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Aspects of the cage effect in the decomposition of azo-bis-isobutyronitrile

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ASPECTS OF THE CAGE EFFECT IN THE DECOMPOSITION OF
AZO-BIS-ISOBUTYRONITRILE

by

Orlin Dalton Trapp

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

Major Subject: Physical-Organic Chemistry

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1957

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INTRODUCTION

The thermal decomposition of 2,2'-azo-bis-isobutyronitrile to produce free radicals has aroused recent interest in industrial polymerization chemistry. In this light, academic as well as industrial research laboratories have endeavored to explain the exact mechanism of this decomposition.

The efficiency of free radical production in the decomposition of 2,2'-azo-bis-isobutyronitrile has been found to vary considerably depending on the solvent used for this decomposition. The so-called "cage effect" has been used to explain this inefficiency. Recently it has been shown that an intermediate, dimethyl-N-(2-cyano-2-propyl)-ketenimine, is formed during this decomposition.

This work was initiated in the hope of furthering the understanding of this much talked about "cage effect" by observing quantitatively the effect of this intermediate, dimethyl-N-(2-cyano-2-propyl)-ketenimine, in relationship to the inefficiency of free radical production in the thermal decomposition of 2,2'-azo-bis-isobutyronitrile.

HISTORICAL

Through the many years prior to today's availability of physical property data by instrumentation, the chemical literature has been filled by the creative compound synthesizers of yesteryear. From two of these many creative minds came the first preparations (1) of 2,2'-azo-bis-isobutyronitrile. Thiele and Heuser observed that the decomposition of the compound in boiling water gave a 50 per cent yield of tetramethylsuccinonitrile. No other products were reported. Later Dox (2) cited thermal decomposition of aliphatic azo compounds as an excellent preparative method for tetrasubstituted succinic acid derivatives.

The classic discovery and study of the free methyl radical by Paneth and Hofeditz (3) in 1929 gave a great stimulus to the interest of organic chemists in free radicals.

Leermakers (4) first suggested a free radical mechanism for the thermal decomposition of azo compounds when it was observed that fragments from the thermal decomposition of azomethane removed a lead mirror. At the same time Rice and Evering (5) observed similar radical properties upon decomposition of 2,2'-azopropane. An early review of aliphatic free radicals is presented in a text by Rice and Rice (6).

Although Rice and co-workers opened the door to a wide field of free radical sources, scientific minds did not

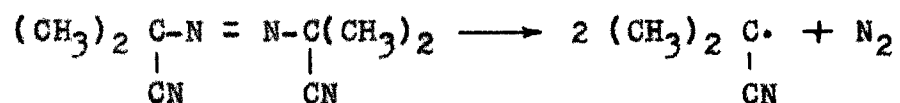
accept this advance until after World War II. At this time industrialists were interested in a clearer picture of free radical polymerization than could be gained by the then accepted initiators, for example, benzoyl peroxide.

In 1949 Lewis and Matheson (7) were the first to show that 2,2'-azo-bis-isobutyronitrile and related azo-bis compounds decompose unimolecularly at approximately the same rate in a variety of solvents. This discovery initiated a flood of publications dealing with 2,2'-azo-bis-isobutyronitrile as a polymerization initiator, and the kinetics and mechanism of the decomposition of 2,2'-azo-bis-isobutyronitrile. Since much of the available literature reporting 2,2'-azo-bis-isobutyronitrile as an initiator for polymerization is not directly related to this problem, the treatise by Flory (8) and a review by Burnett and Melville (9) give excellent coverage.

As a preliminary step to careful explanation of the mechanism of thermal decomposition of 2,2'-azo-bis-isobutyronitrile, Bickel and Waters (10) determined the product distribution of the complete decomposition carried out in dry toluene, which yielded 84 per cent tetramethylsuccinonitrile, 3.5 per cent isobutyronitrile, and 9 per cent 2,3,5-tricyano-2,3,5-trimethylhexane. The latter compound has not been sufficiently characterized to guarantee the structure assignment.

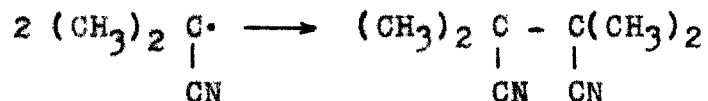
Similar isolation (11) of tetramethylsuccinonitrile from mixtures produced by the decomposition of 2,2'-azo-bis-isobutyronitrile in toluene and in carbon tetrachloride at 80.0° gave yields of 87 per cent and 96 per cent, respectively.

The decomposition of 2,2'-azo-bis-isobutyronitrile produces 2-cyano-2-propyl free radicals.

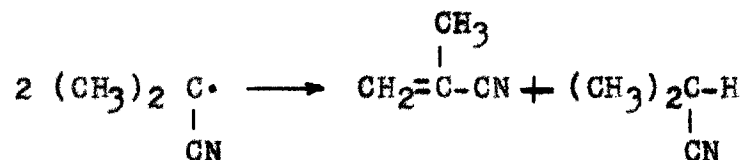


Considering the above product analysis, these free radicals must have several paths by which they can react.

Combination:



Disproportionation:



Disproportionation is a well established phenomenon (12) and involves the abstraction of a hydrogen atom from one

radical species by another, forming two products, an olefin and a saturated hydrocarbon.

The rates of formation of the major products, tetramethylsuccinonitrile (TMSN) and isobutyronitrile (IBN), were reported by Bevington (13), Figure 1. The analysis was carried out using the isotopic dilution technique with 2,2'-azo-bis-isobutyronitrile with a carbon-14 label in the cyano group.

To determine the amount of isobutyronitrile present, the acid, the acid chloride, and then the amide were prepared in sequence. Actually the presence of an intermediate (14, 15) (see page 20) was indicated by this procedure, since this intermediate yields the isobutyramide when these experimental conditions are employed.

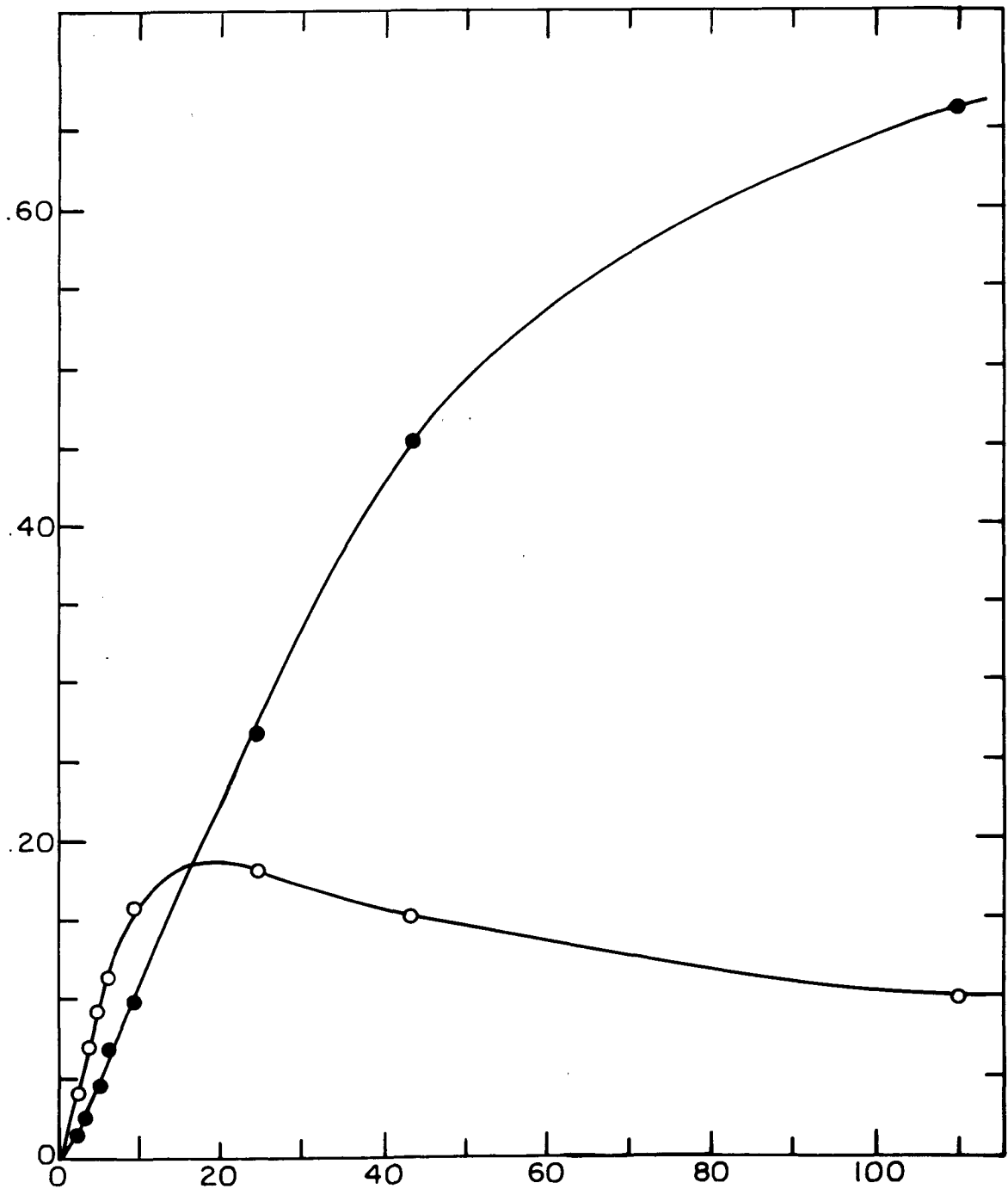
Overberger and Berenbaum (16) gave evidence that free radicals produced from azo-bis-nitriles are relatively free in solution since the decomposition of diastereoisomeric azo compounds produces identical mixtures of stereoisomeric dimerization products.

The first order kinetics of the thermal decomposition of 2,2'-azo-bis-isobutyronitrile have been determined by numerous methods by many workers (7, 11, 14, 17, 18, 19, 20, 21, 22, 23, 24). Several of these references were reviewed by Walling (25), but there are errors in his compilation. Hence all of the reported kinetic data available in the literature

Figure 1. The mole per cent of tetramethylsuccinonitrile and isobutyronitrile formed at various stages in the decomposition of 2,2'-azo-bis-isobutyronitrile at 80°

Abscissa; Time in hours
Ordinate; Yield, mole per cent

Tetramethylsuccinonitrile, ● ; isobutyronitrile, ○



to March 1957 are given in Table 1. The 2,2'-diphenyl-1-picrylhydrazyl (DPPH) data (21) have been corrected according to Lyons and Watson (26). The work (21) using 2,2'-diphenyl-1-picrylhydrazyl as a free radical scavenger has been disputed by many workers (11, 27, 28, 29) on the grounds of the questionable stoichiometry of radical destruction.

Prior to 1952, the efficiency of radical production from 2,2'-azo-bis-isobutyronitrile was assumed to be 1.00 (18, 30). Early in that year Austrian workers, Breitenbach and Schindler (22), reported the efficiency observed in styrene polymerization as less than or equal to 0.72, depending on whether there was or was not chain transfer occurring.

At the same time, in the United States, Arnett and Peterson (19, 31) determined the efficiency of radical production by using carbon-14 labeled 2,2'-azo-bis-isobutyronitrile to initiate polymerizations and then counting the resulting carbon-14 end groups in the polymer formed. Under the conditions of these experiments only a small percentage of the 2,2'-azo-bis-isobutyronitrile was decomposed. The initial efficiencies for monomers methyl methacrylate, vinyl acetate, vinyl chloride, styrene, and acrylonitrile varied between 0.5 and 1.00 in the order given. Arnett attributed the 50 per cent efficiency in methyl methacrylate to the unsymmetrical cleavage of the initiator.



Table 1. Rate of decomposition of 2,2'-azo-bis-isobutyronitrile in various solvents at various temperatures

Temp. (°C)	Solvent	Method	Rate ($10^4 \times$ sec. ⁻¹)	Ref.
80.0	Glacial acetic acid	N ₂ ^a	1.52	7
82.0	Glacial acetic acid	N ₂	1.50	19
80.0	N,N-Dimethyl aniline	N ₂	1.83	7
80.2	Aniline	N ₂	1.68	17
80.0	Dodecyl mercaptan	N ₂	1.46	7
80.2	Isobutyl alcohol	N ₂	1.76	17
80.2	Isobutyl alcohol	N ₂	1.68	17
82.0	Isobutyl alcohol	N ₂	1.67	19
80.2	Tertiary amyl alcohol	N ₂	1.40	17
82.0	n-Butyl alcohol	N ₂	1.55	19
82.0	1-Nitrobutane	N ₂	1.45	19
62.5	Nitromethane	N ₂	0.134	11
82.0	Cyclohexanone	N ₂	1.43	19
50.0	Xylene	N ₂	0.020	19
60.0	Xylene	N ₂	0.100	18
77.0	Xylene	N ₂	0.95	19
80.0	Xylene	N ₂	1.53	7
80.0	Xylene + 0.012 M Chloranil	N ₂	1.50	7

^aThe rate of nitrogen evolution.

Table 1. (Continued)

Temp. (°C)	Solvent	Method	Rate ($10^4 \times$ sec. ⁻¹)	Ref.
82.0	Xylene	N ₂	1.45	19
50.0	Styrene	N ₂	0.0297	22
70.0	Styrene	N ₂	0.472	22
62.5	Nitrobenzene	N ₂	0.179	11
80.0	Nitrobenzene	N ₂	1.99	20
100.0	Nitrobenzene	N ₂	22.5	20
60.2	Carbon tetrachloride	N ₂	0.085	24
62.5	Carbon tetrachloride	N ₂	0.118	11
74.4	Carbon tetrachloride	N ₂	0.675	24
77.0	Carbon tetrachloride	N ₂	1.21	7
62.5	Toluene	N ₂	0.136	24
69.8	Toluene	N ₂	0.38	17
70.0	Toluene	Spectra ^b	0.40	14
80.0	Toluene	N ₂	1.50	23
80.0	Toluene + 0.10 M iodine	N ₂	1.55	23
80.2	Toluene	N ₂	1.66±.06	17
80.4	Toluene	Spectra	1.55	14

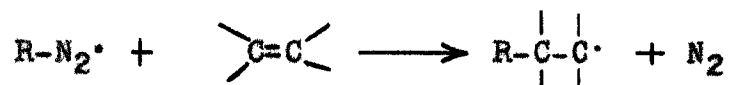
^bThe rate of disappearance of the ultraviolet spectra of 2,2'-azo-bis-isobutyronitrile at 360 m μ , 370 m μ , and 380 m μ .

Table 1. (Continued)

Temp. (°C)	Solvent	Method	Rate ($10^4 \times$ sec. ⁻¹)	Ref.
90.0	Toluene	Spectra	4.86	14
100.0	Toluene	Spectra	16.0	14
105.0	Toluene	Spectra	26.1	14
62.5	Chlorobenzene	N ₂	0.154	11
74.4	Chlorobenzene	N ₂	0.78	24
62.5	Benzene	N ₂	0.142	11
69.5	Benzene	DPPH ^c	0.344	21
60.5	Benzene	DPPH	0.105	21
55.0	Benzene	DPPH	0.0473	21
50.0	Benzene	DPPH	0.0240	21
45.2	Benzene	DPPH	0.01024	21
40.0	Benzene	DPPH	0.00495	21
60.0	Carbon tetrachloride	DPPH	0.0364	21
40.0	Carbon tetrachloride	DPPH	0.00196	21
60.0	Ethyl acetate	DPPH	0.0852	21
40.0	Ethyl acetate	DPPH	0.0043	21

^cDPPH, 2,2'-diphenyl-1-picrylhydrazyl, was corrected according to Lyons and Watson (26). The rate was determined by following the zero order disappearance of the color of DPPH, assuming a 1:1 stoichiometry.

In order to account for this low efficiency Arnett suggested that the two radicals are not equally efficient in polymerization initiation. Specifically he assumed that the reaction,



would occur with high efficiency whereas the efficiency of the simple addition of R^{\cdot} to monomer was assumed to be variable.

Baysal and Tobolsky (32) have reported the efficiency of radical production in the polymerization of styrene as a variable depending on the temperature and mode of termination of the polymer chain. Assuming, according to previous work (31, 33, 34), that nearly all termination is by combination, the efficiency of radical production is about 0.76 at 47.8° , about 0.70 at 60.0° and about 0.50 at 67.8° if the energy of activation for the decomposition is chosen equal to 30.7 kilocalories per mole, an average value obtained from Table 1 data.

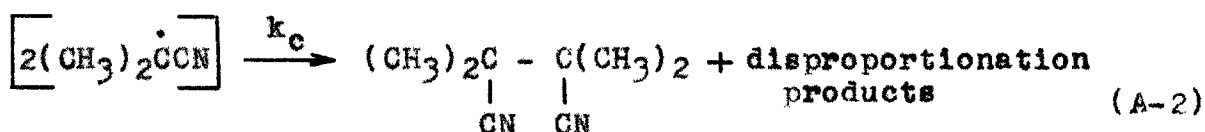
Iodine has been observed by Ford and Waters (35) to be a scavenger for 2-cyano-2-propyl free radicals. Experimentally, 2,2'-azo-big-isobutyronitrile was slowly added to a lesser molar amount of iodine in boiling toluene. It was reported that 74 per cent of the iodine atoms scavenged free radicals, as determined by the α -iodo-isobutyronitrile obtained. Two

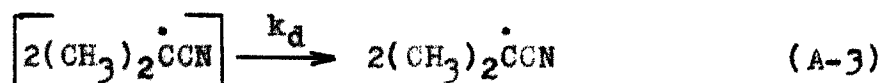
per cent of 2,3,5-tricyano-2,3,5-trimethylhexane was also reported along with an unweighed amount of isobutyronitrile. Tetramethylsuccinonitrile was also quantitatively reported, but it is difficult to estimate the value of this datum, since the ratio of iodine to 2,2'-azo-bis-isobutyronitrile is less than one.

Similarly, 2,2'-azo-bis-isobutyronitrile was decomposed (35) by slowly adding it to bromine in boiling carbon tetrachloride. Although the experiment was only qualitative in nature, α -bromo-isobutyronitrile was isolated as a major product.

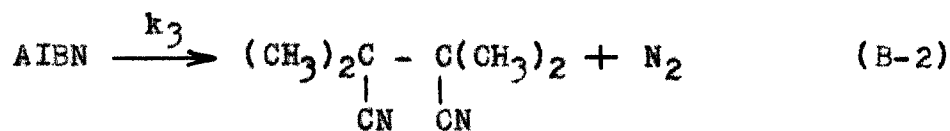
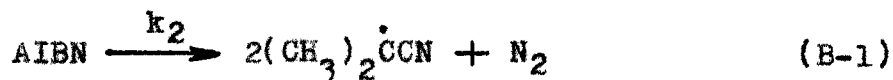
Bateman and Morris (36) reported evidence that the initiation of oxidation of ethyl linoleate, digeranyl, tetralin and other alkenes by 2,2'-azo-bis-isobutyronitrile and benzoyl peroxide was measurably inefficient.

Recently Hammond, Sen and Boozer (11) reported careful efficiency studies on the initial production of scavengable radicals from 2,2'-azo-bis-isobutyronitrile (AIBN). Basic mechanisms to consider are either





or (11)



(cis, non-radical decomposition)



where

$k_1 = k_2 + k_3$ = measurable rate constant for decomposition of AIBN,

$\boxed{2(\text{CH}_3)_2\dot{\text{C}}\text{CN}}$ = "caged" free radicals,

k_c = rate constant for combination,

k_d = rate constant for diffusive separation.

The efficiency factor, \underline{a} , for each case becomes,

Case A:

$$\frac{d[\text{S}]}{dt} = 2 \frac{k_d}{k_c + k_d} k_1 [\text{AIBN}],$$

or,

Case B:

$$\frac{d[S]}{dt} = 2 \frac{k_2}{k_2 + k_3} k_1 [AIBN],$$

$$\underline{a} = \frac{k_d}{k_c + k_d} = \frac{k_2}{k_2 + k_3}.$$

The limits on \underline{a} are first that \underline{a} is one; that is, there is no "caged" combination (Case A) or there is no non-radical decomposition (Case B), second that \underline{a} is zero; that is, k_d is zero, an unobservable radical decomposition (Case A) or there is a complete non-radical decomposition (Case B).

