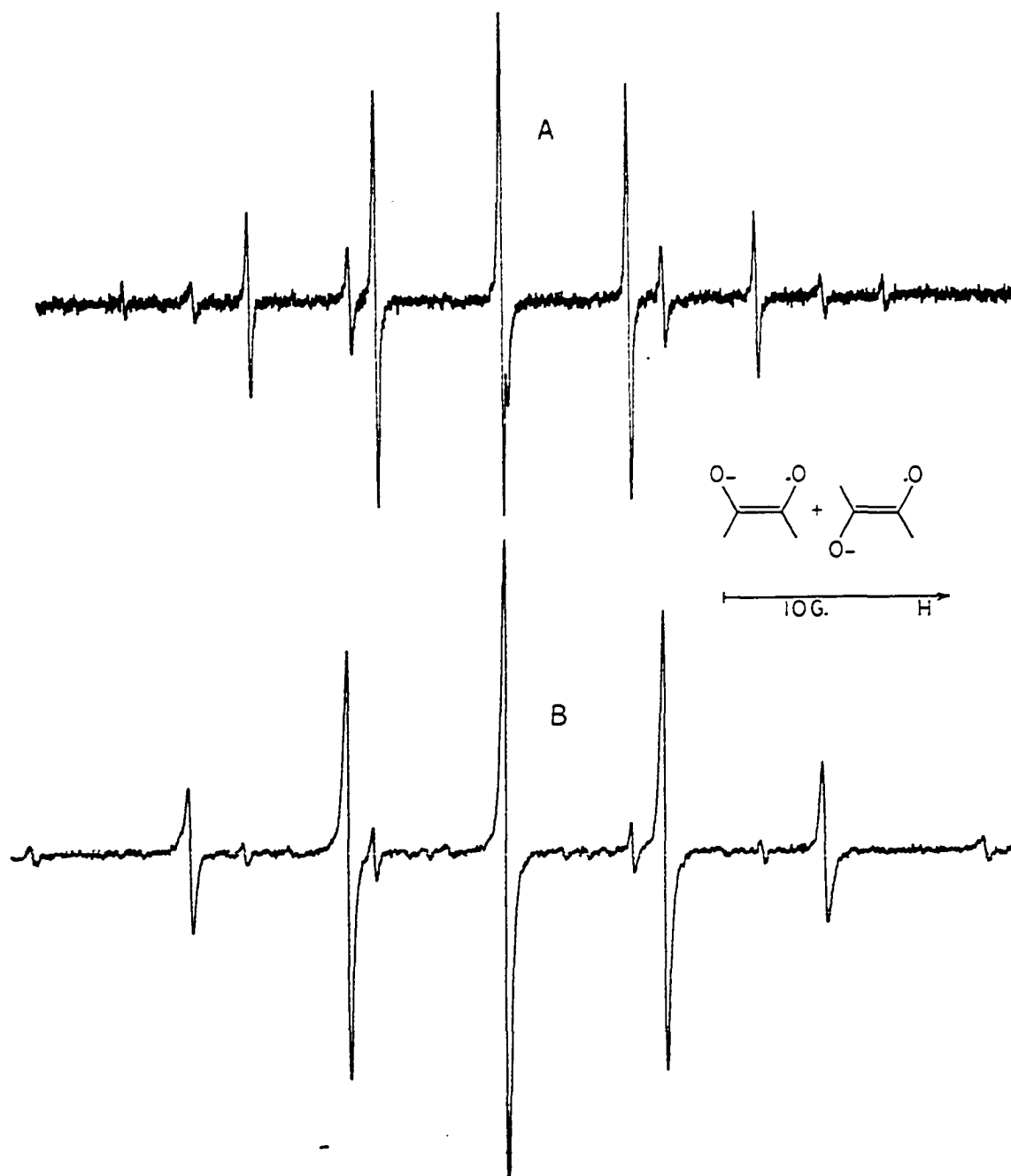
T(C)	$g_E$	$a_E^H$ (G)	$g_Z$	$a_Z^H$ (G)	$[E]/[Z]$
25	2.004980	5.94	2.004910	7.26	---
30	2.004968	5.94	2.004907	7.27	1.0
40	2.004967	5.94	2.004910	7.26	0.94
60	2.004967	5.93	2.004911	7.26	0.85
80	2.004971	5.92	2.004918	7.25	0.75
100	2.004968	5.94	2.004929	7.27	0.63

0.1 M  $K^+DMSO^-$ /[2.2.2]-cryptand

T(C)	$[E]/[Z]$
15	143
30	121
50	92
60	81
70	74

---

Figure 19. Values of  $g$ ,  $a^H$ , and  $[E]/[Z]$  for biacetyl semidione at various temperatures



- A. Dimethylformamide solvent
- B. Tetrahydrofuran solvent

Figure 20. ESR spectra of biacetyl semidione generated with potassium dimsylate

Figure 21. ESR spectra of biacetyl semidione at  $-90^{\circ}\text{C}$  in dimethylformamide, the lines marked with an "X" are the free ion

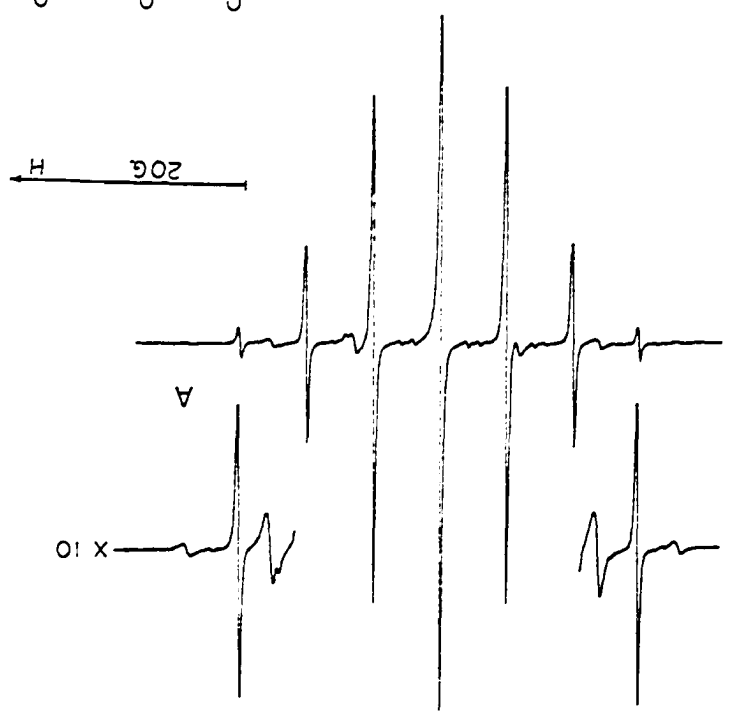
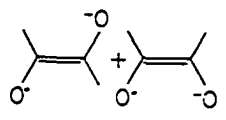
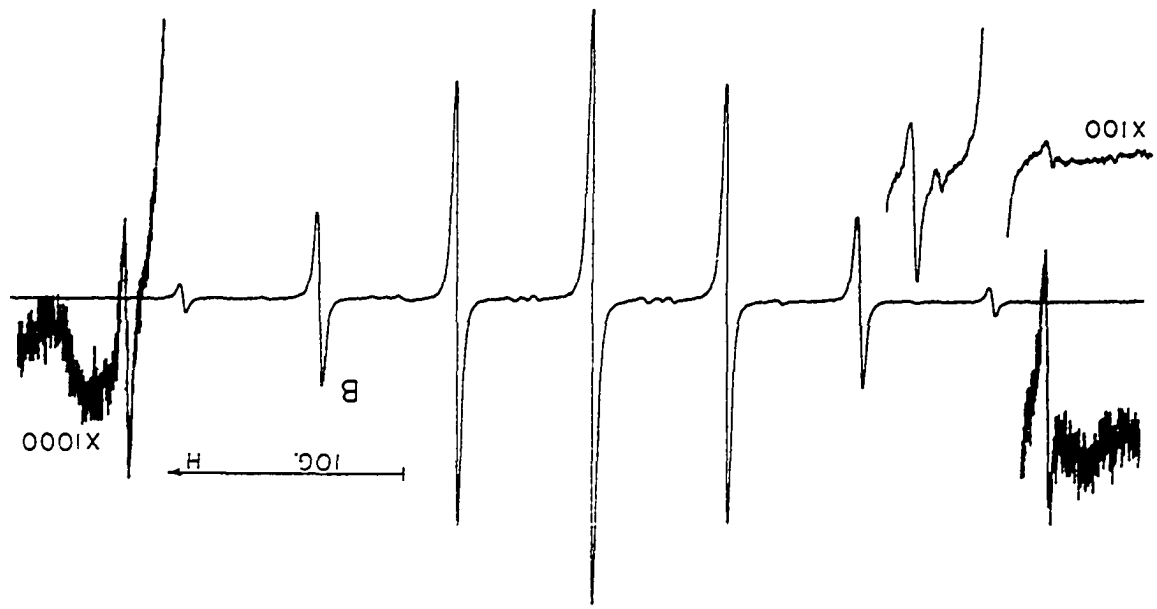
- A. Cesium tert-butoxide was the base
- B. Potassium tert-butoxide was the base



Figure 22. ESR spectra taken of biacetyl semidione in the presence of various salts

- A. Rubidium iodide
- B. Cesium iodide





### 5. Cesium counter ion

When solutions of biacetyl radicals are prepared in the presence of cesium iodide, only the E isomer appears to be present. At high spectrometer gains a second species does appear, this being due to the Z radicals. Figure 18 contains some data for a range of concentrations of cesium iodide. Figure 22 shows a representative spectrum. If DMF is used as the solvent, a spectrum could be observed at low temperature where two different methyl groups appeared to be present (see Figure 21).

### 6. K<sup>+</sup>(18-C-6) counter ion

A number of data were obtained for solutions where K<sup>+</sup>(18-C-6) was the counter ion. These are presented in Figure 18. Only the esr parameters of the Z isomer change, presumably because the E species does not pair with this counter ion.

### 7. K<sup>+</sup>([2.2.2]-cryptand) counter ion

The values of a<sup>H</sup> and g for the "free" biacetyl radical anions are presented in Figure 18. These were obtained in a solution of 0.1 M K<sup>+</sup>DMSO<sup>-</sup> with an excess of [2.2.2]-cryptand present. Figure 23 shows the spectrum obtained for biacetyl semidione under these conditions.

A series of [E]/[Z] ratios were determined at various temperatures in the presence of cryptand. These values are reported in Figure 19.

### 8. Other counter ions

In order to determine the effects of ionic strength on the [E]/[Z] ratio, a few experiments were done with added quaternary ammonium iodides. The results from these investigations are also shown in Figure 18.

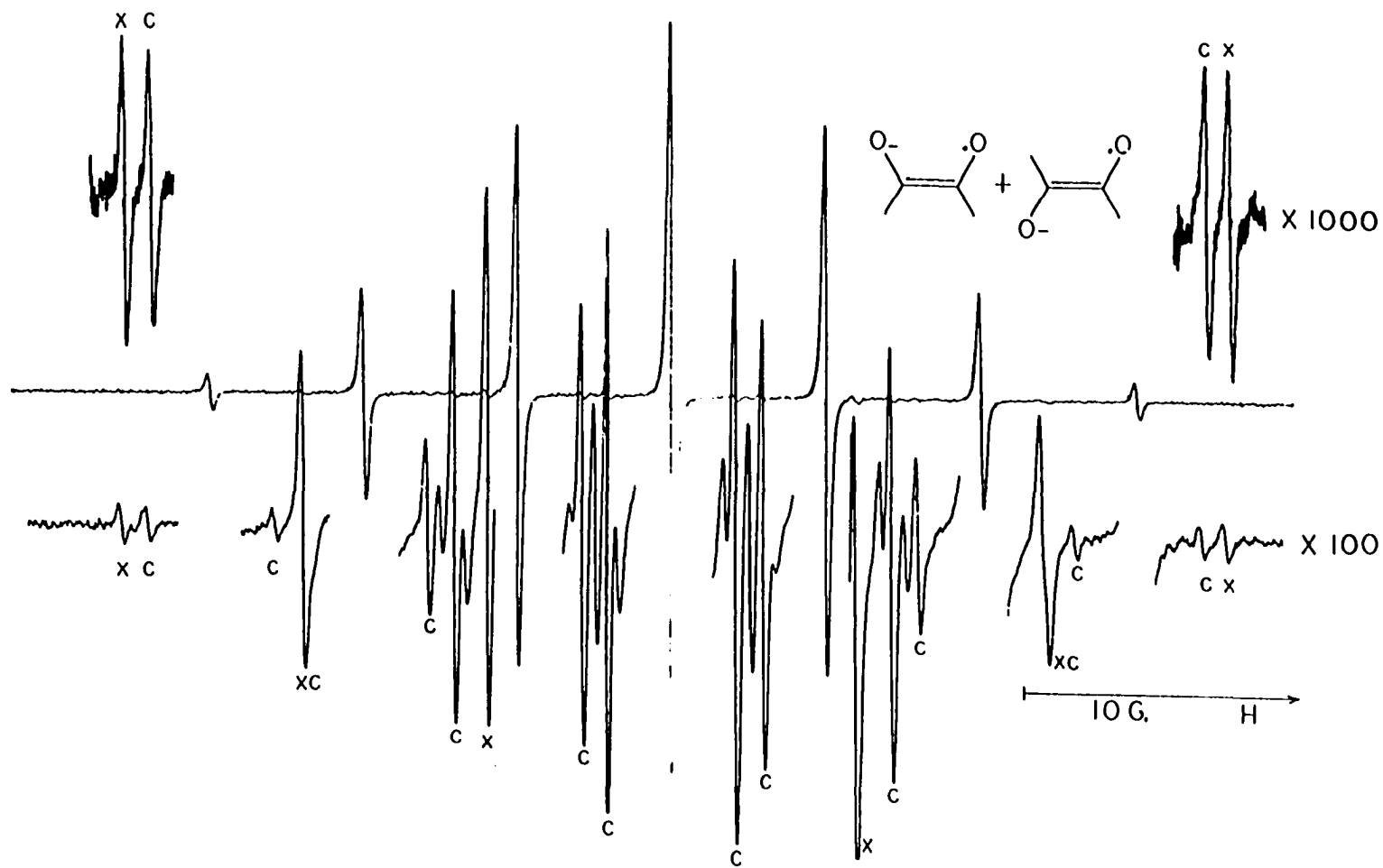


Figure 23. ESR spectrum of biacetyl semidione in the presence of [2,2,2]-cryptand, where the peaks marked with a "C" are <sup>13</sup>C satellites from the E isomer and the peaks marked with an "X" are the lines of the Z isomer

## C. Discussion

1. General observations

Qualitatively speaking, the biacetyl system is fairly well understood. Indeed, the outlines of its behavior have been established for some time.<sup>65,66</sup> Figure 18 shows that the  $[E]/[Z]$  ratio increases along the series lithium, sodium, potassium, rubidium, cesium.

Figure 24 is a summary of the equilibrium constants and values of  $[(a_p^H - a_f^H)/a_f] \cdot 100$  obtained for the biacetyl system. These numbers were determined by the dilution methods discussed in section II of this dissertation. The observed increase in the  $[E]/[Z]$  ratio presumably arises from a decrease in the equilibrium constant for pairing of the  $Z$  isomer with the larger cations. Unfortunately, this could not be verified experimentally since solutions containing rubidium iodide or cesium iodide lose all  $Z$  material upon one or two dilutions. At this point it appears that ( $Z$ )-biacetyl semidione behaves much like a typical cyclic semidione, compare Figure 24 to Figure 15.

The  $E$  ion pair has the metal cation located near one end of the molecule, adjacent to one of the oxygens. This is indicated by the spectra obtained in DMF at low temperature, where the usual septet of lines becomes a quartet of quartets. See Figure 21 for examples of this where the metal ion was either potassium or cesium. It should be noted that the process which averages the two methyls is not completely frozen out on the esr scale even at  $-90^\circ\text{C}$ . (Also note that the spectrum in Figure 21 which was taken with potassium as the counter ion was recorded after a brief irradiation with UV light to enhance the signal.) No

## Biacetyl semidione

	Cation <sup>a</sup>	$\underline{g}^b$	$\underline{a}^H^b$	K	$[(\underline{a}_p^H - \underline{a}_f^H)/\underline{a}_f^H] \cdot 100$
(E) -	"free"	2.00507*	5.66*	---	---
	K	2.00488	6.23	4	10.0
	Cs <sup>c</sup>	2.00496*	6.6(3)*	---	5.8
					5.5(3)*
(Z) -	"free"	2.00511*	6.76*	---	---
	Li	2.00477*	7.70*	large	13.9
	Na	2.00485*	7.40*	large	9.5
	K	2.00491	7.26	250	7.4
	K <sup>+</sup> (18-C-6)	2.00489	6.97	124	3.1

---

<sup>a</sup>"Free" refers to a DMSO/K<sup>+</sup>DMSO<sup>-</sup> solution containing excess [2.2.2]-cryptand.

<sup>b</sup>Numbers marked with an \* were measured directly from a single spectrum.

<sup>c</sup>-90 C, in DMF.

---

Figure 24. Summary of  $\underline{g}$ ,  $\underline{a}^H$ , ion pairing constants and  $[(\underline{\Delta a}^H)/\underline{a}_f^H] \cdot 100$  for various biacetyl semidione ion pairs

metal hyperfine has been observed for the E species. This is similar to the results obtained for the simple E ion pairs of perfluorobiacetyl radical anions.<sup>45</sup> While the Z isomer did show metal hyperfine interaction when the cation was lithium, none of the other cations studied gave spectra exhibiting metal hyperfine. Wallraff has observed sodium hyperfine in (Z)-biacetyl under different conditions.<sup>68</sup> It is interesting to note that for rubidium, and more obviously for cesium, the lines due to the Z isomer are broadened (see Figure 22). With cesium, the effect is gross enough that special care must be taken if the lines from the Z species are to be observed. This effect may be due in part to an intermolecular electron transfer process, a hypothesis supported by the observation that in the rubidium case the lines further from the center of the spectrum are broadened more than those at the center.<sup>69</sup> Alternatively, the effect might be caused by unresolved metal hyperfine splitting, although this seems less likely. Since the Z species becomes too weak to observe after only a few dilutions, it is not possible to say whether or not the lines remain broad at lower cation concentrations. This effect has been noticed for cyclohexane-1,2-semidione when paired with cesium. In that case the lines sharpen as the cation concentration decreases. See Figure 10 for a spectrum of the C<sub>6</sub>-cesium ion pair.

Apparently, the [E]/[Z] ratio of the free ions is not appreciably effected by ionic strength since a DMSO solution saturated with tetramethylammonium iodide containing 0.1 M K<sup>+</sup>DMSO<sup>-</sup> [2.2.2]-cryptand exhibits a ratio of about 100. On the other hand, the apparent ion pairing

constants are sensitive to the presence of quaternary ammonium iodides. Thus, when a solution of radicals is prepared in DMSO which is 0.1 M in  $K^+DMSO^-$  and 0.8 M in trimethylbenzylammonium iodide,  $g_E$  and  $g_Z$  are similar in value, and the amount of  $E$  species is enhanced compared to the case without the salt. Inspection of the formula for  $\gamma_{app}$  derived previously,

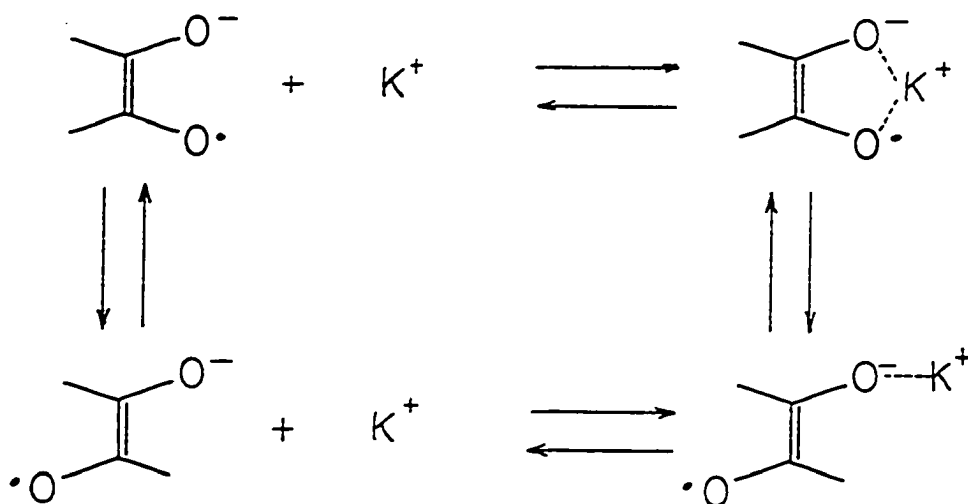
$$\gamma_{app} = \frac{\gamma_{KI}\gamma_f\gamma_{K^+}}{K^+[I^-]\gamma_p\gamma_{K^+}\gamma_{I^-} + \gamma_{KI}\gamma_p} \quad (39)$$

reveals that a decrease in  $\gamma_{app}$  is expected when the iodide concentration is increased. Therefore, this experiment does not really address the question of the effects of ionic strength on the activities of the various species. Note that quaternary ammonium salts do not change the esr parameters of the free ions.

The theoretical work mentioned previously reports values of  $g_Z = 2.00454$  and  $g_E = 2.00512$  for glyoxyl radical anion.<sup>67</sup> It is interesting to note that the calculated order of the  $g$ -values is reversed from the order observed for dimethylsemidione, *e.g.*,  $g_Z < g_E$  was calculated but  $g_Z > g_E$  is observed. What is true and what is observed in a typical experiment is that the ion pair of the  $Z$  isomer has a lower  $g$  value than does the free  $E$  isomer.

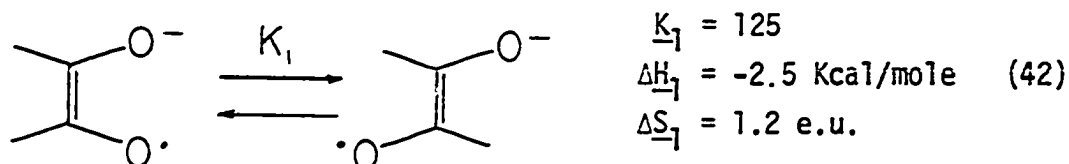
## 2. Thermodynamic parameters

In principle, the following set of equilibria exist in solution,



For the moment ignore the formation of multiple ion aggregates.

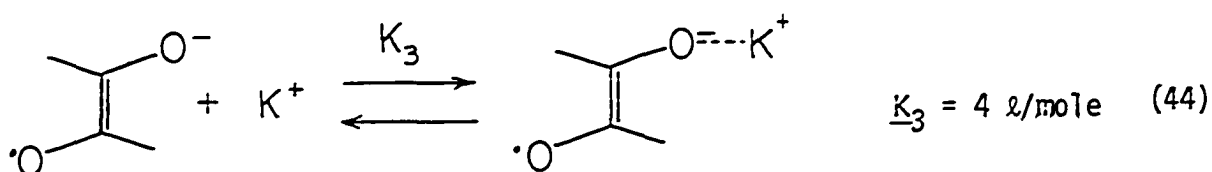
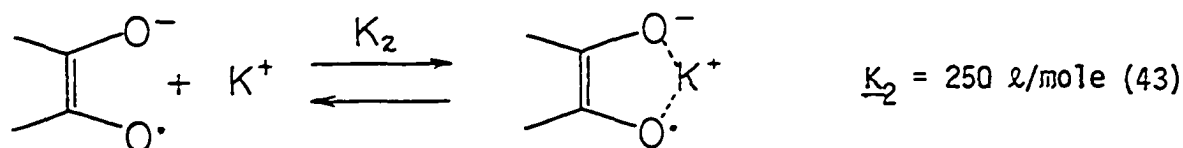
The value of the E-Z equilibrium for the free ions,



may be obtained simply by observing the  $[E]/[Z]$  ratio when an excess of [2.2.2]-cryptand is present. This value is about 125 at room temperature. The results of the temperature study which are reported in part of Figure 19, may be used to calculate  $\Delta H$  and  $\Delta S$  for the interconversion by standard means. (Recall that  $-\Delta H/RT + \Delta S/R = \ln K$ .) This gives values of -2.5 Kcal/mole for  $\Delta H$  and 1.2 e.u. for  $\Delta S$ .

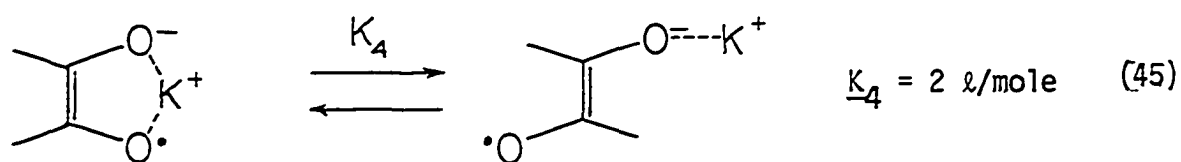


The two ion pairing constants,  $\underline{K}_2$  and  $\underline{K}_3$ ,

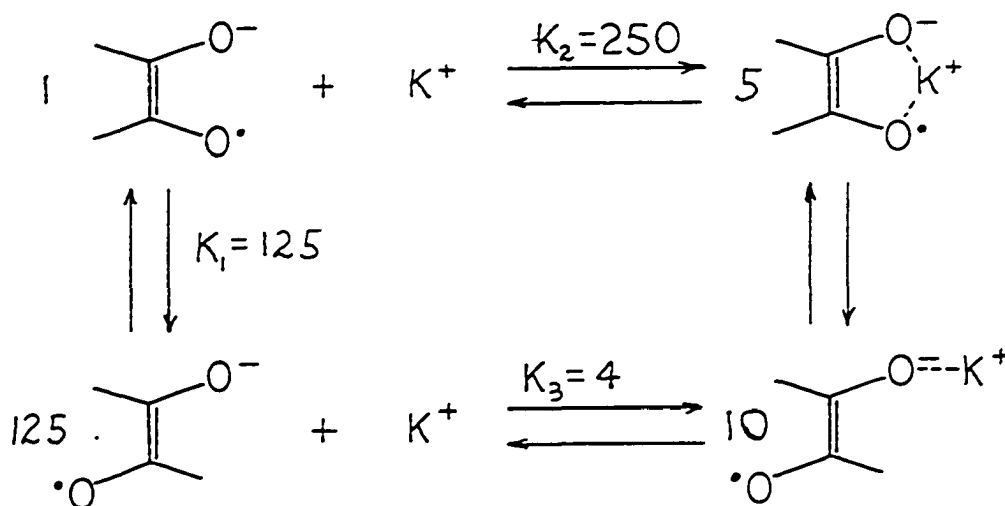


were obtained via the standard dilution technique used in the previous section of this dissertation, from the appropriate data in Figure 18.

