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THE APPLICATION OF THE HAMMETT EQUATION TO THE SOLVOLYSIS OF BENZYL TOSYLATES

by

Jay Kazuo Kochi

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Approved:

Signature was redacted for privacy.

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Head of Major Department

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Dean of Graduate College

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ACKNOWLEDGMENT

> If we consider what persons have stimulated and profited us, we shall perceive the superiority of the spontaneous or intuitive principle over the arithmetic or logical. The first contains the second, but virtual and latent. Logic is the procession or proportionate unfolding of the intuition.
>
> Ralph W. Emerson,
> "Essays".

The conception and completion of the aspect of the problem presented herein owe much to the intellectual stimulation, profundity and encouragement provided the author by Dr. George S. Hammond.

The aid from the Iowa State Research Institute under whose auspices much of this work was undertaken is also gratefully acknowledged.

INTRODUCTION

The correlation of the reaction rates and equilibria of meta and para derivatives of benzene with substituent groups has been successfully undertaken by the Hammett equation. The applicability of this empirical equation in many reaction series is a well-established fact.

There are certain other cases, however, in which the Hammett relationship is not quite so applicable. In particular, it is necessary to assign two values of the substituent constant to the para-nitro group, one for the reactions of phenols and another for the reaction of other benzene derivatives.

A different class of reactions which show anomalous behavior with the Hammett equation is the solvolysis of benzyl chlorides. The studies pertaining to this series of reactions have not been extensively nor systematically carried out with respect to the correlation of substituent effect and reaction velocity. Since this class offers a new and promising approach to the analysis of the Hammett equation, an investigation was undertaken to scrutinize the equation. In particular, a study of substituted benzyl tosylates was made because of the crystalline nature and unambiguous solvolyses of these compounds.

The solvolysis of benzyl tosylates and the saponification of ethyl benzoates represent two reactions of opposed charge requirements. Whereas the solvolysis of benzyl tosylate is facilitated by electron-repelling substituents the saponification of ethyl benzoate is retarded by these same groups. The extent to which substituents promote the solvolysis of benzyl tosylate will depend on the ability of the substituent to stabilize the transition state. The magnitude of the stabilization may be expected to be measured by the deviation of the substituent from the Hammett relationship.

With this interpretation in mind an investigation was initiated to determine the relative conjugative aptitudes of the carbon - carbon double bond and triple bond. From a very qualitative consideration of molecular orbital theory, one may expect the triple bond to conjugate as well as, if not better than, the double bond with an aromatic system. Tolane and Stilbene were chosen as the basic systems to be studied.

HISTORICAL

The Effect of Substituents on Chemical Reactivity

Early attempts to correlate structure with chemical reactivity and physical properties provided a stimulus for the development of modern theoretical organic chemistry. In this respect the interpretation and correlation of effects produced by substituent groups in organic compounds have been one of the foremost problems confronting organic chemists. Numerous empirical rules devised for classifying these effects before the successful application of electronic theory to chemistry by Lewis[1] have been adequately summarized by Watson[2] and Remick[3]. Subsequent studies from varied aspects of mechanistic organic chemistry contributed greatly to the coalescing of fundamental conceptions[4]. Thus, concurrent studies of orientation in aromatic substitution, dipole moment measurements, reaction rates in solvolysis, equilibrium determinations of acid - base systems and oxidation - reduction potentials of organic compounds helped to corroborrate and strengthen the theory.

The basis for the analysis of the problem of substituent effects can be found in the nature of the interaction of a series of substituents, S, with a parent molecule, R. In such a series of compounds, R-S, it is

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[1] G.N. Lewis, J. Am. Chem. Soc., 38, 762 (1916).

[2] H. Watson, "Modern Theories of Organic Chemistry", Second Edition, Oxford University Press, New York, N.Y., 1941.

[3] A. Remick, "Electronic Interpretations of Organic Chemistry", Second Edition, John Wiley and Sons, Inc., New York, N.Y., 1949.

[4] C. Ingold, Chem. Revs., 15, 226 (1934).

important to realize the type and magnitude of the perturbation effected by S across the R-S bond. Of the number of systems of this type that can be studied the benzenoid aromatic system, where R is benzene or its derivatives, has proven to be the most amenable to empirical and theoretical treatments. In subsequent discussion, for the sake of convenience and without too much loss of generality, we shall restrict ourselves to this interesting system.

The influence of substituents on the reactivity of organic compounds has been interpreted in an illuminating manner by the theory of electron displacements[5]. In essence, the theory accounts for two distinct types of electronic effects, termed the inductive effect and electromeric effect. Each perturbation is considered to be independent and no attempt is made to relate the dependence of one on the other.

Inductive effect

Studies on the resting state of a molecule by means of dipole measurements have been used to measure quantitatively the permanent polarization of a molecule[6]. This effect is characterized by the electrostatic interaction of an existing pole[7] (electric change) or dipole[8] with other centers in the molecule, thus causing an unsymmetrical distribution

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[5] C. Ingold, Ann. Rpts. Prog. Chem., 23, 140 (1926).
R. Robinson, J. Chem. Soc., 1445 (1932).

[6] S. Glasstone, "Textbook of Physical Chemistry", Second Edition, D. Van Nostrand Co., Inc., New York, N.Y., 1941, p. 543.

[7] C. Ingold, Ann. Rpts. Prog. Chem., 23, 129 (1926).

[8] W. Waters, J. Chem. Soc., 1554 (1933).

of electrons around these centers. The magnitude of this effect is given by the following equations:

$$F_{pole} = \frac{e^2}{Dr^2}; \quad F_{dipole} = \frac{u(1 + 3\cos^2\theta)^{\frac{1}{2}}}{Dr^3} \qquad (1)$$

where F is the field induced by charge e or dipole u at a distance r in a medium of dielectric constant D. Theta is the angle the dipole makes with the line connecting it and the reaction center. If α is the polarizability of a bond, defined by $m = \alpha F = u$ induced , then the electrostatic energy due to the field will be

$$E_{es} = \frac{1}{2} F^2. \qquad (2)$$

Thus, for a pole, the induced electrostatic energy in a polarized bond will vary as e^2 and for a dipole as u^2. For a particular polarized bond having a dipole moment u the magnitude of the induced charge, Δe, is equal to u/r_{ab}, where r_{ab} is the bond length. From equations (1) it is seen that the transmission of the effects of a pole or dipole fall off rapidly with distance, the decrement depending on the polarizability of the intervening bonds. From values of α it has been calculated that the electrostatically induced energy of a saturated carbon bond is 0.02 times the energy of the previous bond, while for an unsaturated double bond the factor is 0.5[9]. In the case of an induction of charge by a pole or dipole across empty space the term direct or field effect has been applied[10].

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[9] W. Waters, "Physical Aspects of Organic Chemistry", Fourth Edition, D. Van Nostrand and Co., Inc., New York, N.Y., 1950, p. 283.

[10] C. Ingold and R. Vass, J. Chem. Soc., 401 (1926).

This effect differs from the inductive effect only by the medium through which it acts.

Electromeric effect

The apparent anomalies in the orientation in aromatic substitutions on the basis of relative inductive effects[11] together with inexplicable dipole moments of aromatic compounds and ionization constants of substituted benzoic acids[12] led to the postulation of the second electronic effect. The electromeric (mesomeric or tautomeric) effect was found to be operative only in conjunction with multiple bonds between atoms. Using the carbonyl group as an example, the effect prescribes that there exists a certain tendency for a pair of electrons comprising the double bond to be associated exclusively with oxygen, the more electronegative atom. Thus, in the resting state of the carbonyl system the valency of carbon was considered to be somewhere between four and three, and that of oxygen between one and two. The C-O bond thus possesses neither double nor single bond character, but an intermediate one.

A theoretical basis for the semi-empirical electronic theory of organic chemistry has been invoked through the introduction of a more deductive and quantitative theory based on quantum mechanics[13]. The fundamental concepts, however, remain much the same. The theory of the interaction

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[11] C. Ingold and E. Ingold, J. Chem. Soc., 1310 (1926).

[12] H. Watson, et al., ibid., 893 (1933).

[13] J. Van Vleck and A. Sherman, Rev. Mod. Phys., 7, 167 (1935).
L. Pauling, "Nature of the Chemical Bond", Second Edition, Cornell University Press, Ithaca, N.Y., 1940.

of substituent groups with unsaturated hydrocarbon radicals to which they are attached is now considered from a more fundamental standpoint involving the nature of the interaction of atomic and molecular orbitals. Because of its simpler form and adaptability to quantitative calculations, the method of molecular orbitals has been the one most frequently applied to quantum-mechanical formulations of the complex organic systems[14].

In general, the new theory envisages the interaction of groups in two ways:

i) The electric field of the substituent may polarize the radical

ii) The group may form a π-bond with the carbon atom to which it is attached. This effect may have repercussions on the π-bond already present in the radical, i.e., the group participates in a molecular orbital with the carbon atom of the radical.

The polarization of the electric field has been visualized in two ways. Firstly, it is regarded as a purely electrostatic interaction as pictured in the classical inductive effect. This effect is considered to perturb the localized σ-bonds only[15]. Secondly, the electrostatic interaction can also occur with the π-bond system of the radical in which case the field of the substituent causes changes in the π-bond order of the radical. This effect has no counterpart in the classical inductive effect. Moreover, these two effects are not independent since a distortion of the σ-framework by inductive polarization will change the

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[14] R. Brown, Quart. Revs., 6, 63 (1952).

[15] W. Price and A. Walsh, Proc. Roy. Soc., London, A191, 22 (1947).

field in which the more or less nonlocalized π-electrons move. Since the polarizability of the π-bonds is greater than that of the σ-bonds[16] the effect of these latter forces are longer in range.

The classical mesomeric effect has been reinterpreted as a resonance phenomenon[17] in the light of wave mechanics, to include the nonlocalized -bond interaction of the unsaturated radical with the substituent group. The substituent can provide a p_z orbital, perpendicular to the benzene ring, which will extend the conjugation path of the π-electrons in Ar-X (*i.e.*, form new molecular orbitals). As this p_z orbital will in general be occupied by one or two electrons (or can have the same symmetry - hyperconjugation[18]) the change in the number of π-electrons will cause resulting changes in the π-electron energies. Since the non-classical inductive effect and resonance effect both operate on the π-electron system, they are not independent. Electron distribution in the σ-bond will, thus, affect the π-bond energy as well.

The development of an empirical correlation between chemical and physical properties and structure may be conveniently reviewed in the light of the theories which were developed from them. A study of the resting state of the molecule has been provided by dipole moment studies and investigations of the infra-red spectra for vibrational and rotational energies[19]. Further empirical correlations have been made with the

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[16] A. Walsh, *Quart. Revs.*, *2*, 73 (1948).

[17] G. Wheland, "The Theory of Resonance", John Wiley and Sons, Inc., New York, N.Y., 1944.

[18] R. Mulliken and C. Rieke, *J. Am. Chem. Soc.*, *63*, 41 (1941). E. Berliner and F. Berliner, *ibid*, *72*, *222* (1950).

[19] C. Ingold, *et al.*, *J. Chem. Soc.*, 912 (1936).

photochemical excited state utilizing information obtained from ultraviolet spectra. Equilibrium studies on the correlation of structure and reactivity have been provided by acid - base systems and reversible oxidation - reduction potentials. The study of activation processes involving rates of reactions, orientation in aromatic systems and molecular rearrangements have provided another tool for the examination of these effects.

Studies in dipole moments provided a quantitative means of investigating substituent effects. One of the first successful quantitative applications of substituent effects was made by Nathan and Watson[20], who utilized the dipole moments of substituted methanes to obtain ionization constants of the corresponding acetic acids. The empirical equation was formulated as:

$$\log K = \log K^{o} - C(u - \alpha u^{2}) \qquad (3)$$

where the K's represent ionization constants, and C and α are empirical constants. The equation was subsequently extended to aromatic systems. Regular correlations, however, could not be obtained with some *para*-substituted acids (*e.g.*, *p*-methoxybenzoic). The failure of this correlation[21] for these acids was attributed to abnormal mesomeric interaction in the acid, which was not present in the parent compound. Similar discrepancies occurred when attempts were made to apply dipole measurements to the constants and activation energies for the saponification

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[20] H. Watson and B. Nathan, *J. Chem. Soc.*, 438, (1933).