Hammond, et al. (11), used the method of Bawn and Mellish (21) in following the zero order disappearance of the scavenger, iodine. These results (Table 2) were in agreement with other data (11, 37) which warranted the inference of initiation efficiencies from oxygen-scavenged experiments. In the presence of powerful antioxidants, the peroxy radicals produced are immediately converted to unreactive products.

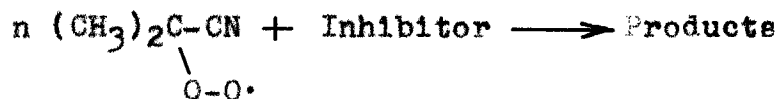
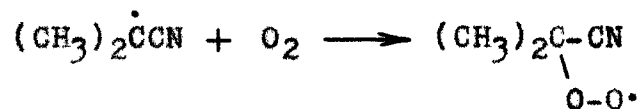


Table 2. Efficiency factor dependence on solvent

Solvent	Method	α	Ref.
Carbon tetrachloride	I ₂	0.45	11
	Oxidation inhibition	0.43	11, 36
Toluene	I ₂	0.59	23
Benzene	I ₂	0.62	11
	Oxidation inhibition	0.61	11, 36
	Radical inhibition	0.59	38
Chlorobenzene	I ₂	0.60	11
	Oxidation inhibition	0.57	11, 36
Nitrobenzene	I ₂	0.75	11
	Oxidation inhibition	0.73	11, 36
Nitromethane	I ₂	0.74	11
	Oxidation inhibition	0.73	11, 36

The stoichiometric factor, n , was substantiated by the isolation of products derived from the inhibitors (37).

An alternate method incorporating the same principle of initial zero order disappearance of iodine was reported by Hamill of Roy, et al. (23). Similar initiator efficiency was observed (Table 2) in toluene solution in the presence of an eight-fold excess of iodine.

Bevington (38) has reported a decrease in the expected yield of tetramethylsuccinonitrile (13) by use of the stable free radical, the oxidized form of N -(3- N -hydroxyanilino-1,3-dimethylbutylidene)aniline oxide. This efficiency factor is tabulated in Table 2.

To explain these anomalies, a physical "picture" was created. As a molecule of 2,2'-azo-bis-isobutyronitrile decomposes the two 2-cyano-2-propyl radicals formed may, owing to restrictions in the motion of molecules in the liquid state, execute many oscillations in its solvent "cage" (39) prior to diffusing apart. Collisions resulting from mutual oscillations may result in a chemical combination. It has been suggested that these combinations be referred to as "primary recombinations" (39). It is extremely unlikely that recombination occurs with every collision, at a rate of 10^{13} seconds⁻¹, due to steric and energetic requirements.

A more probable value for the rate of combination of neighboring radicals would be of the order of 10^9 seconds⁻¹.

Diffusion out of the cage is estimated (39) to occur at a small fraction of the collision rate, smaller by a factor in the neighborhood of 10^{-3} . The mean duration of existence of a pair of radicals as first neighbors should be approximately 10^{-10} seconds; therefore diffusion may well be a more rapid process than recombination, although this may not invariably be true. After a single "jump" out of the cage, there is a considerable probability that the next "jump" will return the original pair, and again expose them to the possibility of recombination. After two or more "jumps" apart, a re-encounter becomes improbable. These free radicals are scavengable or "free".

This explanation describes the model of molecular motion in liquids proposed by Rabinowitch (40). He assumed that displacements or "jumps" are of the order of a molecular diameter and require a finite energy of activation.

A similar explanation was fostered by Matheson (41), although it is not in agreement with the accepted fact that the chain propagation step in styrene polymerization is not fast enough to compete with a diffusion controlled reaction (42).

Early papers by Noyes (43, 44) presented an elegant mathematical treatment of the kinetics of competitive processes with an emphasis on diffusion controlled reactions of reactive fragments produced in pairs. A slightly different

nomenclature was presented, which in itself has added advantages. "Primary recombination" may be considered to be possible only when reactive pairs produced in the "cage" of solvent molecules are less than a molecular diameter apart. In this case recombination takes place in a period of time of the order of a vibration (10^{13} seconds⁻¹) and is certainly less than the time between diffusive displacements (10^{-11} seconds). This "primary cage" could conceivably be scavenged only when an extremely efficient scavenger is present in a concentration approaching a mole fraction of unity.

If the reactive fragments escape the "primary cage" they undergo random diffusive displacement of the order of a molecular diameter with a frequency of roughly 10^{11} seconds⁻¹. During this random diffusion, a fragment may again encounter its original partner and undergo "secondary recombination". If secondary recombination does not take place within 10^{-9} seconds, then the chance of geminate fragments re-encountering is negligible. Thus, by this terminology, the summation of primary and secondary recombination has been generally termed the "cage" recombination.

In later papers, Noyes (45, 46) re-evaluated and expanded previous work to show that current available data suggest that diffusion in liquids involves almost continuous motion and small individual displacements, and does not involve "jumps"

of the order of a molecular diameter that are opposed by significant potential barriers.

There is another explanation for the low efficiencies of radical production in 2,2'-azo-bis-isobutyronitrile decomposition. Hammond and co-workers (11) have suggested that the azonitrile may undergo a non-radical decomposition to give tetramethylsuccinonitrile directly with expulsion of the nitrogen molecule (equation B-2). Such a reaction may involve a transition state such as



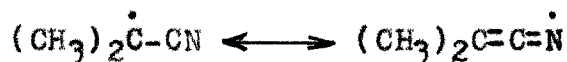
which is closely related to the cis-azo compound.

By the middle of 1955, the mechanism of the decomposition of 2,2'-azo-bis-isobutyronitrile seemed fairly well explained. At this time Talât-Erben and Bywater (14, 15) reported evidence for the existence of a reactive intermediate formed in the decomposition of 2,2'-azo-bis-isobutyronitrile. This intermediate was suggested to be dimethyl-N-(2-cyano-2-propyl)-ketenimine (C-1).

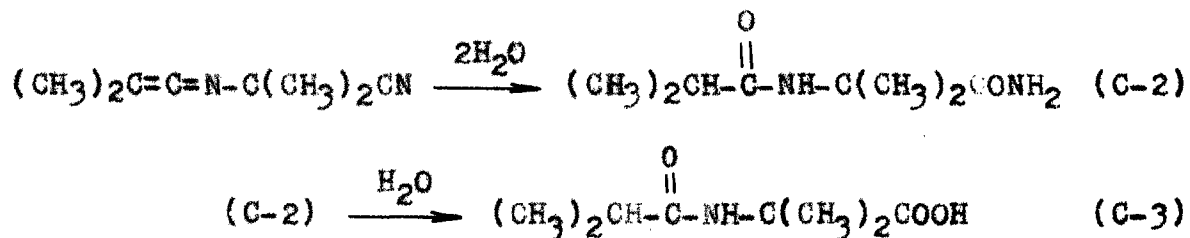


This ketenimine is produced by a C-N coupling, (perhaps) reflecting the fact that some of the odd electron density of

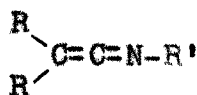
2-cyano-2-propyl radical is associated with the cyano nitrogen.



These workers (15) presented a careful product characterization of dimethyl-N-(2-cyano-2-propyl)-ketenimine. Mild hydrolysis of this ketenimine gave the isolatable amides (C-2) and (C-3).



Staudinger and Hauser (47) reported that ketenimines substituted by two methyl groups or two phenyl groups on the doubly substituted carbon



R = methyl, or

R = phenyl

are fairly unstable in the presence of nucleophilic reagents. Their instability increases upon addition of hydrogen ions. They further noted that oxidative cleavage occurred at the carbon-carbon double bond at temperatures in excess of 150°.

The infrared stretching frequency absorption for the ketenimine linkage ($>C=C=N-$) was observed (14, 15) at 4.96μ in close agreement with Stevens and French (48, 49), who reported infrared data on similar independently synthesized aliphatic ketenimines.

An interesting kinetic approach was reported (14) for the study of the formation of dimethyl-N-(2-cyano-2-propyl)-ketenimine upon decomposition of 2,2'-azo-bis-isobutyronitrile. It was observed that the rate constant for the disappearance of 2,2'-azo-bis-isobutyronitrile multiplied by the time when the maximum in the dimethyl-N-(2-cyano-2-propyl)-ketenimine concentration occurred (as followed by its ultraviolet spectrum) was equal to one, over a temperature range from 70° to 105° . Other results indicated the presence of dimethyl-N-(2-cyano-2-propyl)-ketenimine was a result of consecutive first order reactions. However, their data were lacking the desired quantitative aspect, since they were unable to isolate dimethyl-N-(2-cyano-2-propyl)-ketenimine in pure form.

Talât-Erben and Bywater (50) later reported the presence of ketenimine linkages in polymethacrylonitrile polymerized with the aid of benzoyl peroxide as catalyst.

A recent mathematical treatment of consecutive first order reactions has been presented by Talât-Erben (51, 52). His conclusions were used to explain a previous paper (14).

The discovery of the intermediate, dimethyl-N-(2-cyano-2-propyl)-ketenimine, provided the stimulus for the investigation of the subject of this dissertation.

EXPERIMENTAL

Apparatus and Materials

Constant temperature bath

The constant temperature bath was of conventional design, incorporating several features to insure uniform constant temperature throughout. A Pyrex jar, 16 inches in diameter, filled with mineral oil (Superla White, No. 21, U.S.P. Heavy, Standard Oil) was equipped with four components. The first component was a one-third horsepower Cenco stirring motor with an adjustable gear ratio. The stirrer consisted of two oppositely vented blades positioned to avoid the formation of whirlpools. The second was two heating elements, each regulated by a Variac to a temperature just below that desired. The third was a Bronwill Thermoregulator-Thermometer (Chicago Apparatus Company) adjustable by a rotating magnet over a temperature range from 0° to $100^{\circ} \pm 0.01^{\circ}$. The fourth was a Fisher-Serfass Electronic Relay (Fisher Scientific Company).

The final temperature regulation was maintained with a 150 watt light bulb in connection with the electronic relay and thermoregulator. The fluctuation limits on the bath temperature were $\pm 0.05^{\circ}$.

Qualitative infrared absorption spectra

All qualitative infrared absorption spectra were determined with a Baird Associated Infrared Recording Spectrophotometer (Model B). This is a double beam instrument with sodium chloride optics which automatically recorded the percent transmission of the solution. All spectra taken were done using the solution sampling or capillary cell technique.

Elemental analyses

All elemental analyses were done by Geller Microanalytical Laboratories, 473 Blanchard Terrace, Hackensack, New Jersey.

Sealed tube designs

Several designs of sealed tubes were found convenient for the various experiments. Three designs (D-1, D-2, and D-3) were used.

1. D-1. Pyrex test tubes (150 x 18 millimeters) were soaked overnight in a commercial cleaning solution ("Lakeseal" laboratory glass cleanser, Finger Lakes Chemical Company, Etna, New York). Each tube was

then carefully scrubbed and thoroughly rinsed with hot water and with distilled water before being dried in an oven at 125°. These scrupulously cleaned tubes were specially constricted reserving a bulb 40 millimeters long for the sample. This constriction was approximately 25 millimeters long.

2. D-2. Scrupulously cleaned (as described above) Pyrex test tubes, 200 x 32 millimeters, were constricted in the normal manner. Just below this constriction a 3 inches x 5 millimeters (OD) Pyrex tube was attached. The upper end of this side arm was sealed and bent to parallel the length of the tube.
3. D-3. Clean, one-liter round bottom Pyrex flasks were constricted along the neck. On the upper bulb surface a 1 inch x 5 millimeters (OD) Pyrex tube was attached. The upper end was sealed.

All constricted tubes were annealed overnight at 570° before use.

All runs were sealed by the same procedure. An efficient "pig" with 13 outlets connected to stopcocks by Tygon tubing was used. Each stopcock was fitted with the desired rubber stopper for connection to a constricted tube. This "pig" was adapted for alternate evacuation and nitrogen flushing. All samples were frozen in a dry ice-trichloroethylene bath at -80° prior to initial evacuation. The cyclic operation of

evacuation and nitrogen flushing was repeated three times, before each tube was carefully sealed off with a low flame. In the case of tubes (D-3), the resulting seal had to be flame annealed to prevent cracking by subsequent thermal extremes.

All samples were kept in either a dry ice bath or the freezer compartment of a refrigerator before and after kinetic runs. During a run, as each sample was removed from the constant temperature bath, its reaction was immediately quenched thermally in a dry ice bath.

At the desired time each type of tube could be easily opened by breaking off part of the 5 millimeter (OD) side arm (D-2, D-3) or the elongated constricted neck (D-1) to release any contained pressure.

2,2'-Azo-bis-isobutyronitrile

2,2'-Azo-bis-isobutyronitrile (Blue Recrystallized Grade, Westville Laboratories, Monroe, Connecticut). Filtration of a saturated solution of 2,2'-azo-bis-isobutyronitrile in anhydrous methanol removed the majority of the blue dye as a colloidal precipitate. Cooling the filtrate overnight in a refrigerator yielded almost white crystalline 2,2'-azo-bis-isobutyronitrile. Several crops of crystals were obtained by successive removal of methanol under reduced pressure. A second recrystallization was effected by dissolving

2,2'-azo-bis-isobutyronitrile in boiling diethyl ether and cooling. The melting point in a Hershberg melting point apparatus pre-heated to 95° was 103.5-104.5° (uncorrected) with decomposition.

Benzene

Benzene (Thiophene free, Reagent Grade, Fisher Chemical Company) was dried with sodium and fractionated through a four-foot Oldershaw column at a 10:1 reflux ratio. The fraction boiling at 80.18° (corrected) was collected.

Bromine

Bromine (Eastman White Label, Eastman Kodak Company) was used without further purification.

n-Butyl mercaptan

n-Butyl mercaptan (Eastman White Label, Eastman Kodak Company) was used without further purification in all runs except those carried out at 62.5°. In the latter cases the n-butyl mercaptan was carefully distilled and the middle fraction was collected prior to use.

Carbon tetrachloride

Carbon tetrachloride (Fisher Spectranalyzed Reagent, Fisher Scientific Company) was used without further purification, except for Run 98, in which the carbon tetrachloride was fractionated through a four-foot Oldershaw column at a 10:1 reflux ratio. The fraction boiling at 76.8° (corrected) was collected.

Cyclohexane

Cyclohexane (99 mole per cent Minimum, Pure Grade, Phillips Petroleum Company) was used without further purification.

Skelly B

Skelly B (Skelly Oil Company) was flash distilled prior to chromatographic use.

Tetramethylsuccinonitrile

Tetramethylsuccinonitrile was prepared by the thermal decomposition of 2,2'-azo-bis-isobutyronitrile according to Dox (2). This substance was purified by successive sublimations.

The melting point in a sealed capillary was 169.5-170.5° (uncorrected).

α-Bromo-isobutyronitrile

A modification of the procedure described by Stevens (53) was used to prepare α-bromo-isobutyronitrile. Twenty-five grams (0.36 mole) of isobutyronitrile and 98 grams (0.36 mole) of phosphorous tribromide were mixed together in a 250 milliliter three-neck round bottom flask, provided with a motor driven stirrer, water cooled reflux condenser and a graduated separatory funnel. This apparatus was cooled in an icebath during the slow addition of 58 grams (0.36 mole) of bromine over a 30 minute period. Mild evolution of hydrogen bromide occurred when the icebath was replaced by a heating mantle. After five hours of heating at reflux temperature the reaction mixture was distilled. The collected fraction boiling between 135-143° was a clear yellow liquid. The residual bromine was removed by washing this fraction, dissolved in diethyl ether, with a saturated aqueous sodium bisulfite solution. Redistillation gave 29.0 grams (54.5%) of water-white α-bromo-isobutyronitrile, boiling point 137.5-138° (uncorrected) and refractive index, $n^{25.0} = 1.4437$. The molecular weight determined by the method of Victor Meyer

(54) was $149. \pm 4.$, using five experimental values. The theoretical molecular weight is 148.0.

Dimethyl-N-(2-cyano-2-propyl)-ketenimine

Dimethyl-N-(2-cyano-2-propyl)-ketenimine as reported by Talât-Erben and Bywater (14, 15) was shown to exist as an intermediate in the decomposition of 2,2'-azo-bis-isobutyronitrile. However, they were able to isolate this intermediate only in a grossly impure state, hence all major physical as well as kinetic properties were unobtainable. These workers (14, 15) reported a characteristic infrared band (S) at 4.96μ in accord with the reported (48, 49) infrared absorption of independently authentic, synthesized aliphatic ketenimines. Further, dimethyl-N-(2-cyano-2-propyl)-ketenimine absorbs weakly in the ultraviolet at $287 m\mu$ (15) although the reported extinction coefficient is questionable. Considering this information it was found that dimethyl-N-(2-cyano-2-propyl)-ketenimine is present as an intermediate in the thermal decomposition of 2,2'-azo-bis-isobutyronitrile in carbon tetrachloride, benzene, cyclohexane, and glacial acetic acid. It is understandable that Talât-Erben and Bywater (14, 15) had difficulty in isolating a fairly pure sample of this ketenimine since the remaining reactant, 2,2'-azo-bis-isobutyronitrile, and the major product, tetramethylsuccino-

nitrile, are very soluble in toluene and in benzene, as reported here. However, it has been found that the reactant and major product are insoluble in cyclohexane at temperatures that approximate the freezing point of cyclohexane.

Typical preparation

In a typical preparative run, approximately 15 grams of either recrystallized commercial pure grade or commercial pure grade 2,2'-azo-bis-isobutyronitrile and about 300 milliliters of pure cyclohexane were placed in a specially designed flask (D-3). This flask was attached to an evacuation apparatus and frozen in a dry ice-trichloroethylene bath. When the solution was completely frozen, the flask was evacuated and flushed with nitrogen gas for three consecutive cycles. The reaction flask was sealed under vacuum.

It was found, as will be explained later, that the maximum concentration of dimethyl-N-(2-cyano-2-propyl)-ketenimine occurred after approximately 140 to 160 minutes at 80.9°. This one-liter reaction flask was immersed in the constant temperature bath maintained at $80.9 \pm 0.05^\circ$ for 150 minutes. The flask was then cooled rapidly and the contents were allowed to freeze solid before releasing the nitrogen pressure built up by the decomposition of the 2,2'-azo-bis-isobutyro-

nitrile. This was simply accomplished by carefully breaking off a section of the side-arm.

As the cyclohexane thawed, it was immediately filtered with suction to separate the solution from the insoluble reactant and products.

The solvent was slowly removed at reduced pressures, with no heating, as the desired ketenimine is thermally unstable. The five milliliter yield of light yellow oil deepened in color upon standing at room temperature. Several reactions carried out in this manner yielded 90 per cent pure dimethyl-N-(2-cyano-2-propyl)-ketenimine.

A later preparation, more economical of time and of handling loss of ketenimine, was carried out in a three-neck, five liter, round bottom flask provided with a mechanical stirrer, a reflux condenser, a drying tube containing Drierite, and a nitrogen bubbler. The nitrogen gas was purified by passing over hot copper turnings (55). Three liters of pure cyclohexane was flushed with nitrogen for one hour prior to heating to reflux temperature, then 200 grams of 2,2'-azo-big-isobutyronitrile was added quickly. The reflux temperature was maintained for 145 minutes. The flask was then stoppered and rapidly cooled in a salt and ice water mixture. The solution was removed by decanting from a nearly frozen mixture in 700 milliliter portions and the cyclohexane was removed as previously described. A 25 gram yield (15 per

cent) of dimethyl-N-(2-cyano-2-propyl)-ketenimine was isolated.