The plot of  $\gamma_{\text{app}}$ , as determined for potassium, was utilized. The values of  $\underline{K}_2$  and  $\underline{K}_3$  were found to be 250 and 4, respectively. These two results, plus the previous one, fix the value of the last equilibrium constant,  $\underline{K}_4$ ,



as 2, since the product  $\underline{K}_2 \cdot \underline{K}_4 \cdot 1/\underline{K}_1 \cdot 1/\underline{K}_3$  must be equal to 1. This number is at least of the correct order of magnitude, as verified by the back calculation of  $[\underline{E}]/[\underline{Z}]$  ratios, e.g.; at 0.05 M potassium iodide concentration  $[\text{K}_{\text{app}}^+]$  is 0.02 M so,

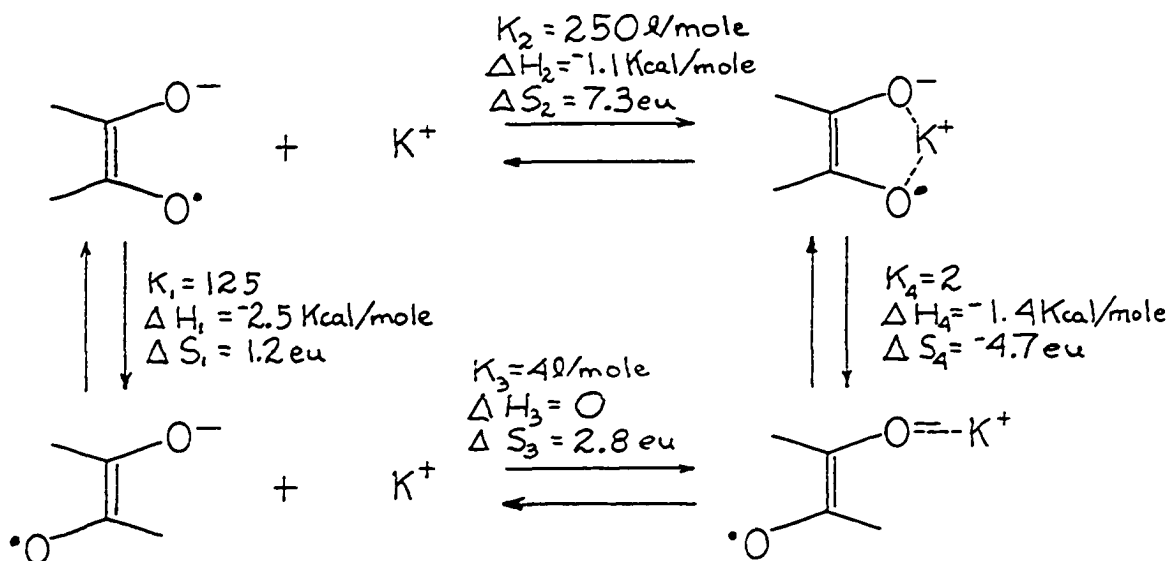


$$\begin{array}{l}
 \text{TOTAL (E)} = 135 \text{ parts} \quad \text{TOTAL (Z)} = 6 \text{ parts} \\
 \therefore \frac{[\text{E}]}{[\text{Z}]} = 22
 \end{array}$$

while data available in Figure 18 show that  $[\text{E}]/[\text{Z}]$  is 17 at  $[\text{KI}] = 0.044 \text{ M}$ . It is true that at high potassium iodide concentrations this value for  $K_4$  tends to give  $[\text{E}]/[\text{Z}]$  ratios which are too large by a factor of two or more. The values of the three experimental equilibrium constants are accurate to about  $\pm 10\%$ , ignoring systematic errors, based on the propagation of experimental error through the calculations.

The values of  $\Delta H$  and  $\Delta S$  associated with  $K_4$  were determined from a plot of  $[\text{E}]/[\text{Z}]$  vs  $1/T$ , where the ratios of  $\underline{\text{E}}$  and  $\underline{\text{Z}}$  were measured in a solution saturated with potassium iodide. (These numbers are included in Figure 19.) The results of this analysis yield  $\Delta H = -1.4 \text{ Kcal/mole}$  and  $\Delta S = -4.7 \text{ e.u.}$  As a check, these values yield a calculated value for  $K_4$  of approximately 1 at room temperature in contrast to the value of 2 obtained for  $K_4$  above. (See below for a further discussion of this point.)

At this stage it was desirable to obtain  $\Delta H$  and  $\Delta S$  for the two ion pairing equilibria. From the data shown in Figure 19, where the solution was saturated with potassium iodide, one can see that  $\Delta H$  for the ion pairing reaction of the E isomer with potassium is approximately zero, i.e., the  $g$  value is essentially independent of temperature. If  $\Delta H_3$  is set equal to zero then  $\Delta S_3$  follows as 2.8 e.u. from the fact that  $K_3$  is equal to 4. Now  $\Delta H_2$  may be set equal to -1.1 Kcal/mole. Then  $\Delta S_2$  must be 7.3 e.u., so that  $K_2$  will be equal to 250 at room temperature. The final scheme is given below.



From this, a number of observations may be made. A) The (Z)-semidione forms a bond to the potassium counter ion the enthalpy content of which is slightly greater than that of the composite "bonds" which must be broken in the act of solvation. B) As indicated by the  $\Delta S$  of 7.3 e.u., the pairing of (Z)-semidione with counter ion frees

solvent molecules. C. The free ions prefer to be in the E configuration, driven by an enthalpy term of -2.5 Kcal/mole, and a small entropy term of 1.2 e.u. The value of  $\Delta H$  may reflect steric interactions between adjacent methyls and/or oxygens in the Z species. Most likely, the entropy term arises from the fact that the E species has no dipole moment and will cause less ordering of the solvent in its vicinity than will the Z isomer. D. The enthalpy content of the (E)-semidione-potassium bond is the same as that of the ion-solvent "bonds" which must be broken upon desolvation. E. In the case of the E isomer, solvent is released from the solvent shell upon pairing, as indicated by the positive entropy term. F. The interconversion of the paired radicals from the Z to the E configuration is favored by enthalpy, presumably because the loss of the chelate structure is offset by solvation of the E ions. Indeed, an increase in solvent ordering occurs, as shown by the decrease in entropy.

### 3. Some assumptions

There were a number of major assumptions made during the arguments presented above.

The values of  $K_1$ ,  $\Delta H_1$ , and  $\Delta S_1$  were determined in DMSO solution with [2.2.2]-cryptand present. Since these numbers were obtained in the presence of "free" ions only, their values must in some sense describe the properties of the two species in solution. The E and Z isomers are believed to be in equilibrium via diamagnetic intermediates.<sup>59,65</sup> This part of the cycle seems relatively well-established.

The ion pairing of the two semidiones with potassium was determined by the methods discussed previously, and all the assumptions involved

then are present here. Of course, the most serious one centers around the determination and use of  $\gamma_{app}$ . The temperature studies of these equilibria merit some comment. Initially one suspects that  $\Delta H$  and  $\Delta S$  could be obtained directly from variable temperature work. However, it must be recalled that  $\gamma_{app}$  is not likely to be temperature independent. Hence, there are two (at least) variables changing with temperature, which makes a conventional treatment unreliable. Disregarding this fact, the value of  $\Delta H_3$  was assumed to be zero simply because the values of  $q_E$  appear to be constant with temperature. Although this is the same as saying that  $\gamma_{app}$  is temperature independent, there appears to be no other rational approach to the problem. This assumption, or some other similarly arbitrary assumption, must be made given the absence of available data.

The numbers associated with the  $\underline{E}$  ion pair may have large errors built into them as well. The equilibrium constant  $K_4$  was determined ad hoc to make the product  $K_2 \cdot K_4 \cdot 1/K_1 \cdot 1/K_3$  equal to one. As was mentioned previously, this value appears to be satisfactory only at the lower potassium iodide concentrations. At high concentrations of potassium iodide, the value is large by a factor of about two. The result of the temperature study is even more surprising. In principle, the data obtained should not fall on a straight line since a significant portion of the  $\underline{E}$  material exists as the free ion. Correcting for this fact by multiplying  $[E]/[Z]$  by a factor (about 0.5) which removes the free  $\underline{E}$  from the ratio, results in data which have a poorer fit to a line. Consequently, the data given in Figure 19 were used as is. A

linear regression was used to find the best line through the points in the graph of  $\ln K_4$  vs  $1/T$ . That this approach works at all seems a coincidence, and may only reflect an ignorance of the complete system.

Presumably, additional problems are generated by the formation of aggregates of the E isomer. It is strange that with cesium as the counter ion the  $g$  value appears to be invariant with concentration until finally at high cesium iodide concentrations the  $g$  value increases.

It appears that the value of  $K_1$ ,  $\Delta H_1$ , and  $\Delta S_1$  are on reasonably secure ground. The value of  $K_2$  is also fairly accurate. However, the other numbers presented should be considered as order of magnitude results, and it should be recognized that additional ion pairing phenomena may be involved, especially with the E isomer which has two effective sites for pairing.

#### 4. Conclusion of section III-C: Ion pairing with biacetyl semidione

Both (E)- and (Z)-biacetyl semidione form ion pairs in DMSO. The Z isomer behaves much like cyclohexane-1,2-semidione. As measured for potassium, the E isomer has a much smaller ion pairing constant than does the Z. The  $[E]/[Z]$  ratio decreases for smaller cations, reflecting a greater increase in the ion pairing constant for Z ion pair formation relative to E ion pair formation. Presumably, the structure of the Z ion pair is such that the metal is located between the two oxygen atoms. The ion pair of the E isomer has the counter ion located near one of the oxygen atoms, resulting in the formation of an asymmetric species. At

room temperature the cation migrates rapidly between the two positions, resulting in two time averaged methyl groups.

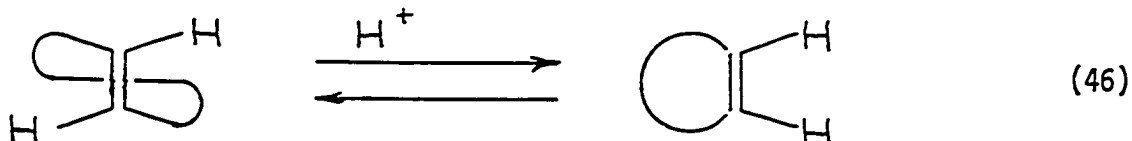
## IV. SEMIDIONES IN LARGE RINGS

## A. Introduction

Once the behavior of biacetyl semidione is understood, it is natural to ask the question, "How large must a ring containing a 1,2-semidione be before the E isomer will be observable by esr?" This section will address that question. Additionally, since a number of heterocyclic semidione precursors were available, there will be a discussion of these systems.

The first observation of a large, cyclic semidione was made over fifteen years ago when Russell and Strom reported the results of experiments with cyclopentadecanone and cyclododecanone.<sup>70</sup> No mention of the E isomer was made at that time. Lown has reported work with cyclic "ketyls" which later turned out to be semidiones produced by adventitious oxygen during his experiments. He reported studies on cyclopentane, cyclohexane, cycloheptane, cyclooctane, cyclononane, cyclodecane, and cyclododecane "ketyls".<sup>71,72,73</sup> Since he believed he was working with ketyls, naturally he made no mention of E configurations.

The question of E-Z isomerization in cyclic olefins has been raised by Cope, who reported thermodynamic data for the acid catalyzed conversion





Number of carbons in cycle	$\Delta G$ (Kcal/mole)	$K$ (298°K)
9	-4.04	$9.2 \times 10^2$
10	-1.86	23
11	0.67	.32
12	0.49	.44

From this, it is apparent that at eleven carbons the E isomer becomes energetically favored.<sup>74</sup>

Roberts has reported data concerning interconversion of the enantiomers of E alkenes.<sup>75</sup> This amounts to rotation of the double bond "through" the hole in the center of the molecule. He gives values for the lifetimes of the eight-, nine-, and ten-membered (E)-cycloalkenes as  $10^8$  years, 10 sec., and  $10^{-4}$  sec., respectively, at room temperature. It will become apparent that the semidione systems resemble simple alkenes in regard to E-Z isomerization, but seem to be poorer models of simple alkenes in regard to ring inversion.

The discussion of conformational effects in large cyclic semidiones will be more meaningful if some discussion of the smaller rings is included. Cyclobutane- and cyclopentane-1,2-semidione appear to be planar or rapidly equilibrating at all temperatures attainable in solution.<sup>76</sup> Cyclohexane-1,2-semidione can be frozen out at  $-90^\circ\text{C}$  to give a spectrum which shows two pairs of nonequivalent protons.<sup>72,76</sup> The seven-, eight- and nine-membered cycloalkyl semidiones have all been re-investigated to some extent during the course of this work, so reference to these cases will be made under the Results and Discussion sections. In addition, the 4-silacyclohexane system will be included since it fits in well with the rest of the silicon containing rings.

## B. Results

### 1. Cycloheptane-1,2-semidione

This radical was prepared from the bis-trimethylsiloxyalkene and subjected to a temperature study in DMSO. Three representative spectra, one at 15°C, one at 70°C and one at 130°C are shown in Figure 25. These spectra were obtained from solutions which had potassium iodide added to them since this was found to enhance the stability of these radicals at high temperatures. One set of spectra were run with [2.2.2]-cryptand present. These spectra were similar to those presented except that at 60°C decomposition became apparent and at 80°C the signal deteriorated very rapidly.

### 2. Cyclooctane-1,2-semidione

At room temperature, this radical anion presented a complex spectrum (see Figure 26). In the presence of [2.2.2]-cryptand, a  $g$ -value of 2.00511 was observed, while in 0.1 M  $K^+DMSO^-/DMSO$  the  $g$ -value was 2.00494. Upon heating to 100°C, a spectrum consisting of a pentet,  $a^H = 3.48$  G could be observed (see Figure 26). Because of the uninterpretable room temperature spectrum, very little work was done with cyclooctane-1,2-semidione.

### 3. Cyclononane-1,2-semidione

At room temperature, cyclononanesemidione gave a spectrum with extensive hyperfine splitting. Upon heating, the spectrum was observed to undergo selective line broadening, reaching the coalescence point around 120°C. See Figure 27 for an example of this. This radical, as

Figure 25. ESR spectra of cycloheptane-1,2-semidione at various temperatures in the presence of potassium iodide

- A. 15°C
- B. 70°C
- C. 130°C

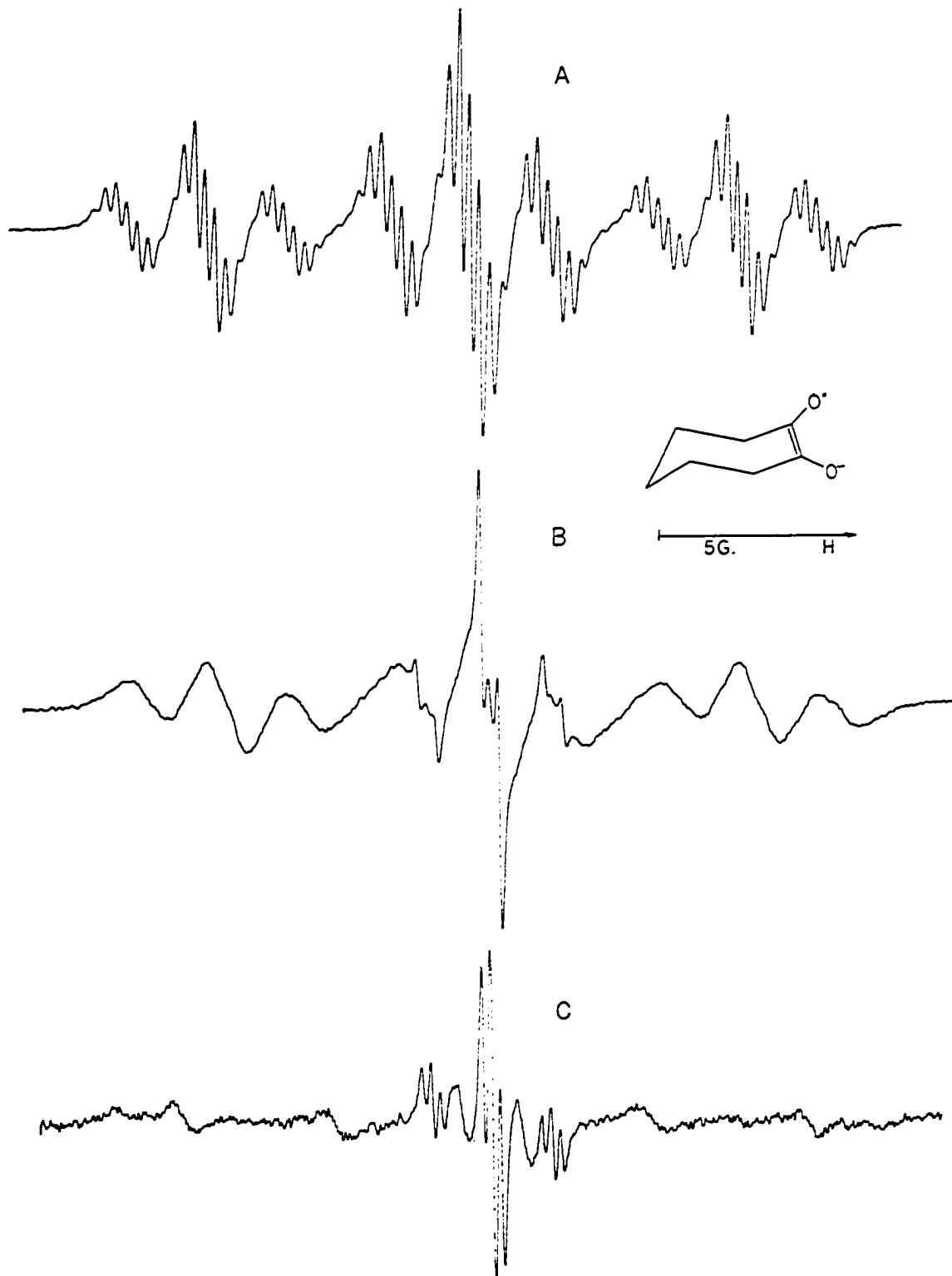


Figure 26. ESR spectra of cyclooctane-1,2-semidione

- A. Room temperature,  $K^+DMSO^-/DMSO$
- B. The same as A, except at 100°C
- C. Cryptand present, room temperature

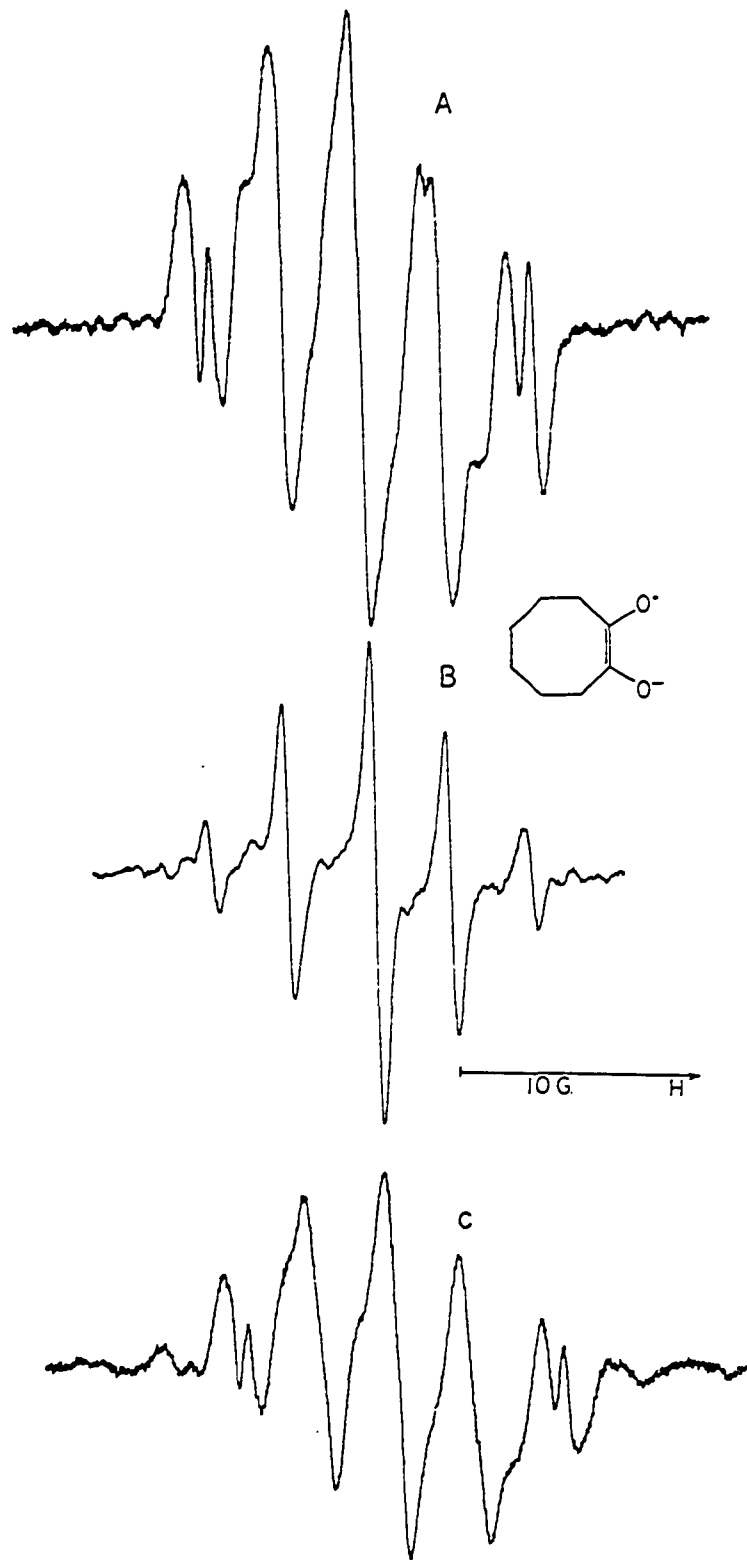
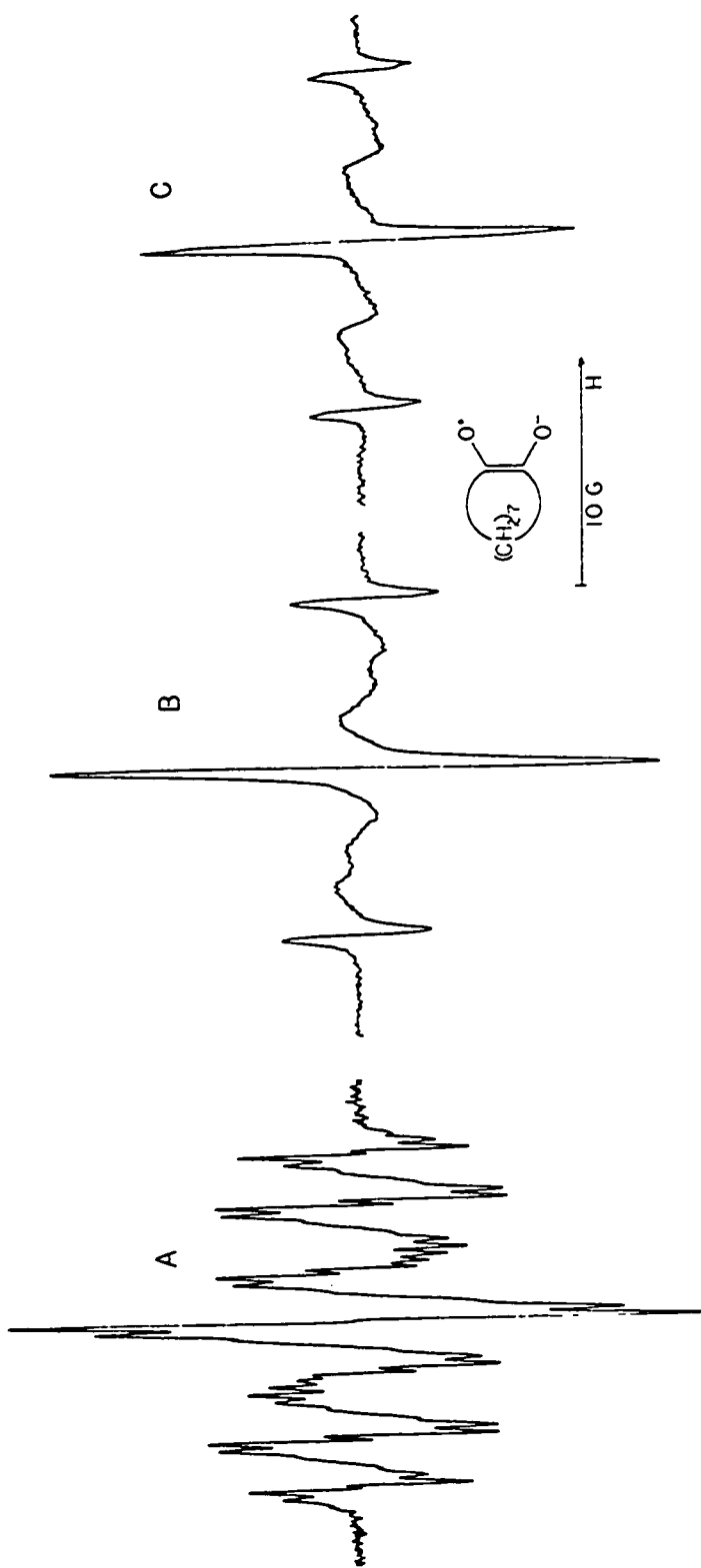


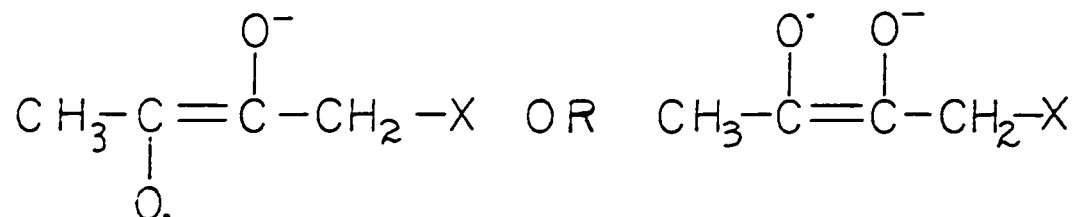
Figure 27. ESR spectra of cyclononane-1,2-semidione in the presence of potassium iodide

- A. 30°C
- B. 100°C
- C. 120°C

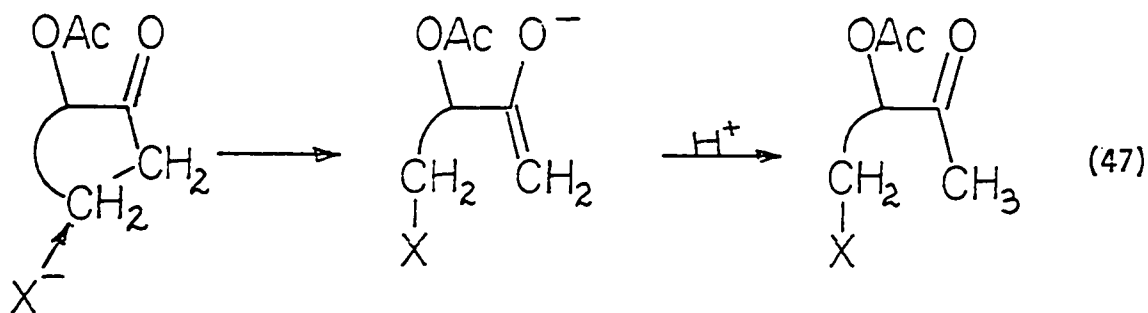




well as the larger carbocyclic radicals, was best generated by reaction of the bis-trimethylsiloxyalkene precursor with base in degassed DMSO. When acetoxy ketones were used to generate the cyclic radicals, ring opening to give E and Z acyclic radicals was a problem. These radicals gave spectra consistent with the structures,



This ring opening may be envisioned as occurring through nucleophilic attack on the acetoxy ketone, followed by protonation and eventual reduction to the radical anion,



The generation of the radicals by the alternative method of air oxidation of the cyclic ketone in basic DMSO, while satisfactory in the sense that radicals could be obtained, suffered in that at high temperatures the radicals were not stable. This is apparently due to oxidative degradation of the radicals by the oxygen remaining in solution.