[21] H. Watson, *Trans. Faraday Soc.*, *34*, 165 (1938).

of esters. Studies by Sutton[22] on mesomeric moments bore out these suspicions. Audsley and Goss[23] have been able to relate the mesomeric moments of halobenzenes to the atomic number of the halogen.

The study of chemical equilibria and equilibrium constants as a function of substituents is important and convenient for several reasons:

(i) The equilibrium constant is independent of the reaction path (*i.e.*, the mechanism of the process), being a function only of the difference in the free energy of the reactants and the products.

(ii) The equilibrium constant is independent of the time of the reaction. A knowledge of the equilibrium constants, thus, enables a study of the variation of substituent groups. From a standpoint of chemical equilibrium, two classes of reactions have been extensively studied, *viz.*, acid - base prototropy and oxidation - reduction potentials of quinones.

Several empirical rules for the determination of ionization constants of non-aromatic acids are given by Branch and Calvin[24]. Their method has been generalized to apply to aromatic acids by McGowan[25]. The equation he used is:

$$F = -RT\ln K = A + BQ \tag{4}$$

where Q is a constant for the substituent and A and B are constants. The equation has recently been expanded to correlate reaction rates[26].

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[22] L. Sutton, *Proc. Roy. Soc., London,* *133A*, 668 (1931).

[23] A. Audsley and F. Goss, *J. Chem. Soc.*, 497 (1942).

[24] G. Branch and M. Calvin, "The Theory of Organic Chemistry", Prentice-Hall, Inc., New York, N.Y., 1941, p.183.

[25] J. McGowan, *Chem. and Ind.*, 632 (1948).

[26] J. McGowan, *J. Soc. Chem. Ind.*, *68*, 253 (1949).

Another empirical equation that has met with limited success is attributed to Hixon and Johns[27]

$$\log K = Q(e^{ax-b} - c) \tag{5}$$

where K represents the ionization constant of a substituted acid, x is a substituent - constant, known as the electron - sharing ability, and Q, a, b and c are empirical constants. The applications and limitations of this equation have recently been reviewed[28].

A more theoretical approach to the problem has been treated by Westheimer[29]. He considers protonic ionization as a problem of the electrostatic interaction of a dipole field of a substituent with the ionizing proton. In this treatment Westheimer considers the free energy difference in ionization between substituted and unsubstituted aromatic acids as the work required to remove the ionizable proton from an electrostatic field due to the dipole of the bond between the ring and the substituent. By considering the solute as occupying an ellipsoidal cavity in the solvent, the effective medium through which the electrical field operates consists of the bulk solvent and the molecule. The difference in free energy is then given for para-substituted benzoic acids as:

$$E_{el.} = \frac{eM\cos\theta}{R^2 De} = 2.303 \log K/K_o \tag{6}$$

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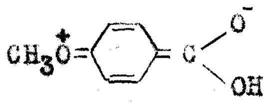
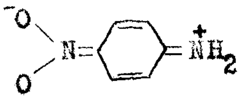
[27] R. Hixon and I. Johns, J. Am. Chem. Soc., 49, 1786 (1927).

[28] F. Schultz, Unpublished Doctoral Dissertation, Ames, Iowa, Iowa State College Library, 1950.

[29] F. Westheimer, J. Am. Chem. Soc., 61, 1977 (1939).

where M is the dipole moment of the substituent, R the distance separating the dipole from the proton, the angle between the dipole and the line joining its center to the proton and D_E the effective dielectic constant, which takes into account the size and shape of the solute molecule and the nature of the medium separating the dipole and the proton. Since the benzene ring introduces the peculiarities mentioned previously, this purely electrostatic treatment has been found to apply well for all substituents in the case of phenylacetic acids only. Good correlations were obtained with most *para*-substituted benzoic acids, the exceptions being *p*-methoxybenzoic and *p*-hydroxybenzoic acids. Phenols and anilines fitted well with experimental values; discrepancies, however, occurred with the *p*-cyano and *p*-nitro derivatives. In general, acids, phenols and anilines deviating were those in which the dipole moment of the molecules was not the sum of the dipoles of the constituent parts. The discrepancies were ascribed to the usual resonance interactions shown below.





The Westheimer-Kirkwood treatment of ionization constants was applied by Sarmousakis[30] to *meta*-substituted aromatic acids, where resonance interactions are not considered to be so important. Instead of using the prolate spheroidal model of Kirkwood and Westheimer to describe the

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[30] J. Sarmousakis, *J. Chem. Phys.*, *12*, 277 (1944).

solute cavity in the solvent, Sarmousakis resorted to the more difficult oblate spheroidal model. In form the equation he obtained was similar to the results obtained by the previous investigators,

$$\log K/K_o = \frac{1}{2.303kT} \; \frac{-e|u_\xi|\cos(u_\xi\vec{i},\vec{r})}{r^2 D_\xi} - \frac{-e|u_\phi|\cos(u_\phi\vec{i},\vec{r})}{r^2 D_\phi}$$

where D_ξ and D_ϕ are effective dielectric constants corresponding to the dipole components u_ξ and u_ϕ. The application of this equation to *meta*-substituted aromatic acids yielded good correspondence with experimental values. An interesting application of this general formula was found for the *para*-substituted acids. The theoretically calculated and experimentally determined values of $\log K/K_o$ showed differences, $\Delta \log K/K_o$, which may be considered a measure of the resonance energy operative over the electrostatic energy in the *para*-acids. The median values of the $\log K/K_o$ showed very little mean deviations in different solvents, which varied from pure alcohols and dioxane to binary solutions with water. Judson and Kilpatrick[31] have extended the treatment further to apply to *meta*- and *para*-substituted phenols with good results.

It has been pointed out by Shorter and Stubbs[32] that the change in ionization constants by two or more substituents in benzoic acid is very nearly the algebraic sum of the effects of the individual groups. This principle of additivity has been applied to a number of di- and tri-substituted benzoic acids with surprising success. Although a uniformity

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[31] C. Judson and M. Kilpatrick, *J. Am. Chem. Soc.*, *71*, 3117 (1949).

[32] J. Shorter and F. Stubbs, *J. Chem. Soc.*, 1181 (1949).

of data was not always possible (thus precluding discussions of small deviations) such compounds as 3-nitro-4-methoxy-, 5-nitro-3-hydroxy-4-methoxy, and 5-nitro-4-hydroxy-3-methoxybenzoic acids showed small deviations from the expected values. Particularly unpredictable were the 2:3- and 2:6-substituted acids.

Another aspect of chemical equilibrium and substituent effect has been the investigation of the reversible oxidation - reduction potentials of substituted quinones. Fieser[33] stated empirically that groups which lower the potential of quinones facilitate substitution in the benzene ring. This was rationalized in terms of the old electronic theory. Analyzing the situation from a more modern viewpoint, Branch and Calvin[34] attribute the driving force (*i.e.*, free energy difference) to a gain in resonance energy in the aromatic hydroquinone system over the quinoidal system. Berliner[35] has shown that the potentials of many quinones are affected by changes in substitution in a manner fairly well predictable by means of the resonance and inductive effect of the substituent groups. Since the oxidation - reduction potential is a measure of the free energy change of quinones to hydroquinones, an examination of the intrinsic difference between the two compounds was considered necessary. He considered the difference in empirical resonance energy of quinones and hydroquinones as an adequate index. A plot of the difference in

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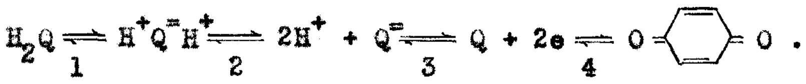
[33] L. Fieser, *J. Am. Chem. Soc.*, *57*, 491 (1935).

[34] G. Branch and M. Calvin, ref. 24, p. 304.

[35] E. Berliner, *J. Am. Chem. Soc.*, *68*, 49 (1946).

resonance energy with oxidation potentials yielded a smooth correlation.

Ri and Takayama[36] have applied a more theoretical treatment to the hydroquinone-quinone equilibrium. They visualized the process as involving the following equilibria:



$$H_2Q \underset{1}{\rightleftharpoons} H^+Q^=H^+ \underset{2}{\rightleftharpoons} 2H^+ + Q^= \underset{3}{\rightleftharpoons} Q + 2e \underset{4}{\rightleftharpoons} O= \quad =O \ .$$

By assuming that the substituents affected only equilibria 2 and 3, i.e., by determining the amount of double bond character in the C-O bond, they were able to calculate the difference in oxidation-potentials of substituted and unsubstituted quinones.

A quantum mechanical study of the oxidation - reduction potentials of quinones was undertaken by Evans, Gergely and deHeer[37]. They applied the basic hypothesis of Branch and Calvin[34], to evaluate the energies of the 10-π and 8-π electrons in hydroquinone and quinone, respectively. The resonance or delocalization energy of the two was then calculated as a function of the electronegativity of the oxygen atoms and the bond energy of the carbonyl link. This molecular orbital method, however, was restricted to quinone and polynuclear quinones. Extension of the method to substituted quinones is possible if a consideration of the σ-bond and π-bond perturbations by substituent groups is taken into account.

In the light of a new and less quantitative molecular orbital theory

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[36] T. Ri and M. Takayama, Rev. Phys. Chem. Japan, 13, 153 (1945); C.A., 44, 2872 (1950) .

[37] M. Evans, J. Gergely and J. deHeer, Trans. Faraday Soc., 45, 312 (1949).

the substituent effect has been restated by Evans and deHeer[38]. Although the overall result is not known, they believe that inductive and resonance effects must be included in the treatment. They suggest a suitable method of attack as consisting of:

(i) Variation of the position of the substituent to determine the role of the inductive effect;

(ii) Variation of both position and nature of the substituent ot determine the importance of the resonance effect. Since the stabilization of the quinone is given by the degree of conjugation, such parameters as the electronegativity of the attached center and the resonance integral between the p_z orbital of the center and the carbon of the ring are included.

The ultraviolet absorption spectra of a series of substituted benzenes have been examined by Doub and Vandenbelt[39] in an effort to correlate structure with the displacement of several bands in benzene, *viz.*, the primary band (203 mu) and the secondary band (280 mu). They studied the regularity in the amount of displacement of both the primary and secondary bands in the derivatives relative to those in benzene. They pictured the absorption of many *meta-* and *para-*substituted benzene compounds as a progression of at least three bands, which, regardless of the degree of displacement, maintained a relatively regular wavelength relationship. The displacement of the primary band of benzene by

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[38] M. Evans and J. deHeer, *Quart. Revs.*, *4*, 101 (1950).

[39] L. Doub and J. Vandenbelt, *J. Am. Chem. Soc.*, *69*, 2714 (1947).

substitution was attributed to the electronic interaction of groups with the benzene nucleus, thus lessening the constraint or force holding the electrons responsible for the absorption of light. The greatest displacement was observed for those groups capable of the greatest electronic interaction across the ring (ortho:para group versus meta group) and least for those groups capable of least interaction across the ring (ortho:para group versus ortho:para, meta versus meta).

A quantity, $\delta\lambda_0$, of the substituent was assigned as a measure of the electron-attracting or electron-repelling power of the substituent. From numerous empirical observations they deduced the following formula:

$$\delta\lambda_0' - \delta\lambda_0'' = 24.05\,(\Delta\lambda_0) \tag{8}$$

where $\Delta\lambda_0$ is the displacement of the primary band of benzene by disubstitution, and $\delta\lambda_0'$ and $\delta\lambda_0''$ are the corresponding displacements of each group separately in monosubstituted benzenes. Despite the limitations inherent in such an empirical correlation the results look impressive. The method was extended[40] to the same type of substituents in the ortho and meta positions. The resulting equation was found to be applicable in these cases:

$$\Delta\lambda_0 = a + b\,(\delta\lambda_0' + \delta\lambda_0'') \tag{9}$$

The success of this correlation was discussed in terms of the resonance stabilization of the ground state relative to the excited state and the

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[40] L. Doub and J. Vandenbelt, J. Am. Chem. Soc., 71, 2414 (1949).

nature of the effect of the substituent on both states.