It was noted in an earlier preparation that dimethyl-N-(2-cyano-2-propyl)-ketenimine could be molecularly distilled in high vacuum. Several types of distillations were attempted in an effort to purify this ketenimine.

A miniature, one piece, Claisen head and condenser were attached to the vacuum system described by Tanaka (56). Distillation through this apparatus approximates one theoretical plate. At a vacuum approaching 10^{-3} millimeters of mercury and a temperature of 35° in the bath surrounding the distillation pot, evaporative distillation occurred.

Fractions of the original distillate were worked up by various methods to effect purification.

1. One fraction, cooled slowly in an ice bath, was fractionally crystallized by scratching the side of the container. Prior to complete crystallization the supposed supernatant liquid was decanted with a specially designed suction filter.

A one millimeter (ID) capillary tube was constructed in a "U" shape. At one end a standard taper male joint with vacuum take-off was incorporated, while the other end was ground and polished flat to accommodate a small circular filter paper. The polished end was sufficiently long to reach the

fluid crystals. The purity did not increase so this approach was discarded.

2. An eighteen inch Spinning Band column (Nester and Faust, Exton, Pennsylvania), with a multiple take-off adapter was attached to the above mentioned vacuum line (56). Distillation occurred at approximately 50° and a vacuum of the order of 10^{-2} millimeters of mercury. The distillation data by this technique can only be approximate in nature since considerable difficulty was experienced in avoiding leaks around the standard ball joints without the application of excess Apiezon N grease (Metropolitan-Vickers Electrical Co., Ltd., England). With an excess of grease the vacuum could be maintained for perhaps an hour, but grease contamination appeared in the distillate.
3. Successive one plate distillations at 22° (3×10^{-3} millimeters) yielded a water-white liquid, freezing point, 12.7° and refractive index, $n^{25^{\circ}} = 1.4473$. The calculated molecular weight for $C_8H_{12}N_2$ is 136.19; by freezing point depression (57), $136. \pm 4$. The infrared spectrum of pure dimethyl-N-(2-cyano-2-propyl)-ketenimine is given in Figure 2.

Anal. Calc. for $C_8H_{12}N_2$: C, 70.55; H, 8.88; N, 20.57.

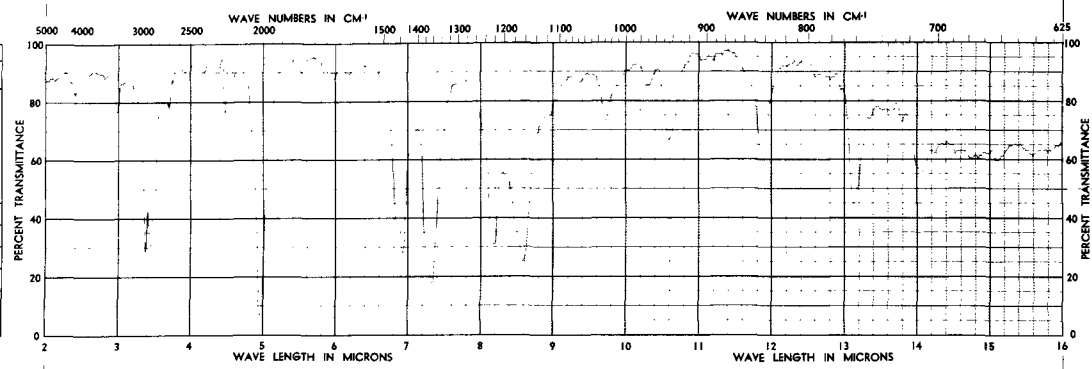
Found: C, 70.63; H, 8.94; N, 20.69.

Figure 2. No. 12725--Dimethyl-N-(2-cyano-2-propyl)-ketenimine

I. R. SPECTROPHOTOMETER
NaCl PRISM

NO.	12720	
DATE	12-27	INDEX
SAMPLE		
C.M. C.H.		
C.H. ₂ C.C.		
C		
FROM	C. T. 100	
SAMP. CELL:	MM	CMS
REF. CELL:	MM	CMS
CHEM:	MG	MG.
SOLV	C. H. 100	C. H. 100
VOL	C.C.	% C.C.
F.S. SOLID	C.	GAS MM

BAIRD ASSOCIATES, INC.
CAMBRIDGE, MASS., U.S.A.
10217



37

Standard of purity. Method 1

Dimethyl-N-(2-cyano-2-propyl)-ketenimine readily hydrolyzes in a slightly acidic solution (14, 47) giving water soluble amides, while the expected impurities 2,2'-azo-bis-isobutyronitrile and tetramethylsuccinonitrile are not appreciably soluble in the hydrolyzing solution. A sample determination of an analytical weight of dimethyl-N-(2-cyano-2-propyl)-ketenimine was carried out in a centrifuge tube with a female standard taper joint at the top. Ten milliliters of distilled water and 2.5 milliliters of one normal hydrochloric acid were added. The tube was stoppered and vigorously shaken over a 24 hour period. The precipitate was filtered quantitatively, washed with distilled water, and pressed between dry filter papers with suction. This precipitate was transferred to a tared screwcap vial, weighed, and carefully dried by admission of a cup containing several crystals of Drierite. After several days, the cup was removed and the vial was again weighed.

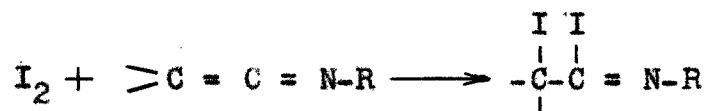
Similar blank determinations were carried out on pure 2,2'-azo-bis-isobutyronitrile and on pure tetramethylsuccinonitrile. It was found that up to 11 milligrams of 2,2'-azo-bis-isobutyronitrile was soluble under these conditions, and up to 18 milligrams of tetramethylsuccinonitrile was soluble.

Standard of purity. Method 2

An alternative analytical scheme was devised to determine the purity of dimethyl-N-(2-cyano-2-propyl)-ketenimine.

An analytical weight of dimethyl-N-(2-cyano-2-propyl)-ketenimine was diluted volumetrically in carbon tetrachloride. An aliquot of this ketenimine solution was added to a 300 milliliter erlenmeyer flask containing a glass-covered magnet. Several small pieces of dry ice were added prior to the addition of an aliquot of 0.1 normal iodine (58) calculated to be in excess. Care was taken to keep a positive supply of dry ice in the flask to exclude oxygen until the titration was completed. A volume of glacial acetic acid equal to the volume of ketenimine sample was added after two to three minutes of vigorous stirring with an external magnet. At this time a volume of distilled water twice that of the sample was added. The excess iodine was titrated with 0.046 normal sodium thiosulfate immediately. Prior to the end-point a large volume of distilled water was added to improve the visual starch-iodine end-point in the presence of acetic acid. The 5 per cent starch solution was a mold resistant solution in formamide prepared as reported by Holler (59).

The expected stoichiometry for iodine addition to dimethyl-N-(2-cyano-2-propyl)-ketenimine is



This rapid addition reaction at room temperature was confirmed by:

1. Infrared spectra: Dimethyl-N-(2-cyano-2-propyl)-ketenimine has a sharp peak at 4.96μ . With addition of a slight excess of bromine or iodine this peak is replaced by a peak at 5.98μ which is due to the $\text{>C} = \text{N-}$ stretching frequency.
2. Ultraviolet spectra: Dimethyl-N-(2-cyano-2-propyl)-ketenimine has an absorption maximum at $287\text{ m}\mu$. Addition of a slight excess of iodine replaces this peak by a much stronger absorbing maximum at lower wave length. This is in agreement with the expected absorption of the $\text{>C} = \text{N-}$ chromophore.
3. An equimolar amount of iodine successfully titrated pure dimethyl-N-(2-cyano-2-propyl)-ketenimine.
4. The ketenimine concentration determined by the hydrolysis method of purity and the iodine titer are in close agreement. A calculated ketenimine-iodide equivalent was 0.0178 and in seven determinations was found to be 0.018 ± 0.001 . Ketene impurities in early samples determined by Method 1 averaged 21 per cent. Impurities in similar samples by infrared analysis calibrated with redistilled ketenimine gave 23 per cent.

Reactions

Decomposition of 2,2'-azo-bis-isobutyronitrile in liquid bromine

The decomposition of 2.5 grams of 2,2'-azo-bis-isobutyronitrile dissolved in 15 milliliters of bromine in a sealed tube (D-2) was carried out by heating at 62.5° for six days. This reaction period is equivalent to approximately 50 half-lives or complete decomposition. The reaction mixture was carefully distilled to remove bromine solvent at room temperature at a reduced pressure. The orange residue was dissolved in methylene chloride and the remaining bromine was removed by an aqueous sodium bisulfite wash. The sample was thoroughly washed with distilled water and dried over Drierite.

The dried sample was chromatographed on a 4 x 36 centimeter column filled to approximately 20 centimeters in depth with Harshaw alumina. The activity of the alumina, according to Brockman (60), was between II and III. The alumina was used without further activation.

Only two fractions could be separated, the first being a conglomerate mixture which flowed freely through the column and was obtained in the first receiver. The weight of this fraction was 5.13 grams. A sodium fusion analysis of this sample indicated the presence of sulfur (lead acetate test),

nitrogen (ferrocyanide test), and halogen (silver halide precipitation). The second fraction was removed by a 1:1 mixture of benzene and anhydrous ether. This small sample sublimed at approximately 120° with a melting point of 138° (uncorrected). The infrared spectrum indicated that the sample was not tetramethylsuccinonitrile. Known tetramethylsuccinonitrile was eluted in a test experiment, and did not appear under the same elution conditions in this reaction chromatogram.

Heating of tetramethylsuccinonitrile in liquid bromine

In run 8, 2.45 grams of tetramethylsuccinonitrile and 15 milliliters of reagent grade bromine were put in a sealed tube (D-2). This sealed tube was heated in a constant temperature bath, maintained at 62.0° , for six days. At the end of this time the excess bromine was removed under vacuum with the help of several 25 milliliter aliquots of carbon tetrachloride. A nitrogen bubbler was used to exclude moist oxygen in the air and to help eliminate bumping. The initial yellow residue had a melting range of $166-168^{\circ}$ (uncorrected) in a sealed capillary. The total residue weighed 2.33 grams (95 per cent recovery by weight).

An analytical portion of this residue upon sublimation yielded white crystalline tetramethylsuccinonitrile melting at $170.0-171.0^{\circ}$ (sealed tube) indicating that the recovered

residue was 95 percent pure. An orange oil, insoluble in ether and soluble in methanol accounted for the remaining five per cent of the initial residue. Thus, 90 per cent of the original tetramethylsuccinonitrile was recovered unreacted.

Decomposition of 2,2'-azo-bis-isobutyronitrile in glacial acetic acid

Glacial acetic acid (250 milliliters) was used as the solvent for the decomposition of 8.30 grams of 2,2'-azo-bis-isobutyronitrile in a specially designed flask (D-3). This exploratory experiment was reacted for 49 hours in a constant temperature bath at 62.0°. The period of reaction approximates three half-lives of the decomposition of 2,2'-azo-bis-isobutyronitrile, assuming this Arrhenius equation

$$k = 6.0 \times 10^{15} e^{-\frac{31,760}{RT}}$$

At the end of 49 hours the solvent was slowly removed at reduced pressures with the pot temperature held below 40°, to avoid any appreciable decomposition of 2,2'-azo-bis-isobutyronitrile. The product mixture (5.71 grams) was extracted with ether in a Soxhlet extractor. The residue, fraction A (1.40 grams), melted at 187° (uncorrected). Fraction A was insoluble in carbon tetrachloride, carbon disulfide, and

chloroform, and very slightly soluble in ether, and soluble in water.

Fraction A was thought to be N-isobutyryl- α -aminoisobutyramide (C-2), as reported by Talât-Erben and Bywater (15).

Anal. Calcd. for $C_8H_{16}N_2O_2$: C, 55.75; H, 9.37; N, 16.27.
Found: C, 55.6; H, 9.2; N, 16.4.

The infrared spectrum of fraction A in a perfluorokerosene mull had the following peaks (units are centimeters^{-1}): 3400 (medium), 3280 (strong), 3190 (shoulder), 2900 (medium), 1645 (strong), 1610 (shoulder), 1530 (medium), 1450 (weak), 1400 (weak).

Confirmation of this structure assignment (C-2) for fraction A was made by alkaline hydrolysis. A sample of fraction A was refluxed in two per cent sodium hydroxide solution for 24 hours, acidified with hydrochloric acid, and extracted with ether in a liquid-liquid extractor. Evaporation of the ether from the extract yielded a white crystalline product. The melting point in a Hershberg melting point apparatus was 148-150 $^{\circ}$ (uncorrected). This is in agreement with the literature melting point, 150-151 $^{\circ}$ (15), for N-isobutyryl- α -aminoisobutyric acid (C-3).

The Soxhlet ether extract, on evaporation of the ether, yielded 2.60 grams of a product mixture which had an extended melting point range, 80-180 $^{\circ}$ (uncorrected), with some sublimation and decomposition occurring at the lower temperatures.

This extract was separated into two fractions (fraction B and fraction C) by fractional crystallization from ether. Although fraction B (1.85 grams) exhibited a large melting point range, 120-180°, the major portion melted between 170-180°. This fraction also had solubility characteristics similar to fraction A. No further separation was carried out. Fraction C (0.75 grams) melted with sublimation at 80° and decomposition and melting between 95-110°. This fraction was probably tetramethylsuccinonitrile and 2,2'-azo-bis-isobutyronitrile.

Decomposition of dimethyl-N-(2-cyano-2-propyl)-ketenimine in high concentrations of n-butyl mercaptan

Dimethyl-N-(2-cyano-2-propyl)-ketenimine (4.475 grams) was decomposed in 250 milliliters of one molar n-butyl mercaptan in carbon tetrachloride. The decomposition was completed in 24 hours in a specially designed flask (D-3) in a constant temperature bath maintained at 80.8°.

It was found in similar runs with tetramethylsuccinonitrile present, that when the solvent and the excess n-butyl mercaptan were removed at reduced pressures, the tetramethylsuccinonitrile could be isolated from an ether extract of the residue.

Tetramethylsuccinonitrile could not be isolated from the reaction mixture by this procedure. The sublimate of the

ether insoluble residue, recrystallized from absolute ethanol, melted at 168.5-170.0° (sealed tube). The infrared spectrum confirmed this product as tetramethylsuccinonitrile. The yield of 27 milligrams (0.4 per cent) was only qualitative in nature since all previously known procedures with their accompanying losses were attempted first.

Decomposition of dimethyl-N-(2-cyano-2-propyl)-ketenimine (1.533 grams) in 250 milliliters of 0.4 molar n-butyl mercaptan in carbon tetrachloride was completed in 24 hours at 80.8°. The solvent and excess n-butyl mercaptan were removed at about 50 millimeters of pressure with heating of the distillation pot. The pressure was reduced to about 3 millimeters and pumping was continued for two hours. The infrared spectrum of the reaction residue indicated that tetramethylsuccinonitrile was probably present, but in very low concentration.

Quantitative Infrared Measurements

It has been reported (48, 49) that ketenimine linkages absorb in the region of 4.9 to 5.0 μ . This corresponds to the presence of a 1:2 diene structure. Talât-Erben and Bywater reported (15) that dimethyl-N-(2-cyano-2-propyl)-ketenimine in toluene solution absorbs at 4.96 μ .

The Perkin-Elmer Model 13 Infrared Instrument, which is available in these laboratories, gave excellent resolution of the 4.96μ peak of dimethyl-N-(2-cyano-2-propyl)-ketenimine in carbon tetrachloride solution (Figure 3), using lithium fluoride optics and a slit width of 0.500 millimeter. (All data were obtained with a 0.500 millimeter slit width unless otherwise indicated.)

Since relatively few compounds and none of the other reaction products of the 2,2'-azo-bis-isobutyronitrile decomposition absorb in the 4.96μ region (Figure 4), the simplest infrared method was chosen for following the concentration of dimethyl-N-(2-cyano-2-propyl)-ketenimine. The techniques of this method, sometimes called the "cell in--cell out" method, consist of:

1. The source is turned on and the battery operated Densitometer is warmed up for one-half hour.
2. The Function on the Perkin-Elmer Model 13 is set for "Direct" reading, the slit width mechanism is set on "Manual" at 0.500 millimeter, the wave length is chosen at 4.96μ , and the second shutter is closed for single beam operation.
3. Zero radiation is adjusted on the Densitometer scale while the single beam shutter is shut.
4. When the sodium chloride sample cell of known length L, determined by its interference pattern, is filled

Figure 3. Perkin-Elmer Model 13 absorption maxima for
 $>C=C=N-$ stretching frequency

Abscissa; Wave length in microns
Ordinate; Per cent transmittance

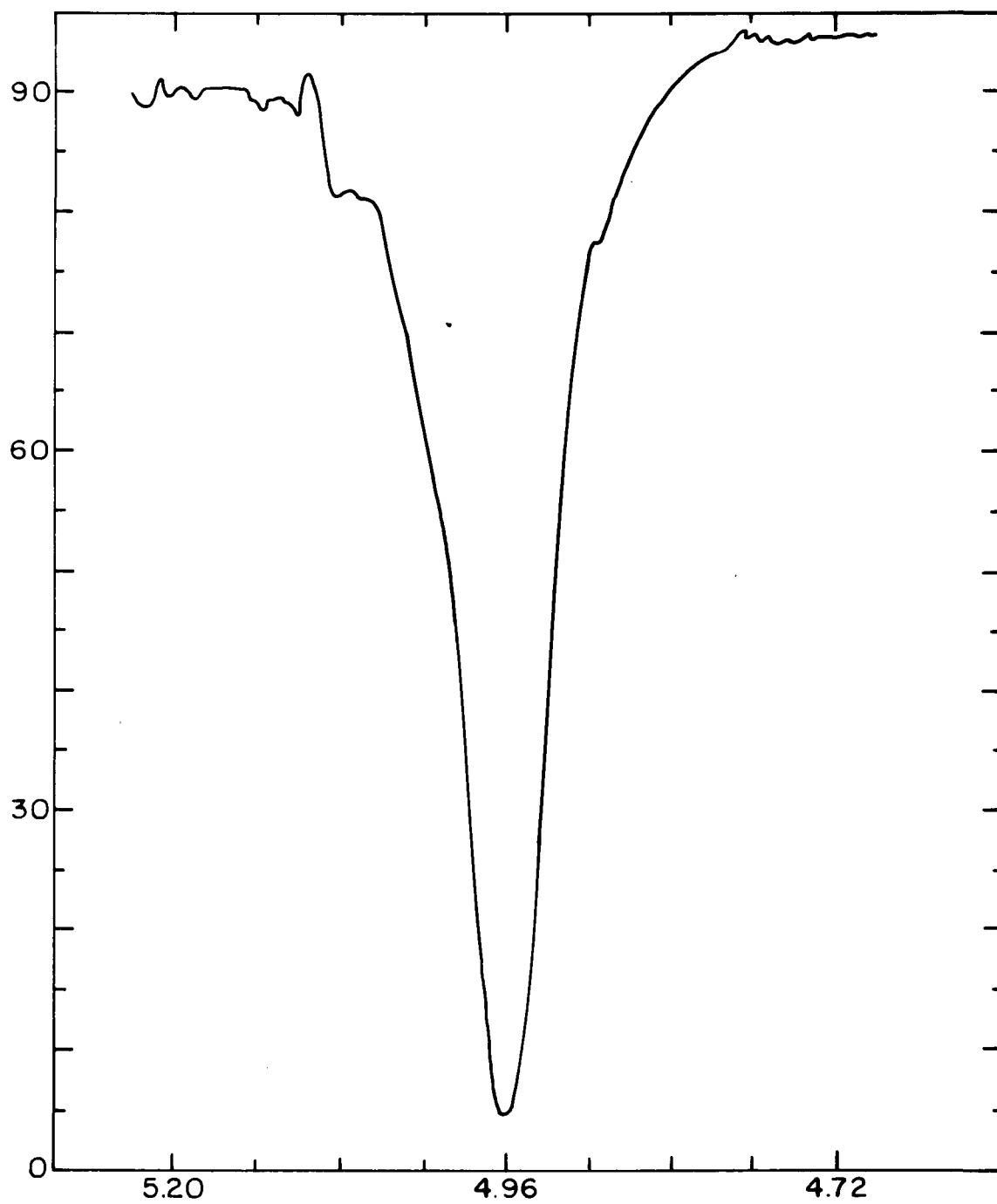


Figure 4. Variance of the spectra of the decomposition of 2,2'-azo-bis-
isobutyronitrile with time, at 80.90