#### 4. Cyclodecane-1,2-semidione

This radical was investigated only briefly. With cryptand present a spectrum with broad lines,  $g = 2.00506$ ,  $a^H = 8.3$  G (2H), was obtained at 80°C. In 0.25 M potassium iodide in DMSO these parameters became 2.00492 and 9.2 G (2H) (see Figure 28).

#### 5. Cycloundecane-1,2-semidione

A number of spectra were run of this radical ion. When an excess of [2.2.2]-cryptand is present, the spectra appear as shown in Figure 29. The esr parameters measured at 170°C were  $g = 2.00507$  and  $a^H = 4.7$  G (2H), 3.1 G (2H). What appears to be a triplet of not particularly well resolved triplets was seen at this temperature. If potassium iodide was added to the solution, a different spectra was seen, Figure 30. The previously mentioned set of lines was still present, but in addition there appeared to be a second set of lines,  $g = 2.00490$ . These lines look somewhat like a spectrum which is coalescing into a pentet. If that is true,  $a^H$  would be 5.6 G. Cooling these radicals in THF resulted in a complex spectrum, Figure 31. Also shown in Figure 31 is a room temperature spectrum of the radicals in 0.1 M  $K^+DMSO^-/DMSO$ .

#### 6. Cyclododecane-1,2-semidione

At 130°C, with cryptand present, this semidione gave a spectrum which seemed to resemble a triplet of triplets,  $a^H = 6.1$  G (2H), 1.9 G (2H) with  $g = 2.00512$ . With potassium iodide added to the solution, the spectral quality was somewhat poorer but it does appear as if a second set of lines,  $a^H = 8.27$  G,  $g = 2.00490$  is present,

Figure 28. ESR spectra of cyclodecane-1,2-semidione

- A, Potassium iodide added
- B. [2.2.2]-cryptand added

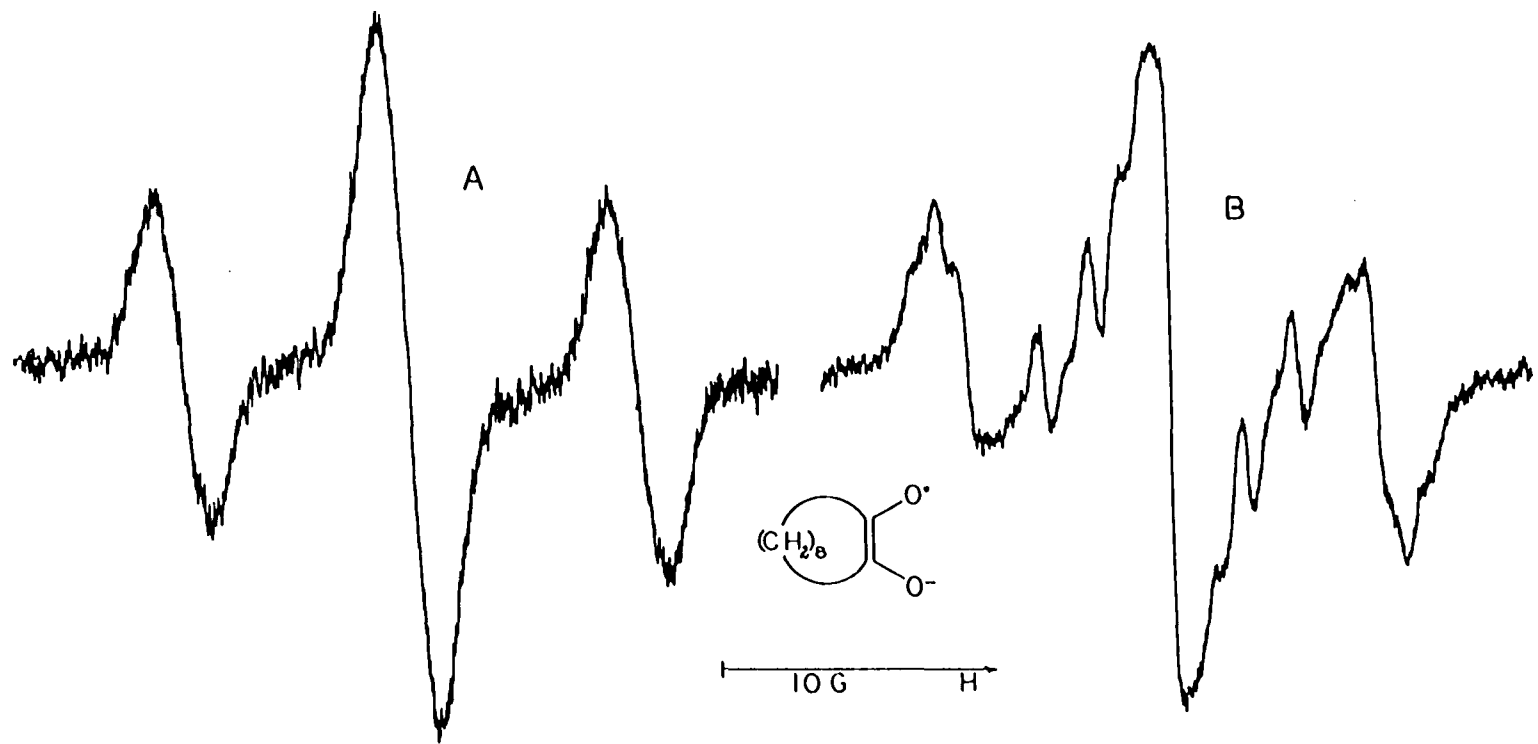


Figure 29. ESR spectra of cycloundecane-1,2-semidione in the presence of [2.2.2]-cryptand

- A. 100°C
- B. Room temperature
- C. 170°C

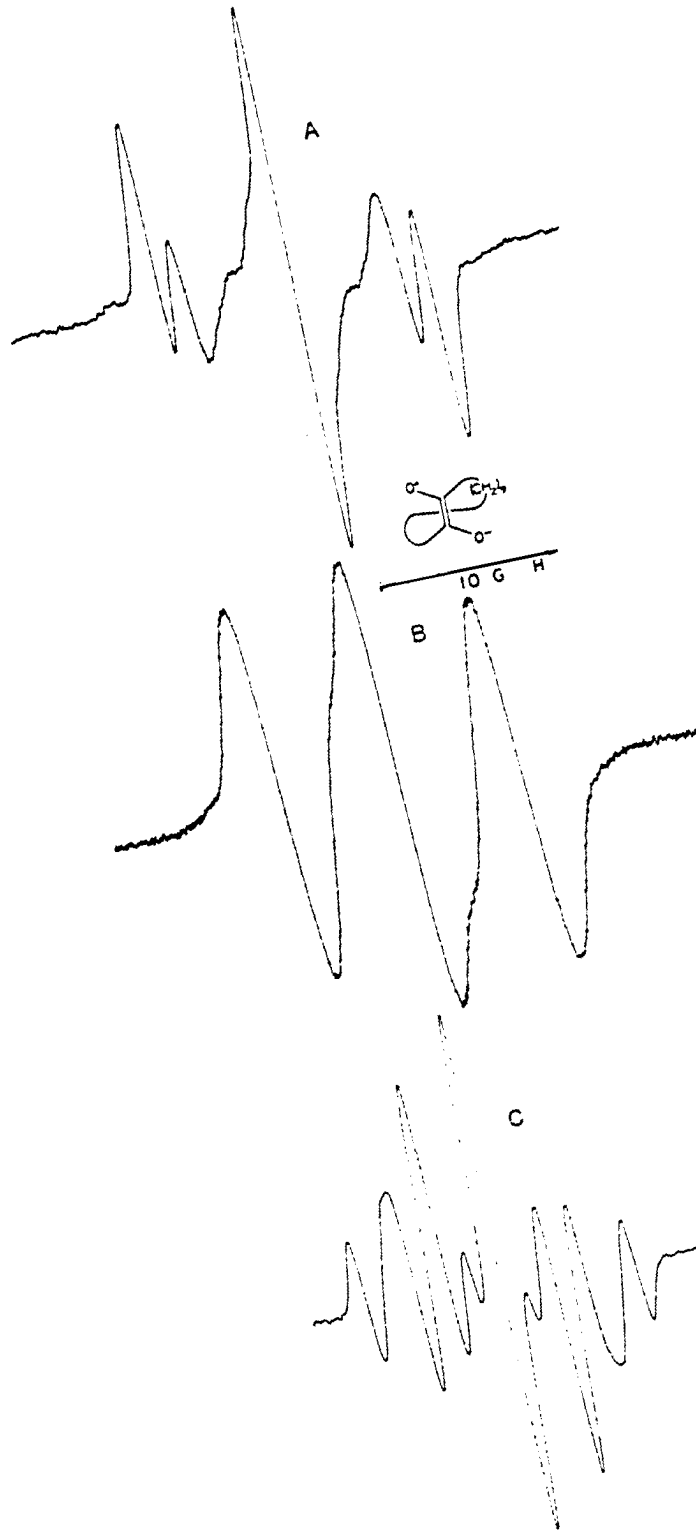


Figure 30. ESR spectra of cycloundecane-1,2-semidione in the presence of added potassium iodide

- A. Room temperature
- B. 100°C
- C. 160°C, marked lines are due to the E isomer

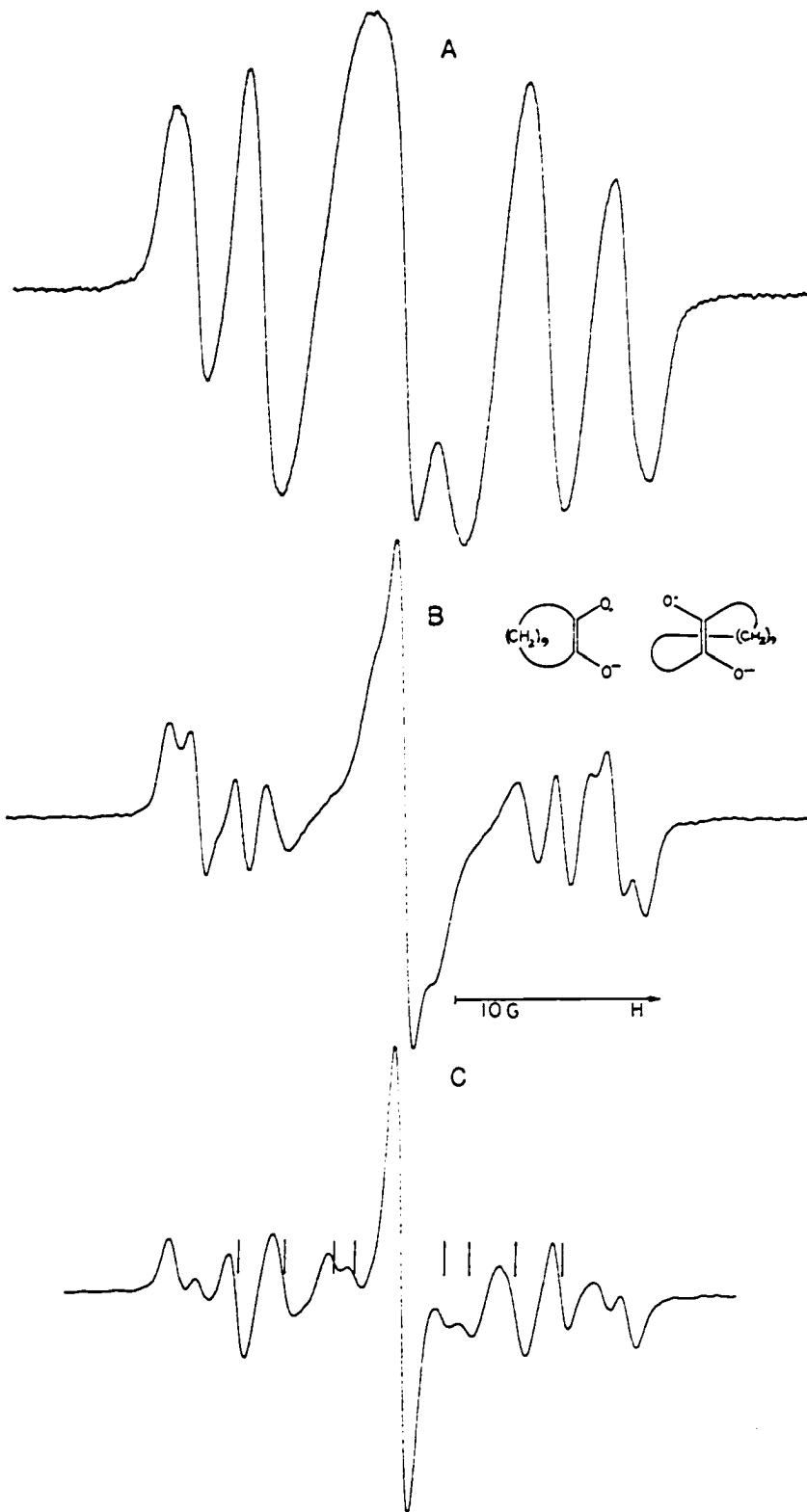




Figure 31. ESR spectra of cycloundecane-1,2-semidione

- A. -30°C in tetrahydrofuran
- B. -90°C in tetrahydrofuran
- C. Room temperature, 0.1 M K<sup>+</sup>DMSO<sup>-</sup>/DMSO

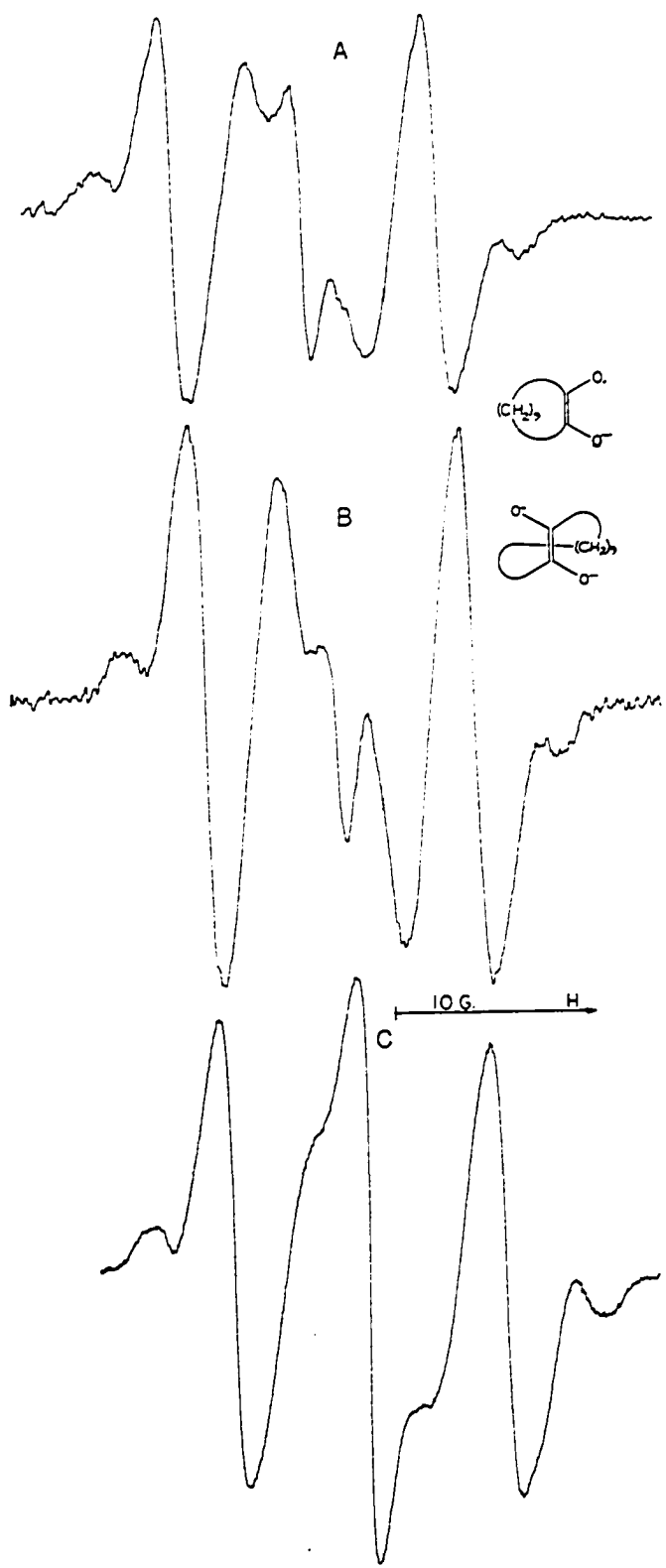


Figure 32. The useable temperature range was limited in this case, since the radicals were generated from cyclododecanone by the action of base and air.

### 7. Cyclotridecane-1,2-semidione

At 80°C with cryptand present, the signal from this semidione was a triplet of triplets,  $g = 2.00513$ ,  $a^H = 6.25$  G (2H), 1.73 G (2H). In 0.74 M potassium iodide solution, a pentet with  $g = 2.00491$  and  $a^H = 5.20$  G (4H) could be observed. In a DMSO solution containing only 0.1 M  $K^+DMSO^-$ , the triplet of triplets was easily seen. Under these conditions,  $g = 2.00504$ ,  $a^H = 6.26$  G (2H), 1.89 G (2H) (90°C) or 6.20 G (2H), 2.09 G (2H) (150°C). See Figures 33, 34 and 35 for examples of spectra of this radical anion. Note that at low temperatures the spectrum is complex.

### 8. Cyclotetradecane-1,3-semidione

Two spectra of cyclotetradecane-1,2-semidione are presented in Figure 36. With [2.2.2]-cryptand in the solution, the esr parameters were  $g = 2.00514$ ,  $a^H = 6.30$  G (2H), 1.74 G (2H). A solution containing potassium iodide shows an additional set of lines. Under these conditions, the esr parameters are  $g = 2.00495$ ,  $a^H = 4.73$  G (4H) and  $g = 2.00504$ ,  $a^H = 6.39$  G (2H), 1.89 G (2H). This radical appears quite similar to the fifteen-membered semidione and no other work was done with it.

Figure 32. ESR spectra of cyclododecane-1,2-semidione

- A. 130°C, [2.2.2]-cryptand added
- B. 100°C, potassium iodide added

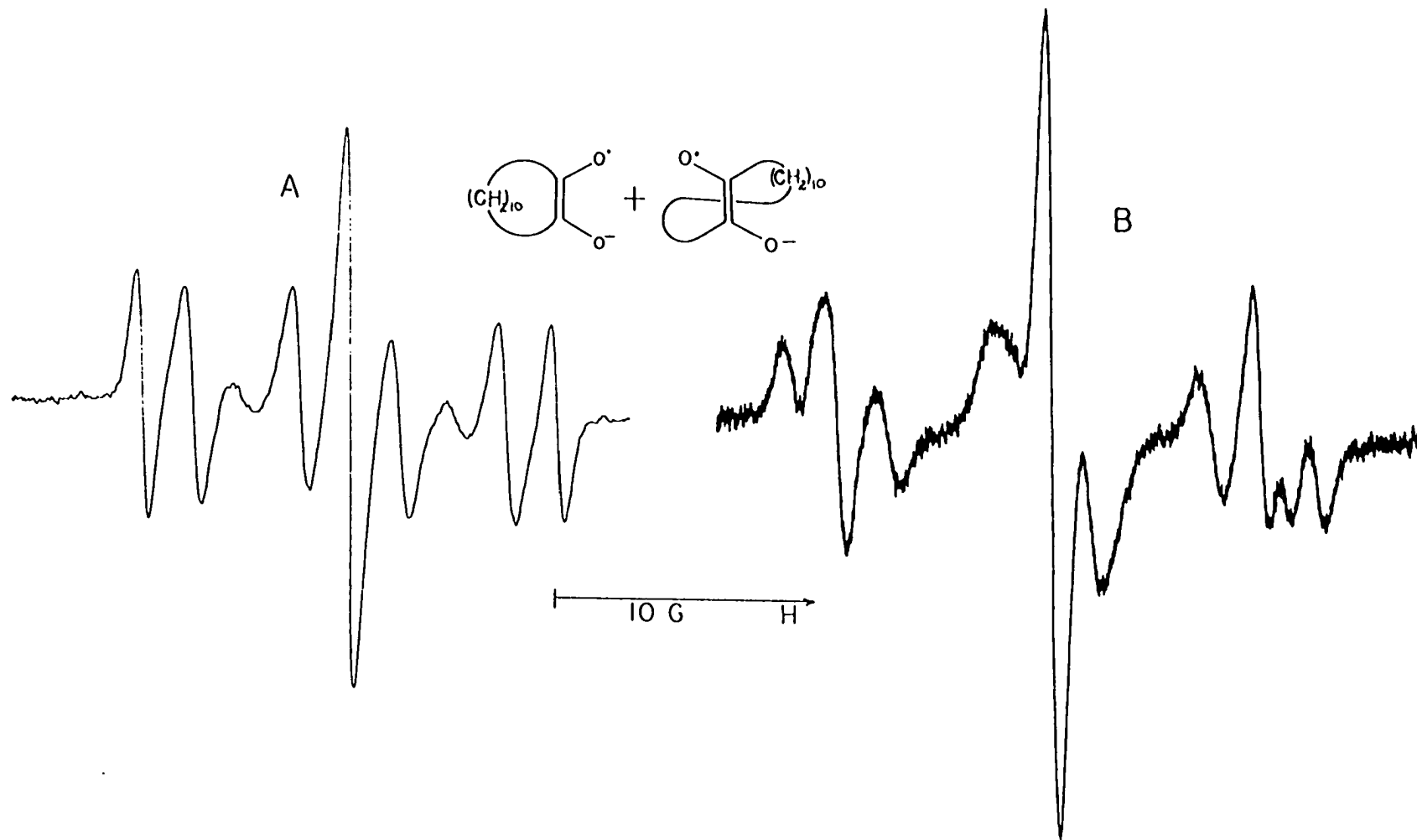


Figure 33. ESR spectra of cyclotridecane-1,2-semidione in the presence of added [2.2.2]-cryptand