Matsen[41] has combined molecular orbital theory and perturbation theory to derive general expressions for resonance energies, resonance (mesomeric) moments, intensities and frequencies of ultraviolet absorption bands and the directing power of substituents and applicable to aromatic systems. He used an experimentally obtainable parameter, δ (a measure of the electronegativity of the substituent), whose value is estimable from ionization energies of the simple compounds containing the substituent. In many of the compounds he considered (*e.g.*, phenol), resonance interaction between the ring and the substituent was so important that other weak effects such as the inductive effect, were neglected. On that basis spectral properties could in general be correlated with differences in ionization energies of substituted benzenes and benzene itself. The smaller the difference in ionization energy the greater was the perturbation of the benzene levels and longer the wavelength and greater the intensity of the near ultraviolet absorption band. However, in the case of the halogenobenzenes a reversal occurred from the expected intensities of the bands. An introduction of a new parameter, δ_1 , (a function of the electron affinity of the substituent), into the Hamiltonian rectified the order.

Sklar[42] has analyzed the intensification of the ultraviolet absorption bands of substituted benzenes over benzene on the basis of the

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[41] F. Matsen, *J. Am. Chem. Soc.*, *72*, 5243 (1950).

[42] A. Sklar, *J. Chem. Phys.*, *7*, 984 (1939).

destruction of the 6-fold symmetry of benzene by partial migration of non-bonding electrons from the substituent into the ring and by charge redistribution by induction of the σ-electrons. The electric moment produced by the migration of charge was calculated by the method of antisymmetrical molecular orbitals, considering parameters involving the ionization potential of the substituent, number of non-bonding electrons on the substituent and the distance of the substituent from the ring. Thespectra of fluorobenzene, aniline, phenol and toluene were discussed on this basis.

The term "spectroscopic moment" has been applied by Platt[43] to the concept introduced by Sklar to describe the induced charge separation in the excited state by substituents in benzene. Platt has inspected the available intensity data for a large number of compounds in order to determine the spectroscopic moment of various substituents. The spectroscopic moments m_i were obtained from the equations

$$I - I_o = Km^2 \quad \text{monosubstituted} \qquad (10)$$

$$= K(m_a^2 + m_b^2 + 2m_a m_b) \quad \text{para-substituted} \qquad (11)$$

$$= K(m_a^2 + m_b^2 - m_a m_b) \quad \underline{\text{ortho}}\text{- or } \underline{\text{meta}}\text{-substituted,} \qquad (12)$$

where I_o is the unsubstituted intensity and I the substituted intensity; K is the proportionality factor. The m_i values have been related to the directing power of the substituent in the aromatic substituents as well as to the mesomeric moments obtained from dipole measurements. Rigorous correlations were not obtained due to the fact that the spectroscopic

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[43] J. Platt, *J. Chem. Phys.*, *19*, 263 (1951).

moment involves the study of the ground and excited states of a molecule, while dipole measurements deal exclusively with the ground state; directive abilities, on the other hand, involve ground state and intermediate complex perturbations. Notable deviations occurred with fluorine and iodine, where m_i and u were of equal magnitude, and with the alkyl groups, where these quantities were in opposite sequence.

Further theoretical calculations of substituent effects on the spectra of benzene derivatives have been made by Price[44] and Herzfeld[45].

The last aspect of substituent effects which we shall review is the activation process. The argument is essentially that treated by Glasstone, Laidler and Eyring[46] in their theory of rate processes. The essential feature of this theory is based on the concept that a chemical reaction is characterized by an initial configuration (reactants) which proceeds by continuous changes into the final configuration (products). The mechanism by which this process occurs is further characterized by some intermediate configuration, an activated complex or transition-state, which is critical for the process in that it is situated at the highest point of the most favorable reaction path on the energy surface. The attainment of this complex usually represents a high probability of the reaction going to completion. The study of reaction processes is

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[44] W. Price, Chem. Revs., 41, 257 (1947).

[45] C. Herzfeld, ibid., 250.

[46] S. Glasstone, K. Laidler, H. Eyring, "The Theory of Rate Processes". McGraw-Hill Book Co., Inc., New York, N.Y., 1941.

centered to a great extent on the requirements for the attainment of this complex.

Orientation in aromatic substitution represents a fertile ground on which to study the effects of substitution on the free energy of activation. The broad outlines have been reviewed recently[47]. Early studies by Ingold and co-workers[48] on competition reactions in aromatic substitutions, utilizing partial rate factors, have been extensively reviewed[49]. These studies led to the early empirical rules based on the electronic theory.

The most fruitful mode of attack on the orientation problem has been achieved by the application of quantum mechanics. In a classic paper Wheland and Pauling[50] applied the molecular orbital approximation. They worked on the assumption that the rate of aromatic electrophilic substitution at a particular nuclear carbon atom increases with increasing negative charge on that carbon atom as the anionoid reagent approaches it in the transition state. They took into account permanent charge distributions in the ring produced by induction and resonance, as well as polarizability factors of the attacking reagent in the transition state. They first made a calculation of the relative electron densities resulting from different electron affinities of the atoms in the systems

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[47] L. Ferguson, Chem. Revs., 50, 52 (1952).

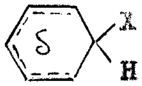
[48] C. Ingold, et al., J. Chem. Soc., 2918 (1927).

[49] E. Remick, ref. 3, p. 357.
C. Price, Chem. Revs., 29, 37 (1941).

[50] G. Wheland and L. Pauling, J. Am. Chem. Soc., 57, 2087 (1935).

(inductive effect) and then explicity included all π-orbitals of the system (resonance effect). A small perturbation, δ, was then placed on each carbon atom at a time (in addition to that due to permanent polarizations) and the result of these charges on the electron densities at the various carbon atoms were calculated. It was found that in cases where strong inductive influences are present (anilinium ion) the external perturbation has little or no effect on the orientation. However, in cases such as the halobenzenes, it was found that the _ortho_ and _para_ positions are more polarizable than the _meta_ position.

Wheland[51] has improved on the underlying assumptions of this treatment by considering more fully the nature of the transition state. Whereas early work included only perturbations by the attacking reagent, the more refined treatment focused attention on the energies of structures contributing to the activated complex, in which a covalent bond is formed between the aromatic system and the reagent as shown below.



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Here δ is positive, negative or neutral depending on whether the attacking species is electrophilic, nucleophilic or free radical. The activation energy is discussed in terms of a polarization energy, which is the change in the π-electron energy between reactants and the transition complex. Coulson[52] prefers to call this "localization energy". Thus, he pictures

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[51] G. Wheland, _J. Am. Chem. Soc._, _64_, 907 (1942).

[52] C. Coulson, _Research_, _4_, 307 (1951).

this quantity as the energy required to localize two, one or zero π-electrons at the tetrahedral carbon while leaving the remainder of the π-electrons undisturbed. Using the values of this polarization energy, Δw, Wheland predicted the most likely position in the ring to be substituted by the various reagents. For example, the following values for nitrobenzene were calculated for Δw in terms of β(resonance integral for the C-C bond):

Point of attack	Δw (β) electrophilic	 nucleophilic	 free radical
ortho	1.886	1.783	1.834
meta	1.852	1.852	1.852
para	1.861	1.757	1.809

Applying the assumption that the smaller the calculated value of Δw for a given position, the more rapidly reaction proceeds at that point, it can be seen that these predictions do hold.

Extensive valence-bond calculations of the effect of substituents have recently been carried out by the French school[53]. The essence of their calculations involves modifications of the nature of the perturbation by substituents on the aromatic ring inherent in the valence-bond approach.

Ri and Eyring[54] approached the problem from the transition state theory of rate processes. They assumed that in the transition state of

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[53] A. Pullman, Compt. rend., 222, 392 (1946);
A. Pullman, Bull. soc. chim., France, 13, 392 (1946);
J. Ploquin, ibid., 15, 646 (1948); 16, 359 (1949);
C. Sandorfy, ibid., 16, 615 (1949).

[54] T. Ri and H. Eyring, J. Chem. Phys., 8, 433 (1940).

the reaction the difference in free energy between substituted benzenes and benzene lay in the electrostatic interaction of the induced charge at a position in the ring with the charged attacking species. Calculating the charge distribution in the ring of the substituted compound due to the inductive effect and resonance effect of the substituent to be e_y, the electrostatic energy was determined to be

$$\Delta\Delta F = \frac{e_y e_n}{rD}, \tag{13}$$

where e_n is the charge on the attacking species and r and D are suitably chosen values for the distance separating the charges and the dielectric constant through which the charges act in the transition state, respectively. The ratio of the rate constants for reactions at any carbon atom y in the substituted compound and benzene is then

$$\frac{k_y}{k_H} = e^{-e_y e_n/rDkT} \quad . \tag{14}$$

This theory was checked by competitive nitration studies.

Assuming that the nature of an intermediate ionic complex is important in aromatic ionic substitution reactions, Price[55] has attempted to determine the effects of substituents on the stability of this complex. He has introduced the "polarizing force" of the substituent as one of the determining factors in the stability. The nature of the force is

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[55] C. Price, J. Am. Chem. Soc., 73, 5833 (1951).

described as electrostatic, being evaluated by the equation

$$E = \sum_b \sum_s \frac{e_b e_s}{r} , \qquad (15)$$

where e_b is the charge on carbon atom b in the ring, e_s is the charge on atom s on the substituent, and r is the distance separating the charges. The magnitude of the charge was obtained from values of the bond moments.

The importance of a consideration of the transition state for aromatic systems has been pointed out by Bordwell and Rohde[56]. Their deductions proceeded from an observation of the *ortho-para* nitration of the negatively substituted side chain of styrene. A similar attention was placed by Waters[57] on the role of the activated complex in determining aromatic orientations. He evaluated the energy difference between the ground and transition states of a bimolecular reaction process by assuming a quinoidal configuration of the activated state. By assigning a large amount of bond localization to the quasi-quinoidal complex, he deduced (from oxidation - reduction potentials of the corresponding quinones) the effects of polar substituents on the relative energy levels of the various quinoidal systems.

Westheimer[58] has applied the Kirkwood - Westheimer treatment of electrostatic influence to the rate of reactions of *para*-substituted aromatic compounds. Assuming that the reaction proceeds via an activated

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[56] F. Bordwell and K. Rohde, *J. Am. Chem. Soc.*, *70*, 1190 (1950).

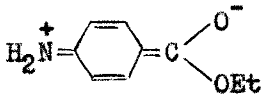
[57] W. Waters, *J. Chem. Soc.*, 727 (1948).

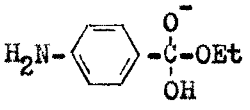
[58] F. Westheimer, *J. Am. Chem. Soc.*, *62*, 1892 (1940).

complex, the effect of a dipolar substituent on the reaction velocity in a bimolecular reaction involving one charged species is:

$$\log k - \log k_o = \frac{eM \cos \theta}{2.303\ kTR^2 D_E} \qquad (16)$$

where k and k_o represent the rate constant of the para-substituted and unsubstituted compounds, respectively. Application to the saponification rates of phenylacetate and hydrocinnamate esters was successful. In the case of benzoates, cinnamates and benzamides deviations were found with p-methoxy and p-amino substituted compounds. He attributed these discrepancies to the stability of the esters relative to the transition state as shown below:





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Attempts to calculate the amount of resonance interaction were made by determining the relative rates of hydrolysis of ethyl 3,5-dimethyl-4-dimethylaminobenzoate and ethyl 3,5-dimethyl-4-aminobenzoate[59].

When a bimolecular reaction occurs between two uncharged molecules, the free energy change is related as

$$\log k = \frac{2M_1M_2}{2.303\ kTR^3 D_i}\ , \qquad (17)$$

where M_1 is the moment of the substituent and M_2 is the moment at the time of the reaction in the transition state. D_i is the internal dielectric constant.

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[59] F. Westheimer, J. Am. Chem. Soc., 63, 1341 (1941).