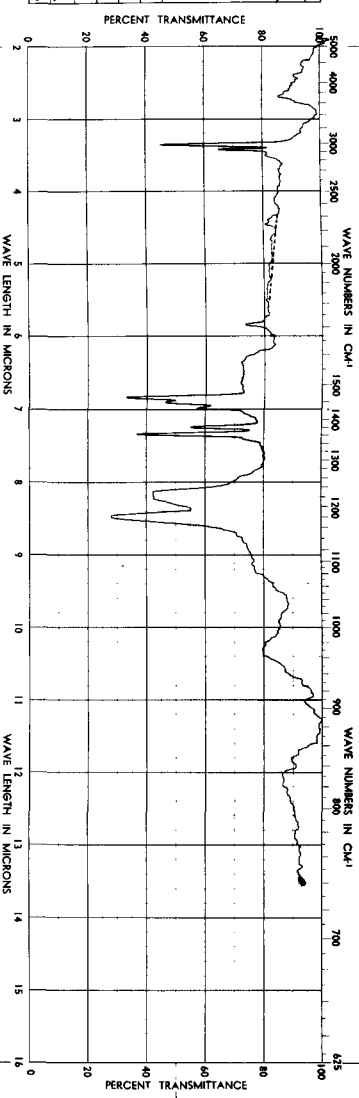
Run 26

No. 10771--0.0 minutes reaction time
No. 10772--40.0 minutes reaction time
No. 10773--62.0 minutes reaction time

I. R. SPECTROPHOTOMETER
 NaCl PRISM

NO.	DATE	INDEX
8-1-58	7-1-58	
SAMPLE		
KNO ₃		
FROM O. Tamm		
SAMP. CELL: 7MM		
REF. CELL: 7MM		
CHEM: KNO ₃		
SOLV: CCl ₄		
VOL. CC: 1.0		
F.S. SOLID: C		
F.S. GAS: MM		

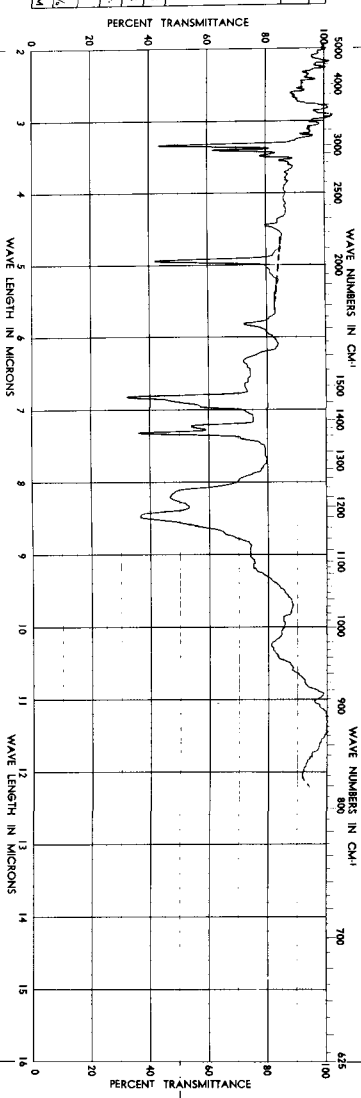
BARBAR ASSOCIATES, INC.
 Cambridge, Mass. U.S.A.



I. R. SPECTROPHOTOMETER
 NaCl PRISM

NO.	DATE	INDEX
8-1-58	7-1-58	
SAMPLE		
KNO ₃		
FROM O. Tamm		
SAMP. CELL: 7MM		
REF. CELL: 7MM		
CHEM: KNO ₃		
SOLV: CCl ₄		
VOL. CC: 1.0		
F.S. SOLID: C		
F.S. GAS: MM		

BARBAR ASSOCIATES, INC.
 Cambridge, Mass. U.S.A.



I. R. SPECTROPHOTOMETER
 NaCl PRISM

NO.	DATE	INDEX
8-1-58	7-1-58	
SAMPLE		
KNO ₃		
FROM O. Tamm		
SAMP. CELL: 7MM		
REF. CELL: 7MM		
CHEM: KNO ₃		
SOLV: CCl ₄		
VOL. CC: 1.0		
F.S. SOLID: C		
F.S. GAS: MM		

BARBAR ASSOCIATES, INC.
 Cambridge, Mass. U.S.A.

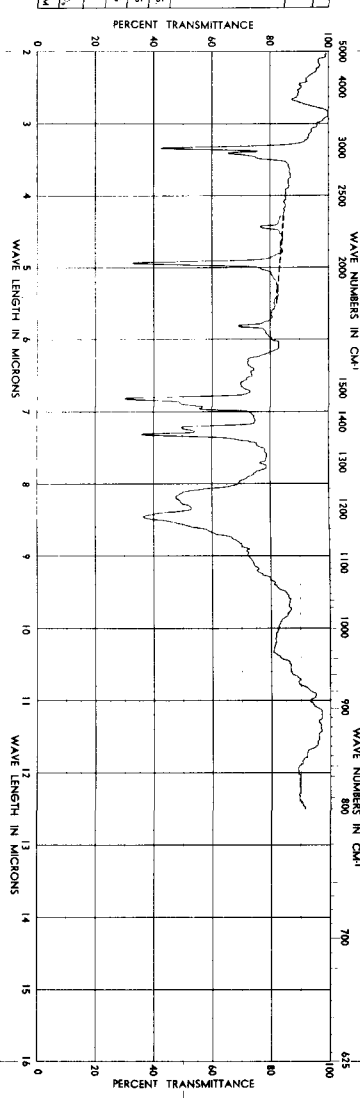


Figure 4. (Continued)

Run 26

No. 10774--90.5 minutes reaction time
No. 10775--120.0 minutes reaction time
No. 10776--152.0 minutes reaction time

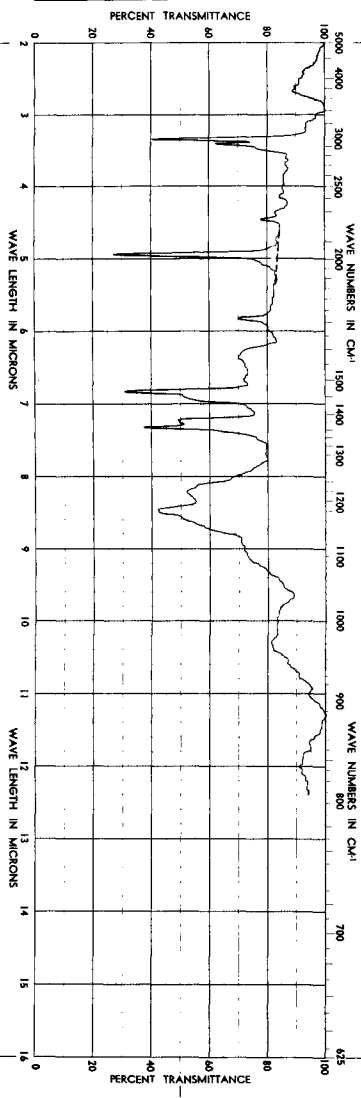
1. B. SPECTROPHOTOMETER
NaCl PRISM

NO.	DATE	INDEX
2-4-56	8-4-56	M. Cook

SAMPLE
Run 26
90.5
Run 100

FROM	O-TOLUENE
SAMP CELL - 7MM	CHKS
REF CELL - 2MM	CHKS
CHEM	MG
SOLV	CC
VOL. CC	% CC
F.S. LIQUID	CL GAS
F.S. LIQUID	CL GAS

FAIRBANKS ASSOCIATES, INC.
CAMBRIDGE, MASS., U.S.A.



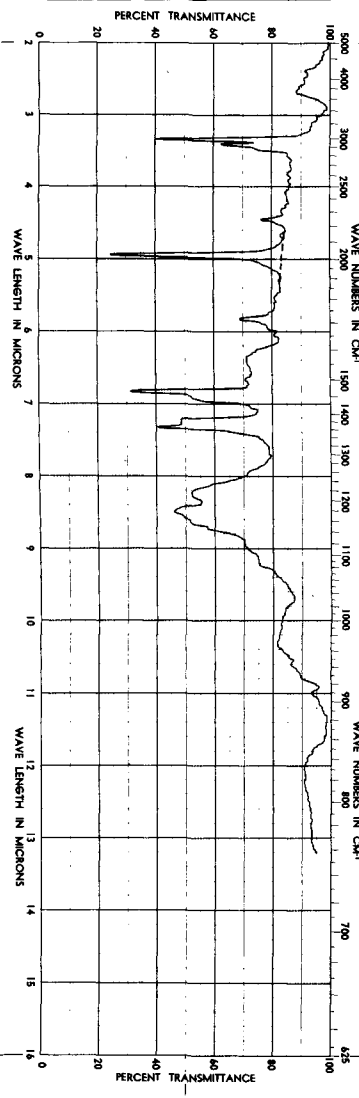
1. B. SPECTROPHOTOMETER
NaCl PRISM

NO.	DATE	INDEX
2-4-56	8-4-56	M. Cook

SAMPLE
Run 26
120
Run 100

FROM	O-TOLUENE
SAMP CELL - 7MM	CHKS
REF CELL - 2MM	CHKS
CHEM	MG
SOLV	CC
VOL. CC	% CC
F.S. LIQUID	CL GAS
F.S. LIQUID	CL GAS

FAIRBANKS ASSOCIATES, INC.
CAMBRIDGE, MASS., U.S.A.



1. B. SPECTROPHOTOMETER
NaCl PRISM

NO.	DATE	INDEX
2-4-56	8-4-56	M. Cook

SAMPLE
Run 26
152
Run 100

FROM	O-TOLUENE
SAMP CELL - 7MM	CHKS
REF CELL - 2MM	CHKS
CHEM	MG
SOLV	CC
VOL. CC	% CC
F.S. LIQUID	CL GAS
F.S. LIQUID	CL GAS

FAIRBANKS ASSOCIATES, INC.
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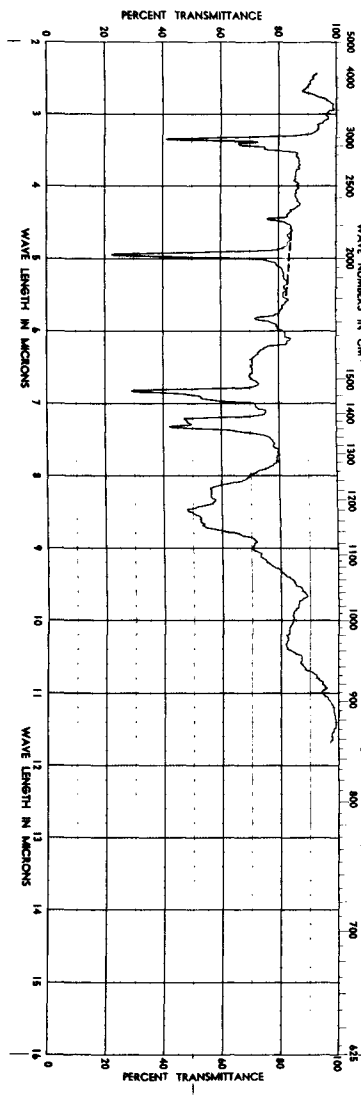


Figure 4. (Continued)

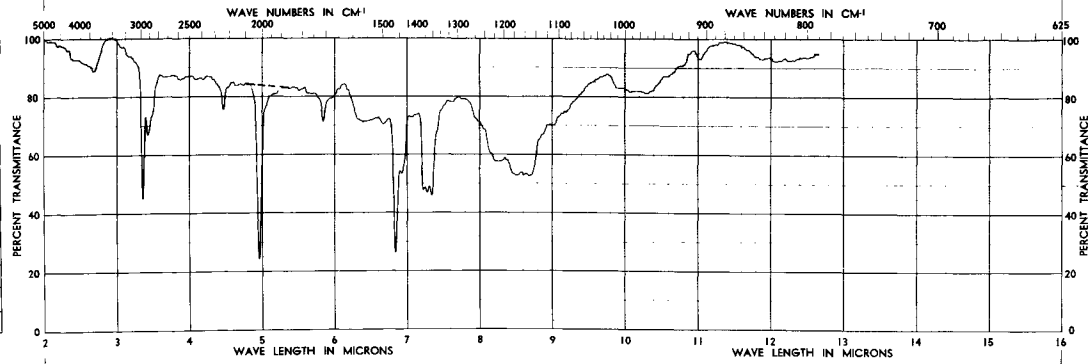
Run 26

No. 10777--185.5 minutes reaction time
No. 10778--25.5 hours reaction time

I. R. SPECTROPHOTOMETER
NaCl PRISM

NO.	DATE	INDEX
	7-26	M. C. G.
SAMPLE		
Kun 20		
1.75 mm		
Kun 10		
FROM O TRAPP		
SAMP CELL: 1	2MM	CMS.
REF CELL: 2	2MM	CMS.
CHEM:	MG	MG.
SOLV:		
VOL: CC	%	C.C. %
F.S. SOLID	C	GAS MM

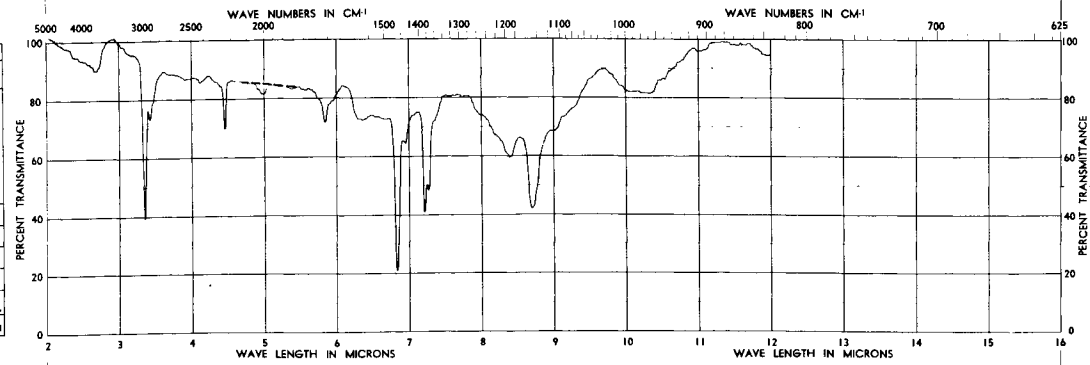
BAIRD ASSOCIATES, INC.
CAMBRIDGE, MASS., U.S.A.
10219



I. R. SPECTROPHOTOMETER
NaCl PRISM

NO.	DATE	INDEX
	7-26	M. C. G.
SAMPLE		
Kun 20		
1.75 mm		
Kun 10		
FROM O TRAPP		
SAMP CELL: 1	2MM	CMS.
REF CELL: 2	2MM	CMS.
CHEM:	MG	MG.
SOLV:		
VOL: CC	%	C.C. %
F.S. SOLID	C	GAS MM

BAIRD ASSOCIATES, INC.
CAMBRIDGE, MASS., U.S.A.
10219



55

with solvent, the Densitometer scale is adjusted to 100 per cent transmission.

5. An aliquot of a sample is transferred into the clean, dry sample cell.
6. The radiation transmittance and absorbance is recorded from the Densitometer.
7. Steps 4, 5, and 6 are repeated with successive samples.

A series of standard solutions of pure dimethyl-N-(2-cyano-2-propyl)-ketenimine in carbon tetrachloride and in benzene were used to determine the linear relationship between absorbance and concentration (Figure 5 and Table 3).

These linear relationships were obtained from these data.

Carbon tetrachloride, L = 0.750 millimeter

$$\text{Concentration} = (2.577 \times 10^{-2})A - 0.022 \times 10^{-2} \quad (\text{E-1})$$

Carbon tetrachloride, L = 0.717 millimeter

$$\text{Concentration} = (2.464 \times 10^{-2})A - 0.016 \times 10^{-2} \quad (\text{E-2})$$

Benzene, L = 0.750 millimeter

$$\text{Concentration} = (2.648 \times 10^{-2})A - 0.025 \times 10^{-2} \quad (\text{E-3})$$

Benzene, L = 0.717 millimeter

$$\text{Concentration} = (2.531 \times 10^{-2})A - 0.024 \times 10^{-2} \quad (\text{E-4})$$

Figure 5. Relationship between concentration of dimethyl-N-(2-cyano-2-propyl)-ketenimine and infrared absorbance

(Sodium chloride cell, L = 0.717 millimeters)

Abscissa; Absorbance

Ordinate; $0.832(\text{Ketenimine}) \times 10^2$

Benzene solution, O ; carbon tetrachloride solution, ●

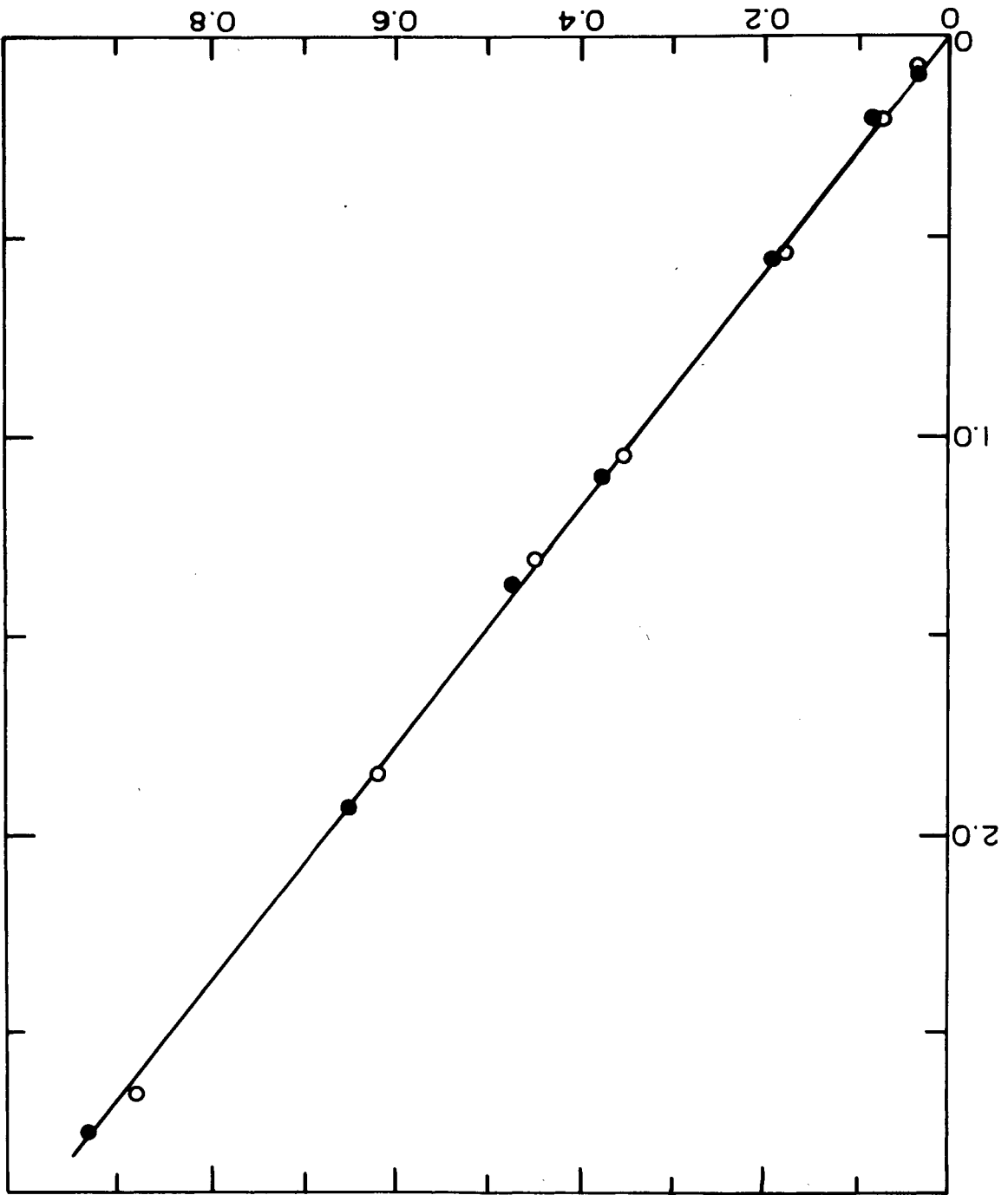


Table 3. Relationship between concentration of dimethyl-N-(2-cyano-2-propyl)-ketenimine and infrared absorbance

(Sodium chloride cell, L = 0.750 millimeter)

Run 93 Carbon tetrachloride		Run 96 Benzene	
Molarity x 10 ²	Absorbance	Molarity x 10 ²	Absorbance
2.360	0.927	2.189	0.837
1.868	0.753	1.751	0.660
1.400	0.543	1.313	0.512
0.952	0.383	0.876	0.347
0.476	0.1975	0.438	0.174
0.280	0.1175	0.263	0.1095
0.190	0.081	0.175	0.076
0.112	0.051	0.105	0.048

Kinetic Runs

Rate of decomposition of 2,2'-azo-bis-isobutyronitrile in liquid bromine

Samples of 2,2'-azo-bis-isobutyronitrile (1.41 grams) in liquid bromine (5 milliliters, $3/4$ molar) were decomposed in sealed tubes (D-2) at 80.8° for varying periods of time.