- A. 40°C
- B. 100°C
- C. 140°C

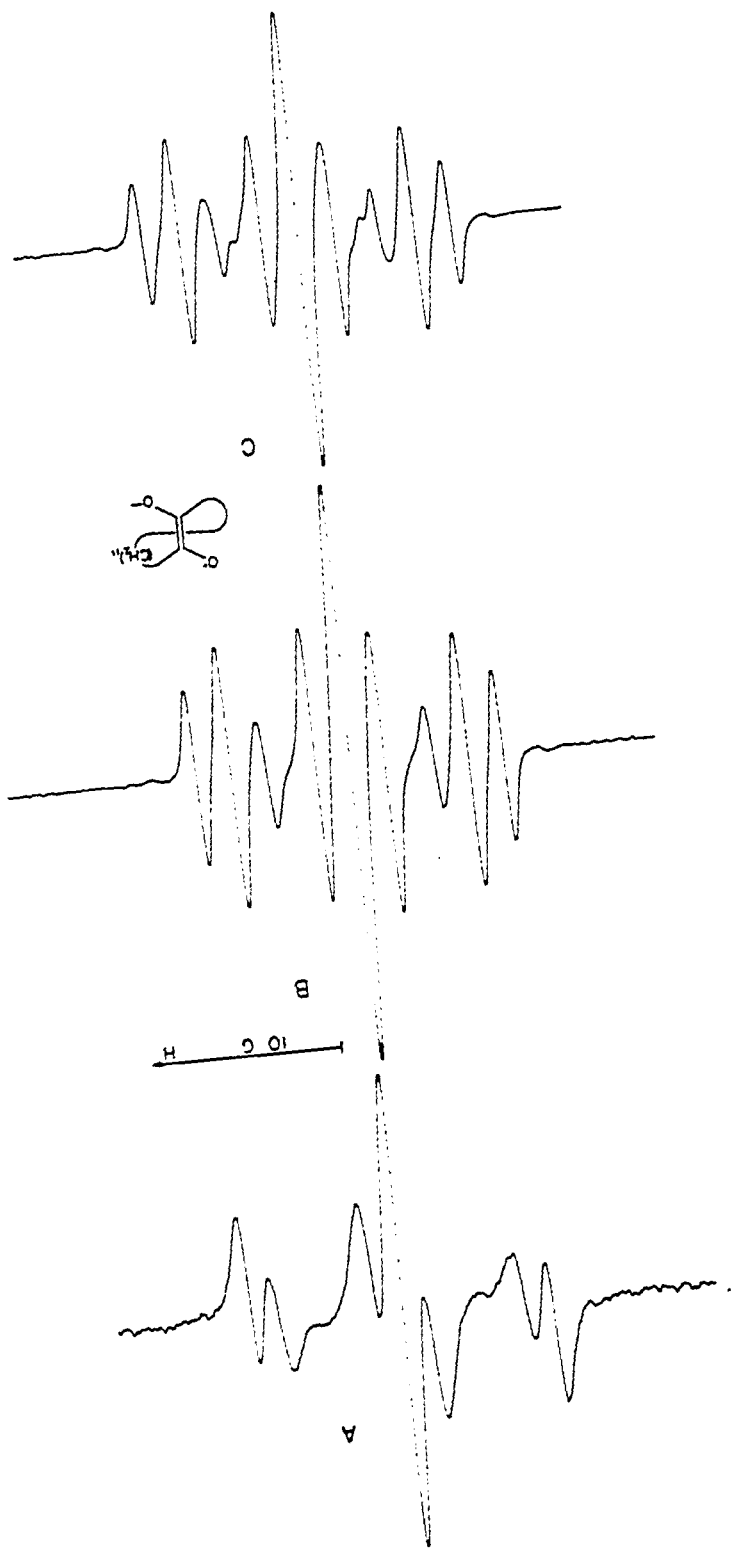
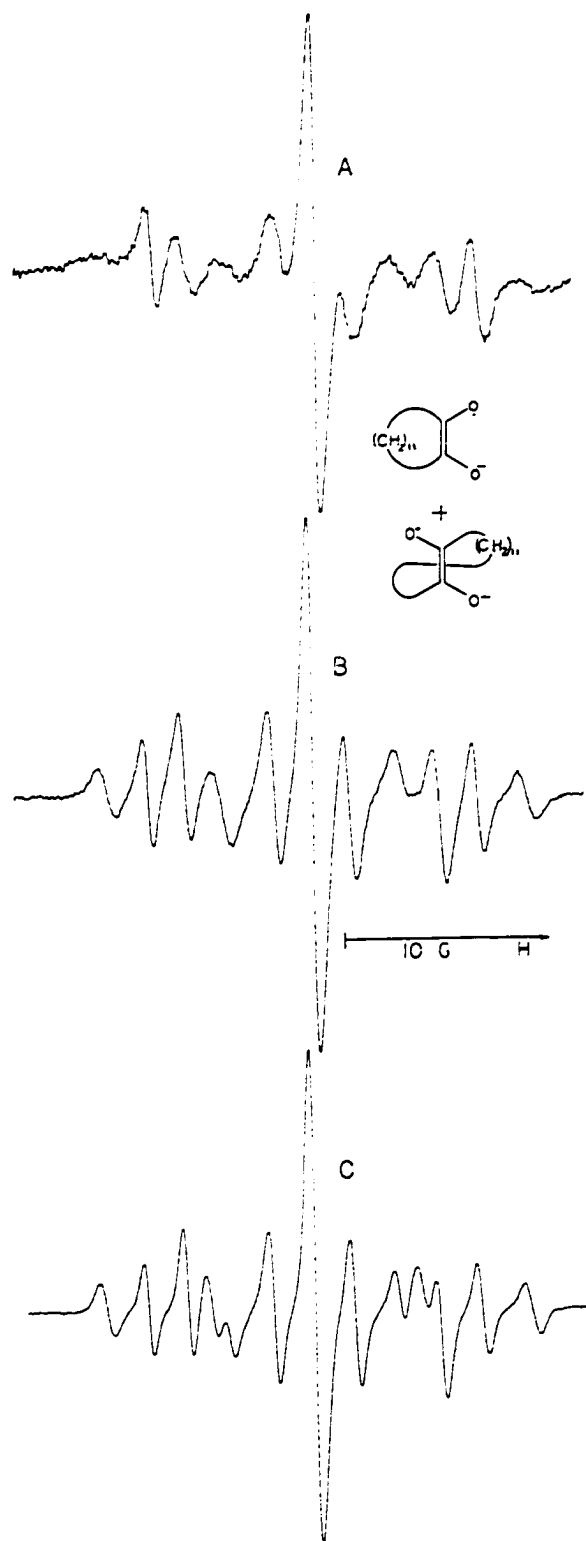


Figure 34. ESR spectra of cyclotridecane-1,2-semidione in the presence of added potassium iodide

- A. 40°C
- B. 100°C
- C. 130°C





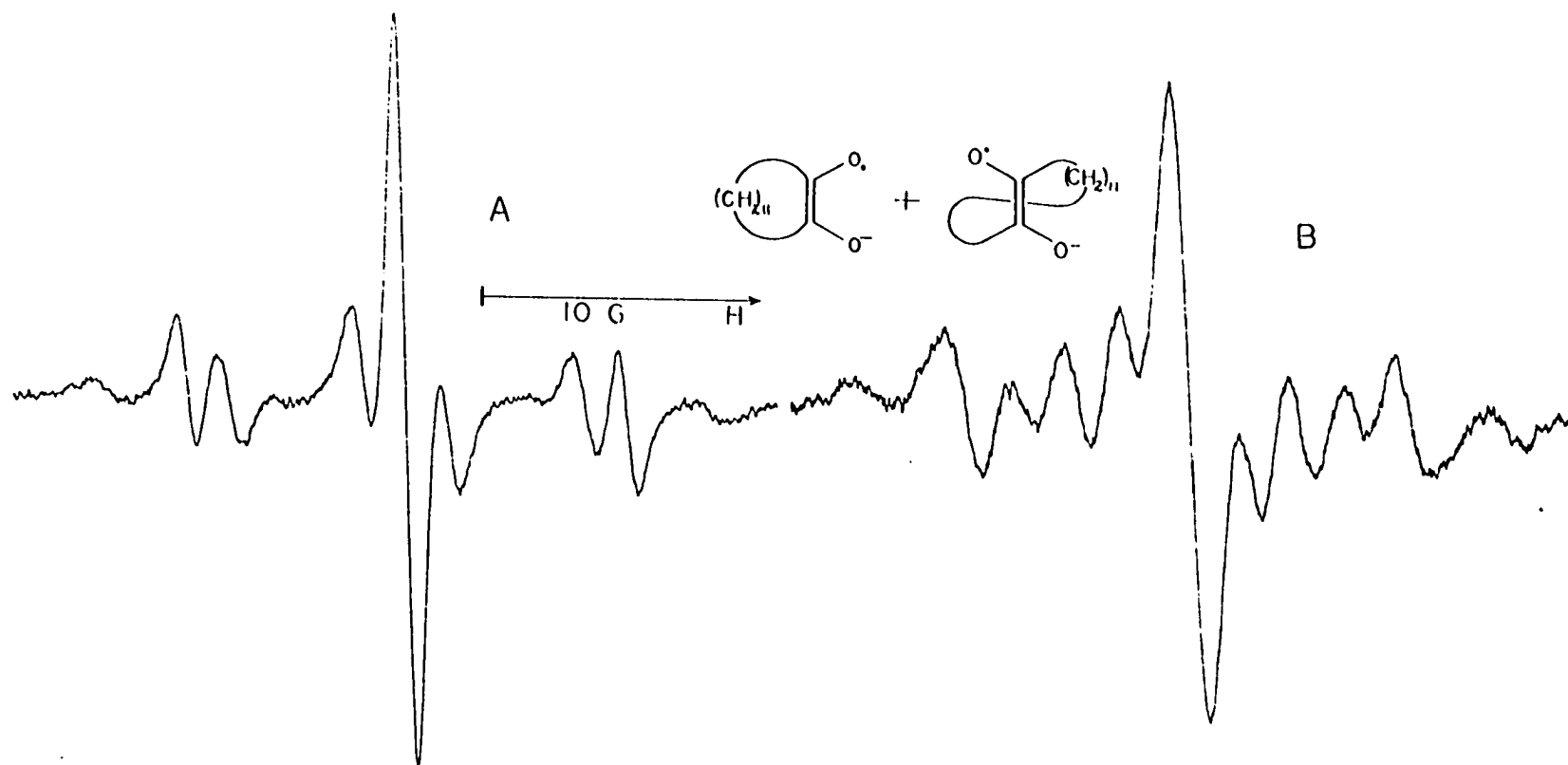


Figure 35. ESR spectra of cyclotridecane-1,2-semidione in tetrahydrofuran solution

- A. 40°C
- B. -100°C

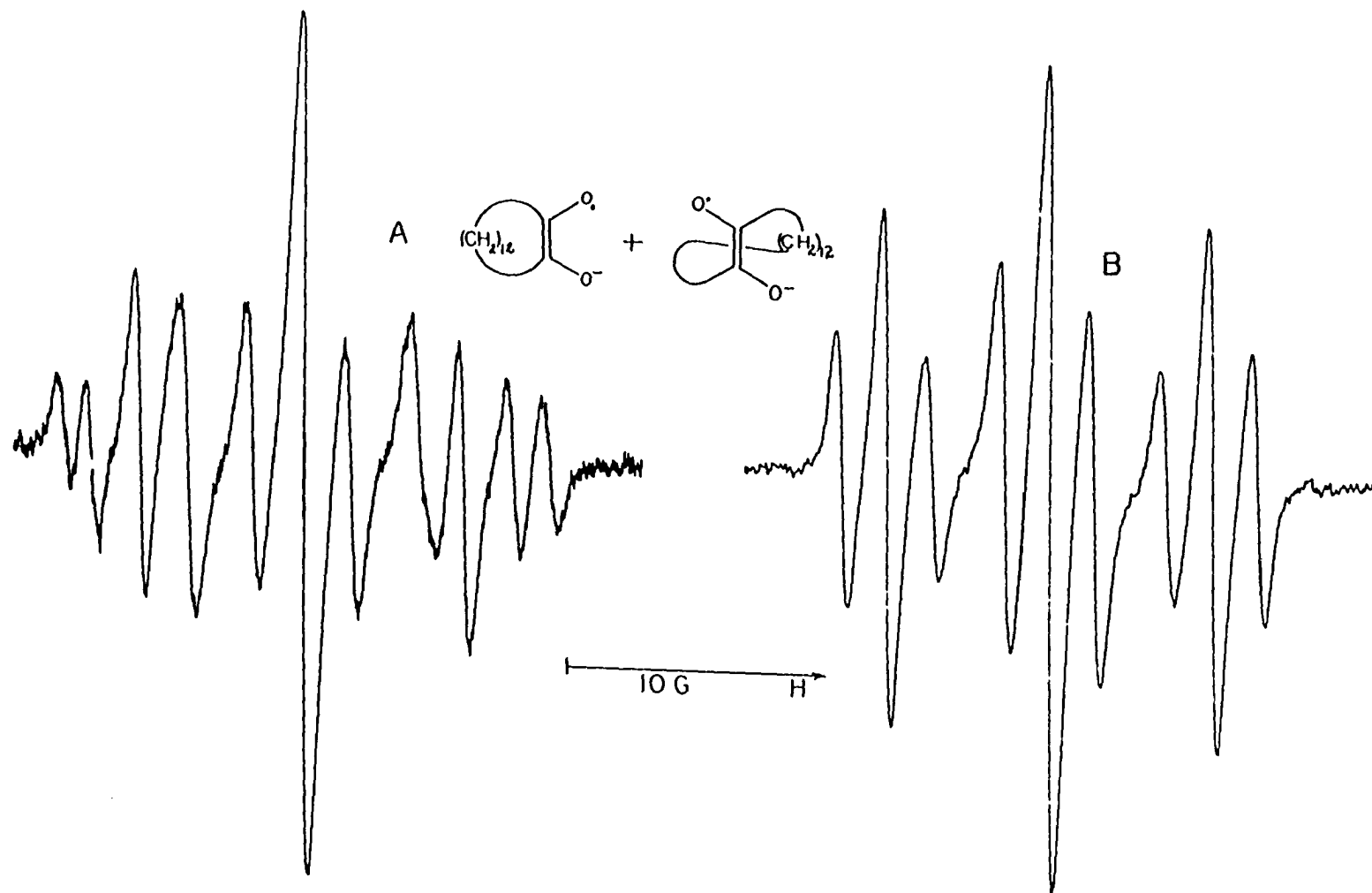


Figure 36. ESR spectra of cyclotetradecane-1,2-semidione

- A. 100°C, potassium iodide added
- B. 80°C, [2.2.2]-cryptand added

### 9. Cyclopentadecane-1,2-semidione

The fifteen-membered cyclic semidione shows what is clearly a triplet of triplets in  $0.1 \text{ M } \text{K}^+ \text{DMSO}^-$ , even at room temperature. The esr parameters were  $g = 2.00504$  and  $a^{\text{H}} = 6.73 \text{ G (2H)}, 2.07 \text{ G (2H)}$ . When potassium iodide is added to the solution, a second set of lines are observable at elevated temperatures. The esr parameters for this set of lines are  $g = 2.00491$ ,  $a^{\text{H}} = 5.19 \text{ G (4H)}$ . Under the same conditions, the triplet of triplets appears at  $g = 2.00502$  with  $a^{\text{H}} = 6.71 \text{ G (2H)}, 2.12 \text{ G (2H)}$ .

In  $0.1 \text{ M } \text{K}^+ \text{DMSO}^-$  at high temperatures, the triplet of triplets begins to show selective line broadening. Unfortunately, the radicals decomposed before the spectrum could be observed to coalesce (see Figures 37 and 38).

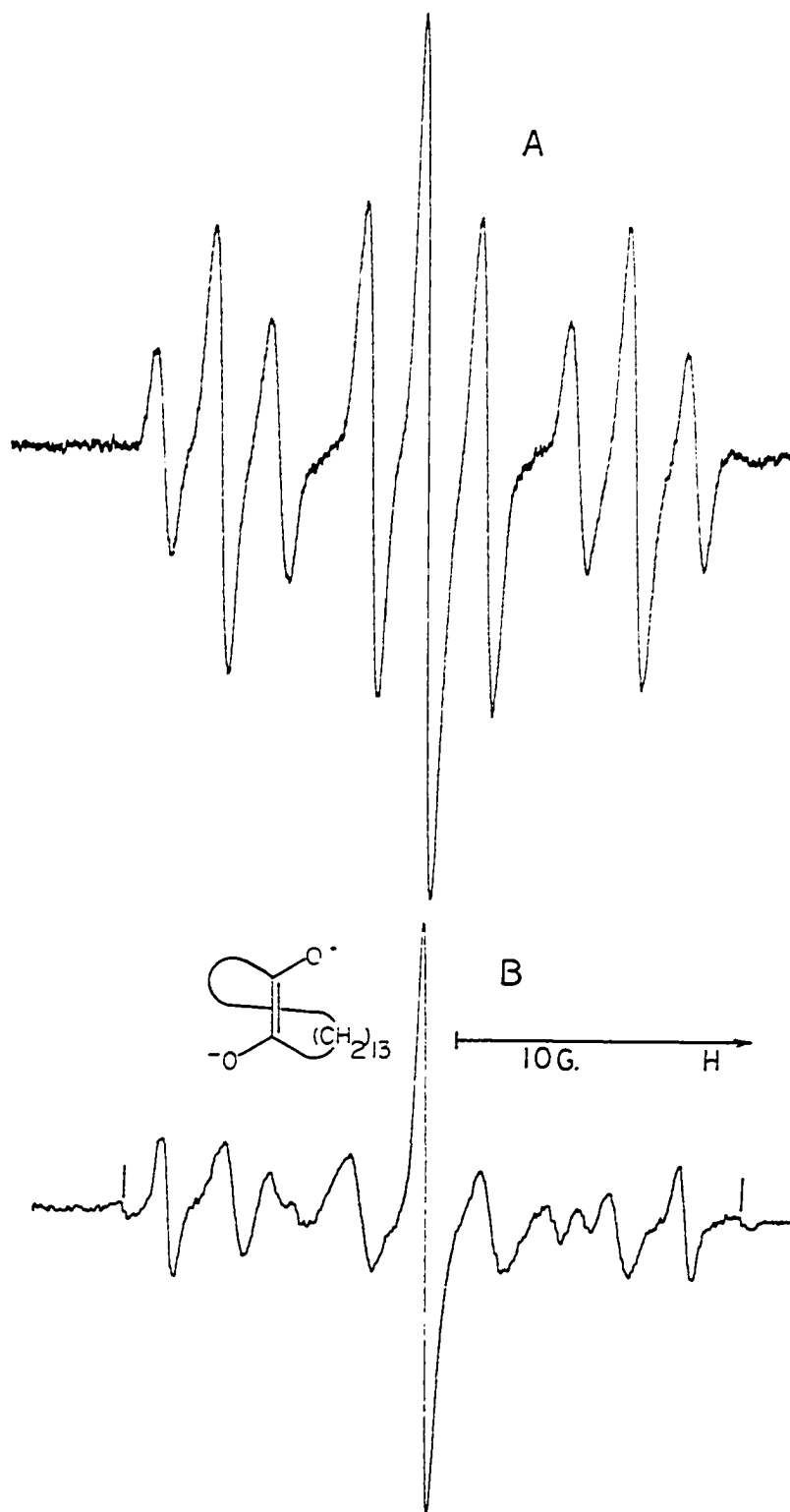
The fifteen-membered carbocyclic system was also investigated when  $\text{DMSO-d}_6$  was the solvent. Under these conditions, the normal spectrum was observed at first. After an hour, the spectrum was much more narrow (see Figure 39). The narrow spectrum was complex and the acquisition of a good record of it was prevented by the poor signal-to-noise ratio. It does appear as if all four of the hydrogen atoms which cause the triplet of triplets are exchanged.

### 10. 4,4-Dimethyl-4-silacyclohexane-1,2-semidione

The precursor which was used in an attempt to generate this radical was the acetoxy ketone,

Figure 37. ESR spectra of cyclopentadecane-1,2-semidione in 0.1 M  $\text{K}^+\text{DMSO}^-/\text{DMSO}$

- A. 40°C
- B. 130°C, marked lines are the wing peaks of the Z isomer



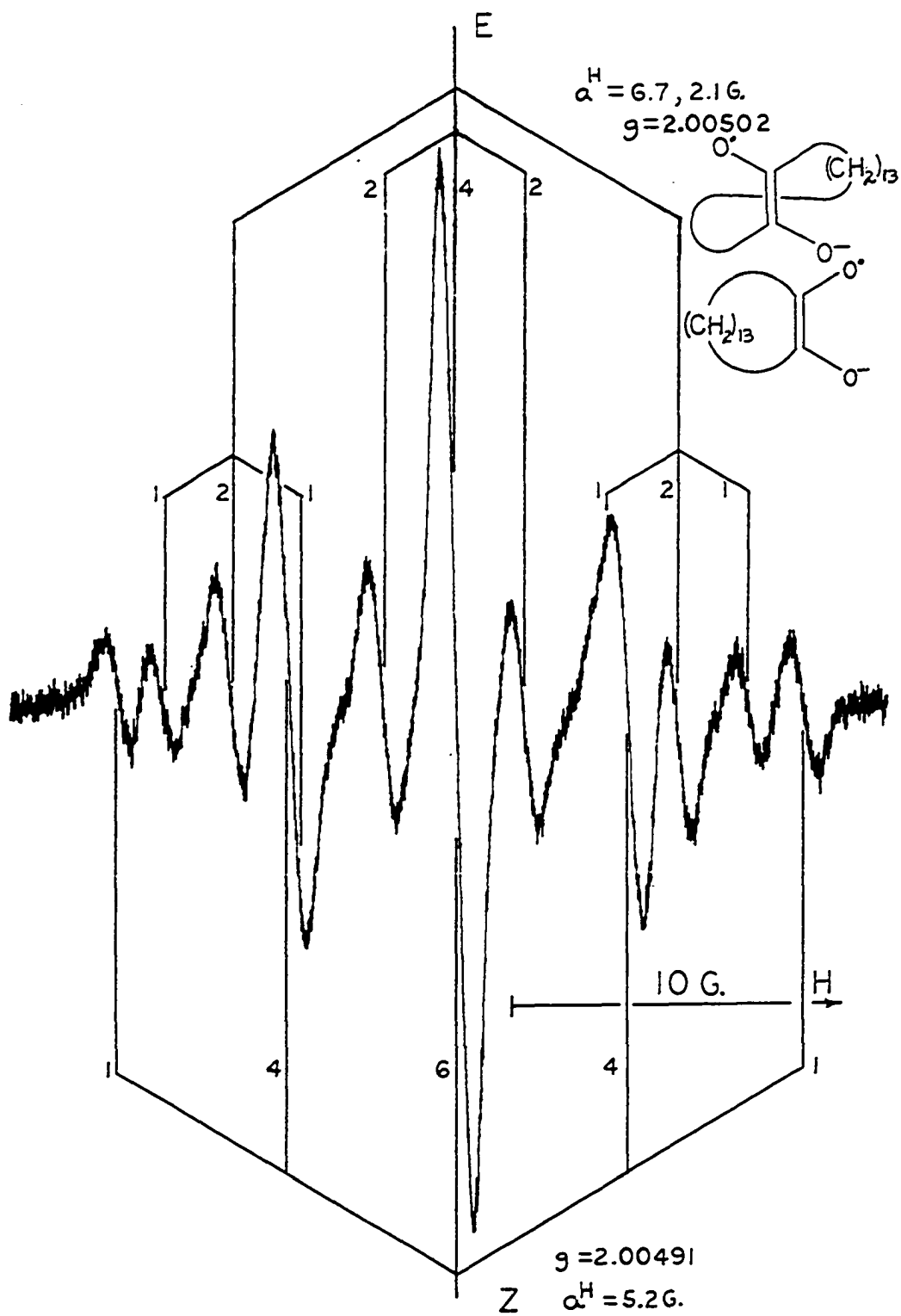


Figure 38. ESR spectrum of cyclopentadecane-1,2-semidione in the presence of added potassium iodide (0.47 M) at 80°C

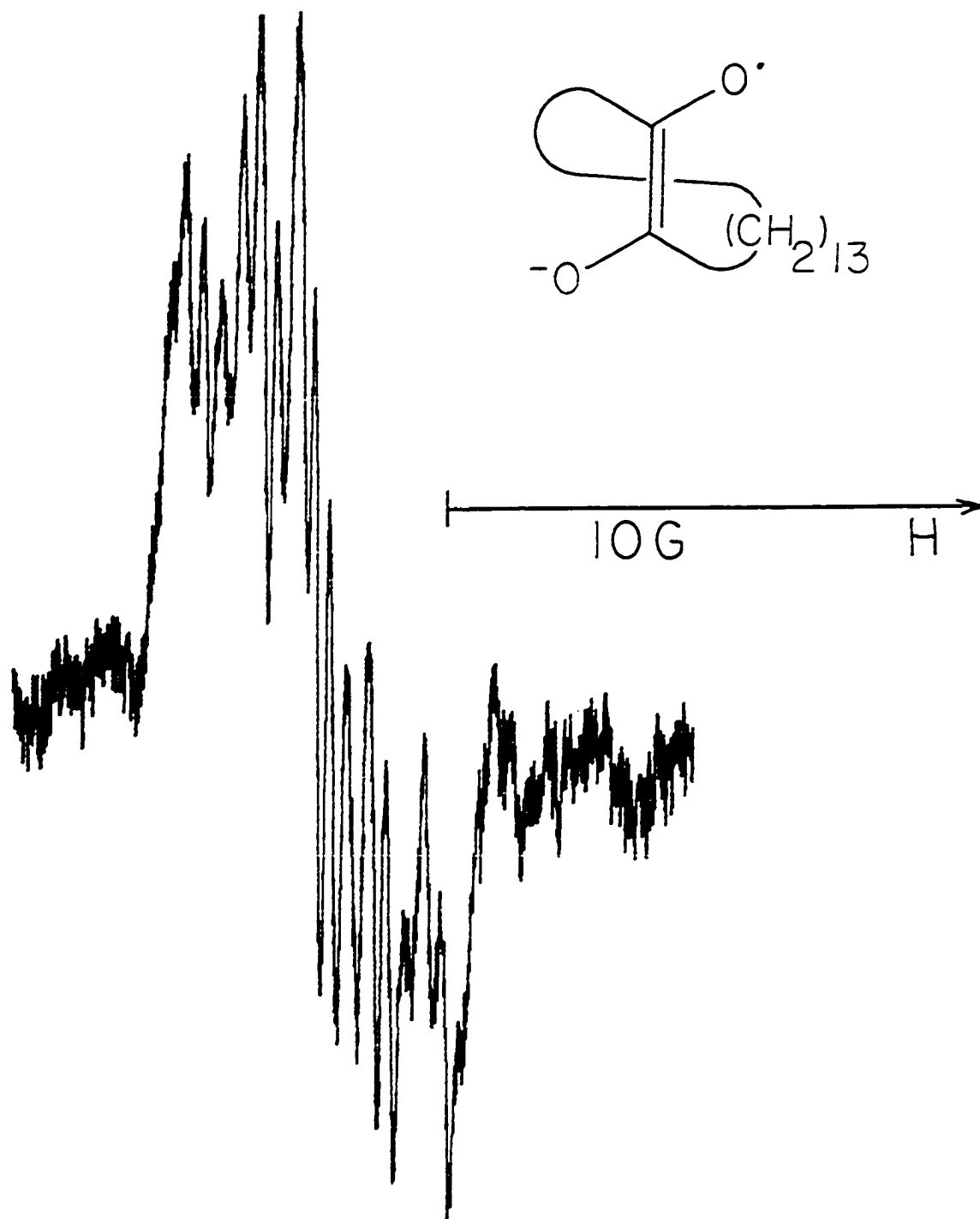
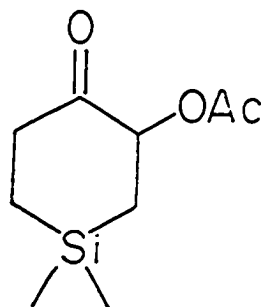


Figure 39. ESR spectrum of cyclopentadecane-1,2-semidione in  $DMSO-d_6$





The only spectrum observed from this precursor was due to ring opened semidiones, presumably due to nucleophilic attack on silicon.