Of all the empirical, semi-quantitative or purely theoretical treatments of structure of aromatic systems and chemical reactivity we have discussed, the Hammett equation[60] is by far the most versatile. The wide applicability of this equation is indicated by its utility in kinetics and equilibria of reversible and non-reversible reactions, respectively, of heterolytic as well as homolytic types. The equation, however, has been limited to meta- and para-substituted derivatives. Complications from ortho (steric or entropy) effects are well-known in organic reactions[61]. The theoretical basis for the Hammett equation shows the necessity of excluding these effects[62]. It is for this reason that the equations are not applicable to ortho-substituted compounds.

The equation is expressible in the forms

$$\log k - \log k_o = \rho\sigma \tag{18}$$

$$\sigma = \log K - \log K_o \quad , \tag{19}$$

where k and k_o represent the rate or equilibrium constants for the substituted and unsubstituted compound, respectively, and K and K_o represent the ionization constants of the substituted and benzoic acids in water at 25°C. The physical relevance of σ is apparent from equation (19). It is a constant depending on the nature of the substituent group.

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[60] L. Hammett, "Physical Organic Chemistry", McGraw-Hill Book Co., Inc., New York, N.Y., 1940, p. 186.

[61] M. Evans, Trans. Faraday Soc., 47, 40 (1951);
J. Baker, J. Chem. Soc., 796 (1941);
P. De LaMare, ibid., 2873 (1949).

[62] L. Hammett, ref. 60, p. 118.

Similarly, ρ as defined by equation (18), is a constant for a reaction series and is independent of the substituents.

In addition to the fifty-seven reactions listed by Hammett which include the saponification rates of esters, dissociations constants of phenols and anilines, and the hydrolysis of benzyl chlorides, in recent years such diverse reactions as the Friedel-Crafts reaction of aromatic compounds with acetyl chloride[63], alkylations with ethyl arylsulfonates[64], acid-catalyzed anionotropic rearrangements of alcohols[65], oxidation-reduction potentials of substituted quinones[66], polarographic half-wave potentials of benzaldehydes and acetophenones[67] and homolytic cleavages of aroyl peroxides[68] have been correlated. The validity of the Hammett equation is, thus, well established. Before 1940 there were 1763 reactions applied to it; of these 332 showed a median deviation of only 15% between the calculated and observed values[69]. The trend recently has been to analyze the equation critically and to apply it to the study of reaction mechanisms and substituent effects.

The Hammett equation has been compared from an empirical standpoint

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[63] H. McDuffie and G. Dougherty, J. Am. Chem. Soc., 64, 297 (1942).

[64] M. Cretcher and L. Morgan, ibid., 70, 375 (1948).

[65] E. Braude and E. Stern, J. Chem. Soc., 1096 (1947).

[66] M. Evans and J. deHeer, Quart. Revs., 4, 108 (1950).

[67] F. Schulz, ref. 28, p. 78.

[68] C. Swain, W. Stockmayer and J. Clarke, J. Am. Chem. Soc., 72, 5427 (1950); J. Cooper, J. Chem. Soc., 3106 (1951).

[69] C. Swain and W. Langsdorf, ibid., 73, 2813 (1951).

by McGowan[70] who has succeeded in correlating it with the empirical constants of the previously cited equation (4). Similar comparison studies have been made with the Hixon-Johns treatment of the electron-sharing abilities of substituents[71].

Price[72] has applied the concepts developed by Ri and Eyring to derive "theoretically" the Hammett equation. In a series of reactions he assumes the difference in activation energy between the substituted and unsubstituted compound to be

$$\Delta\Delta E_{\sigma} = \frac{e_{\sigma} e_{\rho}}{rD} \quad , \qquad (20)$$

where e and e are the parameters defined by Ri and Eyring. The application of the Arrhenius equation leads to

$$\ln k/k_o = \frac{e_{\sigma}}{2.303} \cdot \frac{e_{\rho}}{rRDT} = \sigma\rho \quad .$$

Utilizing Hammett's σ-values, Jaffe[73] has succeeded in applying the molecular orbital method to derive a consistent set of parameters α (Coulomb integral) and β (resonance integral) for a series of meta- and para-substituted benzene derivatives. These parameters were used to calculate with good results electron densities at various positions in the ring, the absorption frequencies, and resonance moments of these

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[70] J. McGowan, J. Soc. Chem. Ind., 68, 254 (1949).

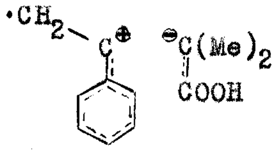
[71] F. Schulz, see ref. 67.

[72] C. Price, Chem. Revs., 29, 37 (1941).

[73] H. Jaffe, J. Chem. Phys., 20, 279 (1952).

compounds. Recently Jaffe[74] has extended the treatment to predict unknown σ constants of substituted biphenylcarboxylic acids.

The application of the Hammett equation in its kinetic form has led some investigators to speculate on the transition state of certain reactions. Walling and co-workers[75] correlated the equation with the bimolecular radical copolymerization of substituted styrene with methyl methacrylate and styrene. From the variation of the ρ constant with the relative reactivities of various substituted styrene monomers with styrene, they were able to speculate on the importance of polar interactions between substituted styrenes and growing radicals in the transition state, and also on the effect of the substituents on the stability of the transition state. Similarly they accounted for deviations of *p*-methoxystyrene in its copolymerization with methyl methacrylate by the importance of non-bonded polar structures in the activated complex as shown below:



An analogous reasoning was applied by Swain, Stockmayer and Clarke[68] to the unimolecular radical decomposition of substituted benzoyl peroxides. By eliminating radical induced decomposition by the addition of

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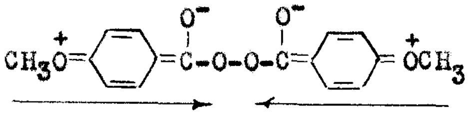
[74] H. Jaffe, Presented before the Buffalo Meeting of the American Chemical Society, April, 1952, p. 8N abstracts.

[75] C. Walling, E. Briggs, K. Wolfstirn and F. Mayo, *J. Am. Chem. Soc.*, *70*, 1537 (1948).

inhibitors, they obtained reasonable fits of the logarithm of the unimolecular rate constant with σ. The weakening of the O-O bond was attributed to the importance of electron-repelling groups in contributing to the creation of two opposed dipoles in the transition state.



Swain and Langsdorf[76] have interpreted the ρ constant in displacement reactions in terms of the extent of bond-forming and bond-breaking processes in the transition state. The interdependence of ρ and σ is shown in the case of the reaction of substituted benzyl chlorides with amines. A similar argument was applied by Braude and Stern[77] to the acid-catalyzed anionotropic rearrangement of arylpropenylcarbinols and styrylmethylcarbinols.

In recent years the Hammett equation has also been frequently utilized to assess electronic influence of substituent groups in aromatic rings. Roberts[78], on the basis of the comparison of the *sigma* constants obtained from the apparent ionization constants of *meta*- and *para*-trimethylsilylbenzoic acids and the reaction rates of these acids with diazodiphenylmethane, together with some dipole moment data, concluded that the effect of the trimethylsilyl group was due largely to the electropositive or electron-releasing properties of silicon relative to

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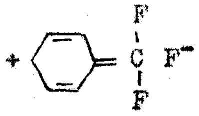
[76] C. Swain and W. Langsdorf, *J. Am. Chem. Soc.*, *73*, 2815 (1951).

[77] E. Braude and E. Stern, *J. Chem. Soc.*, 1098 (1947).

[78] J. Roberts, E. McElhill and R. Armstrong, *J. Am. Chem. Soc.*, *71*, 2923 (1949).

carbon. It seemed that no important resonance interaction occurs between the ring and the substituent group.

Further studies by Roberts and co-workers[79] in determining the sigma constant for trifluoromethyl-substituted anilines and benzoic acids led them to conclude that an important effect of the group can be shown as,



A purely classical inductive effect was attributed to the trimethylammonium group on the basis of similar studies[80]. Corresponding investigations of the electrical effects of methylsulfonyl[81,82,83], methylsulfone[82], methyl sulfide[81,82], acetyl[81], and cyano[84] groups have been made.

The Solvolyses of Benzyl Systems

The benzyl system has been used extensively by early workers to study the effects of side chain reactions of substituted benzene deriva-

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[79] J. Roberts, R. Webb and E. McElhill, J. Am. Chem. Soc., 72, 409 (1950).

[80] J. Roberts, R. Clement and E. McElhill, ibid., 72, 409 (1950).

[81] F. Bordwell and G. Cooper, ibid., 74, 1059 (1952).

[82] C. Price and J. Hydock, ibid., 74, 1943 (1952).

[83] H. Kloosterziel and H. Backer, Rec. trav. chim., 71, 295 (1952).

[84] J. Roberts and E. McElhill, ibid., 72, 628 (1950).

tives. In most cases the unimolecular solvolyses[85] were carried out in binary solutions of acetone or ethanol and water. Studies included those by Olivier[86] and Bennett and Jones[87] of benzyl chlorides in acetone-water, ethanolysis of benzhydryl chlorides by Hughes, Ingold and Taher[88] and hydrolysis of benzyl bromides in aqueous alcohol by Shoesmith and Slater[89]. An interesting observation was made by Miller and Bernstein[90] who found that the hydrolysis of benzyl fluorides in ethanol-water solutions was acid-catalyzed. The trend for the substituted fluorides seemed to be that the more reactive ones showed a higher degree of acid-catalysis. Particular attention was paid by many workers in this field to the abnormal reactivity of p-fluoro- and p-methoxybenzyl compounds.

A detailed study of the solvolysis of benzyl chlorides and benzyl nitrate in dioxane-water solutions was made by Hammett and co-workers[91]:

$$C_6H_5CH_2Cl + H_2O \xrightarrow{k_1} C_6H_5CH_2OH + H_3O^+ + Cl^-$$

$$C_6H_5CH_2ONO_2 + H_2O \xrightarrow{k_1'} C_6H_5CH_2OH + H_3O^+ + NO_3^- \quad .$$

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[85] E. Hughes, Trans. Faraday Soc., 37, 603 (1941).
E. Hughes, Quart. Revs., 5, 245 (1951).

[86] S. Olivier, Rec. trav. chim., 49, 996 (1930).

[87] G. Bennett and B. Jones, J. Chem. Soc., 1815 (1935).

[88] E. Hughes, C. Ingold and N. Taher, ibid., 950 (1940).

[89] R. Shoesmith and T. Slater, ibid., 221 (1926).

[90] W. Miller and J. Bernstein, J. Am. Chem. Soc., 70, 3600 (1948).

[91] G. Beste and L. Hammett, ibid., 62, 2481 (1940).
G. Lucas and L. Hammett, ibid., 64, 1928 (1942).

Both reactions showed a pronounced salt effect. The following tables show the percentage increase of the rate of solvolysis due to added solutes.

Table 1

Solvolysis of Benzyl Chloride

Solute[a]	Percent Increase
Benzyl chloride	-5.9
Benzyl alcohol	-1.7
Dioxane	-0.6
HCl	-2.9
HCl and benzyl alcohol	-7.0
NaCl	-4.3
NaOAc	-8
$NaClO_4$	+7.6
$HClO_4$	+8.0

[a] 0.75 M. ester and 0.05 M. salt.

Table 2

Solvolysis of Benzyl Nitrate

Solute[a]	Percent Increase
$NaClO_4$	15.62
$HClO_4$	15.51
KNO_3	2.61

[a] 0.1 M. ester and 0.1 M. salt.

The authors suggested a possible mechanism for the solvolysis to be:

$$C_6H_5CH_2Cl \xrightarrow{slow} C_6H_5CH_2^+ + Cl^-$$

$$C_6H_5CH_2^+ + H_2O \xrightarrow{fast} C_6H_5CH_2OH + H_3O^+$$

$$C_6H_5CH_2^+ + Cl^- \xrightarrow{fast} C_6H_5CH_2Cl$$

$$C_6H_5CH_2^+ + OAc^- \xrightarrow{fast} C_6H_5CH_2OAc \quad .$$

Studies on the action of salts, however, indicated that the intermediate formation of a carbonium ion was doubtful. A more suitable mechanism is suggested by Swain's hypothesis of termolecular displacement reactions[92].