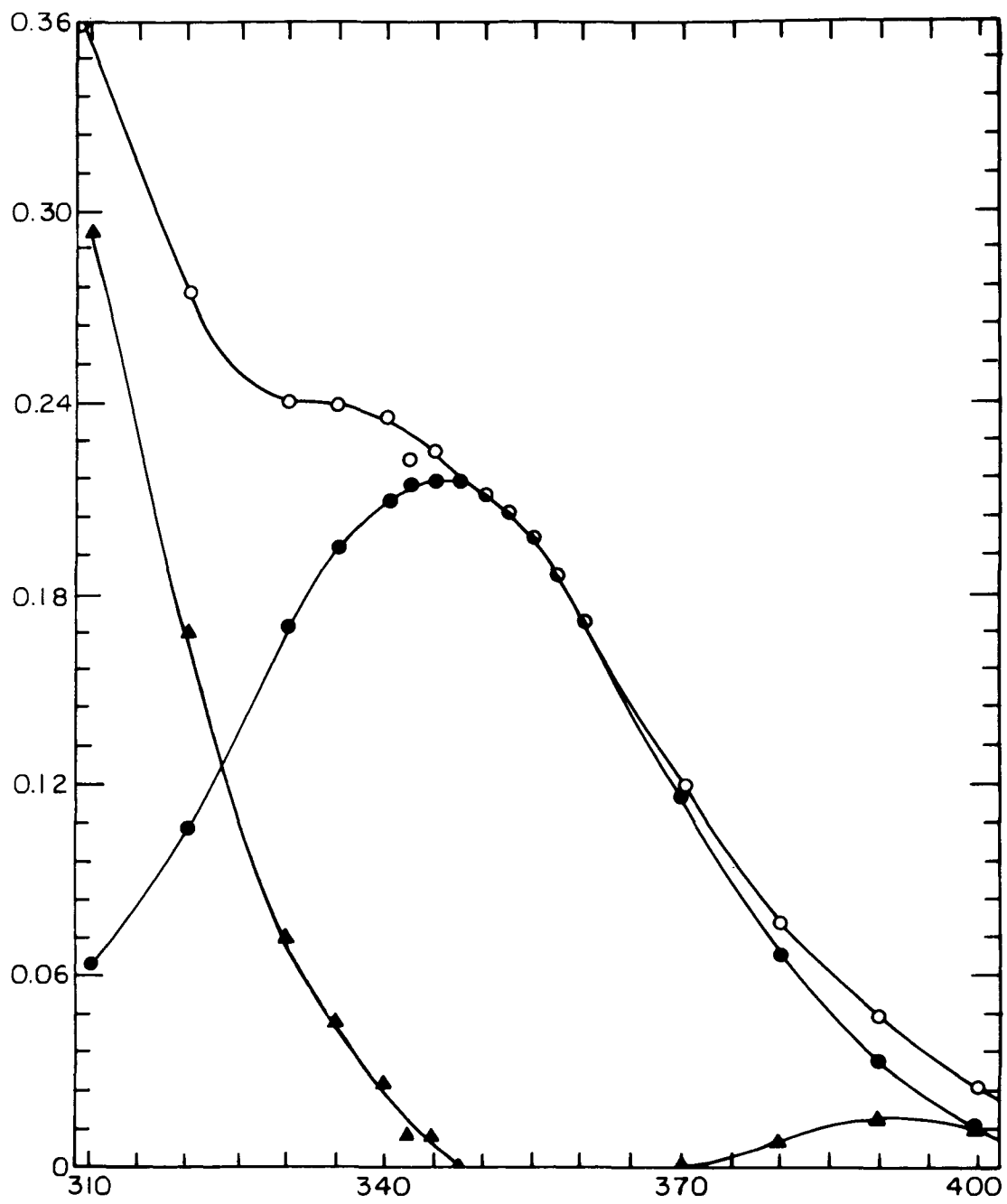
The excess bromine was carefully removed from each sample by vacuum distillation at less than 40° . All but a small portion of the residue dissolved in benzene. The remaining bromine was removed with reagent grade phenol. The resulting tribromo-phenol and any excess phenol were removed by washing with 5 per cent sodium hydroxide solution. The benzene solution was washed repeatedly with distilled water until the washings indicated a pH of 7. The solution was dried for at least four hours with Drierite, filtered, and the Drierite washed with several small portions of dry benzene.

The combined filtrate was made up to 250 milliliters volumetrically. The resulting concentrations of 2,2'-azo-bis-isobutyronitrile were obtained by measuring the ultraviolet absorption spectrum of the filtrate with a Beckman Model DU Spectrophotometer using the extinction coefficients reported by Back and Sivertz (61). Figure 6 expresses the

Figure 6. Resolution of the observed ultraviolet spectra
in determining the rate of decomposition of
2,2'-azo-bis-isobutyronitrile in liquid bromine

Abscissa; Wave length in $m\mu$
Ordinate; Absorbance

Observed spectra, O; absorbance equivalent of
the determined 2,2'-azo-bis-isobutyronitrile
concentration, ●; difference between O and ●, ▲



resolution of this method. The results are tabulated in Table 4 (see "Results").

Rate of formation of dimethyl-N-(2-cyano-2-propyl)-ketenimine

An early analytical method, similar to that reported by Talât-Erben and Bywater (14), for following the formation of dimethyl-N-(2-cyano-2-propyl)-ketenimine upon decomposition of 2,2'-azo-bis-isobutyronitrile, utilized the ultraviolet spectrum. Although this method was reported to be a successful qualitative procedure in toluene solution, it was found unmanageable as a quantitative tool in carbon tetrachloride solution. Limited results were obtained using a Cary Recording Spectrophotometer in conjunction with this experimental procedure.

2,2'-Azo-bis-isobutyronitrile (6.0×10^{-2} molar) in carbon tetrachloride was decomposed in sealed tubes (D-1) for varying periods of time. Each sample was volumetrically diluted two-fold with carbon tetrachloride and the spectrum between 290 and 400 $m\mu$ was recorded. A known concentration of bromine in carbon tetrachloride was similarly diluted and its spectrum was recorded. Then equal volumes of the reaction mixture and of bromine in carbon tetrachloride were mixed and this spectrum was recorded. The initial bromine concentration was chosen so that bromine was in excess after the above

dilution. Using the extinction coefficients for bromine in carbon tetrachloride reported by Lilich (62), the change in bromine concentration was obtained. A 1:1 addition of bromine to the carbon-carbon double bond in dimethyl-N-(2-cyano-2-propyl)-ketenimine was assumed to occur. This would be expected since Stevens and French (49) reported that chlorine rapidly adds to the carbon-carbon double bond in similar ketenimines.

A survey decomposition of 2,2'-azo-bis-isobutyronitrile in sealed tubes (D-1) was followed by semi-quantitative infrared analysis (Figure 4). In these spectra a dotted base line has been inserted to clarify the qualitative revision of the "base line density" technique (63) used. The transmissions of the base line and of the peak at 4.96μ were converted to absorbances. The absorbance difference between each base line and peak was plotted versus time, indicating the usefulness of infrared spectra as an analytical tool for this kinetic analysis.

The quantitative infrared method chosen to obtain tabular data in carbon tetrachloride and in benzene solutions has been previously described.

An attempt was made to observe the rate of formation of dimethyl-N-(2-cyano-2-propyl)-ketenimine in nitromethane and in nitrobenzene. Nitromethane was found to absorb strongly in

the frequency range of the ketenimine, eliminating the infrared as the analytical tool.

A slit width of 1.75 millimeters was used when nitrobenzene was the solvent.

The solvent dependence of the overall formation and subsequent disappearance of dimethyl-N-(2-cyano-2-propyl)-ketenimine is illustrated in Figure 7.

Rate of decomposition of dimethyl-N-(2-cyano-2-propyl)-ketenimine

Dimethyl-N-(2-cyano-2-propyl)-ketenimine was decomposed in sealed tubes (D-1) in various solvent systems; benzene, carbon tetrachloride, n-butyl mercaptan in benzene, and n-butyl mercaptan in carbon tetrachloride. The disappearance of dimethyl-N-(2-cyano-2-propyl)-ketenimine was determined by quantitative infrared measurements as previously described.

Rate of polymerization of styrene initiated by dimethyl-N-(2-cyano-2-propyl)-ketenimine and 2,2'-azo-bis-isobutyronitrile

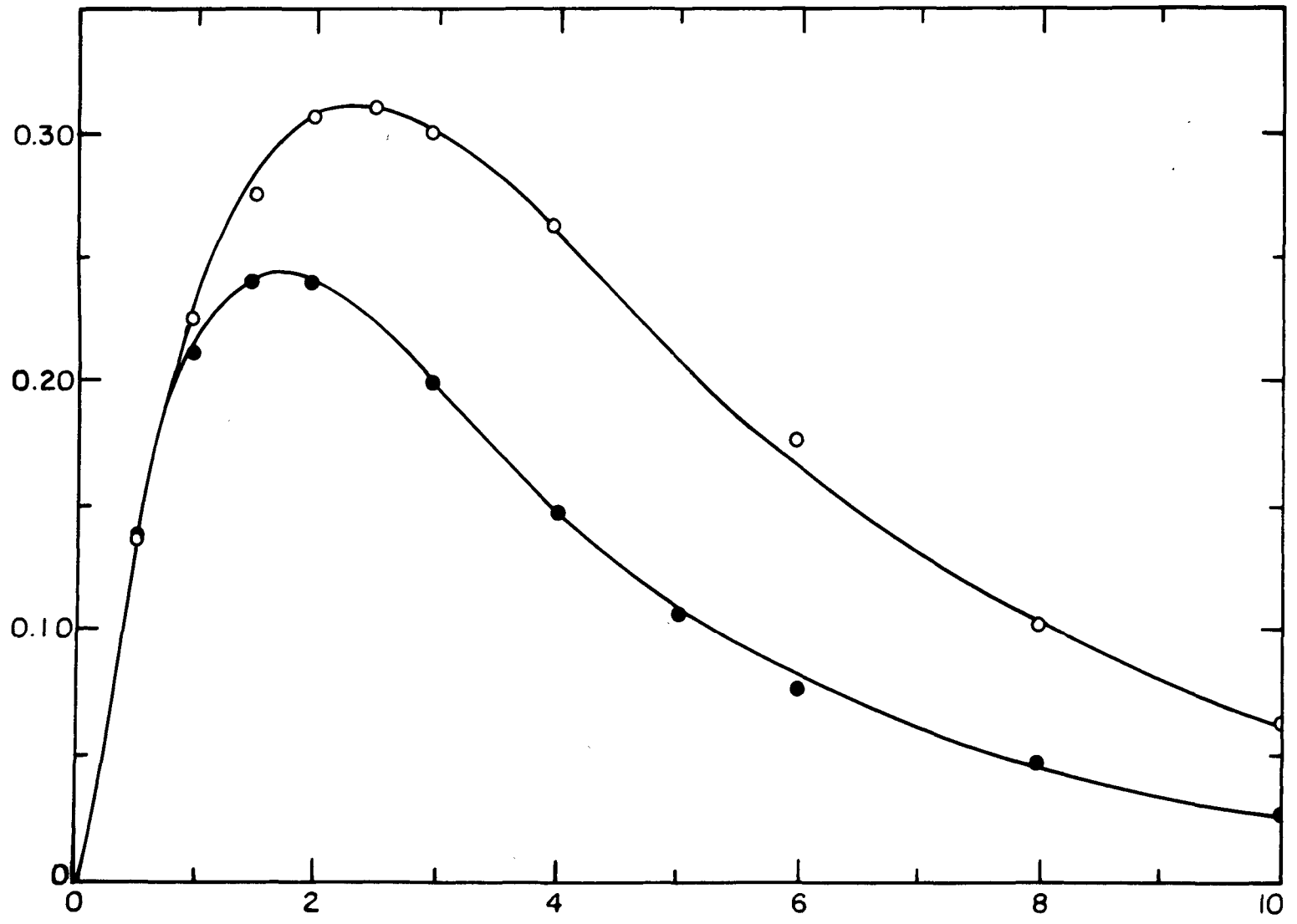
Styrene (Eastman White Label, Eastman Kodak) was washed four times with 5 per cent (by weight) sodium hydroxide solution, twice with water, and dried over anhydrous calcium chloride. The styrene was then distilled in a nitrogen

Figure 7. The solvent dependence of dimethyl-N-(2-cyano-2-propyl)-ketenimine formation and subsequent disappearance

Abscissa; Time in hours at 80.9°

Ordinate; $0.832(\text{Ketenimine})/(\text{AIBN})_0$

Benzene solution \circ ; carbon tetrachloride solution, \bullet



atmosphere at about 50 millimeters pressure through a short Vigreux column. The center one-third of the distillate was collected for use.

Samples of dimethyl-N-(2-cyano-2-propyl)-ketenimine and 2,2'-azo-bis-isobutyronitrile were volumetrically diluted with styrene. The dilatometers used were made of precision bore tubing as designed by Kwert (64). Degassing was done by the freeze-thaw technique with stirring by a magnetic stirrer during the thaw cycle. Liquid nitrogen was used for freezing.

The sealed dilatometers with dimethyl-N-(2-cyano-2-propyl)-ketenimine and 2,2'-azo-bis-isobutyronitrile as initiators were run side by side in the thermostated bath.

Rate of decomposition of dimethyl-N-(2-cyano-2-propyl)-ketenimine in styrene

Pure dimethyl-N-(2-cyano-2-propyl)-ketenimine (1.18×10^{-2} molar) was decomposed in sealed tubes (D-1) in redistilled styrene at 70.0° . After one and one-half hours, the reacted samples could no longer be analyzed by the infrared due to the viscous nature of the samples.

RESULTS

The results of the experimental work appear in Tables 4 through 13.

All accumulated data on the formation and decomposition of dimethyl-N-(2-cyano-2-propyl)-ketenimine as determined by ultraviolet and infrared analyses are presented in Tables 5, 6, and 7.

Values of ketenimine molarity divided by initial 2,2'-azo-bis-isobutyronitrile molarity in Method B in Table 5 are the average values obtained from runs 37, 40, 56, and 87.

Talât-Erben and Bywater (15) reported that water reacts with dimethyl-N-(2-cyano-2-propyl)-ketenimine at room temperature. The decomposition of 2,2'-azo-bis-isobutyronitrile (Table 6) in moist carbon tetrachloride gave a well defined induction period (Figure 8) in the formation of dimethyl-N-(2-cyano-2-propyl)-ketenimine. To determine the initial rate of formation per mole of 2,2'-azo-bis-isobutyronitrile, a correction was made to account for the 2,2'-azo-bis-isobutyronitrile which had decomposed during the induction period.

The rate constants for 2,2'-azo-bis-isobutyronitrile decomposition in carbon tetrachloride and in benzene at temperatures above 62.5° (Table 8) were obtained using this relationship

Table 4. Rate constants for the decomposition of 2,2'-azo-bis-isobutyronitrile in liquid bromine at 80.9°

Run	Initial AIBN ^a molarity x 10 ²	Reaction time in minutes	k x 10 ⁴ (sec. ⁻¹)
83	0.859	72.3	4.6
84	0.963	30.2	5.3

^a2,2'-Azo-bis-isobutyronitrile.

Table 5. Rate of formation of dimethyl-N-(2-cyano-2-propyl)-ketenimine at 80.9° determined by ultraviolet analysis of the bromine titration as compared to infrared analysis

Run 26 reaction time in minutes	Method A ^a $\frac{(\text{ketenimine})^b}{(\text{AIBN})_0^c}$	Method B ^d $\frac{(\text{ketenimine})}{(\text{AIBN})_0}$
40.0	0.14	0.14
62.0	0.17	0.19
120.0	0.25	0.26
152.0	0.26	0.26
185.5	0.26	0.25

^aKetenimine molarity determined by ultraviolet analysis of the bromine titration.

^bDimethyl-N-(2-cyano-2-propyl)-ketenimine molarity.

^cInitial 2,2'-azo-bis-isobutyronitrile molarity.

^dKetenimine molarity determined by infrared analysis in similar runs.

Table 6. Infrared absorbance change on formation of dimethyl-N-(2-cyano-2-propyl)-ketenimine in various solvents at various temperatures

Run	Solvent	Initial AIBN ^a molarity x 10 ²	Reaction time in hours:min.	A ^b	Cell length in mm.	Temp. (°C)
68	I ^c	5.756 ^d	0:00.0	0.003	0.750	62.5
			1:00.0	0.007		
			1:31.0	0.005		
			2:01.0	0.017		
			2:31.0	0.031		
			3:01.0	0.047		
			3:33.0	0.058		
			3:58.0	0.096		
			5:03.0	0.149		
			6:02.0	0.183		
			8:02.0	0.260		
10:00.0	0.338					
69	I	5.896 ^d	0:00.0	0.005	0.750	62.5
			1:02.0	0.0085		
			2:04.0	0.026		
			3:22.0	0.077		
			4:15.0	0.101		
			6:01.0	0.197		
			8:01.0	0.3115		
			12:19.0	0.446		
			16:01.0	0.509		
			22:03.0	0.592		
			28:13.0	0.627		
36:09.0	0.614					

^a2,2'-Azo-bis-isobutyronitrile.

^bInfrared absorbance.

^cI = carbon tetrachloride.

^dCorrected for induction period.

Table 6. (Continued)

Run	Solvent	Initial AIBN ^a molarity x 10 ²	Reaction time in hours:min.	A ^b	Cell length in mm.	Temp. (°C)
70	II ^e	12.96	0:00.0	0.010	0.750	62.5
			1:01.0	0.134		
			1:32.0	0.188		
			2:02.0	0.241		
			2:31.0	0.311		
			3:01.0	0.358		
			3:33.0	0.411		
			3:58.0	0.4425		
			5:04.0	0.529		
			6:02.0	0.617		
			8:02.0	0.732		
10:01.0	0.822					
71	II	11.18	0:00.0	0.004	0.750	62.5
			1:02.0	0.116		
			2:04.0	0.209		
			3:22.0	0.331		
			4:15.0	0.4025		
			6:01.0	0.513		
			8:01.0	0.616		
			12:20.0	0.764		
			16:01.0	0.822		
			22:03.0	0.823		
			28:13.0	0.783		
36:10.0	0.686					
65	I	5.493 ^d	0:00.0	0.0010	0.717	69.6
			0:22.4	0.0245		
			0:49.7	0.0625		
			1:00.7	0.093		
			1:32.4	0.146		
			1:42.5	0.1615		
			2:00.5	0.177		
			2:30.8	0.218		

^eII = benzene.