11. 5,5-Dimethyl-5-silacycloheptane-1,2-semidione

When this radical was prepared in DMSO from the bis-trimethylsilyloxy-cycloalkene, a spectra showing selective line broadening was obtained. The  $g$ -value was 2.00490 and the apparent spacing of the sharp lines was 2.01 G. Upon warming, a pentet of pentets,  $a^H = 3.08$  G (4H), 0.95 G (4H), was obtained along with some ring opened radicals. Cooling the solution only resulted in reversible loss of signal intensity. Adding [2.2.2]-cryptand gave only ring opened radicals. Figure 40 shows some representative spectra taken of this radical.

12. 5,5-Dimethyl-5-silacyclooctane-1,2-semidione

This semidione presented a complex spectrum, Figure 41. Heating did not simplify the spectrum, nor did adding various amounts of potassium iodide. The values of  $g$  obtained were 2.00496 (standard solution), 2.00505 ([2.2.2]-cryptand), and 2.00494 (potassium iodide).

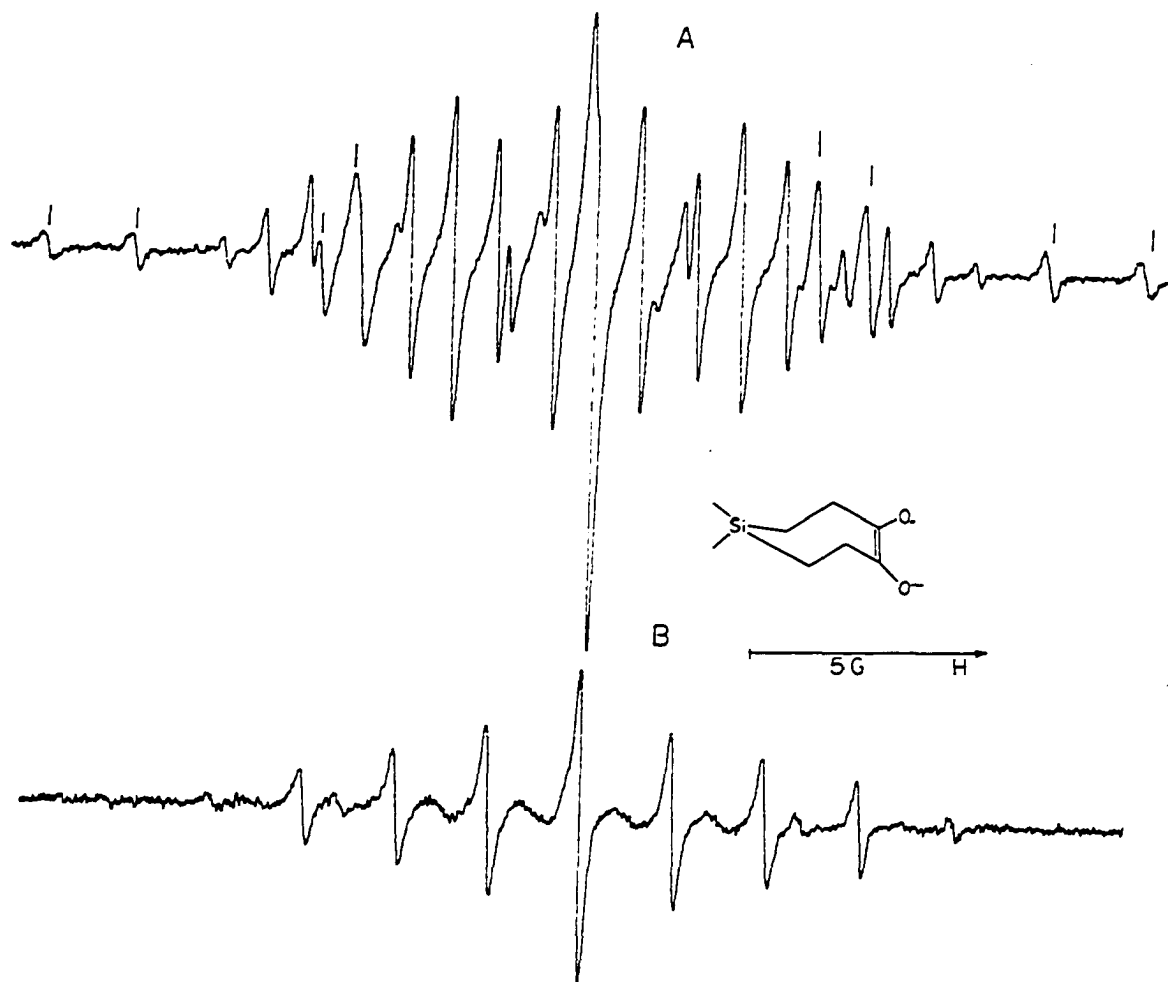


Figure 40. ESR spectra of 5,5-dimethyl-5-silacycloheptane-1,2-semidione in the presence of added potassium iodide

A. 90°C, marked lines are due to ring opened semidiones  
B. 5°C

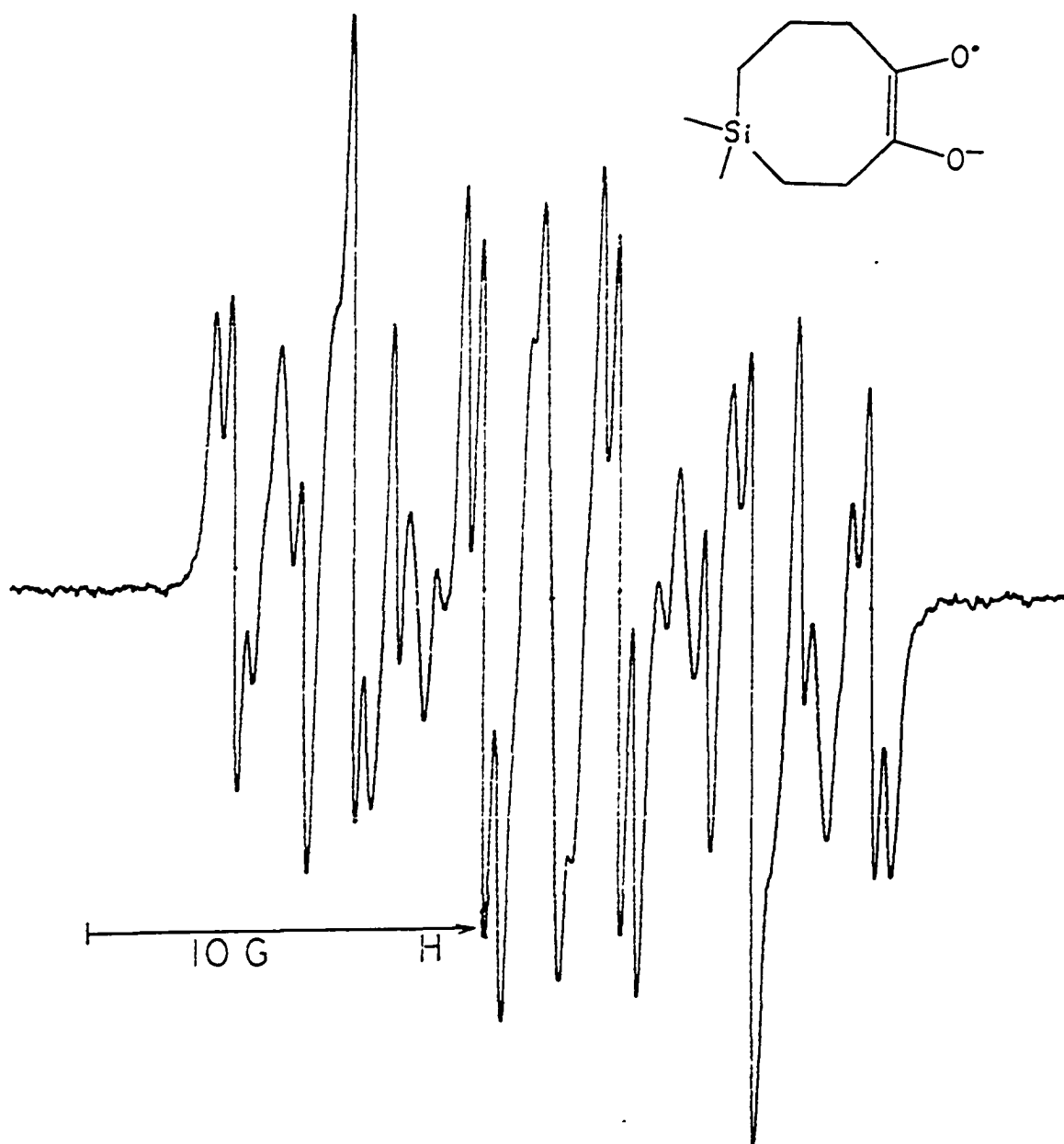


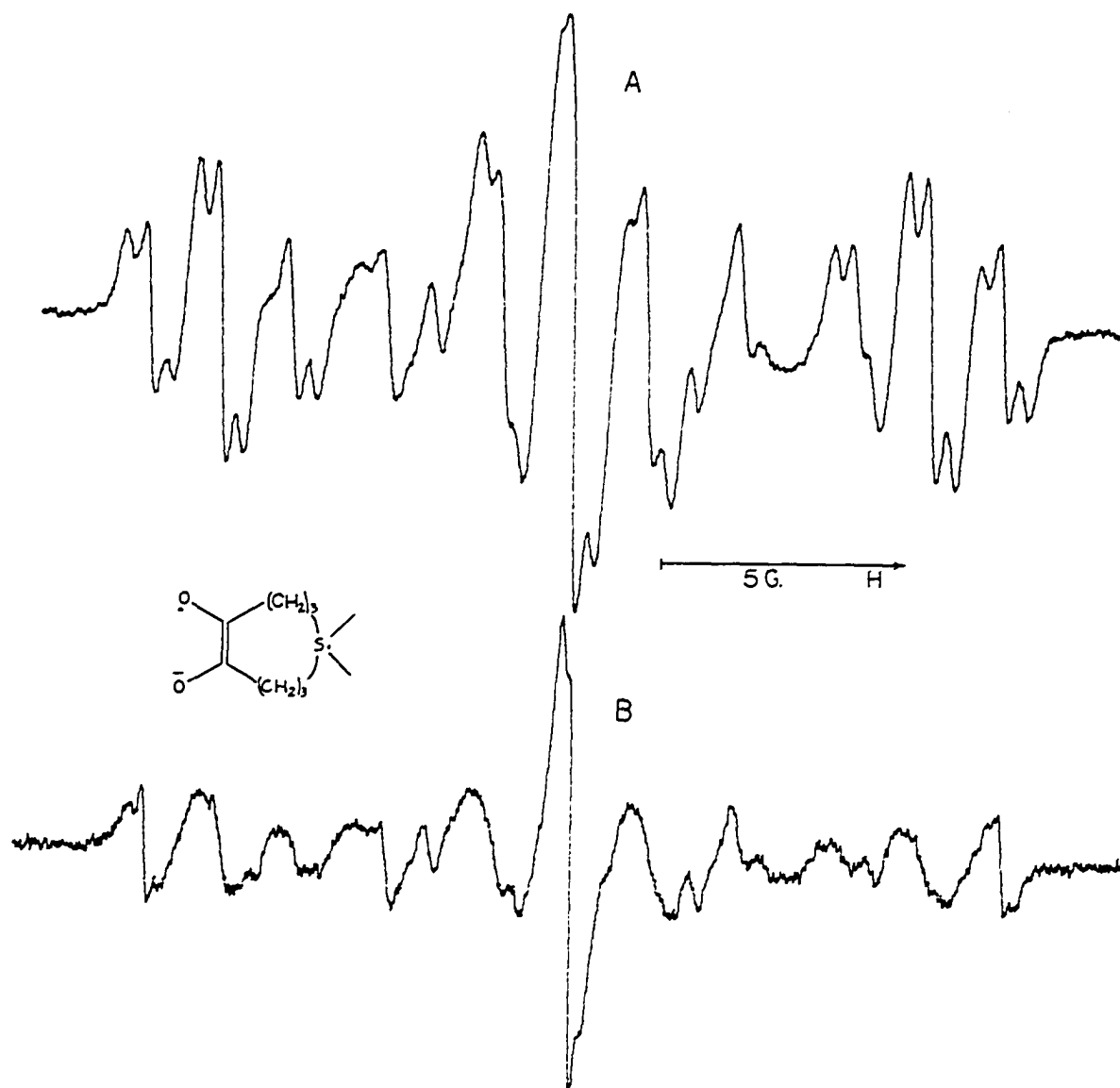
Figure 41. ESR spectrum of 5,5-dimethyl-5-silacyclooctane-1,2-semidione in the presence of added potassium iodide

13. 6,6-Dimethyl-6-silacyclononane-1,2-semidione

At room temperature in the presence of added potassium iodide this semidione gave a spectrum consisting of a triplet of triplets of triplets,  $\underline{a}^H = 7.31 \text{ G (2H)}, 1.35 \text{ G (2H)}, 0.32 \text{ G (2H)}, \underline{g} = 2.00497$ . Warming this sample resulted in line broadening and the eventual transformation to a large triplet at 110°C. This effect was reversible with temperature. When no potassium iodide was added there clearly was an additional set of lines present. The spectrum in the presence of [2.2.2]-cryptand was that of these additional lines. This same spectrum could be generated using cesium tert-butoxide as the base. At a temperature of 60°C, this spectrum consisted of a triplet of triplets,  $\underline{a}^H = 3.50 \text{ G (2H)}, 2.52 \text{ G (2H)}, \underline{g} = 2.00509$ . Cooling a sample of these radicals dissolved in DMF resulted in selective line broadening followed by the formation of a poorly resolved spectrum which could arise from coupling with four nonequivalent hydrogens. Figure 42 shows samples of the spectra which were obtained with added potassium iodide. Figure 43 shows the spectra obtained under standard conditions (0.1 M  $\text{K}^+\text{DMSO}^-$ ) and when [2.2.2]-cryptand was present. Figure 44 presents some of the data for this system as obtained at various temperatures and in various solvents.

14. 7,7-Dimethyl-7-silacycloundecane-1,2-semidione

When generated in DMF with cesium tert-butoxide, this semidione gave a spectrum at -60°C consisting of a broad triplet, the center line of which sharpened into a triplet of triplets upon warming to 0°C. Further warming caused the wing peaks to broaden extensively. However, the

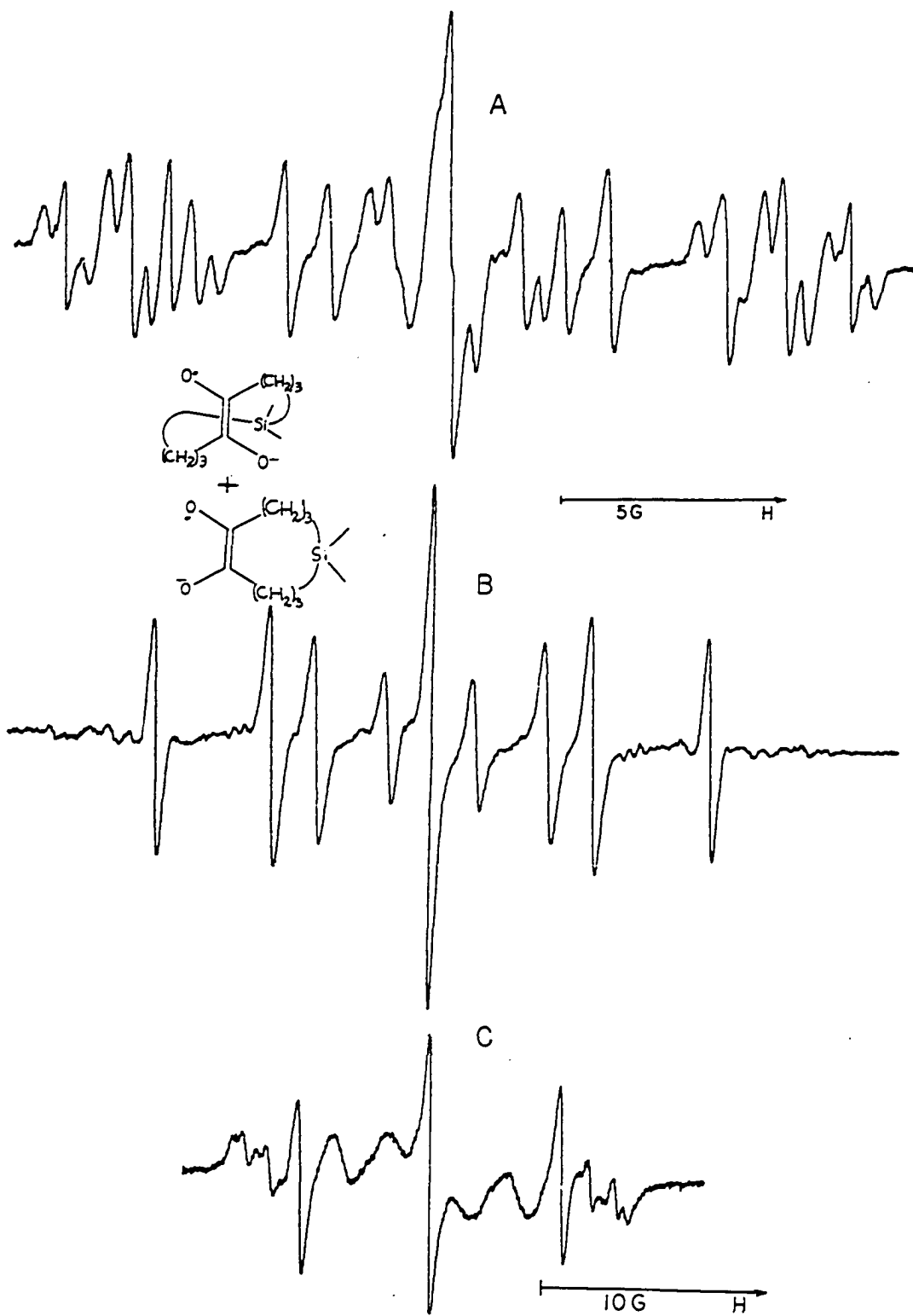


A. 30°C  
B. 90°C

Figure 42. ESR spectra of 6,6-dimethyl-6-silacyclononane-1,2-semidione in the presence of added potassium iodide

Figure 43. ESR spectra of 6,6-dimethyl-6-silacyclononane-1,2-semidione

- A. Standard solution
- B. [2.2.2]-cryptand added
- C. Tetrahydrofuran/[2.2.2]-cryptand at  $-70^{\circ}\text{C}$



## 6,6-Dimethyl-6-silacyclononane semidione

Temperature (°C)	Splittings (G)	g	Configuration
20	7.31, 1.35, 0.32 T X T X T	2.00497	Z <sup>a</sup>
120	1:4:1 (Selective line broadening)	---	Z <sup>a</sup>
-80	6.47, 4.28, 1.72 D X D X D	---	E <sup>b</sup>
60	3.58, 2.59 T X T	2.00509	E <sup>b</sup>
25	3.5, 2.6 T X T	---	E <sup>c</sup>
70	3.52, 2.59 T X T	---	E <sup>d</sup>

---

<sup>a</sup>DMSO/potassium iodide added.

<sup>b</sup>DMF/cesium tert-butoxide.

<sup>c</sup>DMF/[2.2.2]-cryptand/potassium tert-butoxide.

<sup>d</sup>DMSO/[2.2.2]-cryptand/K<sup>+</sup>DMSO<sup>-</sup>.

---

Figure 44. Values of  $\underline{a}^H$  and  $\underline{g}$  obtained under various conditions for 6,6-dimethyl-6-silacyclononane-1,2-semidione



Temperature (°C)	Splittings (G)	g	Configuration
25	3.54, 2.56 T X T	2.00509	E <sup>e</sup>
25	7.29, 1.40, 0.35 T X T X T	2.00487	Z <sup>e</sup>
25	3.48, 2.50 T X T	2.00509	E <sup>f</sup>
25	6.47, 1.45, 0.37, 0.16 T X T X T X T	2.00507	Z <sup>f</sup>

---

<sup>e</sup>DMSO/K<sup>+</sup>DMSO<sup>-</sup>/TLC purified sample (see text).

<sup>f</sup>DMSO/[2.2.2]-cryptand/K<sup>+</sup>DMSO<sup>-</sup>/TLC purified sample (see text.)

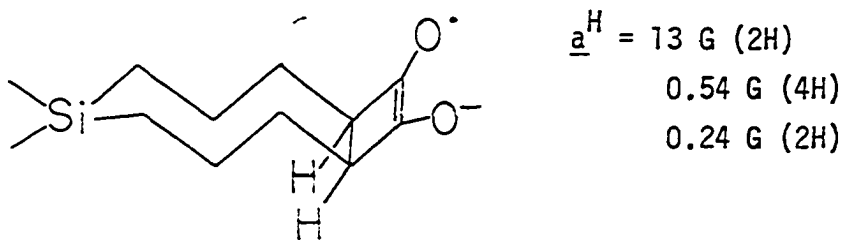
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Figure 44. (Continued)

central line remained narrow. Figure 45 shows this effect. Finally at 80°C, the spectrum became a triplet of triplets again with a narrower width than at the lower temperature. The esr parameters were, -70°C  $g = 2.00511$ ,  $a^H = 9.73$  G (2H), 0°C  $a^H = 8.41$  G (2H), 1.32 G (2H), 80°C  $a^H = 6.99$  G (2H), 1.62 G (2H), and 110°C  $a^H = 6.72$  G (2H), 1.46 G (2H). The  $g$ -value increased upon warming to  $g = 2.0518$  at 80°C.

When the spectrum was obtained in the presence of potassium iodide at room temperature, the resolution was better. Upon warming, the spectra continued to sharpen until at 90°C the spectrum shown in Figure 46 was obtained. This appears to be a superposition of the spectrum taken at 80°C when cesium was the counter ion plus another set of lines. The total width was about 20 G and the small splitting was 0.25 G (4H). Furthermore, the wider set of lines seemed to be at slightly higher field than the second set. Continued warming caused some change in line intensities, although the spectra appeared fundamentally similar.

On one occasion, a spectrum (Figure 47) was obtained which seemed to be due to some species such as



This was not observed at any other time, although no intentional effort was made to reproduce this result. The radicals had been generated from the corresponding hydroxyketone by the action of  $K^+DMSO^-$ . Potassium iodide had been added.