Additional studies by Hammett and McCleary[93] on the reaction of ethyl tosylate with water and halide ion yielded the relative reactivities with the corresponding halides.

$$TsOEt + 2H_2O \longrightarrow TsO^- + EtOH + H_3O^+$$

$$TsOEt + X^- \longrightarrow TsO^- + EtX$$

The order of reactivity was given as:

EtOTs : EtI : EtBr : EtCl in a ratio 5.5 : 1.0 : 0.96: 0.048.

No salt and little common-ion effect was found.

Baker[94] has attempted to analyse the variation in reactivity of substituted benzyl halides by considering the nature of the difference between the ground state and the transition state of the solvolysis.

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[92] C. Swain, J. Am. Chem. Soc., 70, 1119, 2989 (1948).

[93] H. McCleary and L. Hammett, ibid., 63, 2254 (1941).

[94] J. Baker, Trans. Faraday Soc., 37, 635 (1941).

Table 3

Solvolysis of Ethyl p-Toluenesulfonate

Solute[a]	Percent Increase
EtOTs	-0.5
$NaClO_4$	0
NaTsO	-2.3
NaCl	-6.0
KBr	-6.0
KI	12.5

[a] 0.1 M. ester and 0.1 M. salt

On the basis of qualitative reasoning he has assigned quantitative values of the contributions of the inductive and mesomeric effects to the energy levels of substituted benzyl chlorides, both in the transition state and in the ground state. The differences of the summed effects were directly related to the reactivity of the side chain.

A more quantitative interpretation of side chain effects has been treated by Swain and Langsdorf[95]. From analysis of the rho constant from the Hammett equation they discuss the deviation of p-methoxybenzyl chloride in its reaction with amines. A consideration of the various bond orders in the transition state of the reaction was given.

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[95] C. Swain and W. Langsdorf, J. Am. Chem. Soc., 73, 2813 (1951).

A Comparison of Ethylenes and Acetylenes

The reactions involving acetylenic linkages have been well documented[96]. The comparison of the acetylenic bond with ethylenic bond may be conveniently made from two aspects, chemical reactivity and physical properties and the theories deduced from them.

The earliest study of these two unsaturated systems was made by Baker, Cooper and Ingold[97] who analyzed the relative amounts of the various isomers resulting from the quantitative nitration of phenylpropiolic and cinnamic acids and their ethyl esters. They found the percentage of the isomers to be:

Compound	*ortho*	*meta*	*para*
propiolic acid	8	65	27
ethyl propiolate	6	58	36
cinnamic acid	*ortho-para* exclusively		
ethyl cinnamate	" " "		.

Recently Bordwell and Rohde[56] have interpreted the directivity of the *beta*-substituted side chain in terms of the transition state of the reaction.

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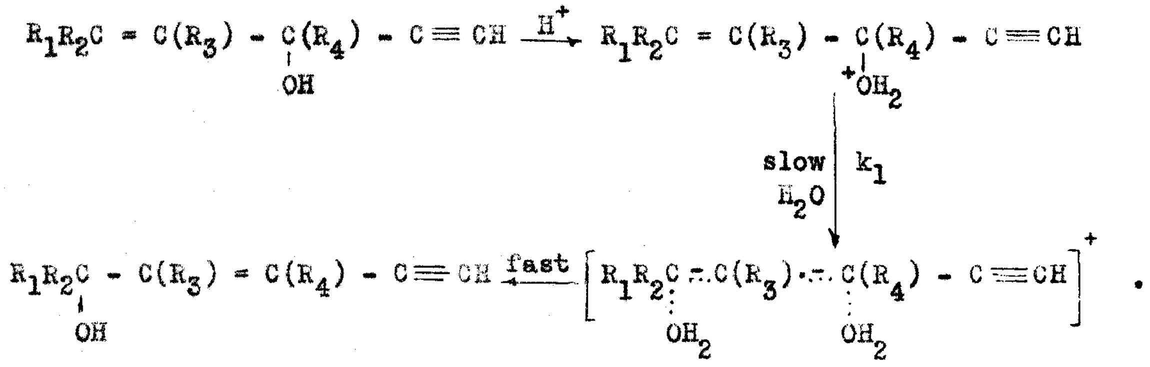
[96] A. Johnson, "The Chemistry of Acetylene Alcohols", Edward Arnold Co., London, 1948.
A. Johnson, "The Chemistry of Acetylene Acids", Edward Arnold Co., London, 1950.

[97] J. Baker, K. Cooper and C. Ingold, *J. Chem. Soc.*, 427 (1928).

A kinetic analysis of the rearrangement of non-conjugated unsaturated alcohols was made by Braude and Jones[98]. After establishing the first-order acid-catalyzed rearrangements of these systems, they postulated the following mechanism:



$$R_1R_2C = C(R_3) - \underset{OH}{C}(R_4) - C\equiv CH \xrightarrow{H^+} R_1R_2C = C(R_3) - \underset{^+OH_2}{C}(R_4) - C\equiv CH$$

$$\downarrow \text{slow}\ H_2O \quad k_1$$

$$R_1R_2\underset{OH}{C} - C(R_3) = C(R_4) - C\equiv CH \xleftarrow{\text{fast}} \left[R_1R_2\underset{OH_2}{C} \cdots C(R_3) \cdots \underset{OH_2}{C}(R_4) - C\equiv CH\right]^+ .$$

They obtained the ratios of the first order rate constants, k_1, for several substituted isomers of the acetylenic alcohol and the analogous ethylene compound. The results were:

$\frac{k_{vinyl}}{k_{ethynyl}}$ = 12,000 , R's all H

= 3,000 , R_1 and R_3 = Me

= 3,200 , R_1 = Me

= 240 , R_1 and R_4 = Me .

They accounted for this variation in the ratio of rate constants by attributing smaller electron-attracting powers to the vinyl group as compared to the ethynyl group. Thus they state:

> The higher the multiciplicity of the linkage, *i.e.*, the greater number of electrons shared, the greater is the electron deficiency of the constituent atoms and thus the negative inductive effect of the acetylenic group would be expected to be much greater than that of the ethylenic group.

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[98] E. Braude and B. Jones, *J. Chem. Soc.*, 129 (1946).

Table 4

Rates of Rearrangement and Ionization Constants

Compound	$10^4 k_1$	Acid	$10^5 K_i$
CH_3-CH=CH-CH(OH)-C≡CH	0.11	HC≡C-COOH	1400
CH_3-CH=CH-CH(OH)-C≡C-C_4H_9	16.5	C_4H_9-C≡C-COOH	140
CH_3-CH=CH-CH(OH)-CH=CH_2	345	CH_2=CH-COOH	5.5

Further evidence for this was cited in listing the ionization constants of several acids.

Dippy[99] has arrived at a similar conclusion to this by inspecting the K_i's of various acids. On comparing acetylenes with ethylenes, he states, "....the greater the degree of unsaturation the more pronounced the intrinsic attraction for electrons becomes". The obscurity of this interpretation has been pointed out by Burawoy[100].

Hennion and Maloney[101] have attempted to determine the stabilities of structures such as I and II in the transition state of the solvolysis of 3-chloro-3-methylbutyne-1.

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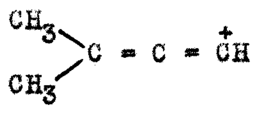
[99] J. Dippy, Chem. Revs., 25, 179 (1939).

[100] A. Burawoy, Vol. Commemoratif Victor Henri, Liege, 1948, p. 78.

[101] G. Hennison and D. Maloney, J. Am. Chem. Soc., 73, 4735 (1951).



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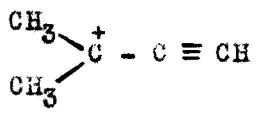

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The values for the unimolecular processes at 25°C. are compared for similar compounds.

Table 5

Ionization Constants of Unsaturated Acids

Acid	10^5K_i
$C_6H_5-C\equiv C-COOH$	590
$C_6H_5-CH=CH-COOH$	3.65
$C_6H_5-CH_2-CH_2-COOH$	1.67
$CH_3-C\equiv C-COOH$	222.8
$CH_3-CH=CH-COOH$	2.03
$CH_3-CH_2-CH_2-COOH$	1.54

Although solvolyses have not been carried out on analogous olefinic compounds, Young and Andrews[102] have determined the solvolysis rate at 25°C. of the nor-3-methyl compound under slightly different conditions.

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[102] W. Young and L. Andrews, *J. Am. Chem. Soc.*, *66*, 421 (1944).

Table 6

Solvolyses of Unsaturated Alkyl Chlorides

Compounds	Conditions	$k(\text{hr}^{-1})$
3-Chloro-3-methylbutyne-1	80% EtOH - H_2O	7.4×10^{-4}
	60% EtOH - H_2O	4.3×10^{-4}
	60% acetone - H_2O	1.93×10^{-3}
1-Chloro-3-methylbutadiene-1,2	80% EtOH - H_2O	0
t-Amyl chloride	80% EtOH - H_2O	5.55×10^{-2}

Table 7

Solvolyses of Unsaturated Alkyl Chlorides

Compound	Conditions	$k(\text{hr}^{-1})$
3-Chlorobutene-1	50% EtOH - H_2O	4.11×10^{-2}
	100% EtOH	2.11×10^{-4}
1-Chlorobutene-2	50% EtOH - H_2O	5.32×10^{-2}
	100% EtOH	2.20×10^{-4}

Robertson and co-workers[103] studied the bimolecular addition of bromine to a series of olefins and their acetylenic analogs. An interesting interpretation of the relative effects of substituents on the reactivities of the unsaturated compounds was given.

The quantum-mechanical representation of ethylenic and acetylenic bonds has been described lucidly by Coulson[104]. In brief, the ethylenic bond is considered to consist of a σ-bond, composed of two overlapping sp^2 atomic orbitals of trigonally hybridized carbon atoms, together with a π-bond resulting from the overlap of two p-π atomic orbitals. In acetylene, the overlap of two sp hybrid orbitals of digonally hybridized carbon forms a σ-bond, which is supplemented by two pairs of p-π orbitals, p_z and p_y, to form two mutually perpendicular π-bonds.

The far-ultraviolet absorption spectra of these unsaturated systems have been theoretically resolved by Walsh[105]. The π^{-1} ionization potential of ethylene has been found to be 10.50 volts, which compares with 11.41 volts for acetylene. The larger ionization potential of acetylene was interpreted as a consequence of the larger s character, and hence tighter binding of the σ-electrons[106], of the σ-bond in acetylene (sp-sp) as compared to ethylene (sp^2-sp^2). Thus, the repulsion between these σ-electrons and the π-electrons is considered to be less in the case of

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[103] P. Robertson, W. Dasent, P. Milburn and W. Oliver, J. Chem. Soc., 628 (1950).

[104] C. Coulson, Quart. Revs., 2, 144 (1947).

[105] A. Walsh, Ann. Rpts., 44, 32 (1947).

[106] A. Walsh, Disc. Faraday Soc., 2, 19 (1947).

acetylenes than in ethylenes. Moreover, the tighter binding of the π-electrons in acetylene, as a result of this, led Walsh to postulate a smaller conjugating power with other unsaturated systems. Thus, the shift in the absorption maxima of various systems is:

Compound	max.(Å)	Region (Å)
benzene	1,790	2,000
phenylacetylene	1,910	2,390 - 2,200
styrene	1,950	2,400 - 2,300

Pullman and Pullman[107] observed a similar shift in the longer wavelength region. The following values are listed for the near-ultraviolet absorption spectra:

Compound	max.(mu)
styrene	282
stilbene	295
phenylacetylene	278
tolane	279

The correlation between atom hybridization and electronegativity has been further clarified by Walsh[108].

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[107] A. Pullman and B. Pullman, *Disc. Faraday Soc.*, *9*, 51 (1950).

[108] A. Walsh, *ibid.*, *2*, 21 (1947).