Table 6. (Continued)

Run	Solvent	Initial AIBN ^a molarity $\times 10^2$	Reaction time in hours:min.	A ^b	Cell length in mm.	Temp. (°C)
			2:58.0	0.249		
			4:25.4	0.3475		
			6:02.4	0.405		
			8:53.6	0.395		
66	II	5.356	0:00.0	0.0065	0.717	69.6
			0:21.7	0.054		
			0:49.4	0.116		
			1:00.1	0.1355		
			1:32.0	0.186		
			1:42.3	0.200		
			2:00.2	0.2225		
			2:30.6	0.266		
			2:57.6	0.289		
			4:24.9	0.352		
			6:01.9	0.390		
			8:53.3	0.392		
36	III ^f	6.131	0:00.0	0.0045	0.717	80.9
			0:30.0	0.007		
			1:00.0	0.000		
			1:30.0	0.000		
			2:00.0	0.000		
			2:20.0	--g		
			2:40.0	0.000		
			3:00.0	--g		
			3:20.0	--g		
			4:01.0	0.000		
			5:01.5	--g		

^fIII = carbon tetrachloride + 0.06 M iodine.

^gNo data collected.

Table 6. (Continued)

Run	Solvent	Initial AIBN ^a molarity $\times 10^2$	Reaction time in hours:min.	A ^b	Cell length in mm.	Temp. (°C)
37	I	6.128	0:00.0	0.002	0.717	80.9
			0:30.0	0.284		
			1:00.0	0.476		
			1:30.0	0.569		
			2:00.0	0.622		
			2:20.0	0.630		
			3:00.3	0.604		
			3:20.0	0.589		
			4:00.5	0.517		
		5:00.3	0.442			
38	IV ^h	6.136	0:00.0	0.009	0.717	80.9
			0:25.0	0.0075		
			0:45.0	0.006		
			1:05.0	--E		
			1:25.0	--E		
			1:45.0	--E		
			2:05.0	0.0085		
			2:35.3	--E		
			3:10.5	--E		
			4:01.3	--E		
			5:00.5	--E		
39	II	6.130	0:00.0	0.0025	0.717	80.9
			0:25.0	0.2525		
			0:45.0	0.370		
			1:05.0	0.442		
			1:25.0	0.483		
			1:45.0	0.474		
			2:05.0	0.482		
			2:35.0	0.444		
			3:10.5	0.384		
			4:01.5	0.307		
			5:01.0	0.228		

^hIV = benzene + 0.06M iodine.

Table 6. (Continued)

Run	Solvent	Initial AIBN ^a molarity $\times 10^2$	Reaction time in hours:min.	A ^b	Cell length in mm.	Temp. (°C)
40	I	6.134	0:30.0	0.285	0.717	80.9
			2:00.3	0.648		
			4:00.3	0.557		
			6:00.0	0.356		
			8:02.0	0.217		
			9:30.0	0.157		
41	II	6.166	0:30.0	0.281	0.717	80.9
			2:00.3	0.486		
			4:00.3	0.305		
			6:00.0	0.163		
			8:02.0	0.102		
			9:30.0	0.066		
55	II	4.795 ^d	0:00.0	0.005	0.717	80.9
			0:05.0	0.037		
			0:10.2	0.074		
			0:15.1	0.125		
			0:20.0	0.150		
			0:25.0	0.1725		
			0:30.0	0.2075		
			0:40.0	0.262		
			0:50.0	0.283		
			1:00.3	0.314		
56	I	4.624 ^e	0:00.0	0.0065	0.717	80.9
			0:04.9	0.027		
			0:10.4	0.044		
			0:15.4	0.073		
			0:19.9	0.114		
			0:24.9	0.131		
			0:29.9	0.205		
			0:39.9	0.217		
			0:49.9	0.298		
			1:00.1	0.331		

Table 6. (Continued)

Run	Solvent	Initial AIBN ^a molarity $\times 10^2$	Reaction time in hours:min.	A ^b	Cell length in mm.	Temp. (°C)
87	I	5.899 ^d	0:00.0	0.010	0.750	80.9
			0:07.6	0.034		
			0:15.8	0.144		
			0:22.8	0.164		
			0:31.6	0.254		
			0:59.9	0.434		
			1:30.1	0.536		
88	II	2.312	0:00.0	0.007	0.750	80.9
			0:07.7	0.281		
			0:16.0	0.597		
			0:22.9	0.812		
			0:31.7	1.03		
			1:00.1	1.48		
			1:30.2	1.615		
34	V ¹	1.799	0:38.0	0.022	2.92	80.9
			1:14.8	0.015		
			1:40.0	0.037		
			2:17.0	0.033		
			3:10.5	0.018		
64	II	4.868 ^d	0:00.0	0.0024	0.717	89.6
			0:03.6	0.0675		
			0:06.3	0.127		
			0:09.0	0.184		
			0:12.1	0.2255		
			1:01.1	0.303		
			0:22.0	0.338		
			0:30.4	0.354		
			0:40.4	0.363		
			0:16.1	0.284		

¹V = nitrobenzene, slit width = 1.75 millimeters.

Table 6. (Continued)

Run	Solvent	Initial AIBN ^a molarity $\times 10^2$	Reaction time in hours:min.	A ^b	Cell length in mm.	Temp. (°C)
			1:20.1	0.243		
			1:45.6	0.1665		
			2:11.9	0.1095		
63	I	4.688 ^d	0:00.0	0.0065	0.717	89.6
			0:03.7	0.051		
			0:06.4	0.102		
			0:09.1	0.150		
			0:12.4	0.204		
			0:16.3	0.252		
			0:22.1	0.308		
			0:30.5	0.357		
			0:40.5	0.393		
			1:01.3	0.382		
			1:20.4	0.334		
			1:45.4	0.266		
			2:11.7	0.196		

Table 7. Infrared absorbance change on thermal decomposition of dimethyl-N-(2-cyano-2-propyl)-ketenimine in various solvents, with and without scavengers, at several temperatures

Run	Solvent	Initial ketenimine ^a molarity $\times 10^2$	Initial RSH ^b molarity $\times 10^2$	Reaction time in hours:min.	A ^c	Cell length in mm.	Temp. (°C)
72	I ^d	1.82	--	0:00	0.727	0.750	62.5
				0:30	0.708		
				1:00	0.703		
				1:35	0.683		
				2:00	0.674		
				2:30	0.670		
				3:00	0.648		
				3:34	0.627		
				4:00	0.608		
				5:00	0.607		
				6:01	0.574		
8:00	0.557						
10:02	0.504						
73	I	1.78	--	0:00	0.698	0.750	62.5
				1:00	0.671		
				2:02	0.648		
				3:01	0.618		
				4:02	0.606		
				6:07	0.548		
				10:01	0.491		
74	II ^e	1.83	--	0:00	0.701	0.750	62.5
				0:30	0.697		
				1:00	0.672		

^aDimethyl-N-(2-cyano-2-propyl)-ketenimine.

^bn-Butyl mercaptan.

^cInfrared absorbance.

^dI = carbon tetrachloride.

^eII = benzene.

Table 7. (Continued)

Run	Solvent	Initial ketenimine ^a molarity $\times 10^2$	Initial RSH ^b molarity $\times 10^2$	Reaction time in hours:min.	A ^c	Cell length in mm.	Temp. (°C)
				1:35	0.649		
				2:00	0.634		
				2:30	0.619		
				3:00	0.589		
				3:34	0.575		
				4:00	0.566		
				5:01	0.510		
				6:02	0.478		
				8:00	0.414		
				10:02	0.3725		
75	II	1.85	--	0:00	0.708	0.750	62.5
				1:00	0.666		
				2:01	0.624		
				3:01	0.587		
				4:03	0.562		
				6:00	0.505		
				9:57	0.3875		
76	I	1.87	0.087	0:00	0.735	0.750	62.5
				1:00	0.694		
				2:02	0.661		
				3:01	0.636		
				4:02	0.627		
				5:08	0.601		
				6:07	0.5825		
				8:05	0.516		
				10:01	0.439		
77	I	1.89	0.043	0:00	0.743	0.750	62.5
				1:02	0.722		
				2:00	0.689		
				3:00	0.664		
				4:03	0.636		
				5:01	0.626		
				6:13	0.596		
				8:02	0.554		
				9:24	0.538		

Table 7. (Continued)

Run	Solvent	Initial ketenimine ^a molarity $\times 10^2$	Initial RSH ^b molarity $\times 10^2$	Reaction time in hours:min.	A ^c	Cell length in mm.	Temp. (°C)
78	II	1.80	0.094	0:00	0.689	0.750	62.5
				1:00	0.633		
				2:02	0.598		
				3:01	0.554		
				4:02	0.524		
				5:08	0.494		
				6:07	0.461		
				8:05	0.414		
				10:01	0.350		
79	II	1.75	0.047	0:00	0.669	0.750	62.5
				1:02	0.612		
				2:00	0.575		
				3:00	0.541		
				4:03	0.498		
				5:01	0.468		
				6:14	0.448		
				8:02	0.385		
				9:24	0.365		
80 ^f	I	1.52	87.0	0:00	0.597	0.750	62.5
				1:00	0.037		
				2:01	0.016		
				3:00	0.016		
				4:03	0.005		
				5:07	0.000		
				6:00	0.001		
				8:01	0.000		
				9:57	0.000		
81 ^f	II	1.71	94.1	0:00	0.654	0.750	62.5
				1:00	0.011		
				2:01	0.008		
				3:00	0.007		

^fAbsorbances corrected for n-butyl mercaptan absorption.

Table 7. (Continued)

Run	Solvent	Initial ketenimine ^a molarity $\times 10^2$	Initial RSH ^b molarity $\times 10^2$	Reaction time in hours:min.	A ^o	Cell length in mm.	Temp. (°C)
				4:03	--8		
				5:07	0.006		
				6:00	--8		
				8:01	--8		
				9:57	0.004		
97 ^h	II	2.06	4.06	0:00	0.789	0.750	62.5
				0:30	0.729		
				1:01	0.692		
				1:31	0.643		
				2:01	0.608		
				3:22	0.512		
				3:42	0.489		
				4:12	0.457		
				5:07	0.403		
				6:04	0.356		
				7:05	0.308		
98 ^h	I	1.97	4.05	0:00	0.773	0.750	62.5
				0:30	0.740		
				1:01	0.700		
				1:31	0.657		
				2:01	0.637		
				3:22	0.563		
				3:42	0.537		
				4:12	0.491		
				5:07	0.444		
				6:04	0.421		
				7:05	0.393		
91	III ⁱ	1.18	--	0:00	0.457	0.750	70.0
				0:10	0.453		

^gNo data collected.

^hLiquid nitrogen was used to cool tubes during evacuation-nitrogen flush cycle prior to sealing off each tube.

ⁱIII = styrene.

Table 7. (Continued)

Run	Solvent	Initial ketenimine ^a molarity $\times 10^2$	Initial RSH ^b molarity $\times 10^2$	Reaction time in hours:min.	A ^c	Cell length in mm.	Temp. (°C)
				0:20	0.430		
				0:30	0.426		
				0:41	0.413		
				0:51	0.394		
				1:00	0.347		
				1:20	0.333		
				1:41	--8		
				2:00	--8		
				2:32	--8		
				3:03	--8		
44	I	2.28	--	0:00.0	0.932	0.717	80.9
				0:10.5	0.879		
				0:20.0	0.828		
				0:30.0	0.789		
				0:40.5	0.740		
				0:50.0	0.703		
				1:00.5	0.652		
				1:20.0	0.594		
				1:40.0	0.529		
				2:03.0	0.473		
				24:30.0	0.046		
45	II	2.25	--	0:00.0	0.898	0.717	80.9
				0:10.5	0.823		
				0:20.0	0.749		
				0:30.0	0.674		
				0:40.5	0.615		
				0:50.0	0.566		
				1:00.5	0.513		
				1:20.0	0.416		
				1:40.0	0.349		
				2:03.0	0.276		
				24:30.0	0.022		
42	I	2.16	2.99	0:00.0	0.883	0.717	80.9
				0:10.0	0.792		
				0:25.0	0.684		
				0:40.0	0.583		

Table 7. (Continued)

Run	Solvent	Initial ketenimine ^a molarity $\times 10^2$	Initial RSH ^b molarity $\times 10^2$	Reaction time in hours:min.	A ^c	Cell length in mm.	Temp. (°C)
				0:51.0	0.511		
				1:10.0	0.422		
43	II	2.23	3.11	0:00.0	0.891	0.717	80.9
				0:10.0	0.777		
				0:25.0	0.645		
				0:40.0	0.531		
				0:51.0	0.454		
				1:10.0	0.352		
58	II	1.02	8.53	0:00.0	0.412	0.717	80.9
				0:12.0	0.3375		
				0:26.8	0.1825		
				0:41.9	0.152		
				0:57.0	0.095		
				1:11.9	0.060		
				1:26.9	0.042		
				1:41.9	0.0305		
				2:02.0	0.027		
				2:21.9	0.0235		
59	I	1.08	9.28	0:00.0	0.444	0.717	80.9
				0:10.8	0.370		
				0:24.9	0.2675		
				0:40.3	0.181		
				0:55.0	0.118		
				1:10.2	0.068		
				1:25.0	0.047		
				1:40.0	0.038		
				2:00.1	0.032		
				2:20.0	0.0245		
60	I	1.09	9.17	0:00.0	0.4505	0.717	80.9
				0:12.0	0.359		
				0:26.9	0.2425		
				0:42.1	0.169		
				0:57.1	0.107		
				1:12.0	0.068		
				1:27.0	0.044		
				1:42.0	0.033		
				2:01.9	0.031		
				2:22.0	0.028		

Table 8. Initial rate of formation of dimethyl-N-(2-cyano-2-propyl)-ketenimine

Run	Solvent	Temp. (°C)	k_2^a $\times 10^5$	k_{AIBN}^b $\times 10^5$	$\frac{k_2}{k_{AIBN}}$
68	I ^c	62.5	0.69	1.18	0.58
69	I	62.5	0.67	1.18	0.57
65	I	69.6	1.45	3.10	0.47
56	I	80.9	7.4	13.3	0.56
87	I	80.9	7.2	13.3	0.54
63	I	89.6	16.7	38.5	0.43
70	II ^d	62.5	0.68	1.42	0.48
71	II	62.5	0.68	1.42	0.48
66	II	69.6	1.75	3.73	0.47
55	II	80.9	6.8	16.0	0.43
88	II	80.9	7.0	16.0	0.44
64	II	89.6	18.6	46.2	0.40

^aInitial fractional rate constant of dimethyl-N-(2-cyano-2-propyl)-ketenimine formation.

^bRate constant of 2,2'-azo-bis-isobutyronitrile decomposition.

^cCarbon tetrachloride.

^dBenzene.

Table 9. Solvent and temperature dependence of the first order rate constants of the decomposition of dimethyl-N-(2-cyano-2-propyl)-ketenimine

Run	Solvent	Temp. (°C)	Ketenimine ^a molarity x 10 ²	k x 10 ⁵ (sec. ⁻¹)
72	I ^b	62.5	1.82	1.02
73	I	62.5	1.78	1.04
44	I	80.9	2.28 ^c	9.64
74	II ^d	62.5	1.83	1.71
75	II	62.5	1.85	1.71
45	II	80.9	2.25 ^c	16.3

^aDimethyl-N-(2-cyano-2-propyl)-ketenimine.

^bCarbon tetrachloride.

^cCorrected to account for 25 per cent impurity.

^dBenzene.

Table 10. Solvent dependence of the Arrhenius energy of activation and frequency factor for the decomposition of dimethyl-N-(2-cyano-2-propyl)-ketenimine

Solvent	Z ^a	ΔE_a (Kcal/mole)
Carbon tetrachloride	4.86×10^{13}	28.7
Benzene	1.14×10^{14}	28.9

^aFrequency factor in $k(\text{sec.}^{-1}) = Z \exp. (-\Delta E_a/RT)$.

Table 11. Solvent and temperature dependence of the first order rate constants of the decomposition of dimethyl-N-(2-cyano-2-propyl)-ketenimine in the presence of scavengers

Run	Solvent	Temp. (°C)	Ketenimine ^a molarity $\times 10^2$	RSH ^b molarity $\times 10^2$	$k \times 10^5$ (sec. ⁻¹)
77	I ^c	62.5	1.89	0.043	1.00 ^f
76	I	62.5	1.87	0.087	0.99 ^f
98	I	62.5	1.97	4.05	2.74
80	I	62.5	1.52	87.0	77.0 ^f
42	I	80.9	2.16	2.99	17.4
59	I	80.9	1.08	9.28	45.9
60	I	80.9	1.09	9.17	47.3
79	II ^d	62.5	1.75	0.047	1.90
78	II	62.5	1.80	0.094	1.75 ^f
97	II	62.5	2.06	4.06	3.73
81	II	62.5	1.71	94.0	180. ^f
43	II	80.9	2.23	3.11	22.3
58	II	80.9	1.02	8.53	48.8
91	III ^e	70.0	1.18	--	7.1 ^f

^aDimethyl-N-(2-cyano-2-propyl)-ketenimine.

^bn-Butyl mercaptan.

^cCarbon tetrachloride.

^dBenzene.

^eStyrene.

^fConsiderable scatter.

Table 12. Polymerization of styrene initiated by dimethyl-N-(2-cyano-2-propyl)-ketenimine and 2,2'-azo-bis-isobutyronitrile

(Styrene molarity, 8.28)

Run	Initiator ^a molarity x 10 ²	Time in minutes	Readings ^b in cm.	Dilatometer	Temp. (°C)
51	I ^c --1.667	40.0	38.730	A ^d	70.2
		45.0	37.100		
		49.0	35.805		
		55.5	33.950		
		61.0	32.220		
		65.0	30.885		
50	II ^e --1.934	39.0	41.790	B ^f	70.2
		44.0	39.940		
		48.0	38.415		
		54.0	36.530		
		59.5	34.490		
		62.0	33.085		

^aInitiator molarity calculated at run temperature.

^bReadings made with a precision cathetometer.

^cI = dimethyl-N-(2-cyano-2-propyl)-ketenimine.

^dA = volume of dilatometer A is 19.959 cc.

^eII = 2,2'-azo-bis-isobutyronitrile.

^fB = volume of dilatometer B is 17.320 cc.

Table 12. (Continued)

Run	Initiator ^a molarity x 10 ²	Time in minutes	Readings ^b in cm.	Dilatometer	Temp. (°C)
86K	I--1.167	12.0	33.345	A	70.0
		15.0	32.320		
		18.0	31.245		
		20.0	30.525		
		22.0	29.815		
		24.0	29.110		
		28.0	27.710		
		30.0	27.015		
		34.0	25.685		
		37.0	24.670		
		39.0	24.020		
		41.0	23.350		
		43.0	22.695		
		45.0	22.040		
		51.0	20.115		
		53.0	19.480		
55.0	18.845				
57.0	18.255				
60.0	17.315				
67.0	15.190				
94K	I--1.161	1.0	31.975	A	70.0
		5.0	30.720		
		7.0	30.015		
		10.0	28.955		
		13.0	27.880		
		16.0	26.860		
		19.0	25.830		
		22.0	24.815		
		25.0	23.830		
		28.0	22.835		
		32.0	21.515		
		35.0	20.540		
		38.0	19.590		
		42.0	18.355		
		49.0	16.180		
51.0	15.575				
53.0	14.970				
55.0	14.375				

Table 12. (Continued)

Run	Initiator ^a molarity x 10 ²	Time in minutes	Readings ^b in cm.	Dilatometer	Temp. (°C)
95K	II--0.998	9.0	31.460	C8	70.0
		13.0	30.840		
		15.0	30.345		
		20.0	29.020		
		25.0	27.690		
		30.0	26.375		
		35.0	25.080		
		40.0	23.780		
		45.0	22.525		
		50.0	21.270		
		55.0	20.010		
		60.0	18.800		
		65.0	17.590		
		72.0	15.885		
		75.0	15.195		
		80.0	14.005		
		83.0	13.340		

^aC = volume of dilatometer C is 23.993 cc.