Figure 45. ESR spectra of 7,7-dimethyl-7-silacycloundecane-1,2-semidione in dimethylformamide solution with cesium tert-butoxide as the base

- A.  $-70^{\circ}\text{C}$
- B.  $0^{\circ}\text{C}$
- C.  $50^{\circ}\text{C}$
- D.  $120^{\circ}\text{C}$

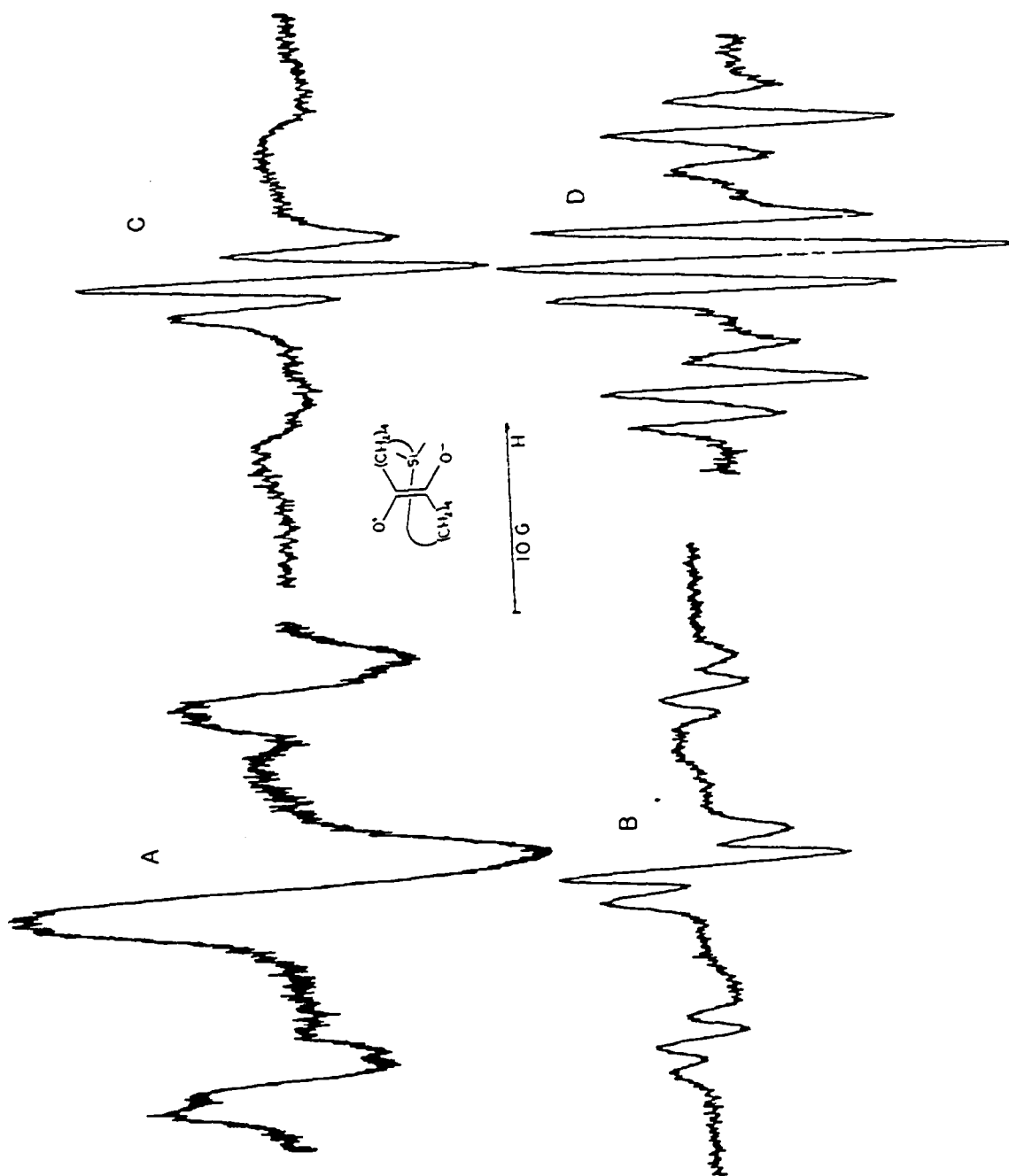


Figure 46. ESR spectra of 7,7-dimethyl-7-silacycloundecane-1,2-semidione in DMSO with added potassium iodide

- A. 40°C
- B. 90°C

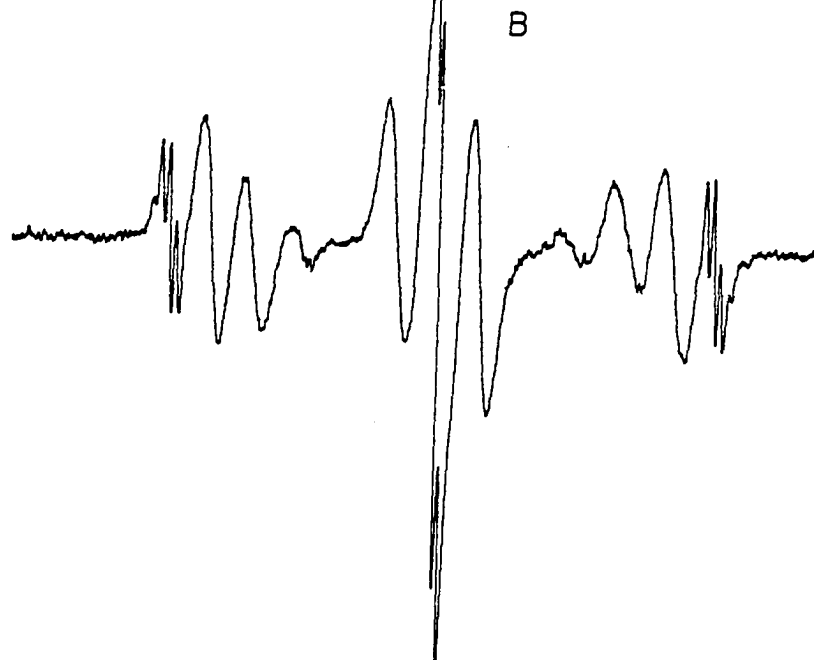
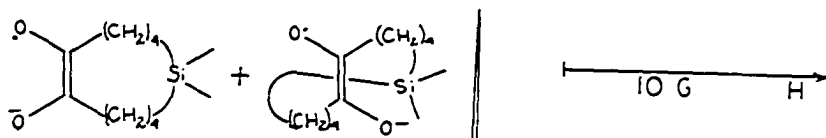
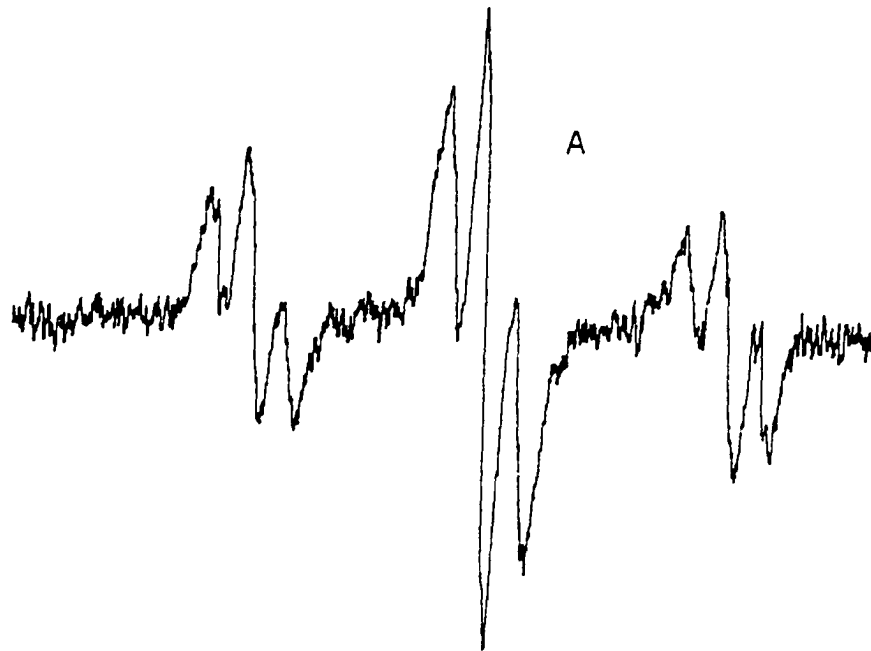


Figure 47. Unusual esr spectrum obtained from the precursor for 7,7-dimethyl-7-silacycloundecane-1,2-semidione in DMSO with added potassium iodide, at 60°C (see text)

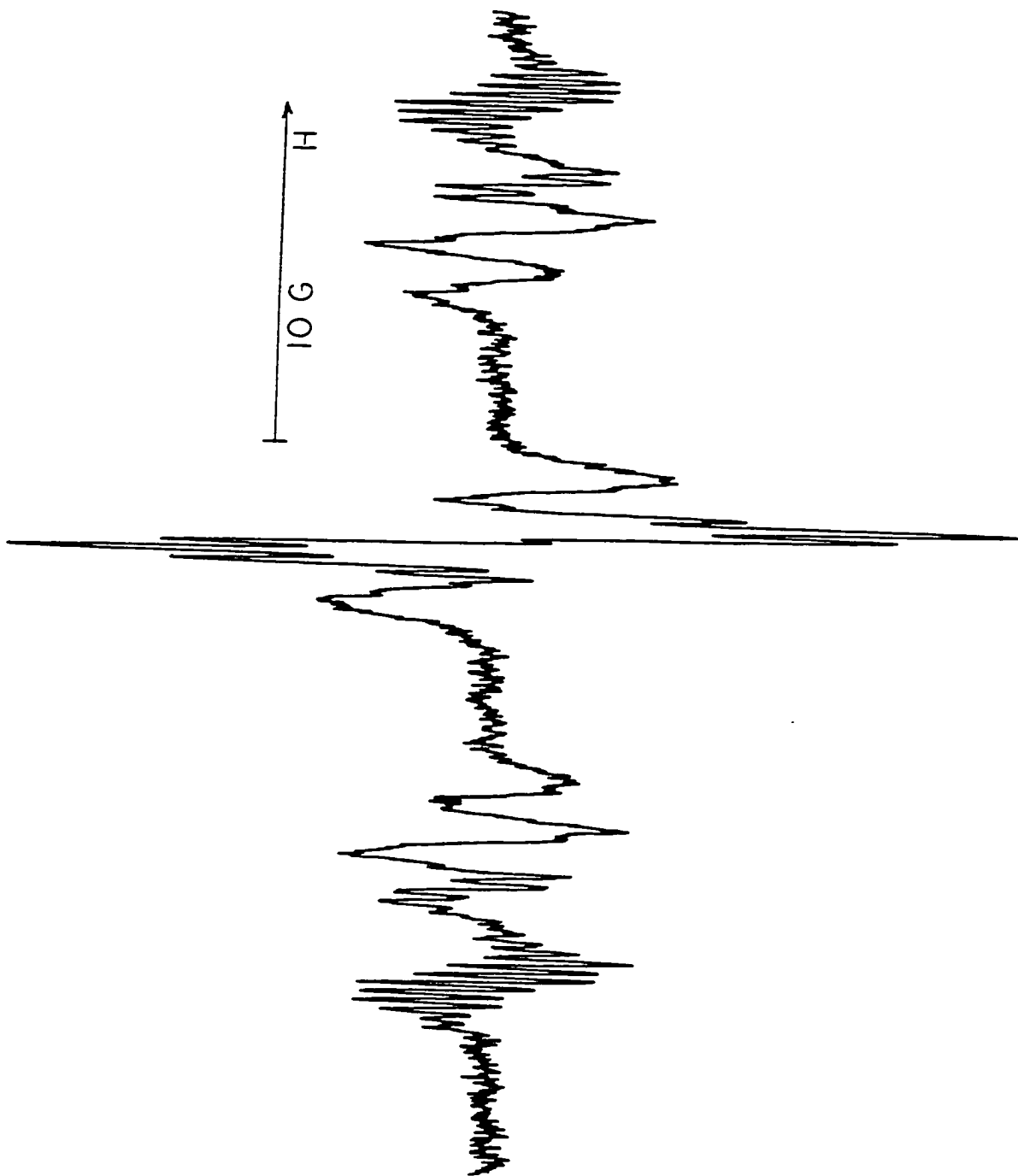




Figure 48 presents some of the data for the eleven-membered sila-cycle. This attempts to show the effects described above in a more concise form.

15. 7,7-Dimethyl-7-germacycloundecane-1,2-semidione

At 100°C in the presence of [2.2.2]-cryptand, this ring showed a spectrum which consisted of a triplet of triplets,  $g = 2.00505$   
 $a^H = 6.25$  G (2H), 1.79 G (2H). The spectrum became complex at lower temperatures. In the standard solution at high temperatures two species appeared, one being the previously mentioned spectrum. Under these conditions the esr parameters for this species were  $g = 2.00504$   
 $a^H = 6.42$  G (2H), 2.00 G (2H). The second had  $g = 2.00496$  and  
 $a^H = 4.83$  G (4H). The room temperature spectrum was broad, except for the central peak, although the broadening was essentially removed at the temperature of 60°C. See Figure 49 for examples of the spectra obtained with this system. The wing peaks of the spectrum taken when potassium iodide was added had a  $g$ -factor of 2.00489.

Figure 50 is a compilation of some of the data obtained from the germacycloundecanesemidione system.

16. 8,8-Dimethyl-8-silacyclotridecane-1,2-semidione

In DMF with cesium counter ion, this radical gave an esr spectrum consisting of a broad triplet (-60°C)  $g = 2.00506$ ,  $a^H = 8.73$  G (2H). As the temperature was raised, the spectrum began to sharpen. At 70°C the signal was an essentially perfect triplet of triplets,  
 $a^H = 6.94$  G (2H), 1.72 G (2H),  $g = 2.00509$ . If a solution containing

## 7,7-Dimethyl-7-silacycloundecane semidione

Temperature (°C)	Splittings (G)	g	Configuration
50	?, 1.46 ? X T	---	E <sup>a,b</sup>
40	8.83, 1.27 T X T	---	E <sup>c,d</sup>
80	8.75, 1.54, 0.28 T X T X P	---	E <sup>c,e</sup>
120	8.25, 1.75, 0.28 T X T X P	---	E <sup>c,e</sup>
140	8.11, 1.83, 0.25 T X T X P	---	E <sup>c,e</sup>

---

<sup>a</sup>K<sup>+</sup>DMSO<sup>-</sup>/DMSO/0.1 M

<sup>b</sup>Wing peaks broad

<sup>c</sup>K<sup>+</sup>DMSO<sup>-</sup>/DMSO/potassium iodide added

<sup>d</sup>Wing peaks sharp

<sup>e</sup>Pentet splitting visible on outermost lines only

---

Figure 48. Values of  $\bar{a}^H$  and  $\bar{g}$  obtained under various conditions for 7,7-dimethyl-7-silacycloundecane-1,2-semidione

Temperature (°C)	Splittings (G)	g	Configuration
120	4.84 P (?)	---	Z <sup>C,f</sup>
140	4.64 P	---	Z <sup>C,g</sup>
0	8.86, 1.18 T X T	---	E <sup>b,h</sup>
50	?, 1.49 ?, T	---	E <sup>b,h</sup>
140	6.57, 1.82 T X T	---	E <sup>b,h</sup>
25	8.75, 1.32 T X T	2.00507	E <sup>a</sup>
25	8.94, 1.27 T X T	2.00502	E <sup>c</sup>

---

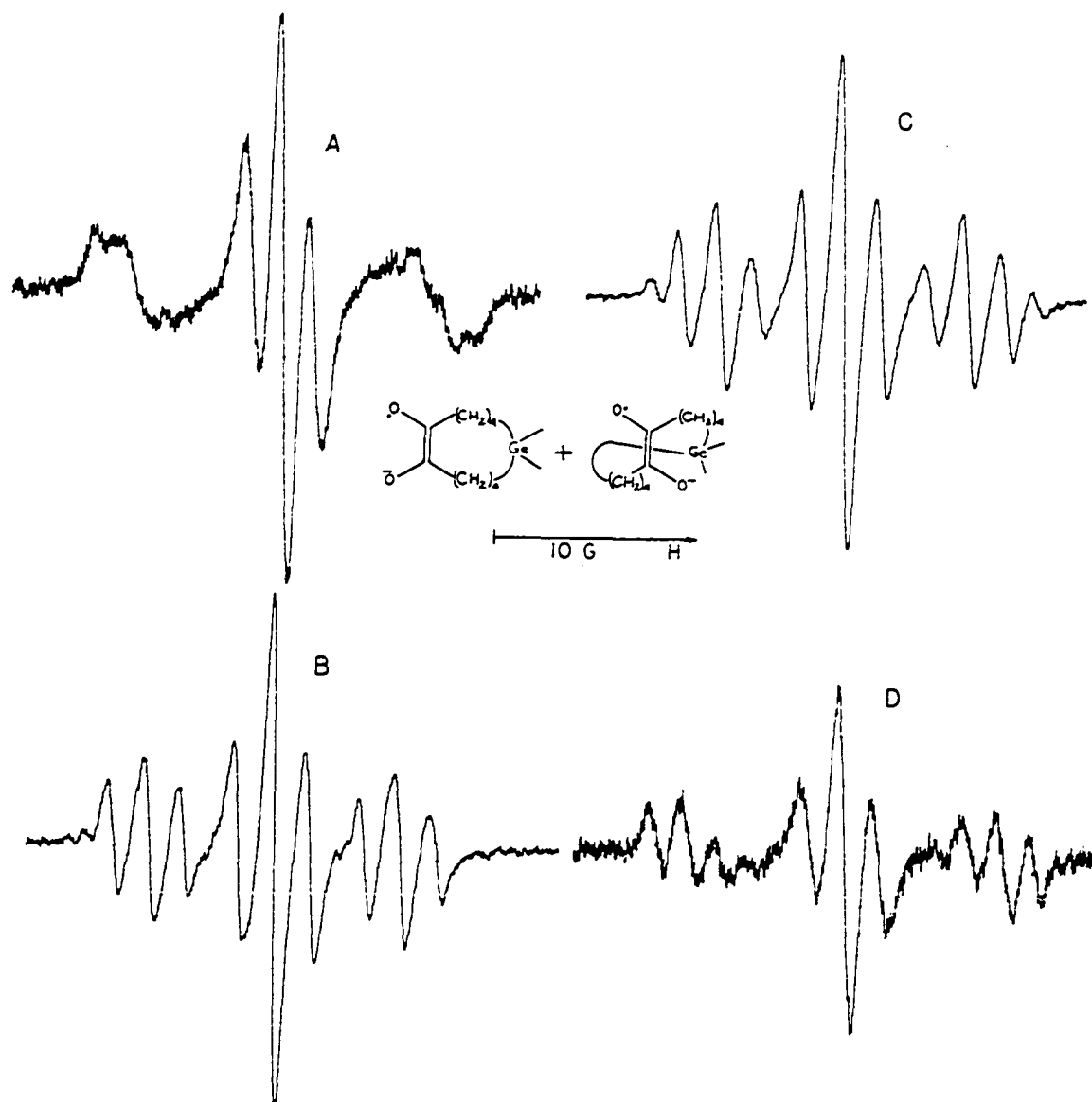
<sup>f</sup>All lines broad

<sup>g</sup>At lower g than the lines from the E isomer

<sup>h</sup>DMF/cesium tert-butoxide

---

Figure 48. (Continued)



- A. 40°C, [2.2.2]-cryptand added  
 B. Same as A, except at 100°C  
 C. 120°C, 0.1 M K<sup>+</sup>DMSO<sup>-</sup>/DMSO  
 D. 80°C, potassium iodide added (0.5 M)

Figure 49. ESR spectra of 7,7-dimethyl-7-germacycloundecane-1,2-semidione

## 7,7-Dimethyl-7-germacycloundecane semidione

Temperature (°C)	Splittings (G)	g	Configuration
25	7.48, 1.43 T X T	---	E <sup>a</sup>
60	6.55, 1.68 T X T	2.00504	E <sup>b</sup>
80	4.66 P	2.00496	Z <sup>c</sup>
80	6.31, 1.76 T X T	2.00504	E <sup>c</sup>
130	4.62 P	---	Z <sup>c</sup>
130	5.97, 1.82 T X T	---	E <sup>c</sup>
25	7.80, 1.62 T X T	---	E <sup>d</sup>

---

<sup>a</sup>Broad wing peaks

<sup>b</sup>DMSO/[2.2.2]-cryptand

<sup>c</sup>DMSO/standard conditions

<sup>d</sup>DMSO/potassium iodide added

---

Figure 50. Values of  $\underline{a}^H$  and  $\underline{g}$  obtained under various conditions for 7,7-dimethyl-7-germacycloundecane-1,2-semidione

the radicals and added potassium iodide was observed at room temperature, two superimposed spectra could be seen. As this sample was warmed, the wings of the set of lines at lower  $g$  began to sharpen so that by 90°C the spectrum consisted of a triplet of triplets and a pentet.

( $\underline{a}^H = 6.83$  G (2H), 1.81 G (2H) and 5.61 G (4H).) Figures 51 and 52 are copies of typical spectra which have been observed in this system.

Figure 53 presents a condensed form of the data obtained for this system.

### C. Discussion

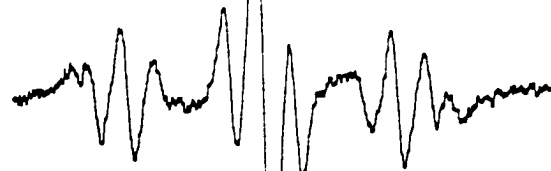
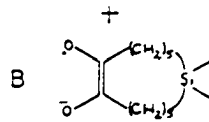
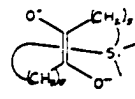
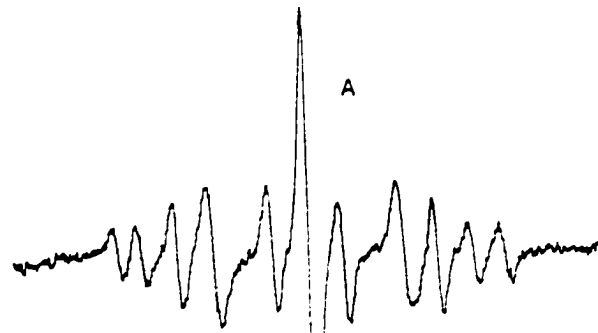
#### 1. E-Z isomerization

Consider for the moment the case of cyclopentadecane-1,2-semidione presented in part 9 and Figures 37 and 38 of the Results section. It is apparent that two sets of lines are present in the esr spectrum. One of these sets consists of a pentet, indicating four equivalent hydrogens, and is most reasonably assigned to the (Z)-1,2-semidione. The  $g$ -value and splitting constant fit into the pattern established by the small and medium sized rings where only the Z isomer can exist, as well as with (Z)-biacetyl.

Carbons in Cycle	$\underline{a}^H$ G (4H)	$g$ ( $K^+$ counter ion)
4	14.20	2.00498
5	13.85	2.00490
6	10.04	2.00490
7	4.0 (120°C)	2.00480 (R.T.)
8	3.48 (100°C)	2.00494 (R.T.)
9	4.0 (120°C)	2.00491 (R.T.)

Figure 51. ESR spectra of 8,8-dimethyl-8-silacyclotridecane-1,2-semidione taken in the presence of added potassium iodide

- A. 90°C
- B. 30°C
- C. 120°C



10 G H

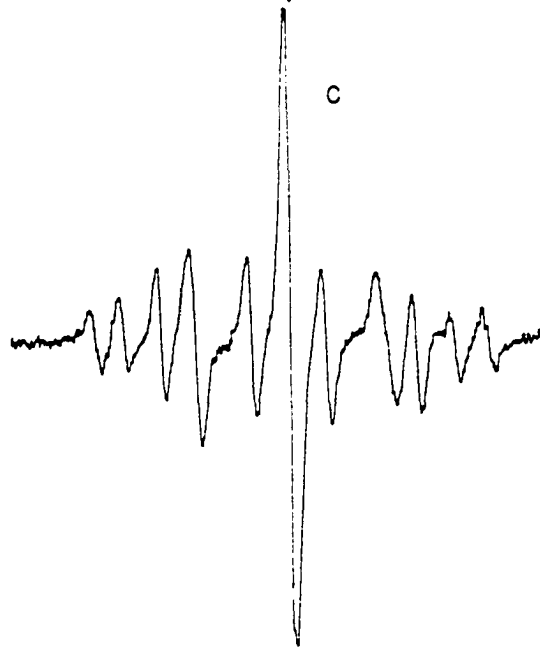
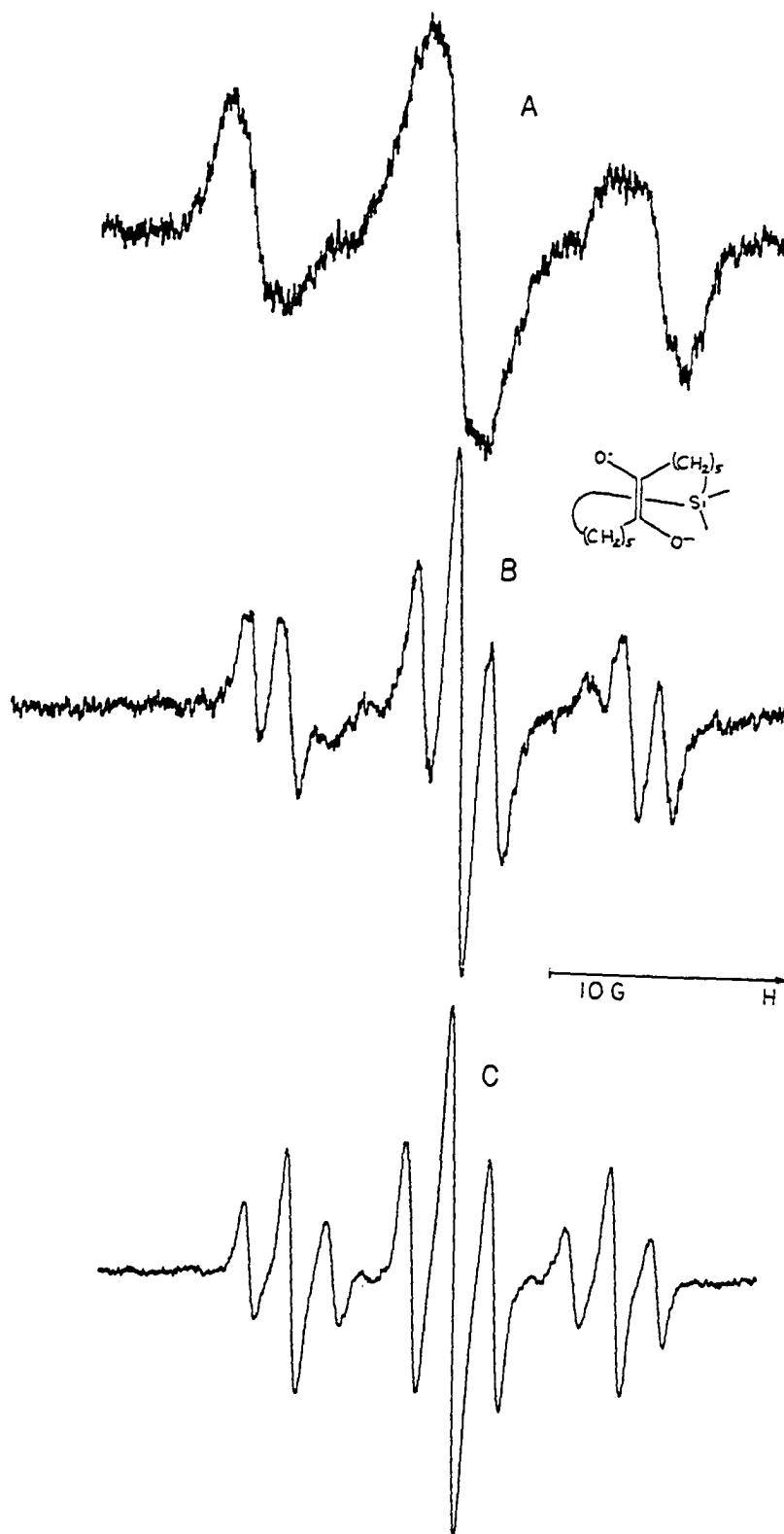




Figure 52. ESR spectra of 8,8-dimethyl-8-silacyclotridecane-1,2-semidione taken in dimethylformamide with cesium tert-butoxide as the base

- A. -60°C
- B. 0°C
- C. 70°C



## 8,8-Dimethyl-8-silacyclotridecane semidione

Temperature (°C)	Splittings (G)	$\underline{g}$	Configuration
-40	8.09, 0.99 T X T	2.00506	E <sup>a,b</sup>
60	6.82, 1.65 T X T	---	E <sup>a</sup>
90	6.68, 1.76 T X T	2.00507	E <sup>a</sup>
40	4.90 P	---	Z <sup>c,d</sup>
40	7.04, 1.65 T X T	---	E <sup>c</sup>
130	5.10 P	---	Z <sup>c,d</sup>
130	6.60, 1.95 T X T	---	E <sup>c</sup>

---

<sup>a</sup>DMF/cesium tert-butoxide.

<sup>b</sup>Broad wing peaks.