Table 8

Properties of Some Hydrocarbons

Valency	C Atom Hybrid.	r_{CH} (Å)	$10^{-5}K(CH)$ (dyne/cm.)	E(CH) (kcal./mole)	Dipole
CH radical	p	1.120	4.09	80	$C^{\delta++}$ $H^{\delta--}$
CH_4	sp^3	1.094	4.79	104	$C^{\delta+}$ $H^{\delta-}$
C_2H_4	sp^2	1.087	5.10	106	$C^{\delta-}$ $H^{\delta+}$
C_2H_2	sp	1.059	5.85	121	$C^{\delta--}$ $H^{\delta++}$

Two fundamental principles are stated by Walsh:

> (i) The more s character in a carbon valency, the more electronegative is the carbon atom in that valency,
> (ii) If a group X, attached to carbon, is replaced by a more electronegative group Y, then the carbon valency toward Y has more p character than it had toward X.

Matsen[109] has applied a simplified molecular orbital theory to calculate the wave-length of maximum absorption of styrene and phenylacetylene. In his calculations he assumed that in acetylene only one p-π orbital interacts strongly with the benzene ring at a time, as in styrene. The difference in the two arose in the calculations from the difference in bond order between the alpha and beta carbon atoms of the side chain; these bond orders are two in acetylene and one in ethylene. The results are given as:

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[109] F. Matsen, J. Am. Chem. Soc., 72, 5256 (1950).

Compound	Frequency (cm.$^{-1}$)	$1 - v/v_B$	
		calc.	obs.
styrene	34,761	0.14	0.087
phenylacetylene	36,370	0.093	0.045 ,

where v_B and v represent the frequencies of the 0-0[110] band in benzene and substituted benzene, respectively.

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[110] F. Matsen, J. Am. Chem. Soc., 72, 5245 (1950).

EXPERIMENTAL

The Preparation of Substituted Stilbenes and Tolanes

Preparation of 3- and 4-carboxystilbene

The 4-carboxystilbene was prepared by the method of Meerwein, Buchner and Emster[111], which involves the reaction of cinnamic acid with 4-carboxybenzenediazonium acetate. The yields, based on several attempts, were not as good as that reported in the literature[112]. Yield - 12%. Melting point - 248.1-248.4°C.

The corresponding 3-carboxy-isomer was prepared in an analogous manner using the 3-carboxybenzenediazonium salt. The maximum yield from several attempts was 6%. Melting point - 197.0-197.5°C.

Preparation of 3- and 4-carboxytolane

To a suspension of 1.6 g. of 3-carboxystilbene in 160 ml. carbon tetrachloride, a solution of 1.5 ml. of bromine in 25 ml. of carbon tetrachloride was added dropwise. The solution was then warmed on a water bath at 70°C. and allowed to react for twenty minutes, cooled and filtered. The resulting light yellow colored solid was recrystallized from absolute ethanol. The colorless dibromide, obtained in 87% yield, melted at 246-248°C.

To a solution of 60 g. of potassium hydroxide in 100 ml. absolute ethanol was added 2.4 g. of 3-carboxystilbene dibromide, in order to

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[111] Meerwein, Buchner and Emster, J. prakt. Chem., 152, 237 (1939).

[112] R. Fuson and H. Cooke, J. Am. Chem. Soc., 62, 1180 (1940).

effect dehydrobromination. After the solution was refluxed for twenty hours, it was poured into a slurry consisting of 200 g. crushed ice and 500 ml. water. Twenty percent hydrochloric acid was then slowly stirred in until the solution was acid to litmus. The crude 3-carboxytolane was recrystallized several times from aqueous ethanol solution. Yield - 78%. Melting point - 160-161°C.

Preparation of 4-carboxytolane

The preparation of 4-carboxytolane was carried out in a similar manner. Seventeen grams of 4-carboxystilbene was suspended in 500 ml. carbon tetrachloride. A solution of 5.2 ml. bromine in 200 ml. carbon tetrachloride was then added slowly. The mixture was then heated on a water bath for one-half hour, cooled and filtered, and then washed twice with boiling ethanol. The white crystalline dibromide in the form of a fine powder melted at 267-269°C. It was obtained in 91% yield. To dehydrohalogenate the dibromide, 20 g. was treated with a solution of 80 g. potassium hydroxide in 140 ml. absolute ethanol and refluxed for thirty-six hours. The solution was then filtered and the filtrate acidified in the usual manner. The crude, flocculent 4-carboxytolane, after recrystallization from ethanol, twice, melted at 220.5-221.0°C. Yield - 74%.

Table 9

Physical Constants of the Unsaturated Acids

Acid	Melting Point ($^{\circ}$C.)	Neutralization Equivalent[a]		Analysis (%)[b]			
				Calculated		Found	
		Calc.	Found	C	H	C	H
4-Carboxystilbene	248.1-248.4	224.3	226.6	80.33	5.39	80.07	5.29
3-Carboxystilbene	197.0-197.5	224.3	223.8	80.33	5.39	78.83	5.38
4-Carboxytolane	220.5-221.0	222.3	222.2	81.06	4.54	80.80	4.71
3-Carboxytolane	160 -161	223.3	223.9	81.06	4.54	80.50	4.66

[a] The neutralization equivalents were obtained potentiometrically.

[b] The analyses were supplied by Strauss and Weiler, Oxford, England.

The preparation of 3- and 4-carbethoxystilbene

The 4-carbethoxystilbene was prepared by the procedure given by Fuson and Cooke. It involved the Meerwein reaction using 4-carbethoxybenzenediazonium acetate. The product was obtained in poor yields of about 13.7%. It melted at 108.5-109.0°C.

The preparation of 3-carbethoxystilbene was not successful using the method described above. This compound was prepared by the Fischer esterification. Five and two-tenths grams of 3-carboxystilbene was dissolved in 50 ml. absolute ethanol. One milliliter concentrated sulfuric acid was added and the solution was refluxed for seventy-two hours. The hot solution was then poured quickly into 900 ml. water, and the oily suspension extracted successively with 500 ml. and 200 ml. ether. The combined ethereal extracts were then washed with 5% sodium bicarbonate until the wash solution, on acidification, showed no solid acid. The combined weight of the recovered acid was 0.5 g.

The ethereal solution was washed with water twice and then dried with Drierite. The residue from the evaporation of the ether was a slightly colored oil. The short path distillation of this oil gave a colorless liquid which solidified on cooling. The solid was recrystallized from Skelly A twice. The melting point of the ester, compound I, was 63.2-64.0°C. When the combined mother liquors were chilled in a dry-ice acetone bath, a second crop of crystals, compound II, was obtained. This compound, however, melted when it warmed to room temperature. Evaporation of the Skelly A solvent from the resulting mother liquor led to a third material, compound III. In appearance, it was a yellow solid of no definite melting point. It appears to be a mixture of the first two compounds mentioned, and it probably represents a mixture of cis-trans isomers. The yield of the ester melting at 63°C. was 2.0 g.

The preparation of 3- and 4-carbethoxytolane

The 3-carbethoxytolane was prepared by the Fischer esterification of the acid. Five and six-tenths g. 3-carboxytolane was dissolved in 75 ml. absolute ethanol and 2 ml. of concentrated sulfuric acid, and then refluxed for 75 hours. The subsequent treatment of the solution was the same as that for the dihydro compound. The combined weight of the recovered acid was 0.4 g. The evaporation of the ether left a yellow colored oil. The microdistillation of this oil could not be effected satisfactorily. At a pressure of 1.2 mm. and bath temperature of 230°C. the viscous liquid could not be distilled without flooding the column. A partial separation, however, was obtained into six fractions. The corrected refractive indices at 29°C. were as follows:

Fraction	Volume of Distillate (ml.)	Refractive Index
I	0.3	1.6108
II	0.3	--
III	0.2	1.6122
IV	0.4	--
V	0.2	--
VI	0.1	1.6125

Table 10

Physical Constants of the Unsaturated Esters

Ester	Melting Point (°C.)	Saponification Equivalent[a]		Analysis (%)[e]			
		Calc.	Found	Calc.		Found	
				C	H	C	H
3-Carbethoxystilbene	63.2- 64.0	252.3	253	80.92	6.39	81.29	6.14
4-Carbethoxystilbene	108.5-109.0	252.3	251	80.92	6.39	80.44	6.36
3-Carbethoxytolane	liquid[b]	250.3	255[d]	81.58	5.63	81.37	5.76
3-Carbethoxytolane	liquid[c]	250.3	--	81.58	5.63	81.41	5.63
4-Carbethoxytolane	83.5- 84.0	250.3	250	81.58	5.63	81.55	5.60

[a] Fraction III

[b] Fraction V

[c] Fraction IV

[d] Saponification equivalents determined as stated in a later section.

[e] Carbon and hydrogen analyses determined by Strauss and Weiler, Oxford, England.

Subsequent studies on the saponification rate of the ester showed that fractions III and VI were the same compound.

The esterification of 4.0 g. 4-carboxytolane was carried out in 75 ml. absolute ethanol and 1.8 ml. concentrated sulfuric acid. The solution was refluxed eighty hours. It was treated in a manner similar to the previous synthesis. The recovered tolanecarboxylic acid amounted to 0.5 g. A light yellow solid was obtained from the ethereal solution after the solvent was evaporated. Recrystallization of the crude 4-carbethoxytolane yielded 3.0 g. of ester melting at 83.5-84.0°C. The physical constants of these esters are given in Table 10.

The preparation of 3- and 4-hydroxymethylstilbene

To 3.8 g. powdered lithium aluminum hydride suspended in 175 ml. absolute ether in a three-neck round bottom flask attached with a Trubore stirrer, condenser and graduated dropping funnel, was added dropwise a solution of 2.4 g. 4-carboxystilbene in 50 ml. absolute ether. The solution was added at a rate which maintained the refluxing of the ether. After the addition was complete the suspension was refluxed for an additional five hours. The flask was then cooled in an ice bath and water added dropwise cautiously, through the dropping funnel. When the violent evolutions of gas were no longer evident 50 ml. of water was added. This was followed by 20 ml. of 10% sulfuric acid added portionwise. The two layers were then transferred to a separatory funnel and shaken. The aqueous phase was extracted again with 50 ml. ether. The combined ether extracts were treated three times with 25 ml. 10% sodium bicarbonate and then twice with 25 ml. portions of water. The ethereal solution was

Table 11

Physical Constants of the Unsaturated Alcohols

Alcohol	Melting Point (°C.)	Analysis (%) Calc. C	Analysis (%) Calc. H	Analysis (%) Found C	Analysis (%) Found H
3-Hydroxymethylstilbene	97.8- 98.5	85.68	6.70	86.43	6.67
4-Hydroxymethylstilbene	170.0-170.5	85.68	6.70	85.83	6.66
3-Hydroxymethyltolane	47.5- 48.5	86.50	5.81	86.47	5.77
4-Hydroxymethyltolane	125.8-126.5	86.50	5.81	86.59	5.89

dried overnight over Drierite and filtered. The evaporation of the ether left 4-hydroxymethylstilbene which on two recrystallizations from Skelly D melted at 170.0-170.5°C. Yield - 3.0 g. The sodium bicarbonate extracts did not yield any acid on acidification with sulfuric acid.

In a manner similar to the previous synthesis, 3.1 g. of 3-carboxystilbene was reacted with 4.0 g. lithium aluminum hydride. The evaporation of the ether solution _in vacuo_ yielded a light yellow solid. This crude 3-hydromethylstilbene was recrystallized three times from Skelly D. The colorless platelets melted at 97.8-98.5°C. Acidification of the bicarbonate extracts gave no acid. The yield of the ester was 2.5 g.

The preparation of 3- and 4-hydroxymethyltolane

The reduction of 4-carboxytolane (10.3 g.) with 5.0 g. lithium aluminum hydride was effected similarly to its stilbene analog. Three recrystallizations of the crude 4-hydroxymethyltolane yielded colorless platelets melting at 125.8-126.5°C. Yield - 9.2 g.

The 3-carboxytolane was treated similarly. The reduction of 14.1 g. of acid with 4.0 g. lithium aluminum hydride produced 10.1 g. of 3-hydroxymethyltolane, which, recrystallized twice from Skelly D, produced 9.1 g. colorless platelets melting at 47.5-48.5°C.

The Determination of Apparent Ionization Constants of Substituted Benzoic Acids

Solvents - ethanol and water

Stockroom grade absolute ethanol was used without further purification. Carbon dioxide-free water, prepared by the usual boiling process, was used in all the solutions.