Table 13. Comparison of the efficiency of radical production by dimethyl-N-(2-cyano-2-propyl)-ketenimine and 2,2'-azo-bis-isobutyronitrile in styrene polymerization

(Temperature, 70.0°; styrene molarity, 8.28)

Run	Initiator ^a molarity $\times 10^2$	Initial rate $R_p \times 10^4$ moles/l.-sec.	$\frac{a_1}{a_2}$ ^b
95K	I ^c --0.998	2.254	--
94K	II ^d --1.161	2.358	0.636
86K	II--1.167	2.376	0.642

^aInitiator molarity calculated at run temperature.

^bRatio of dimethyl-N-(2-cyano-2-propyl)-ketenimine efficiency to 2,2'-azo-bis-isobutyronitrile efficiency (Run 95) using the rate constant for decomposition of dimethyl-N-(2-cyano-2-propyl)-ketenimine in styrene as 0.71×10^{-4} seconds⁻¹ (Run 91) and the rate constant for decomposition of 2,2'-azo-bis-isobutyronitrile in styrene as 0.48×10^{-4} seconds⁻¹ (as determined by nitrogen evolution by Dr. S. K. Liu in these laboratories).

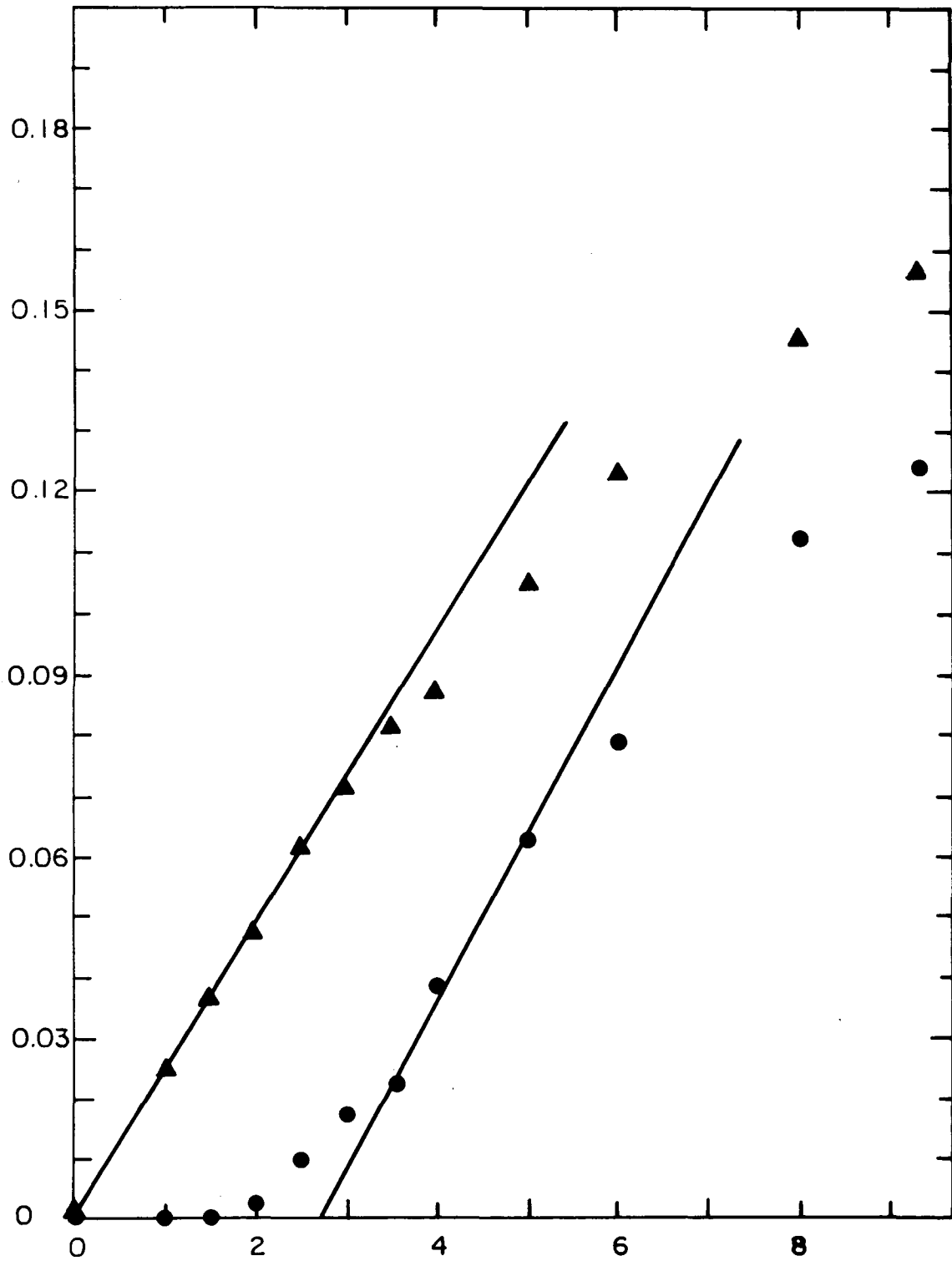
^c2,2'-Azo-bis-isobutyronitrile.

^dDimethyl-N-(2-cyano-2-propyl)-ketenimine.

Figure 8. Induction period, due to water, in the formation of dimethyl-N-(2-cyano-2-propyl)-ketenimine

Abscissa; Time in hours at 62.5°
Ordinate; (Ketenimine)/(AIBN)₀

Run 70, benzene solution, ▲; Run 68, moist carbon tetrachloride solution, ●



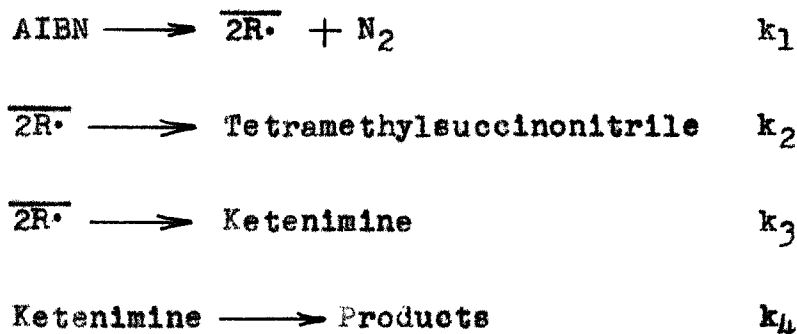
$$\frac{k_1'}{k_2'} = \exp.(-\Delta E/R(1/T_1 - 1/T_2)) = \frac{k_1''}{k_2''}$$

and the data of Talât-Erben and Bywater (14) in toluene solution where the k' are in toluene and the k'' are in a second solvent. This method assumes the Arrhenius activation energies for 2,2'-azo-bis-isobutyronitrile decomposition in these three solvents are equal. Values of k'' at 62.5° used were

carbon tetrachloride, $k'' = 1.18 \times 10^{-5}$ seconds⁻¹

and benzene, $k'' = 1.42 \times 10^{-5}$ seconds⁻¹ .

The k_2/k_{AIBN} data in Table 8 and the first order rate constants for decomposition of dimethyl-N-(2-cyano-2-propyl)-ketenimine in Table 9 could also be obtained by computations using basic (ketenimine)/(AIBN)₀ data. If this basic mechanism is used



The integrated rate equation for ketenimine is

$$\frac{(\text{ketenimine})}{(\text{AIBN})_0} = \left(\frac{k_3}{k_2 + k_3} \right) \frac{k_1}{k_4 - k_1} (e^{-k_1 t} - e^{-k_4 t}),$$

where

$$\overline{2R\cdot} = \text{"caged" free radicals,}$$

$$\frac{k_3}{k_2 + k_3} = \text{the rate fraction of formation of the ketenimine proportional to } k_2/k_{\text{AIBN}} \text{ in Table 8,}$$

and

$$k_4 = \text{rate of decomposition of the ketenimine.}$$

The value for $k_3/(k_2 + k_3)$ is constant throughout an entire run provided that the correct k_4 is fitted into the equation. As a check on the data in Tables 8 and 9, Table 14 gives a sampling of the computed values.

These computations are rather tedious for several reasons; first, successive approximations of k_4 are necessary, and, second, the data are not sufficiently uniform.

The Arrhenius energies of activation (Table 10) were determined for benzene and carbon tetrachloride solutions from the average rate constants at two temperatures.

Table 14. Computed rates of decomposition of dimethyl-N-(2-cyano-2-propyl)-ketenimine and the initial fraction of formation of dimethyl-N-(2-cyano-2-propyl)-ketenimine

Run	Solvent	Temp. (°C)	$k_4 \times 10^5$	$k_3/(k_2 + k_3)$
70	Benzene	62.5	1.65	0.54
55	Benzene	80.9	16.5	0.49

All decompositions were observed to be first order in dimethyl-N-(2-cyano-2-propyl)-ketenimine irrespective of the solvent system (Table 11), except decompositions in the presence of high concentrations of n-butyl mercaptan. These appear to follow pseudo-first order kinetics; first order in dimethyl-N-(2-cyano-2-propyl)-ketenimine and first order in n-butyl mercaptan.

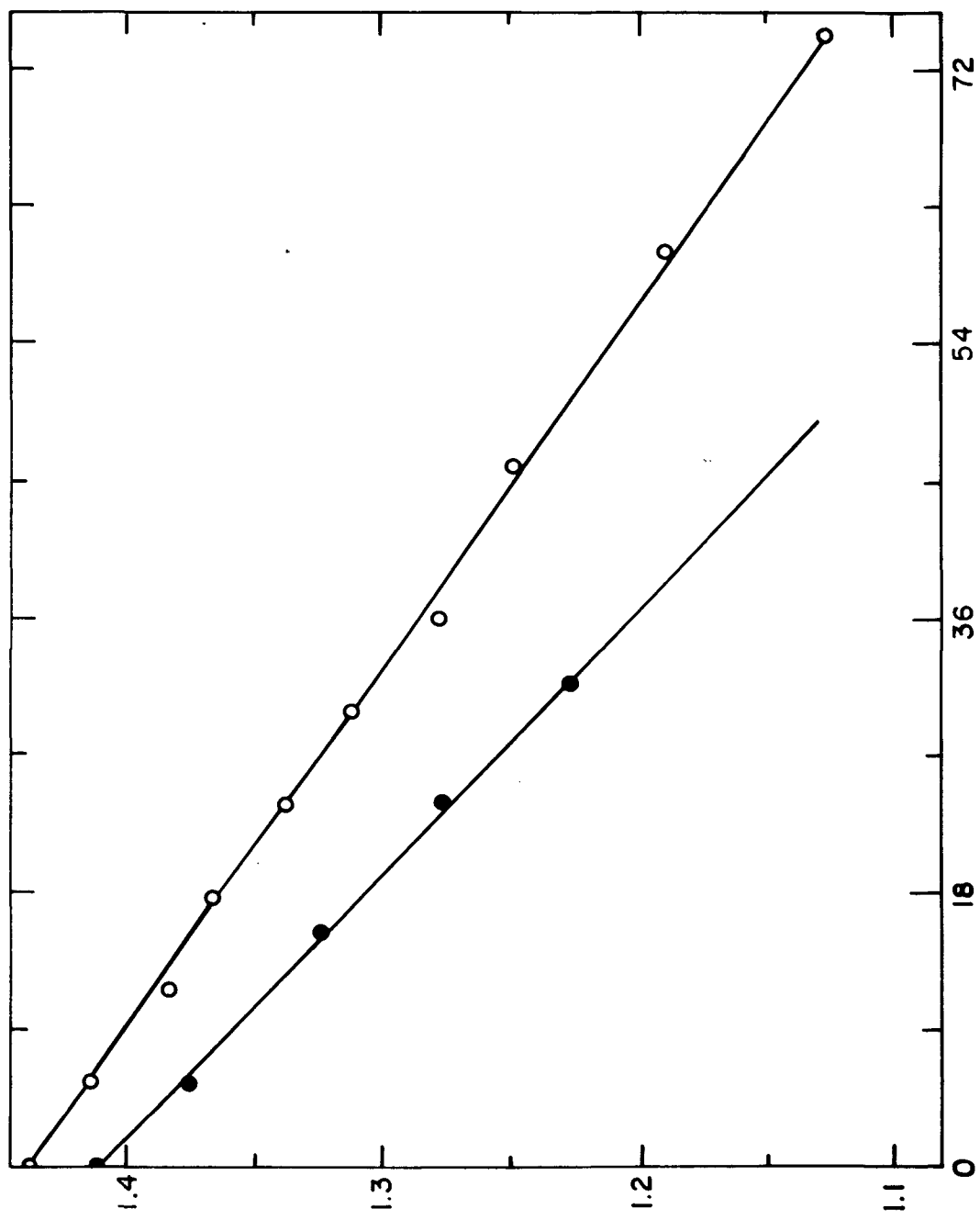
Figure 9 illustrates the increased first order rate constant for decomposition of dimethyl-N-(2-cyano-2-propyl)-ketenimine, observed in the presence of an approximately equimolar amount of n-butyl mercaptan.

The comparison of efficiency factors of Run 51 to Run 50 does not appear in Table 13 since the dimethyl-N-(2-cyano-2-propyl)-ketenimine used in Run 51 was measurably impure.

Figure 9. Increase in the first order rate constant for decomposition of dimethyl-N-(2-cyano-2-propyl)-ketenimine in the presence of n-butyl mercaptan

Abscissa; Time in seconds $\times 10^{-2}$ at 80.9°
Ordinate; $\log_{10}(\text{ketenimine}) + 3.08$

Run 44 in carbon tetrachloride, (ketenimine) = $2.26 \times 10^{-2}M$,
O; Run 42 in carbon tetrachloride, (ketenimine) =
 $2.16 \times 10^{-2}M$, (n-butyl mercaptan) = $2.99 \times 10^{-2}M$, ●



The other tables are self explanatory and will be discussed later. Runs marked by a K were made by Mr. Richard T. Keys.

DISCUSSION

The inefficient yield of scavengable free radicals upon thermal decomposition of 2,2'-azo-bis-isobutyronitrile (Table 2) has prompted publication of several hypotheses (11, 38, 43) to explain this abnormality. The most often cited explanation is that of the "cage" effect (see "Historical"). Another suggestion (11) is that 2,2'-azo-bis-isobutyronitrile may undergo a non-radical cis expulsion of nitrogen



producing tetramethylsuccinonitrile directly.

The decomposition of 2,2'-azo-bis-isobutyronitrile in liquid bromine (34 molar) was found (Table 4) to follow first order kinetics. Although the first order rate constant is slightly higher than those observed in other solvents, this constant is not large enough to be considered a pseudo-first order rate constant. This implies that the decomposition of 2,2'-azo-bis-isobutyronitrile in bromine is probably via free radicals. The absence of tetramethylsuccinonitrile as a product of the decomposition of 2,2'-azo-bis-isobutyronitrile in bromine rules out the views (11) that 2,2'-azo-bis-isobutyronitrile may decompose by a cis non-radical path producing tetramethylsuccinonitrile directly.

The recent reports (14, 15) of the presence of an intermediate, dimethyl-N-(2-cyano-2-propyl)-ketenimine, in this decomposition in dry toluene suggest the possibility of a correlation between inefficiency of radical production and the presence of this intermediate. Early experimental work reported herein confirmed the presence of dimethyl-N-(2-cyano-2-propyl)-ketenimine as an intermediate in the decomposition of 2,2'-azo-bis-isobutyronitrile in a variety of solvents: benzene, carbon tetrachloride, cyclohexane, and glacial acetic acid.

This intermediate was suggested to form and to decompose by consecutive first order reactions (14, 15, 51). This has been confirmed in terms of a generalized mechanism (Tables 8, 9, and 14). These calculations are of particular value since the rate constant for decomposition of dimethyl-N-(2-cyano-2-propyl)-ketenimine can be determined without actually isolating pure dimethyl-N-(2-cyano-2-propyl)-ketenimine and measuring its rate of decomposition independently.

That radicals are produced in this decomposition was explicitly demonstrated by the ability of the ketenimine to initiate the polymerization of styrene (Tables 12 and 13). Further, comparison of the rates of polymerization, R_p , of styrene by dimethyl-N-(2-cyano-2-propyl)-ketenimine and 2,2'-azo-bis-isobutyronitrile by the accepted relationship

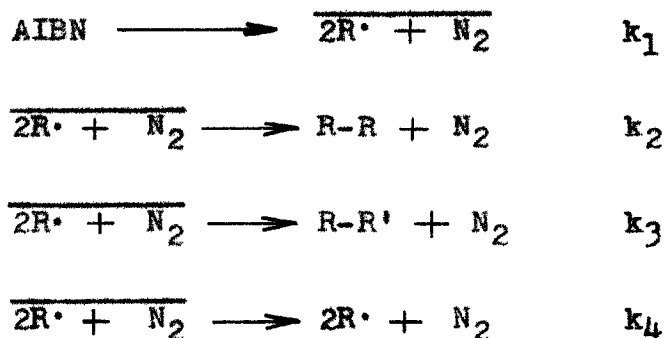
$$\frac{(R_{p1})^2}{(R_{p2})^2} = \frac{a_1 k_1 (I_1)}{a_2 k_2 (I_2)} \quad (\text{E-1})$$

where the subscripts 1 and 2 distinguish between initiators, and a and k are the efficiency factors and rates of decomposition in styrene, gives the ratio

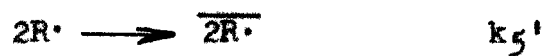
$$\frac{a_{\text{ketenimine}}}{a_{\text{AIBN}}} = 0.64. \quad (\text{E-2})$$

This would suggest the view that the radicals produced from 2,2'-azo-bis-isobutyronitrile are in a looser "cage" than the radicals from dimethyl-N-(2-cyano-2-propyl)-ketenimine. This view is consistent with the fact that a nitrogen molecule is produced on decomposition of 2,2'-azo-bis-isobutyronitrile but is not present in the ketenimine produced "cage".

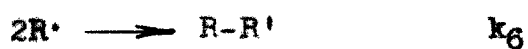
The most plausible mechanism for the decomposition of 2,2'-azo-bis-isobutyronitrile (AIBN) in the light of these experimental results, is



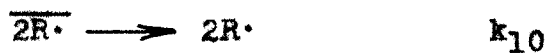
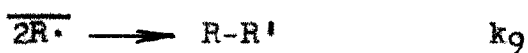
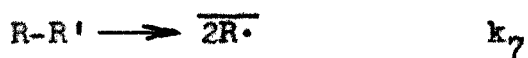
either



or



and



where

$R\cdot$ = 2-cyano-2-propyl radical,

$\overline{2R\cdot + N_2}$ = two $R\cdot$, formed in the presence of a nitrogen molecule, in a "cage", also referred to as a "loosely caged pair",

$R-R$ = tetramethylsuccinonitrile,

$R-R'$ = dimethyl-N-(2-cyano-2-propyl)-ketenimine,

and

$$\overline{2R\cdot} = 2R\cdot \text{ in a "cage".}$$

By this mechanism the initial rate of dimethyl-N-(2-cyano-2-propyl)-ketenimine formation is 48 per cent of the 2,2'-azo-bis-isobutyronitrile decomposition rate (Runs 70 and 71, Table 8). In terms of the proposed mechanism, this is

$$\frac{\left(\frac{d(R-R')}{dt}\right)_0}{k_1(AIBN)_0} = \frac{k_3}{k_2 + k_3 + k_4} + \frac{k_4 k_6}{(k_2 + k_3 + k_4)(k_5 + k_6)} \quad (E-3)$$

The first term represents the fraction of the "loosely caged pair" which combine to generate the ketenimine and the second term, the fraction separated by diffusion multiplied by the fraction of the freely diffusing radicals which combine at a later encounter to give ketenimine. The fraction separated by diffusion as measured by efficiency studies (11, 36, 38) is 61 per cent. If the assumption is made that only two per cent of the loosely caged radicals produce dinitrile, then

$$0.48 = 0.37 + 0.61 \frac{k_6}{k_5 + k_6}$$

or

$$\frac{k_6}{k_5 + k_6} = 0.18 \quad (E-4)$$

This assumption may seem low. However, Dr. J. N. Sen in 1952 in these laboratories completely decomposed 2,2'-azo-bis-isobutyronitrile in an excess of iodine in carbon tetrachloride at 80.0°. Dr. Sen isolated approximately a five per cent yield of tetramethylsuccinonitrile. Since iodine scavenges ketenimine over the period of the reaction, the only source of tetramethylsuccinonitrile is from the original loose cage. Evidence to suggest that tetramethylsuccinonitrile yield is lower in benzene than in carbon tetrachloride is provided by Hammond, et al. (11). The observed mole per cent yield of tetramethylsuccinonitrile decreases with increasing concentration of n-butyl mercaptan at 80.0°; in carbon tetrachloride with initial mercaptan molarity equal to 0.6 M, the dinitrile yield is reduced to 12 per cent, while in toluene under similar conditions the dinitrile yield is five per cent.