<sup>c</sup>DMSO/potassium iodide added.

<sup>d</sup>Lower  $\underline{g}$  value than the E isomer.

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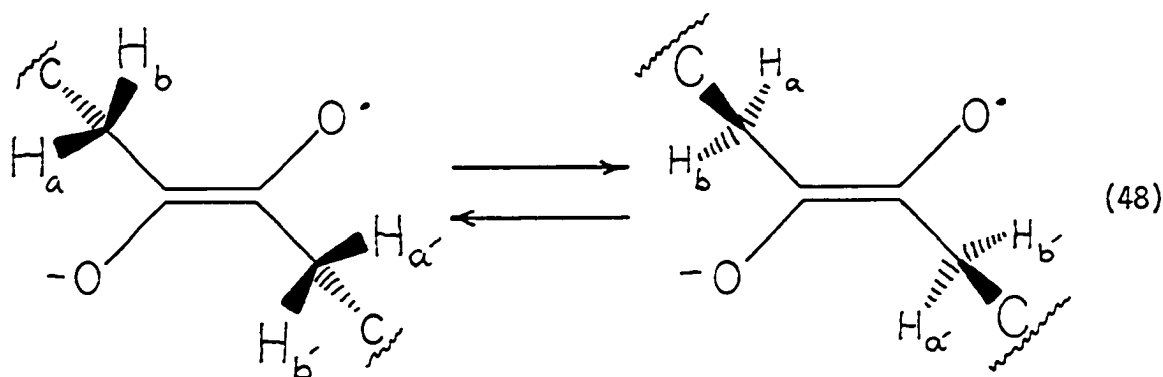
Figure 53. Values of  $\underline{a}^H$  and  $\underline{g}$  obtained under various conditions for 8,8-dimethyl-8-silacyclotridecane-1,2-semidione

Carbons in Cycle	$\underline{a}^H$ G (4H)	$\underline{g}$ ( $K^+$ counter ion)
15	5.2 (100°C)	2.00491 (R.T.)
( <u>Z</u> )-biacetyl	7.26 (6H)	2.00491

The fact that this species is favored by high potassium ion concentrations also argues in favor of ascribing the pentet to the Z isomer, since the Z isomer would be expected to have an ion pairing constant larger than the E isomer.

The second set of lines is a triplet of triplets which indicates the existence of two pairs of equivalent hydrogens. The fact that both of these pairs of hydrogens exchange in DMSO- $d_6$  indicates that these hydrogen atoms are alpha to the semidione group. (Semidiones are known to exchange their alpha hydrogen atoms when generated under basic conditions in DMSO- $d_6$ .<sup>77</sup>) The high  $\underline{g}$ -value of the triplets in the presence of potassium counter ion, as well as the fact that they are disfavored relative to the pentet upon addition of potassium iodide, suggests that the triplets arise from (E)-cyclopentadecan-1,2-semidione. If one makes a model of this system, one can see that there are two kinds of  $\alpha$ -hydrogens, one cisoid to the neighboring oxygen atom (labeled (a) below) and one transoid to this oxygen. It is true that in a given conformation the spatial orientation of (a) does not appear to equal that of (a'), but a minor movement of the atoms of the ring will cause (a) and (a') to become time averaged. On the other hand, (a) and (b) cannot be exchanged except by rotating the ring around the semidione group, a molecular motion which intuitively seems much more difficult to achieve. This relationship can be seen in the diagram below, where the

four carbons and the two oxygens associated with the semidione moiety are in the plane of the paper. On the left, the ring goes back into the page and the  $\alpha$ -hydrogens stick out toward you, while on the right the opposite is true. The pair of atoms labeled (a) and (a') are one set of equivalent hydrogens at room temperature, and the pair labeled (b) and (b') are the other set.



The  $g$ -value for the triplet of triplets is similar to that of (E)-biacetyl under the same conditions (0.1 M  $K^+$ DMSO),  $g = 2.00504$ ,  $g_{\text{biacetyl}} = 2.00506$ .

The formation of the E semidione is in keeping with the previously mentioned observations of Cope, who noticed that cyclic olefins with eleven or more carbon atoms in the ring were more stable in the E configuration than in the Z configuration. Indeed, it appears as if E semidiones become more stable than Z semidiones when there are eleven or more carbon atoms in the ring.

The spectrum of the ten-membered semidione looks the same both in the presence and in the absence of potassium counter ion. The spectrum consists of a broad triplet,  $a^H = 8.27$  G ([2.2.2]-cryptand present) or

9.20 G (0.25 M KI). The difference in the  $g$ -values under these two sets of conditions is  $1.4 \times 10^{-4}$  with the solution high in potassium ion concentration giving the lower value. This is typical of the smaller  $\underline{Z}$  rings,  $C_4$ ;  $1.2 \times 10^{-4}$ ,  $C_5$ ;  $2.1 \times 10^{-4}$ ,  $C_6$ ;  $2.0 \times 10^{-4}$ ,  $C_7$ ;  $1.8 \times 10^{-4}$ , and  $C_9$ ;  $1.9 \times 10^{-4}$ ) or ( $\underline{Z}$ )-biacetyl,  $2.0 \times 10^{-4}$ , and as we have seen, arises from ion pairing. ( $\underline{E}$ )-biacetyl semidione shows a change in  $g$ -value of  $4 \times 10^{-5}$  upon going from the free ion to a solution containing added potassium iodide (0.3 M). These two pieces of evidence indicate that the ten-membered ring is in the  $\underline{Z}$  configuration only. On the contrary, the eleven-membered ring shows two different splitting patterns, depending on the conditions chosen. When the potassium counter ion is complexed with cryptand, an incompletely resolved triplet of triplets is seen. The spectra for this system are not perfect, owing to the strain of the  $\underline{E}$  configuration which prevents the (a) and (a') hydrogens from equilibrating. At the other extreme, when high concentrations of potassium are used a second set of triplets is observed. These different sets of lines may be seen by referring to Figures 29 and 30.

The behavior of the members between  $C_{11}$  and  $C_{15}$  is intermediate, as would be expected. That is, as the ring size increases, the  $\underline{E}$  isomer appears to become more symmetrical as the (a) and (a') protons become more easily time averaged. Finally, by  $C_{15}$  the spectrum from the  $\underline{E}$  ring is a reasonably well-defined triplet of triplets at room temperature.

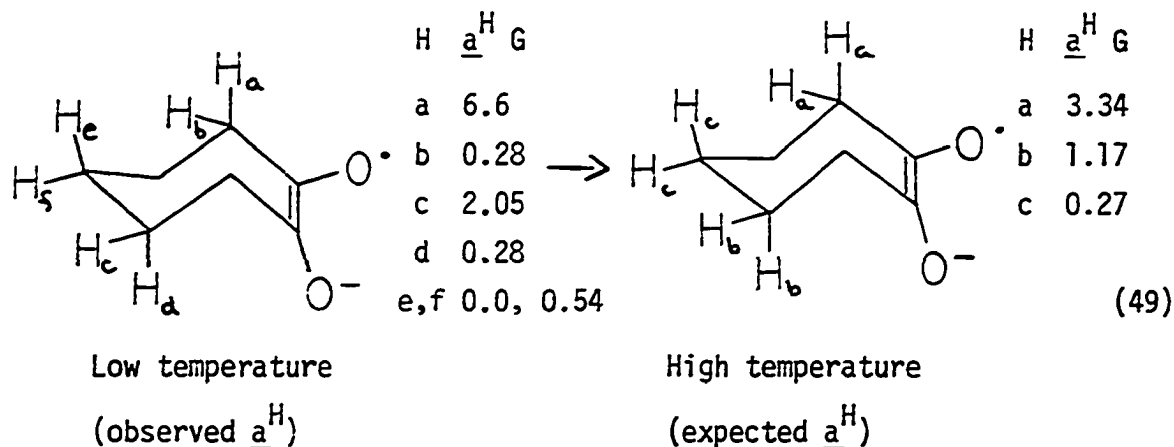
It appears that the interconversion of  $\underline{E}$  and  $\underline{Z}$  species does not occur by simple rotation about the carbon-carbon bond of the semidione,

but rather through a diamagnetic intermediate. This point will be discussed later in section 3.

## 2. Conformation of the Z isomers

As mentioned earlier, the seven-membered semidione has been studied extensively.<sup>18</sup> During the course of this investigation, the previously neglected variable temperature experiment was done.<sup>78</sup> It is qualitatively obvious from Figure 25 that cycloheptane-1,2-semidione is undergoing observable conformational motion on the esr time scale at room temperature. The complexity of the spectrum, plus the fact that the high temperature limit cannot be reached before the radicals decompose, makes quantitative analysis of the data impossible. It does seem safe to say that additional conformations are being populated at the higher temperatures. The argument supporting this claim follows.

Consider the following,



The coupling constants determined at room temperature are shown above on the left. If the only process occurring is interconversion of two degenerate conformations, then the splittings which would result at

high temperatures are those on the right. The two smallest splittings may be determined experimentally from the high temperature spectrum as 0.20 G (2H), and 0.77 G (2H). The large splitting is not known since the equilibration process is not yet fast enough to sharpen all the lines of the spectrum. There is a considerable discrepancy between the expected value of 1.17 G and the observed value of 0.77 G. This discrepancy presumably arises from the population of conformations other than those populated at room temperature. (These would have different splitting constants, which would change the expected time averaged values.)

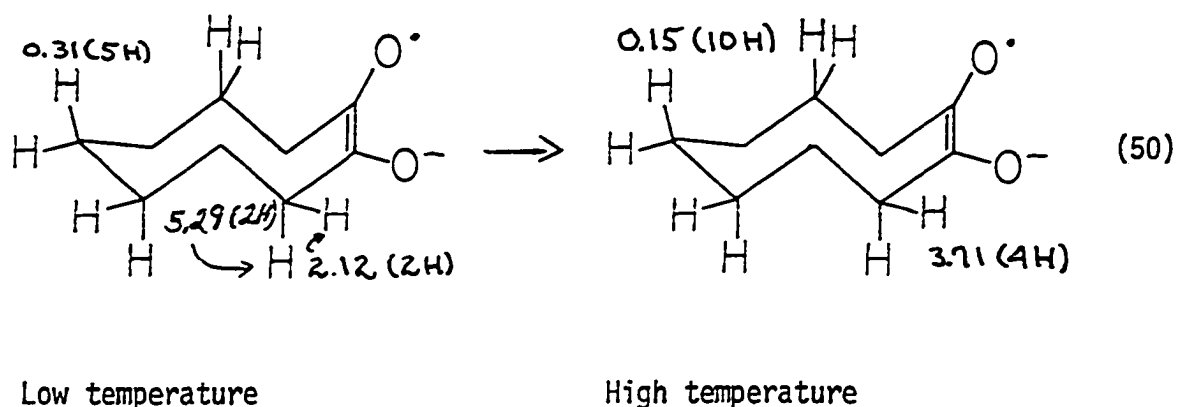
Models confirm that there may be more than one type of molecular motion involved in the conformational interconversion. The chair form actually prefers to be slightly twisted. These two twist-chair conformations may be interconverting at room temperature. At higher temperatures the boat form may become populated. Simultaneously, the chair-chair interconversion becomes rapid so that at a high enough temperature the esr spectrum would appear as a pentet of pentets of triplets. This spectrum would not necessarily have the same total width as the one at lower temperatures.

The eight-membered ring must exist in two (or more) different conformations at room temperature. Warming this radical causes a reversible change to a pentet which is most reasonably ascribed to the fluxional cyclooctane-1,2-semidione. The spectrum taken at low temperature (-80°C) in THF may be interpreted as a doublet, doublet,



doublet, doublet, with splitting constants of 1.8, 3.5, 5.0, and 5.4 gauss.

The nine-membered ring is also fairly rigid at room temperature and its spectrum, like those of the seven- and eight-membered rings, also shows a variation with temperature. It is not possible to obtain much information about the high temperature splitting constants of the nine-membered ring, since the radicals decay rapidly below the coalescence temperature. However, it does appear that the total spectral width does not change. Also, it looks as if the major splitting is going to be a large pentet, of  $a^H = 3.7$  G, with much smaller (if any) additional splittings. This is in keeping with what one would predict for a simple interconversion of two degenerate conformations,



Although a few spectra were run of the ten carbon system, the results are not particularly spectacular. The broad triplet which is seen does not change appreciably with temperature.

The behavior of the Z configuration of the larger rings is interesting. The eleven- and twelve-membered rings do not seem to be completely time averaged at 110°C. This effect is present, but to a

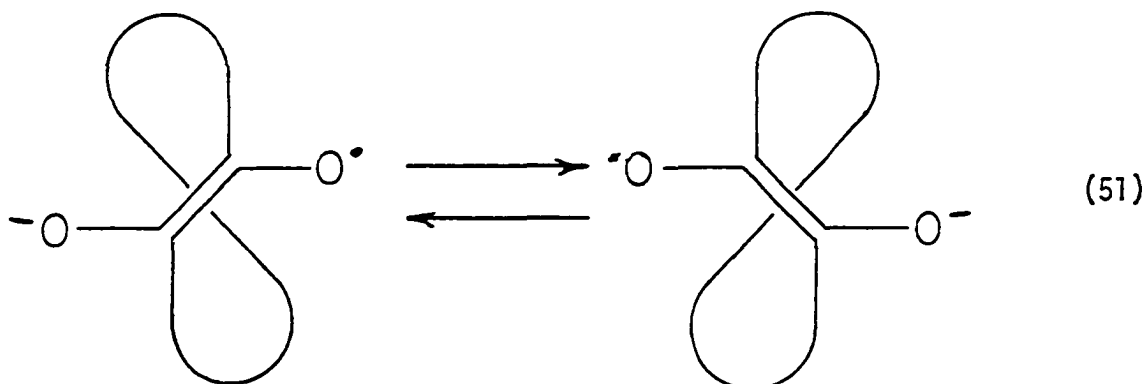
lesser degree, in the higher homologs as well. To observe the lines from the Z isomers, the samples must be warmed to sharpen the lines. Even the fifteen carbon cyclic semidione shows this effect. There must be enough rigidity in the ring so that interconversion of the  $\alpha$ -hydrogens is slowed. Additionally, a number of conformations appear to be accessible to the larger Z systems, as is indicated by the change in total spectral width with temperature. This fact makes quantitative determination of entropies and enthalpies of activation difficult.

In summary, the picture we have of (Z)-semidiones in the medium and large rings is one of moderately slow or slow rates of conformational inversion at room temperature. At modest temperatures, the four  $\alpha$ -hydrogens of the twelve-, thirteen-, fourteen-, and fifteen-membered rings are rapidly equilibrating on the esr time scale. Remarkably, the six-membered ring has a higher rate of conformational interconversion at room temperature than any of the larger rings studied. It is amusing to consider that the increased "floppiness" of the larger rings is offset by the greater difficulty of constraining a large number of atoms in the transition state. In other words, the lower enthalpy of activation expected for the large rings does not result in a greater rate of conformational motion because of the higher entropy of activation. Parallels between this and the operation of human social organizations abound.

### 3. Conformation of the E isomers

As mentioned in section one, the E isomers have two sets of two equivalent hydrogens at, or above, room temperature. The eleven- and twelve-membered E rings appear to be asymmetric, giving spectra which resemble triplets of triplets, but which do not have the proper line intensities. In principle, each of the four  $\alpha$ -hydrogens of the E rings could be different, resulting in a set of lines which would be a d. X d. X d. X d. Although low temperature experiments are consistent with this expectation, they do not prove it conclusively since the lines are not well-enough resolved to determine the exact splitting pattern.

Cyclopentadecane semidione shows an interesting effect at high temperature where the triplet of triplets begins to coalesce, presumably to a pentet. This is caused by the interconversion of one E "enantiomer" into the other by rotation of the double bond through the ring. (Note that at no time is either enantiomer isolated, nor is there ever an enantiomeric excess.)



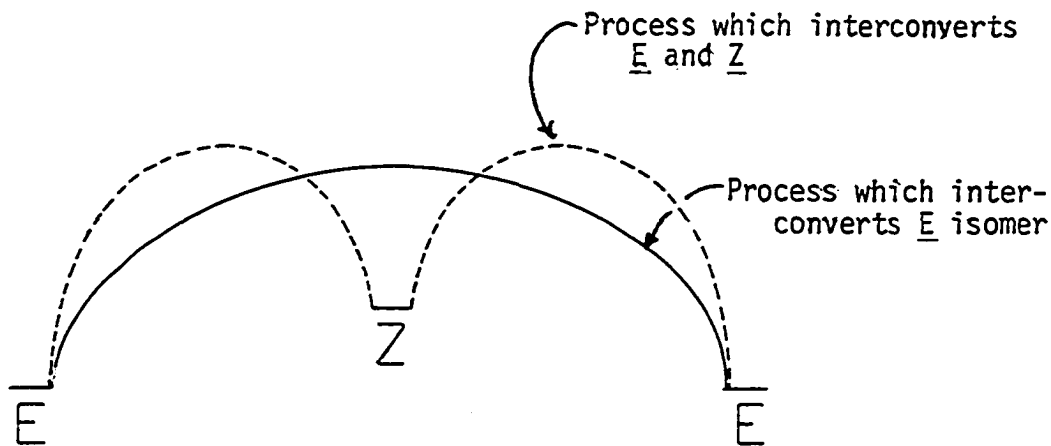
The two hydrogens of a given  $\alpha$ -methylene group are diastereotopic. Rapid equilibration of the two enantiomers removes the distinction between these hydrogens in the time frame of the esr experiment which causes the hydrogens to become equivalent. The rate at which interconversion must occur to cause this is approximately  $3 \times 10^6 \text{ sec}^{-1}$ . (This is determined from the separation of the esr lines.) This gives a lifetime of about  $10^{-6}$  to  $10^{-7}$  sec at  $130^\circ\text{C}$ . Compare this to  $10^{-4}$  sec for (E)-cyclodecene (at room temperature) as reported by Roberts. Although it is not possible to draw any firm conclusions from this observation, it suggests that a cyclic semidione can invert less easily than the corresponding cycloalkene. This is to be expected considering the size of the oxygens in the semidione moiety.

There was no attempt made to obtain ion pairing data, or [E]/[Z] ratios, for the large rings. This was because of experimental difficulties. At room temperature the wing peaks of the Z isomers are broadened. Additionally, the signal strength was often poor at room temperature. This made it necessary to warm the solutions during the observation of the spectra, which in turn introduced a number of complications, including the fact that  $\gamma_{\text{app}}$  is unknown at the elevated temperatures. Furthermore, the overlap of the two sets of lines often made precise identification of  $g$ ,  $a^{\text{H}}$ , and [E]/[Z] difficult.

Casual inspection of the spectra of the fifteen carbon system shows that in  $0.1 \text{ M } \text{K}^+ \text{DMSO}^- / \text{DMSO}$  the [E]/[Z] ratio is approximately the same as that of biacetyl under identical conditions. It is tempting to conclude that cyclopentadecane semidione behaves the same as does

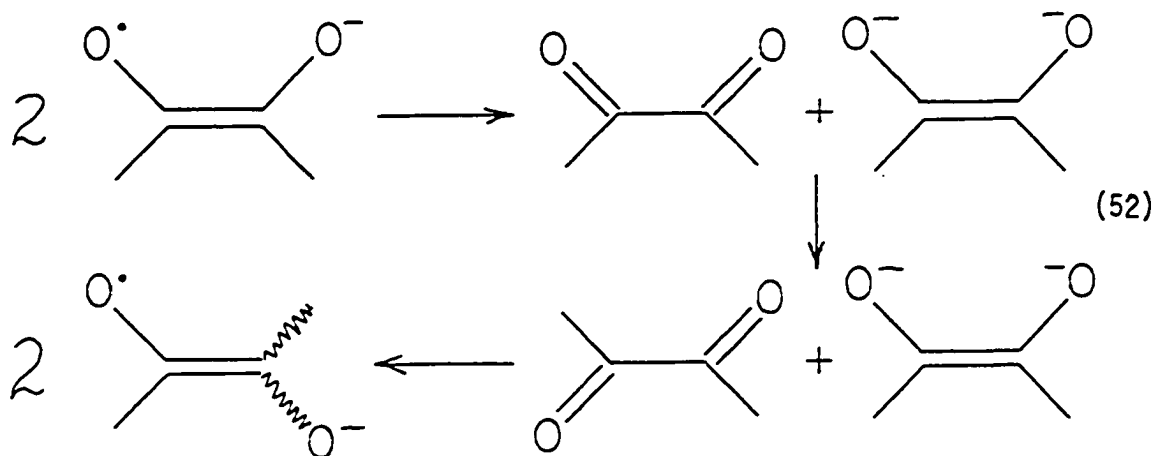
biacetyl with respect to ion pairing and the intrinsic, free ion,  $[E]/[Z]$  ratio. This has not been rigorously proven, however.

One additional point may be made concerning the  $E-Z$  interconversion. If you look at the high temperature spectrum of cyclopentadecane-1,2-semidione, you will see small wing peaks corresponding to the  $Z$  isomer even though the  $E$  spectrum is showing alternating line width due to the previously discussed isomerization. This shows that isomerization does not occur through an intermediate  $Z$  configuration. This is true because if the contrary were the case, the wing peaks of the  $Z$  species would be broadened too, and they are not. (If the lifetime of the  $E$  material is becoming short on the esr time scale, then certainly any intermediate in the conversion between  $E$  isomers must also have a short lifetime.) Yet, the  $E$  and  $Z$  material are in equilibrium. The potential energy diagram for this might look like,



At this point, twisting about the carbon-carbon double bond has not been ruled out as the mechanism of  $E-Z$  interconversion. An alternate

mechanism involving a disproportionation-comproportionation pathway,



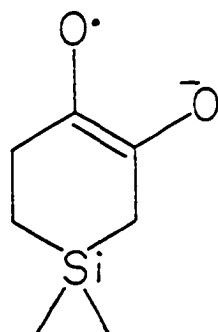
has traditionally been invoked to explain E-Z equilibration, but no data exists, which I know of, to allow a firm distinction between these two mechanisms to be made. Simple molecular orbital calculations do show a significant amount of double bond character for the C-C bond. Of course, the isomerization is less likely to occur via rotation around the C-C bond if this bond has a large amount of double bond character.

Summarizing, cyclic (E)-semidiones appear to form when eleven or more carbon atoms are included in the ring. As the ring size increases, the rigidity of the (E)-ring decreases. The largest ring studied, (E)-cyclopentadecane-1,2-semidione, has an [E]/[Z] ratio similar to biacetyl. This suggests that the relative strain in the E configuration compared to the Z configuration is the same in this semidione as it is in biacetyl.

4. The effect of including a silicon atom in a medium sized ring

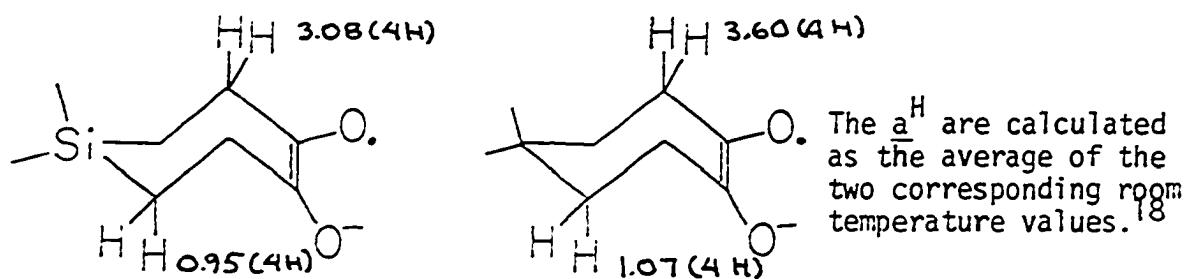
So far the discussion has been concerned only with carbocyclic rings. Since it would be interesting to know the effect of substituting a larger hetero-atom for one of the carbon atoms in the ring, I ran a series of experiments with sila- (and germa-) cycloalkane semidiones.

The first member of this series to be investigated was the six-membered ring,



(Note that the silicon (or germanium) atoms are always substituted with two methyl groups. Strictly speaking, the proper hydrocarbon systems to compare these results with would be the corresponding dimethylcycloalkanesemidiones.) The cyclic semidione could not be observed. In this instance only acyclic semidiones were seen.

The seven-membered ring proved to be more tractable. At room temperature, a spectrum showing alternating line width effects is observed. At high temperature, the spectrum coalesces to a pentet of pentets, due to the four  $\alpha$ -hydrogens and the four  $\beta$ -hydrogens. Unfortunately, the signal strength decreased drastically as the temperature was lowered making the observation of the completely frozen



radicals impossible. Adding [2.2.2]-cryptand, which typically improves the signal strength under these conditions, resulted in opening of the ring. The room temperature spectrum can be interpreted as arising in part from splittings of 2 and 4 gauss, due to the four  $\alpha$ -hydrogens. Using established methods<sup>79</sup> the enthalpy and entropy of activation could be obtained for this system (see section 6). Qualitatively speaking, the seven-membered ring containing the silicon atom appears to be less rigid than the simple carbocyclic system as might be expected from consideration of the carbon-silicon bond length vs the carbon-carbon bond length.

The spectrum of the eight-membered ring is just as complex with the silicon atom present as it is without it. The complexity arises from the co-existence of two or more different conformations at room temperature. The behavior of the  $g$ -value and of the spectrum's shape upon addition of [2.2.2]-cryptand or potassium iodide, implies that the eight-membered ring is always in the Z configuration even with the larger silicon atom present.