Aqueous alcoholic bicarbonate-free sodium hydroxide (0.IN)

A concentrated aqueous solution of sodium hydroxide (I:I by weight) was filtered through a fine grade sintered glass crucible. The appropriate volume of this solution was dissolved in a medium consisting of 75 volume-percent ethanol in water.

Benzoic acids

The sources and properties of the benzoic acids used are listed in Table 12.

The titration

The titration was performed with a Beckmann Model G pH meter. All acid solutions were prepared to the same molar concentration by weighing out the required amount of acid. This precaution was necessitated by the sensitivity of the pH meter and the ionization constants of the acids to the ionic strength of the solution. It was found that a ten percent difference in the acid concentration (at 0.0079 M.) did not affect the pH appreciably at the midpoint of the titration.

A weighed amount of acid was transferred quantitatively to a 100 ml. volumetric flask and washed down with a small amount of ethanol. Twenty-

Table 12

Sources and Properties of Benzoic Acids

Acid	Mol. Wt.[a] Calc.	Found	Melting Point ($^\circ$C.)[b] Literature	Found	Source[c]
Benzoic	122.1	122	121.7	122.8-123.4	Merck purified
Anisic	152.1	151	182-4	182.7-183.4	Eastman white
Toluic	136.1	137	179-80	179.1-179.4	Eastman white
p-Bromobenzoic	201.0	200	251-3	252 - 253	Eastman white
m-Iodobenzoic	248.0	248	187-8	185 - 186	Eastman white
m-Nitrobenzoic	167.1	167	140-1	139 - 140	Matheson reagent
p-Nitrobenzoic	167.1	168	240-2	241 - 242	Matheson reagent
4-Carboxystilbene	224.3	222		248.0-248.4	This thesis
3-Carboxystilbene	224.3	222	194-5	197.0-197.5	This thesis
4-Carboxytolane	223.3	221		220.5-221.0	This thesis
3-Carboxytolane	223.3	220		160 - 161	This thesis

[a] The molecular weight is based on the titration curves obtained potentiometrically.

[b] All melting points are uncorrected. They were obtained from a Fisher hot stage block.

[c] Each acid was sublimed under vacuum before use.

five milliliters of water was pipetted into the flask and ethanol added to the mark. The solutions were allowed to equilibrate overnight, and the levels readjusted. The composition of the medium was dictated by the solubility of the most insoluble acid, 4-carboxystilbene. The maximum solubility of this acid at 25°C. is only 100 mg./100 ml. in this medium.

Fifty milliliters of the acid solution was pipetted into the titration cell. The cell was attached to the air-driven stirrer and electrode assembly. A five milliliter capacity microburette calibrated in 0.01 ml. units was then inserted through the stopper. The contents of the cell were, in this way, exposed to a minimum amount of atmosphere. The whole assembly was immersed in a thermostated bath maintained at 25.3 ± 0.01°C. and the potentiometric titrations were carried out within one-half hour. The electrodes were immersed before and after each run in a buffer solution. In all cases, the pH meter maintained a steady balance throughout the titration. Particular attention was paid to the buffered region and the end-point during the titration. In all cases the end-point was ascertained to within 0.07%. Moreover, the pH readings should be acceptable to 0.02 pH unit.

The titration curves were plotted for each acid. In each case values of the pH were plotted against the corresponding burette readings. The end-points were determined by means of the familiar differential method. The apparent pK_a's of the various acids were obtained with the

Table 13

Apparent pK's of Substituted Benzoic Acids

Acid	Volume of 0.1043 N. NaOH		$-pK_a$		Average pKa
		1/3	1/2	2/3	
p-Methoxybenzoic	3.785	7.06	7.02	6.97	-7.02
p-Bromobenzoic	2.673	6.25	6.23	6.22	-6.24
m-Nitrobenzoic	3.856	5.50	5.48	5.46	-5.48
p-Methylbenzoic	3.671	6.86	6.83	6.80	-6.83
m-Iodobenzoic	3.750	6.11	6.06	6.09	-6.09
p-Nitrobenzoic	3.760	5.28	5.28	5.30	-5.29
Benzoic	3.810	6.50	6.57	6.62	-6.57
3-Carboxytolane	3.728	6.41	6.35	6.32	-6.36
3-Carboxystilbene	3.719	6.56	6.52	6.51	-6.53
4-Carboxystilbene	2.340	6.70	6.69	6.67	-6.69
4-Carboxytolane	3.689	6.36	6.31	6.29	-6.39

Table 14

Variation of pK_a with Constitution of Medium

Vol. H_2O/100 ml. Solution	Vol. base used (ml.)	Apparent pK_a
25	2.200	-6.60
25	3.970	-6.59
50	3.592	-5.69
65	3.975	-5.16

aid of the Henderson equation[113]:

$$pH = pK_a + \log \frac{\left[(\text{salt}) + (H^+)\right]}{\left[(\text{acid}) - (H^+)\right]} - A(u)^{\frac{1}{2}} + Cu$$

where A is a constant. C is a function of the particular anion and u is the ionic strength. The first approximation for dilute solutions, such as were used in these titrations, is to make C a constant for all the acids. Furthermore, the low ionic strength of the solutions may justify elimination of activity coefficient terms altogether. The hydrogen ion terms (H^+) may be dropped altogether in comparison with the salt and undissociated acid concentrations for acids with pK's approximately equal to 10^{-5} in water. Thus

$$pH = pK_a + \log (\text{salt})/(\text{acid}) .$$

That these approximations are valid is apparent from the values listed in Table 13. Here the pK_a values were obtained from the titration curves at one-third, one-half and two-thirds neutralization.

Under slightly different experimental conditions, the pK_a's were determined as a function of water concentration and acid concentration in the case of benzoic acid only. The results are shown in Table 14.

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[113] S. Glasstone, "Introduction to Electrochemistry", D. Van Nostrand Co., New York, N.Y., 1940.