In this mechanism

$$\frac{k_5}{k_6} = \frac{k_8}{k_9} \quad (\text{E-5})$$

since radicals separated by diffusion must re-encounter before recombination. The only possible result of such an encounter, the life of which is long enough to result in combination, is that a cage identical to $\overline{2R\cdot}$ is formed. This is also equivalent to

$$\frac{k_6}{k_5 + k_6} = \frac{k_9}{k_8 + k_9} = 0.18 \quad (\text{E-6})$$

from equation (E-4).

Applying steady state kinetics to this mechanism, the observed rate constant for the decomposition of dimethyl-N-(2-cyano-2-propyl)-ketenimine in the absence of scavenger is

$$-\frac{d \ln(R-R')}{dt} = k_7 \left(1 - \frac{k_9}{k_8 + k_9 + k_{10}} \right) + k_7 \left(\frac{-k_{10} k_6}{(k_8 + k_9 + k_{10})(k_5 + k_6)} \right). \quad (\text{E-7})$$

The second fraction of the first term represents the fraction of the caged pair which recombine to regenerate the ketenimine, and the second term, the fraction separated by diffusion multiplied by the fraction of the freely diffusing radicals which recombine at a later encounter to give ketenimine.

This equation can be condensed and rewritten as

$$-\frac{d \ln(R-R')}{dt} = k_7 \left(1 - \frac{k_9}{k_8 + k_9} \right) \quad (\text{E-8})$$

or

$$-\frac{d \ln(R-R')}{dt} = 0.82 k_7 .$$

From the observed rate constant for decomposition of dimethyl-N-(2-cyano-2-propyl)-ketenimine in benzene at 62.5° (Runs 74 and 75, Table 9), the rate constant

$$k_7 = 2.08 \times 10^{-5} \text{ seconds}^{-1}. \quad (\text{E-9})$$

n-Butyl mercaptan (BuSH) is observed to react directly with the ketenimine in addition to scavenging the diffused free radicals.



The observed rate constant for decomposition of dimethyl-N-(2-cyano-2-propyl)-ketenimine in the presence of n-butyl mercaptan is

$$-\frac{d \ln(\text{R-R}')}{dt} = k_7 \left(1 - \frac{k_9}{k_8 + k_9 + k_{10}} \right) + k_{11}(\text{BuSH}) \quad (\text{E-10})$$

or for simplicity

$$-\frac{d \ln(\text{R-R}')}{dt} = k_7 X + k_{11}(\text{BuSH}). \quad (\text{E-11})$$

In this nomenclature, the observed rate constant in the absence of scavenger (E-7) becomes

$$-\frac{d \ln(R-R')}{dt} = k_7 X + k_7 Y . \quad (\text{E-12})$$

Inserting the concentrations and rate constants from Runs 74, 79, and 97 (Tables 9 and 11), in benzene at 62.5°, into a set of simultaneous equations, gives

$$k_7 X = 1.88 \times 10^{-5} \text{ seconds}^{-1} \quad (\text{E-13})$$

$$k_7 Y = -0.170 \times 10^{-5} \text{ seconds}^{-1} \quad (\text{E-14})$$

$$k_{11} = 4.56 \times 10^{-4} \text{ liters/mole-second} . \quad (\text{E-15})$$

Insertion of the values of X and Y into equations (E-13) and (E-14) gives

$$k_7 X = 1.88 \times 10^{-5} = \left(1 - \frac{k_9}{k_8 + k_9 + k_{10}} \right) k_7$$

or

$$k_7 = \frac{1.88 \times 10^{-5}}{\left(1 - \frac{k_9}{k_8 + k_9} \right)} \quad (\text{E-16})$$

and

$$k_7 Y = -0.17 \times 10^{-5} = \left(\frac{-k_{10} k_6}{(k_8 + k_9 + k_{10})(k_5 + k_6)} \right) k_7$$

or

$$k_7 = \frac{0.17 \times 10^{-5}}{\frac{a_k k_6}{k_5 + k_6}} \quad (E-17)$$

Equating equations (E-16) and (E-17), the efficiency of radical production, a_k is

$$a_k = 0.45 \quad (E-18)$$

This implies that

$$\frac{k_9}{k_8 + k_9 + k_{10}} = 0.099 \quad (E-19)$$

the fraction of the caged pairs which recombine to regenerate the ketenimine. While

$$\frac{k_{10} k_8}{(k_8 + k_9 + k_{10})(k_5 + k_6)} = 0.082 \quad (E-20)$$

is the fraction of radicals separated by diffusion multiplied by the fraction of freely diffusing radicals which recombine at a later encounter to give ketenimine.

To check these calculations, the efficiency of radical production from 2,2'-azo-bis-isobutyronitrile is obtainable from equations (E-2) and (E-18)

$$\frac{d[AIBN]}{dt} = 0.70 . \quad (E-21)$$

This is in excellent agreement with the reported efficiency in styrene (31, 33, 34) of 0.70 at 60.0°.

Support for the hypothesis that only two per cent of the loose cage, $\overline{2R \cdot + N_2}$, produces dinitrile is present in the expression for $k_3/(k_2 + k_3)$ tabulated in Table 14 (Run 70). This fraction in terms of the proposed mechanism is

$$\frac{k_3}{k_2 + k_3 + k_4} + \frac{k_4}{k_2 + k_3 + k_4} \left(\frac{k_9}{k_8 + k_9 + k_{10}} + \frac{k_6}{k_5 + k_6} \right) = 0.54.$$

Solving for $k_3/(k_2 + k_3 + k_4)$

$$\frac{k_3}{k_2 + k_3 + k_4} = 0.37 , \quad (E-22)$$

a value identical to that chosen in equation (E-4) is obtained.

A relatively straight forward experiment exists that could further support this hypothesis. Data on the quantitative recovery of the dinitrile formed in the decomposition of 2,2'-azo-bis-isobutyronitrile in the presence of an excess of iodine in benzene at 62.5° would be very useful.

It is observed that the initial rate fraction of formation of dimethyl-N-(2-cyano-2-propyl)-ketenimine decreases with increasing temperature (Table 8). This would be expected since the observed energy of activation for decomposition of

dimethyl-N-(2-cyano-2-propyl)-ketenimine is lower than that of the parent azo compound. Therefore the ketenimine is less stable at higher temperatures. This is in agreement with the work of Talât-Erben and Bywater (50), who observed fewer ketenimine linkages in higher temperature polymerization of methacrylonitrile. At higher temperatures the loose cage should be expected to produce proportionally more dinitrile than the tight cage ($\overline{2R\cdot}$), which already yields a high per cent of dinitrile, accounting for the major reduction in the initial rate fraction of formation of dimethyl-N-(2-cyano-2-propyl)-ketenimine. This would then agree with the reported five per cent limiting yield of tetramethylsuccinonitrile in toluene at 80.0° and the two per cent value in benzene as shown in the above equations.

Therefore a choice of

$$\frac{k_2}{k_2 + k_3 + k_4} = 0.08 \quad (\text{E-23})$$

in carbon tetrachloride at 62.5° seems reasonable. The measured efficiency of radical production from 2,2'-azo-bis-isobutyronitrile (11) is

$$\frac{k_4}{k_2 + k_3 + k_4} = 0.45 . \quad (\text{E-24})$$

The initial rate of formation of dimethyl-N-(2-cyano-2-propyl)-ketenimine is 57.5 per cent of the 2,2'-azo-bis-iso-butyronitrile decomposition rate (Runs 68 and 69, Table 8). Substituting these values into equation (E-3) gives

$$0.575 = 0.47 + 0.45 \frac{k_6}{k_5 + k_6}$$

or

$$\frac{k_6}{k_5 + k_6} = \frac{k_9}{k_8 + k_9} = 0.23 . \quad (\text{E-25})$$

The observed rate constant for the decomposition of dimethyl-N-(2-cyano-2-propyl)-ketenimine (Runs 72 and 73, Table 9) and (E-25) fit equation (E-9), giving the rate constant

$$k_7 = 1.34 \times 10^{-5} \text{ seconds}^{-1} . \quad (\text{E-26})$$

The rate constant for decomposition of dimethyl-N-(2-cyano-2-propyl)-ketenimine in carbon tetrachloride appears not to change in the presence of small amounts of n-butyl mercaptan. Unfortunately, considerable scatter was observed which is attributed to the lowered freezing point of the carbon tetrachloride and n-butyl mercaptan solution, with the result that the concentration of n-butyl mercaptan is far from certain in all carbon tetrachloride solvent runs, except for

Run 98. (In this case liquid nitrogen was used as the freezing coolant in the evacuation and sealing operations.) This error would be particularly noticeable at the very low concentrations of n-butyl mercaptan. Therefore the error in the rate constants associated with these lower concentrations of n-butyl mercaptan is very large.

If the assumption is made that the ratio of efficiency factors found in styrene is valid in carbon tetrachloride solution, then

$$\frac{k_{10}}{k_8 + k_9 + k_{10}} = 0.29 . \quad (\text{E-27})$$

This implies that

$$\frac{k_8 + k_9}{k_8 + k_9 + k_{10}} = 0.71 , \quad (\text{E-28})$$

and

$$\frac{k_9}{k_8 + k_9 + k_{10}} = 0.16 , \quad (\text{E-29})$$

the fraction of caged radicals which recombine to regenerate the ketenimine.

With these calculations and the observed rate constant and mercaptan concentration of Run 98 (Table 11), determination of the second order rate constant for addition of

n-butyl mercaptan to dimethyl-N-(2-cyano-2-propyl)-ketenimine is possible.

$$k_{11} = 4.00 \times 10^{-4} \text{ liters/mole-second.} \quad (\text{E-30})$$

In terms of the proposed mechanism the mole fraction yield of tetramethylsuccinonitrile (TMSN) at infinite time is

$$\frac{(\text{TMSN})}{(\text{AIBN})_0} = \frac{k_2}{k_2 + k_3 + k_4} + \frac{k_8 k_7 (k_{13} + k_{14} + k_{15})}{(k_8 + k_9 + k_{10})(k_{12} + k_{11}(\text{BuSH}) - k_1)} \left(1 - \frac{k_1}{k_{12} + k_{14}(\text{BuSH})}\right) \quad (\text{E-31})$$

where

$$k_{12} = \frac{k_7 k_{10}}{k_8 + k_9 + k_{10}} \left(\frac{k_8}{k_8 + k_9 + k_{10}} + \frac{k_6}{k_5 + k_6} \right)$$

$$k_{13} = \frac{k_3}{k_2 + k_3 + k_4}$$

$$k_{14} = \frac{k_4 k_9}{(k_2 + k_3 + k_4)(k_8 + k_9 + k_{10})}$$

$$k_{15} = \frac{k_4 k_6}{(k_2 + k_3 + k_4)(k_5 + k_6)} .$$

Using the rate constants and rate constant ratios calculated above for decompositions in carbon tetrachloride at

62.5°, the mole fraction yield of tetramethylsuccinonitrile expected in the presence of 0.6 M n-butyl mercaptan would be

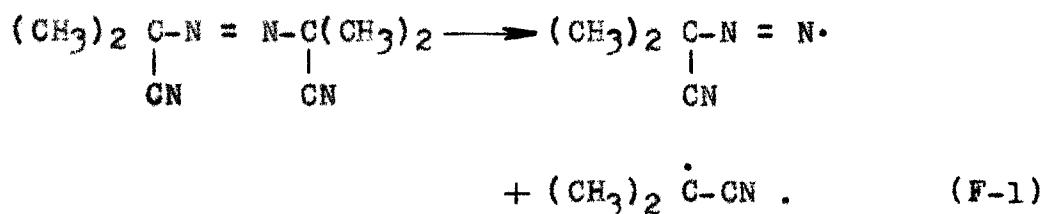
$$\frac{(\text{TMSN})}{(\text{AIBN})_0} = 0.10 ,$$

as compared to 12 mole per cent reported (11) at 80.0°.

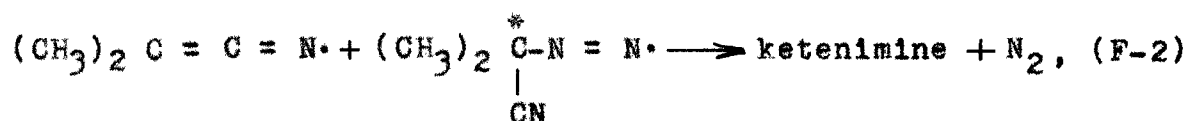
Similar agreement exists for calculation of decomposition in benzene solution.

It will be noted that although the cis-non-radical decomposition of 2,2'-azo-bis-isobutyronitrile producing tetramethylsuccinonitrile directly has been ruled out, such a cis non-radical decomposition of 2,2'-azo-bis-isobutyronitrile giving dimethyl-N-(2-cyano-2-propyl)-ketenimine is conceivable. The fact that the "loosely caged radicals", $2\overline{\text{R}}\cdot + \text{N}_2$, produce a very small fraction of tetramethylsuccinonitrile while the "caged" radicals, $\overline{2\text{R}}\cdot$, give tetramethylsuccinonitrile a considerable advantage in product ratio, strongly suggests this alternative. Further, molecular models show that 2,2'-azo-bis-isobutyronitrile has an appropriate geometry for such a non-radical formation of dimethyl-N-(2-cyano-2-propyl)-ketenimine.

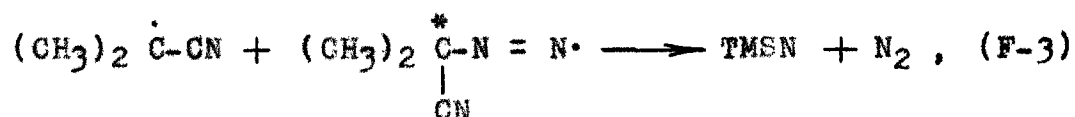
Another view having the same end result consists of decomposition of 2,2'-azo-bis-isobutyronitrile initially giving two different radical fragments,



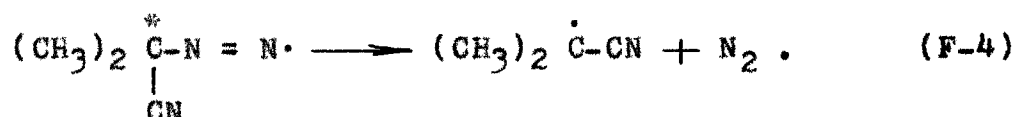
The azo radical could lose nitrogen on formation of ketenimine,



or, on formation of tetramethylsuccinonitrile (TMSN),



or, independent decomposition,



Of the first two paths, the second (F-3) would be the less favorable since more steric hindrance exists as the sp^2 trigonal hybrid 2-cyano-2-propyl radical moves in on the tetrahedral carbon ($\overset{*}{\text{C}}$, above). Hence, the former path (F-2) would account for almost all of the reactions with the azo radical.

This view explains the temperature effect on what was previously referred to as the "loose cage", although it is actually a normal cage containing an unlike pair of radicals. Increasing temperature would decrease the difference in the steric hindrance between these two paths, hence an increased fraction of tetramethylsuccinonitrile would be produced.

The second view is preferred since free radicals are known to be produced on decomposition of 2,2'-azo-bis-isobutyronitrile. Thus if the major portion of the ketenimine were produced by a non-radical path as suggested in the first view, this would imply that there is little or no cage effect in the decomposition of 2,2'-azo-bis-isobutyronitrile forming free radicals. This would be in sharp contrast with the large observed cage effect in the decomposition of dimethyl-N-(2-cyano-2-propyl)-ketenimine.

The energies of activation reported in Table 10 are probably not very realistic since the true energy of activation for the decomposition of dimethyl-N-(2-cyano-2-propyl)-ketenimine should be obtained using the calculated k_7 rate constants.

The magnitude of the errors has been estimated for a sampling of these measurements. The purity of dimethyl-N-(2-cyano-2-propyl)-ketenimine is very critical in the determination of the initial rate fraction of formation of dimethyl-N-(2-cyano-2-propyl)-ketenimine. Comparison of values determined by the disappearance of the bromine spectrum on

titration of ketenimine solution and the values determined by infrared analyses (Table 5) gives a standard deviation of 0.006, or approximately three per cent, supporting the validity of the infrared measurements.

The best linear fit of the data in several runs was determined by the method of least squares. The samples chosen for these calculations represent the extremes in precision. Run 81 (Table 11) represents the best data and the least squares calculations of the rate constant and probable error are $(3.71 \pm 0.02) \times 10^{-5}$ seconds⁻¹. The least precise data, Run 91 (Table 11) give $k = (7.19 \pm 0.57) \times 10^{-5}$ seconds⁻¹. Therefore the data scatter ranges from 0.5 per cent at best to 8.0 per cent.

The computed fraction of formation of dimethyl-N-(2-cyano-2-propyl)-ketenimine (Table 14, Run 70) has a standard deviation of approximately three per cent.

Dimethyl-N-(2-cyano-2-propyl)-ketenimine provides a unique source of free radicals and should provide an avenue for obtaining understanding of some polymerization and photolysis free radical mechanisms.

SUMMARY

On the basis of the experimental results reported in this thesis and the previously reported kinetic studies of others, certain hypotheses have been developed in the discussion.

The most significant experimental observations are:

1. Dimethyl-N-(2-cyano-2-propyl)-ketenimine is an intermediate in the decomposition of 2,2'-azo-bis-isobutyronitrile.
2. This intermediate forms and decomposes by consecutive first order reactions.
3. Dimethyl-N-(2-cyano-2-propyl)-ketenimine can be isolated in the pure state.
4. Quantitative infrared analysis is an excellent tool for following the ketenimine concentration.
5. The decomposition of dimethyl-N-(2-cyano-2-propyl)-ketenimine produces free radicals.
6. No tetramethylsuccinonitrile is formed when 2,2'-azo-bis-isobutyronitrile is decomposed in bromine.

The hypotheses advanced to account for these facts are:

1. The mechanism for decomposition of 2,2'-azo-bis-isobutyronitrile and ketenimine involves two different "cages"; one for decomposing

2,2'-azo-bis-isobutyronitrile, which favors dimethyl-N-(2-cyano-2-propyl)-ketenimine formation; and one for decomposing ketenimine, which favors tetramethylsuccinonitrile formation.

2. Dimethyl-N-(2-cyano-2-propyl)-ketenimine is initially formed by either a non-radical decomposition of 2,2'-azo-bis-isobutyronitrile, or, 2,2'-azo-bis-isobutyronitrile on decomposition gives an azo radical and a 2-cyano-2-propyl radical, which preferentially yield dimethyl-N-(2-cyano-2-propyl)-ketenimine for steric reasons.

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