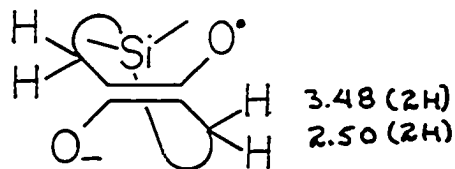
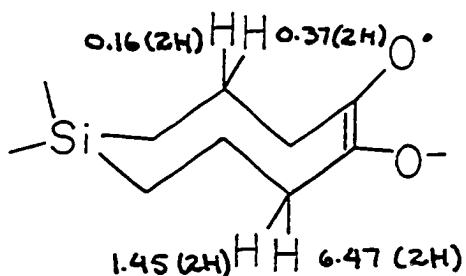
5. The effect of including a silicon or germanium atom in a large sized ring

The precursors for the six-, seven- and eight-membered rings discussed in the previous section were synthesized in these laboratories. Those for the systems to be discussed now were given to us by other workers. Since the samples had been stored in small septum-stoppered vials for a few years before I received them, a fair amount of decomposition had occurred. (Presuming the samples were pure when they were originally received.) The precursor for the nine-membered semidione was purified by means of preparative thin layer chromatography (TLC). Since the spectra obtained from the purified sample and the unpurified sample were identical, none of the other precursors were purified. Since there were only small amounts of these materials available, this had the advantage not only of saving time, but also of avoiding the risk of loss through some accident. In retrospect, this was probably an error, since somewhat different results were obtained from the eleven- and thirteen-membered substituted rings. The best approach would be to synthesize the appropriate bis-trimethylsiloxy alkene precursors which have always given good spectra in the past and re-investigate these few systems. At the point where this course of action had obviously become the preferred route, the experimenter's patience had been (grossly) exceeded. Therefore, I leave this for someone else should they be so inclined.

The results of the study of 6,6-dimethyl-6-silacyclononane-1,2-semidione are relatively clear cut. There appear to be two radical

species in solution even when the starting  $\alpha$ -hydroxy ketone is purified by TLC. The ratio of these two species may be altered by adding [2.2.2]-cryptand or potassium iodide. In light of the previously described results, the most likely explanation for this is the existence of both E and Z isomers in solution. At room temperature, the E isomer appears as a not quite perfectly shaped triplet of triplets, while the Z isomer is a t. X t. X t. X t. (Often the smallest two sets of triplets are broadened to an ill-defined peak consisting of three lines.) As expected, the E species predominates in solutions which are lacking suitable counter ions, e.g.,  $K^+$ [2.2.2]-cryptate or cesium ion. The spectrum for the E isomer has a narrower width and a higher  $g$ -value than that of the Z isomer under standard conditions. Cooling a DMF/cesium tert-butoxide solution to low temperature caused the spectrum of the E isomer to show selective line broadening and then to coalesce into a set of three doublet splittings ( $a^H = 1.72, 4.28, 6.45$  G). In all the experiments, the total line width of both E and Z species remained constant (see below). If a solution of Z radicals was warmed, an alternating line width effect was observed. At elevated temperature no change in the spectrum of the E species was noticed.

All the results are in agreement with the following interpretation,

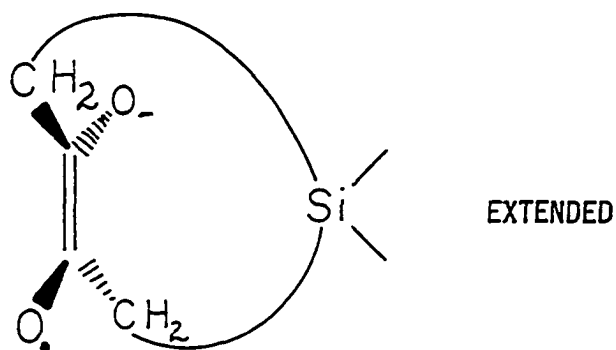


The E isomer is asymmetric and at low temperatures the splitting constants reflect this. The Z isomer may also be asymmetric since at low temperatures the spectra of these radicals were poorly resolved, relative to those taken at room temperature. This point was not investigated carefully due to the difficulty of generating high concentrations of radicals at low temperature. At high temperatures, the Z isomer undergoes conformational inversion rapidly enough to cause line broadening.

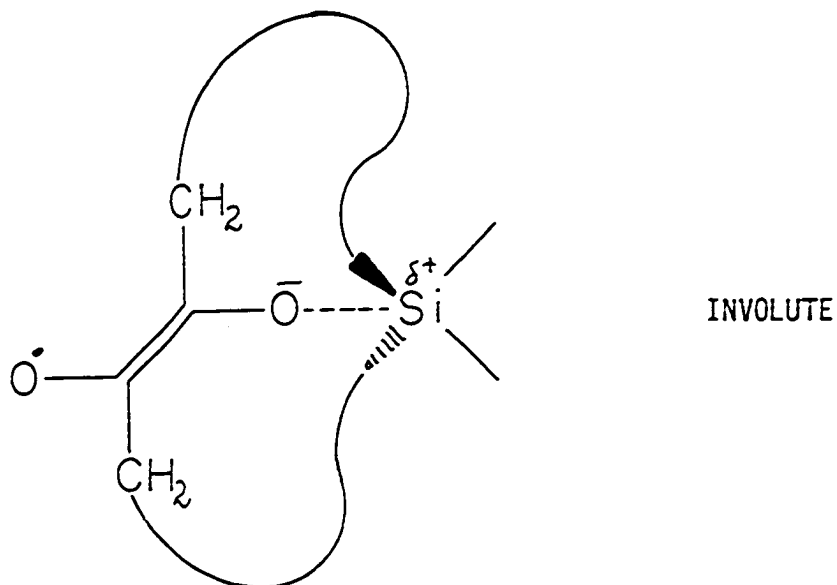
The analysis of the eleven- and thirteen-membered systems is somewhat more complex. In DMF/cesium tert-butoxide solution, the thirteen-membered sila-substituted ring shows a marked change in line width with temperature. At  $-40^{\circ}\text{C}$ , the spectrum is something like a triplet of triplets with the other line being sharper than the wings. As the temperature rises, the splitting constants are seen to change and the total spectral width becomes less. The  $g$ -value of 2.00507 does not change significantly. This same radical in potassium iodide/ $\text{K}^+\text{DMSO}^-$  shows a fairly well resolved triplet of triplets along with a second set of lines which, at higher temperatures, can be seen to be a pentet. The pentet appears at higher field (lower  $g$ -value) than does the triplet of triplets. The most reasonable assignment for the pentet is the Z isomer of the cyclic semidione. The broadness of these lines at room temperature is in accord with the behavior of the carbocyclic analogs. The E species presumably produces the triplets. Why the spectrum of the E isomer should show such an effect of temperature is not obvious from the previous studies. A reasonable explanation would be that there are two

(or more) conformations which have different splitting constants in equilibrium in solution. The rate of interconversion between these two conformations must be intermediate on the esr time scale at room temperature. If the two conformations had different enthalpy content, the relative populations of the two states would change with temperature. This would explain the change in spectral width. When the temperature is low, the radicals are mostly in the state with larger width, and the resulting spectrum is the spectrum of the semidione in that state. As the temperature rises, the second state is populated and the spectrum becomes broad in the wings due to uncertainty in the value of the splitting. (Recall that the rate of exchange has been defined as intermediate.) As the temperature continues to rise, the rate of exchange increases, causing the lines to sharpen. Concomitantly, the population of the second species continues to increase causing a further shrinking of the spectrum's width.

The qualitative temperature effects suggest that the conversion from the species seen at low temperature to the one seen at high temperature has a positive value for both  $\Delta H$  and  $\Delta S$ . One might suppose that the low temperature species is an extended conformation where the semidione moiety is surrounded by solvent and the silicon atom is distant from it.



The higher temperature species could be an involute conformation where an oxygen of the semidione moiety would be associated with the silicon atom.



This is reasonable in light of the polarization of the carbon silicon bond and seems possible based on Dreiding models of the two conformations. (Note, Dreiding models are so floppy that almost anything seems reasonable with this large a ring.)

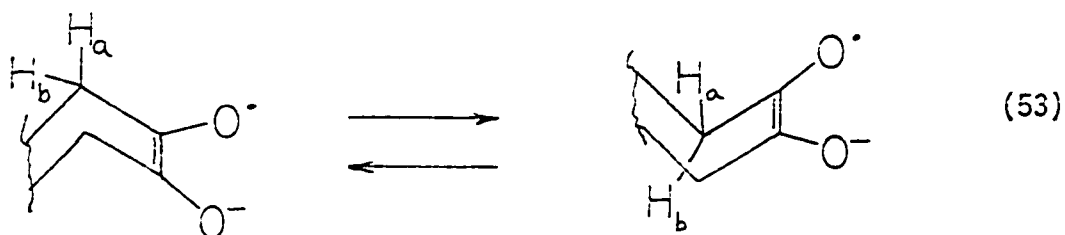
The eleven-membered ring containing a silicon atom also shows this behavior. That is, when potassium counter ion is present, a pentet can be observed and the triplet spectra show marked variation in width as the temperature changes. It was observed that addition of potassium iodide to a solution showing broad wing peaks sharpened those peaks and resulted in the spectrum of larger total width. This is consistent with the picture presented above, *i.e.*, the pairing with potassium favors the extended conformation. It may be true that some counter ion ( $K^+$  or  $Cs^+$ ) must be

present for the extended conformation to be observed at all, although this is not proved. The 6-germa-derivative also shows these changes in spectral width as well as the additional pentet of lower  $g$ -value.

The behavior of these substituted semidiones is similar to the carbocyclic analogs if the radicals are in the  $\underline{Z}$  configuration. However, in the  $\underline{E}$  configuration a pair of conformations appears to be present, one of which may involve a transannular interaction. This is not observed in the carbocyclic analogs where only one  $\underline{E}$  species has been detected. (It is true, however, that small changes in total line width occur in many of the carbocycles as well.)

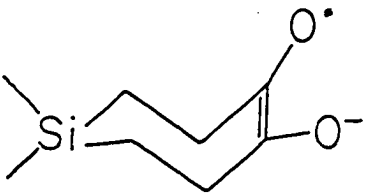
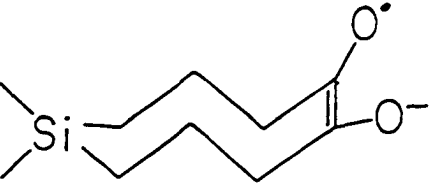
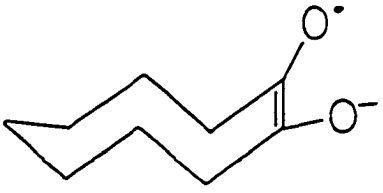
#### 6. Quantitative values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for conformational inversion

It was originally hoped that by using studies of the line shapes the rates of conformational interconversion of the rings could be obtained.



Varying the temperature would allow the values of the enthalpy and entropy of activation to be obtained graphically. It would have been interesting to compare these numbers for the various sizes of rings, and for various hetero-atoms in the rings. However, as we have seen, there are apparently a number of conformations involved in many of these systems. Consequently, when this approach was tried poor results were obtained.

Since the situation is more complex than a two jump (between degenerate conformers) model, the standard approach to line shape analysis is useless. A few of the systems did give reasonably good results and are shown below. The values for  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  which were calculated are reproduced here without further comment.

Ring	$\Delta H^\ddagger$ (Kcal/mole)	$\Delta S^\ddagger$ (e.u.)
	6.28	-7.04
	2.30	-22.7
	4.95	-14.8

#### 7. Conclusion of section IV-C: Semidiones in large rings

Large rings containing the 1,2-semidione moiety have been observed to form both the E and the Z configurations. As expected, the E configuration appears to show greater conformational mobility in the larger sized rings. Unexpectedly, the Z configuration seems to be only slightly more fluxional in the fifteen-membered case than in the eleven-membered one suggesting that a plateau has been reached for the rate of conformational interconversion in the cyclic-(Z)-1,2-semidiones.

The inclusion of a silicon or a germanium atom in the ring causes the ring to behave like a carbocyclic one containing two more methylene groups as far as formation of the E isomer is concerned. This may be due to the combination of the larger physical length of the Si-C (or Ge-C) bond and the possibility of trans-annular interaction with the polarized Si-C (or Ge-C) group.

Figure 54 displays the values of  $\underline{g}$  and  $\underline{a}^H$  which were obtained for all the large and medium sized rings. This figure is useful for a quick comparison but it must be noted that not all of the data which have been discussed within this dissertation are included in the figure.



Ring	$\underline{a}_Z^H$ (G)	$\underline{g}_Z$	$\underline{a}_E^H$ (G)	$\underline{g}_E$
7	6.19, 1.97 <sup>b</sup>	2.00498 <sup>b</sup>	---	---
8	3.48 <sup>b,c</sup>	2.00511 <sup>b</sup>	---	---
9	5.10, 2.14 <sup>b</sup>	2.00513 <sup>b</sup>	---	---
10	8.27 (T) <sup>b,c</sup>	2.00506 <sup>b,c</sup>	---	---
11	5.6 <sup>d,e</sup>	2.00490 <sup>d,e</sup>	4.7, 3.1 <sup>b,d</sup>	2.00507 <sup>b,d</sup>
12	8.27 <sup>c,e</sup>	2.00492 <sup>c,e</sup>	6.1, 1.9 <sup>b,d</sup>	2.00512 <sup>b,d</sup>
13	5.20 <sup>c,e</sup>	2.00491 <sup>c,e</sup>	6.26, 1.73 <sup>b,c</sup>	2.00513 <sup>b,c</sup>
14	4.73 <sup>c,e</sup>	2.00495 <sup>c,e</sup>	6.30, 1.74 <sup>b,c</sup>	2.00514 <sup>b,c</sup>
15	5.19 <sup>c,e</sup>	2.00491 <sup>c,e</sup>	6.73, 2.07 <sup>b,c</sup>	2.00408 <sup>b,c</sup>
5-sila- 7	3.08 (P), 0.95 (P) <sup>c</sup>	2.00490	---	---
5-sila- 8	---	2.00497	---	---
6-sila- 9	7.31, 1.35, 0.32	2.00497	3.50, 2.52 <sup>b</sup>	2.00509 <sup>b</sup>
7-sila- 11	4.84 <sup>d,e</sup>	---	8.11, 1.83 <sup>d,e</sup>	---
7-germa- 11	4.83 <sup>c,e</sup>	2.00496 <sup>c,e</sup>	6.25, 1.79 <sup>b,c</sup>	2.00505 <sup>b,c</sup>
8-sila- 13	4.80 <sup>f</sup>	---	7.19, 1.60	2.00509
biacetyl	7.03 (Sep.)	2.00495	5.71 (Sep.)	5.00506

<sup>a</sup>Except as marked, all  $\underline{a}^H$  values with one listed number are pentets, the remainder are triplets.

<sup>b</sup>[2.2.2]-cryptand present.

<sup>c</sup>Measured at  $\sim 100$  °C.

<sup>d</sup>Measured at  $\sim 150$  °C.

<sup>e</sup>Measured with added potassium iodide.

<sup>f</sup>Measured at  $\sim 50$  °C.

Figure 54. A summary of some  $\underline{g}$  and  $\underline{a}^H$  values determined for the medium and large sized rings

## V. EXPERIMENTAL

### A. ESR Measurements

The esr spectra were taken with a Varian V-4500 spectrometer. A dual cavity was used. The field was measured with a modified Alpha Scientific gauss meter. This is a simple nmr which uses water as a sample. The nmr frequency was counted with a Hewlett-Packard counter to eight significant digits, and the field strength calculated from this by,

$$H \text{ (G)} = 234.873 \cdot \nu_p \text{ (MHz)} \quad (54)$$

where  $\nu_p$  is the measured resonance frequency of the protons in  $\text{CuSO}_4$  doped water. With care, the field could be measured reproducibly to within 1 ppm.

The reference for  $g$ -value measurements was perylene radical cation with a  $g$  factor of  $2.002583 \pm 6 \times 10^{-6}$ .<sup>80</sup> The dual cavity was calibrated at the beginning of each set of runs by measuring perylene vs perylene. This allowed the field difference between the two sections of the cavity to be obtained. Typically, the correction was about 60 mG.

Variable temperature work was done with a standard V-4540 variable temperature controller which was calibrated against a chromel-alumel thermocouple.

At one point, it was necessary to obtain the ratios of peaks. Since the esr presentation is the first derivative of the spectrum, a double integrator was constructed using LM-301A op amps. The output of this integrator was used to drive a DVM. Although this worked fairly well

for integral ratios no larger than about ten to one, the presence of noise in the spectrum made the use of this circuit difficult due to drift.

Irradiation with light was accomplished with either a small "pen-lite" UV source, or a Phillips 500 W high pressure mercury arc which was focussed with a quartz lens upon the window of the cavity.

#### B. Preparation of Samples

The radical ions were prepared from suitable precursors using the standard "H" cell with a flat quartz active region.<sup>81</sup> The solvents used were dried with calcium hydride (DMF, DMSO) or lithium aluminum hydride (THF). The potassium tert-butoxide was commercial material (Aldrich Chemical Co.) and was vacuum sublimed prior to use. Cesium tert-butoxide, sodium tert-butoxide and lithium tert-butoxide were prepared by the reaction of the corresponding alkali metal with dried and distilled (over potassium) tert-butyl alcohol. They were then vacuum sublimed.

The alkali metal iodides were commercial materials (Alpha-Ventron) and were used after drying in an oven at 125°C, except for lithium iodide which was used from the bottle as is. Lithium iodide has one water of hydration which cannot be removed at atmospheric pressure at 125°C. Further, it decomposes upon stronger heating in air. The anhydrous salts were purchased.

[2.2.2]-Cryptand was obtained from PCR Inc. and was a product of the West German firm of E. Merck. It was not purified.

The 18-crown-6 macrocyclic ether was obtained from Aldrich and used without further purification.

Potassium dimsylate was made from potassium hydride (Alpha-Ventron) and dry DMSO and was titrated for total base concentration. This value was used as the potassium ion concentration of the sample. Aliquots were stored frozen under argon in ampules. The material was melted and withdrawn via syringe when needed.

To prepare a sample, the precursor (if solid), the base (if solid), the alkali metal iodide (if used) and complexing agent (if used), were weighed on an analytical balance in a glove bag purged with nitrogen and kept dry with indicating silica gel. (Liquids were measured with a syringe.) The vials containing the solid materials were sealed and transferred to a hood where an argon line was available. The contents of the vials were transferred to the appropriate legs of the "H" cell and a measured amount of DMSO (or other solvent) added. No attempt was made to take into account volume change upon dissolution of the salts, so the molarities reported here can only be approximately correct. The liquids were dispensed directly into the "H" cell.

Typically, 1 ml total volume was prepared. With the smaller variable temperature cell, a volume of 0.5 ml was used. When variable temperature work was done with  $K^+DMSO^-$  as the base, a concentrated (1.5 M) stock solution of base in DMSO was used if DMSO was not the solvent for the experiment. This means that the low temperature experiments run with dimsylate as the base (in THF or DMF) have a small amount of DMSO in them.

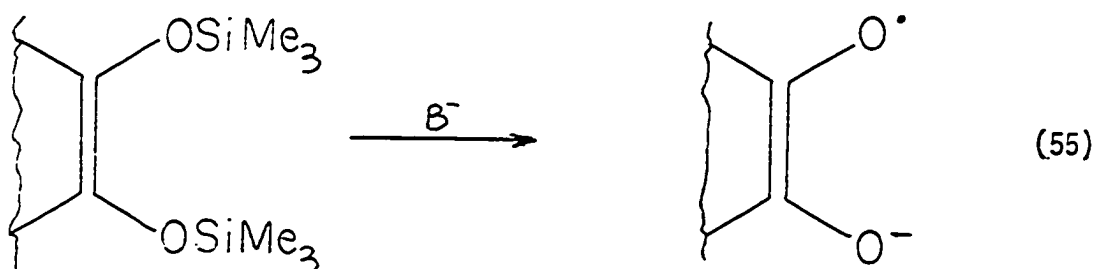
The standard conditions were 1 ml of 0.1 M  $K^+DMSO^-$  in DMSO with a semidione precursor concentration of 0.05 M.

To perform a dilution experiment, the sample was removed from the esr spectrometer and shaken back down into the "H" part of the cell. Then 0.50 ml (of the 1.00 ml total) of the solutions was removed from the cell under argon pressure with a syringe. (One must be careful to account for the dead volume of the syringe.) Finally, 0.50 ml of dry, degassed DMSO was added to the cell which was then shaken thoroughly to insure complete mixing. The result of this operation is a solution one-half as concentrated as before. This could be done a number of times until the radicals became too weak to observe, or until the experimenter made an error.

A smaller version of the "H" and quartz flat cell were used for the variable temperature studies.

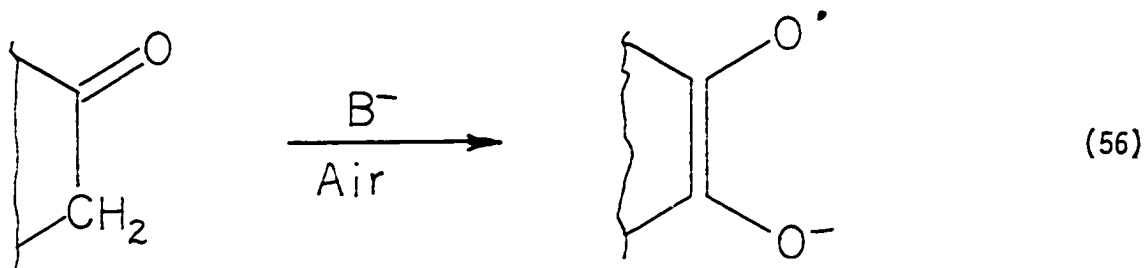
### C. Semidione Precursors

A number of the semidiones were prepared by reaction of the corresponding bis-trimethylsiloxyalkene with base.



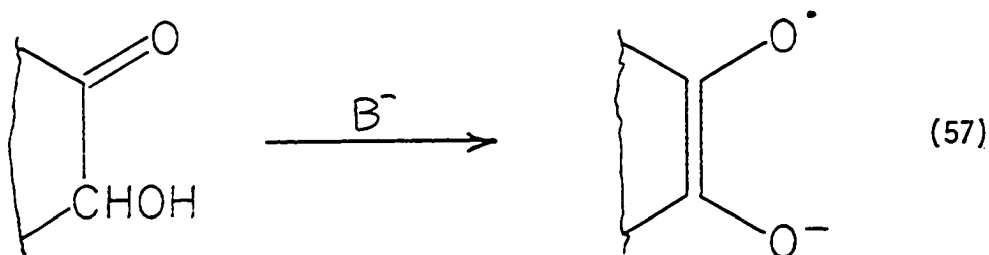
The siloxy alkenes, which were known compounds, were prepared from the corresponding diacid esters via the aciloin condensation.<sup>82</sup> The compounds made in this fashion exhibited the expected physical properties (IR, NMR, Bp). The diacid esters or the diacids needed for the carbocyclic systems were all commercially available (Aldrich, Fisher, J. T. Baker). The radical anions prepared via this route include: cyclobutyl, cyclopentyl, cycloheptyl, cyclooctyl, cyclononyl, cycloundecyl, cyclotridecyl, and biacetyl semidiones, as well as dimethyl sila-cycloheptyl and dimethyl sila-cyclooctyl semidiones.<sup>83</sup>

Other radicals were generated from the corresponding ketones by the action of base and air,



The radical anions prepared via this route include: cyclodecyl, cyclododecyl, cyclotetradecyl, and cyclopentadecyl semidiones. The ketones were purchased commercially, all from Aldrich except for cyclotetradecanone which came from Pfaltz and Bauer, Inc.

Most of the remaining radicals were made by the action of base on the  $\alpha$ -hydroxy ketones,



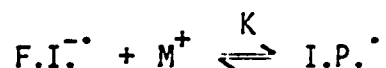
The systems obtained in this fashion included cyclohexyl semidione (The hydroxy ketone came from Aldrich.), and the 9-, 11- and 13-membered silacycles and the 11-membered germa-cycle. In these latter cases, the hydroxy ketones were provided by Professor P. Mazerolles.<sup>84,85,86</sup>

The only other route used for the generation of radicals was the reaction of  $\alpha$ -acetoxy ketones with base. Only the six-membered silacycle was generated in this fashion.<sup>83</sup>

## VI. SUMMARY

Ion pairing and conformational effects in aliphatic semidiones have been discussed. ESR spectroscopy was used to study the radical ions. The  $g$ -values and splitting constants of the radicals were the primary probes of the investigation.

Cyclic-1,2-semidiones have been shown to ion pair in dimethylsulfoxide solution with the following cations: lithium, sodium, potassium, rubidium, cesium, and potassium/(18-crown-6). The ion pairing constants,  $K$ , were found to be a function of the nature of both



the counter ion and the semidione. In general, the larger cations had smaller ion pairing constants although this trend was not strictly observed. The order of ion pairing constants in the series, cyclobutyl, cyclopentyl, cyclohexyl semidione was  $C_4 < C_5 < C_6$ . This was rationalized on the basis of changing oxygen-oxygen spacing in the semidione moiety.

Biacetyl semidione was extensively studied in the presence of potassium cations. The enthalpies and entropies of reaction for  $\underline{E}$ - $\underline{Z}$ -interconversion of both the free ion and the potassium ion pair were determined.  $\Delta H$  and  $\Delta S$  were also estimated for the ion pairing reactions of both  $\underline{E}$  and  $\underline{Z}$  isomers with potassium.

Cyclic semidiones with eleven or more carbon atoms in the ring were observed to form  $\underline{E}$  as well as the "normal"  $\underline{Z}$  isomers. The stability of the  $\underline{E}$  isomer increased with increasing ring size. Cyclopentadecane-1,2-semidione appeared to behave much like biacetyl



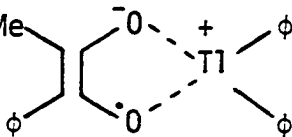
semidione. Cyclopentadecyl semidione also showed an interesting effect, the semidione moiety could be observed to rotate through the center of the ring.

The addition of a heteroatom such as silicon or germanium to a cyclic system caused a given sized ring to behave like a carbocyclic ring containing two more methyl units. The E isomers of the eleven- and thirteen-membered rings containing a heteroatom were observed to show an unusual variation of line width with temperature. This was attributed to a change in the conformation of these radicals with changing temperature.

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87. After Paul Feyerabend of the University of California, Berkeley.
88. With apologies to W. Dobson (Lewis Carroll).

## VIII. ACKNOWLEDGEMENTS

I would like to thank Professor G. A. Russell for putting up with me for five (long!) years. Also, I would like to thank the National Science Foundation for kindly providing a pre-doctoral fellowship which constituted a good portion of my support for those years, and Iowa State University which provided a teaching appointment that supplied the rest.

"said once, said twice, said thrice...

PROVED!"<sup>87,88</sup>