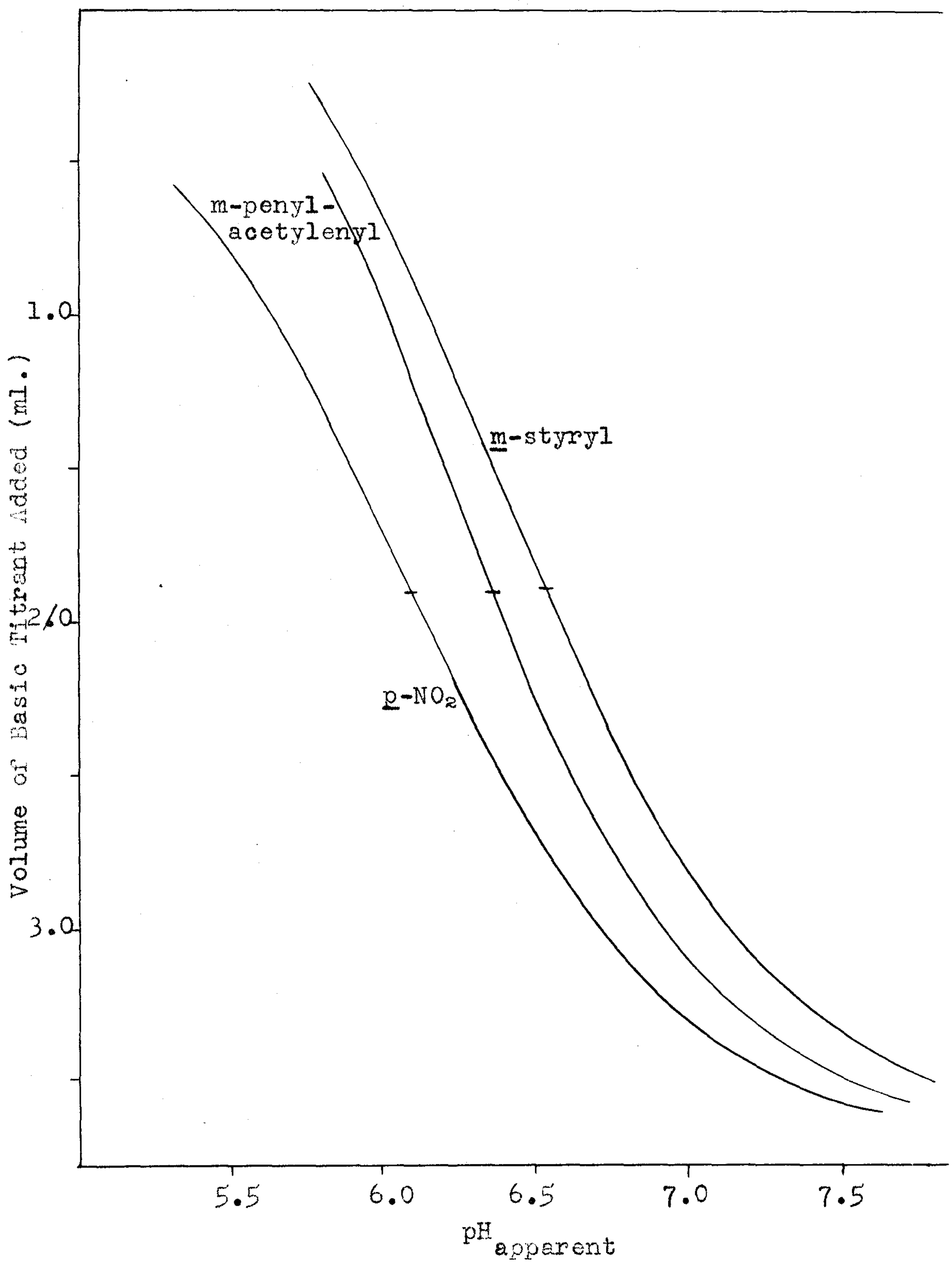

Figure Ia

Potentiometric Titrations of Benzoic Acids

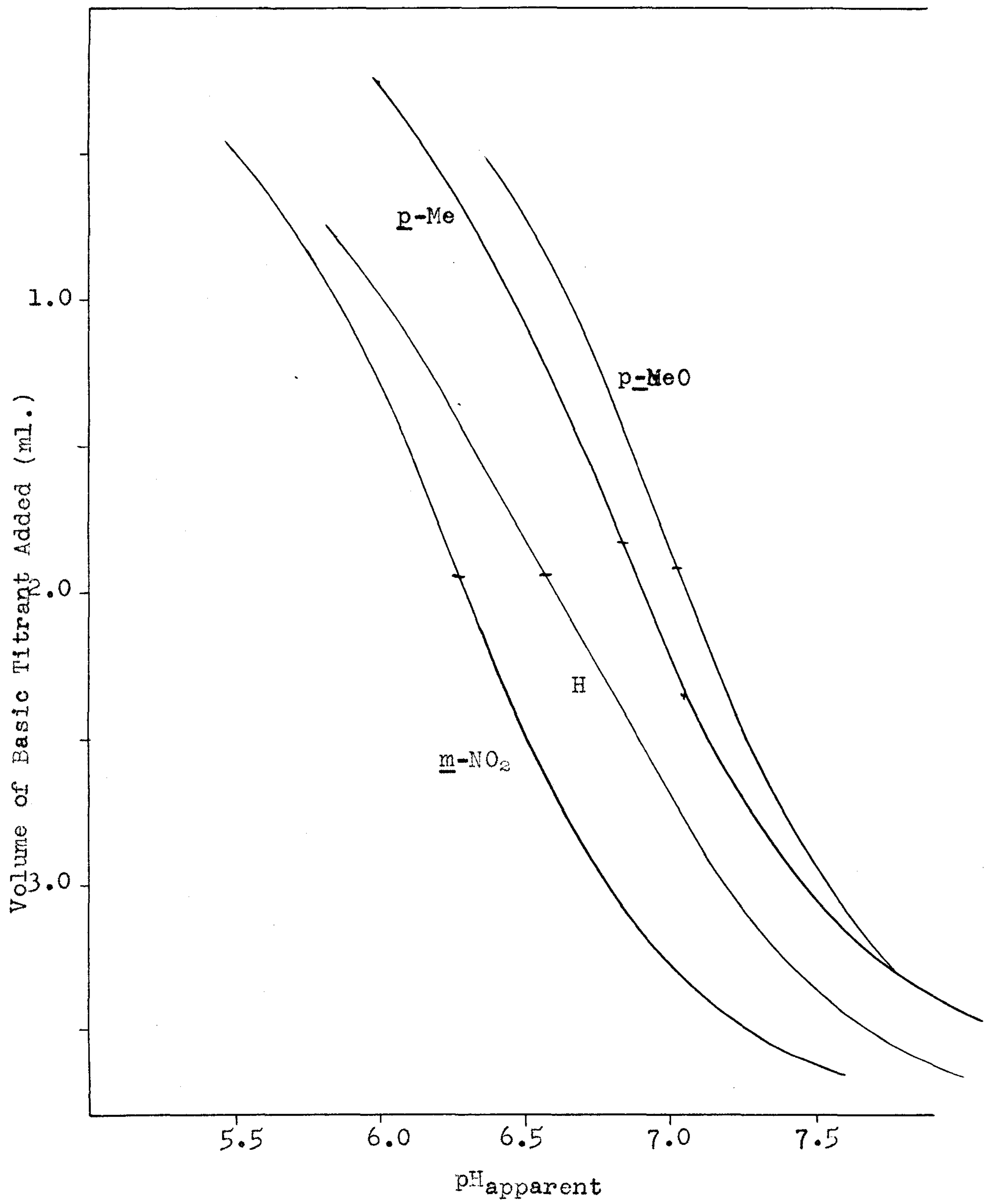

Figure Ib

Potentiometric Titration of Benzoic Acids

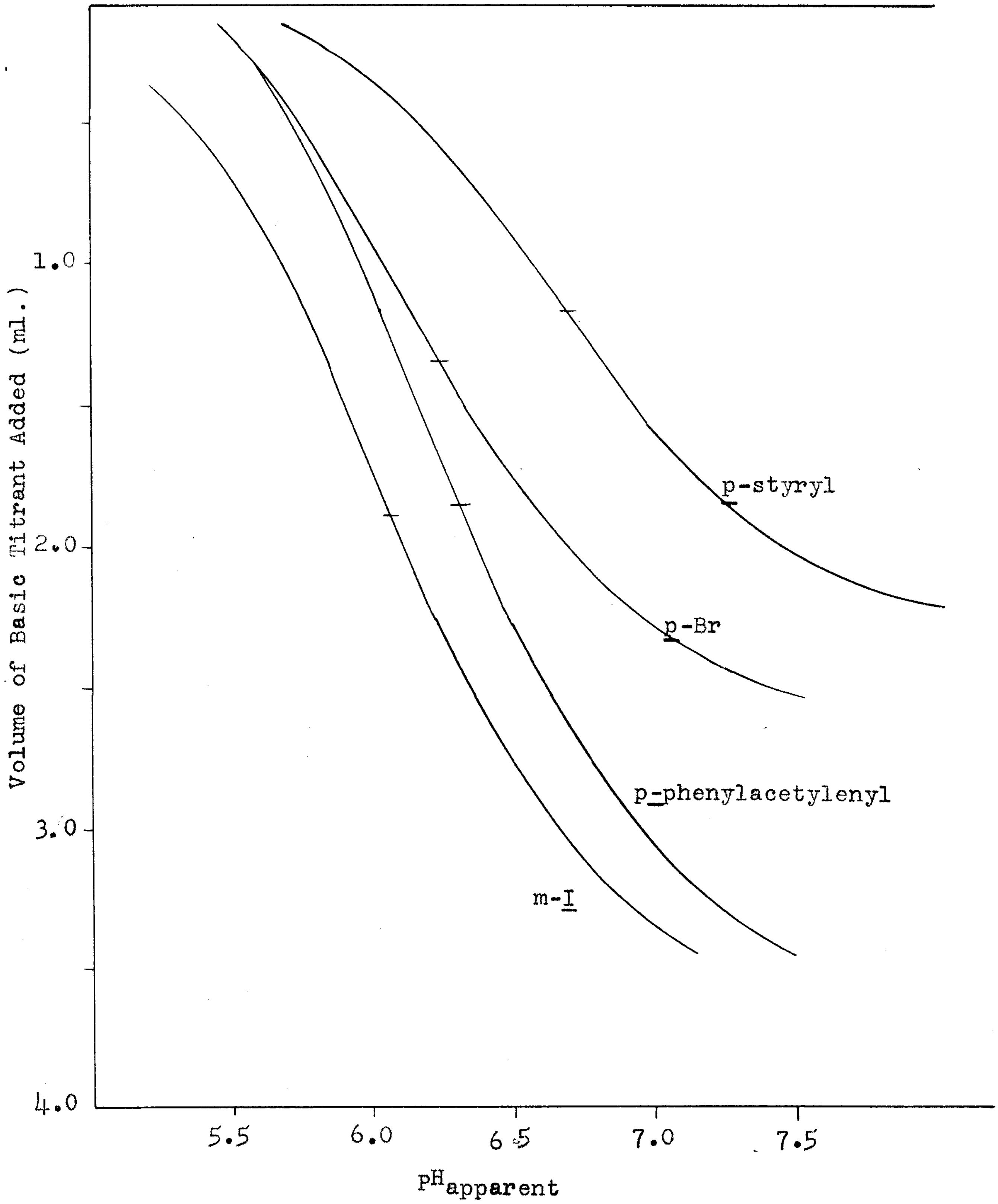

Figure Ic

Potentiometric Titration of Benzoic Acids

The Ester Saponifications

Acetone

Stockroom grade acetone was treated with potassium permanganate (1 g. per liter) and Drierite (10 g. per liter) for two days at room temperature. The liquid was filtered and then distilled through a five-foot helix packed, vacuum jacketed still. A two hundred milliliter forerun was rejected. Two and a half liters boiling at 55.1°C. was collected.

Bicarbonate-free sodium hydroxide

A concentrated solution of sodium hydroxide in water (57% by weight water) was filtered through a fine grade sintered glass crucible. Five and six-tenths milliliters of this solution was added to two liters of carbon dioxide-free water in a paraffin-lined bottle protected with an Ascarite tube. The normality of this solution did not change throughout the experiments (two weeks). This solution was used to make up solutions for conducting the saponification rates.

A more dilute solution of sodium hydroxide than the one above was made by dissolving 1.1 ml. of a filtered solution of sodium hydroxide (50% by weight water) in two liters of CO_2-free water. This solution was used for titrating aliquots.

Hydrochloric acid solution

Stockroom grade C.P. hydrochloric acid (7.6 ml.) was dissolved in two liters of distilled water and allowed to stand two days before standardizing.

Potassium acid phthalate

Baker and Adamson C.P. minimum assay 99.9% potassium acid phthalate was dried in an oven for twenty-four hours at 110°C. It was stored in a desiccator and used for all subsequent standardizations.

Indicator

Cresol red solution was made by triturating 0.04 g. cresol red with 0.7 ml. 0.15 N. sodium hydroxide and 10 ml. water. The resulting solution was diluted to 100 ml. in a volumetric flask. Five drops of this indicator were used in all the titrations.

Esters

Ethyl benzoate was Eastman Kodak white label material. Two hundred milliliters of the ester was distilled through a short path still. A fifty milliliter forerun was discarded. Material boiling at 99.0-100.0°C. at 20.0 mm. pressure was collected. The total volume of collected material was 50 ml.

Ethyl m-bromobenzoate was prepared* by the Fischer esterification of m-bromobenzoic acid, and distilled through a Claisen head. The ester was purified by distilling through a semimicro-Vigreux column. A 10 ml. forerun was rejected; material boiling at 100-100.5°C. at 7mm. was collected.

The stilbene and tolane esters prepared previously were used without further purification.

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*Courtesy of Mr. F. Borduin of this Laboratory.

The saponification rates of the esters

The procedure used here is essentially that of Hinshelwood and Tommila[114]. One hundred milliliters of approximately 0.04 N. sodium hydroxide was pipetted into a 250 ml. volumetric flask. Acetone was added to the mark with swirling and the solution allowed to equilibrate overnight. The volume was adjusted with acetone and the flask put into a constant temperature bath maintained at 25.3°C. The ester was weighed carefully into a 250 ml. standard taper round bottom flask attached with a female "Trubore" assembly. One hundred milliliters of stock sodium hydroxide solution was then quickly pipetted into the flask, the flask corked and then immersed in the bath. Four runs were made simultaneously. Eight points were taken and recorded in the usual manner.

A 10 ml. aliquot was pipetted out of the flask at the designated time, quenched with 5 ml. hydrochloric acid and then back-titrated with 0.01 N. NaOH. In the case of the unsaturated esters it was found necessary to add a slight amount of acetone to the quenched solution in order to effect solution of the precipitated acid and/or ester.

An infinite-time titer was obtained by transferring the flask, after the "Trubore" attachment was replaced by a standard taper stopper suitably tied down, to a bath maintained at 55°C. Twelve hours was sufficient to hydrolyze the esters completely. The stock solutions were titrated before and after each run in order to be sure that no change in titer occurred.

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[114] E. Tommila and C. Hinshelwood, *J. Chem. Soc.*, 1801 (1938).

The alkaline solutions were titrated before and after each run with standard solutions of potassium acid phthalate. The hydrochloric acid solution was in turn standardized with the sodium hydroxide solutions. All titrations were reproducible to within 0.1%. The volumetric glassware used in the experiments were within the limits of acceptable tolerance (0.1%). Saponification equilavents were found in the usual manner. The rate constants for the saponification of esters are listed in Table 15.

The second order rate constants were obtained from the integrated equation,

$$k_2(t_2 - t_1) = \frac{1}{a - b} \ln \left[\frac{b - x_2}{b - x_1} - \frac{a - x_2}{a - x_1} \right]$$

where b and a are the initial concentrations of ester and sodium hydroxide, respectively. The subscripts 1 and 2 refer to two different points. In this manner, the rate constants were obtained between two successive points. A representative experiment is given in Table 16.

Table 15

Rate Constants for Saponification of the Esters

	Mol. Wt.		Infinite	10^4k_2
Ester	Calc.	Found	Titer (%)	(liters/mole-sec.)
Ethyl benzoate	150.2		100	31.3
			100	30.6
			100	31.8
			100	32.6
				Ave. 31.8 ± 0.6
Ethyl *m*-bromobenzoate	229.0		100	192
			100	192
				Ave. 192 ± 0
Ethyl 3-carbethoxystilbene	252.3	253	91.7	34.6
			97.2	37.0
			100	34.1
			101[a]	40.2
				Ave. 35.2 ± 1.1
Ethyl 4-carbethoxystilbene	252.3	251	106	24.2
			103	27.1
			100	27.0
Ethyl 3-carbethoxytolane	250.3	255[b]	99.4[c]	80.2
			98.4[d]	80.7
				Ave. 80.4 ± 0.3
Ethyl 4-carbethoxytolane	250.3	250	97.6	107.8
			97.5	106.8
				Ave. 107.3 ± 0.5

[a] Compound III

[b] Fraction IV

[c] Fraction V

[d] Fraction II

Table 16

Saponification Rate of Ethyl Benzoate at 25.3°C.[b]

NaOH Titer (ml.)[a] (0.01280 N.)	Time (min.)	$\left[\log \frac{(b-x_2)}{(b-x_1)} - \log \frac{(a-x_2)}{(a-x_1)}\right] \times 10^4$
2.04		
3.22	00.0	
4.03	41.7	5.76
4.53	77.7	5.25
5.05	116.9	5.22
5.84	182.0	5.43
6.62	282.5	5.32
7.63	471.4	5.22
10.03	infinite	
		Ave. 5.29

[a] Initial base titer - 2.04 ml;
Final base titer - 10.03 ml;
Five milliliters 0.0383 N. HCl added to each aliquot;
Initial concentration of ester - 1.022 meq. per 100 ml;
Initial concentration of NaOH - 1.639 meq. per 100 ml.

[b] k_2 - 32.6 x 10^{-4} liters/mole-sec.

The Solvolysis of Substituted Benzyl Tosylates

Acetone

Stockroom grade acetone was dried over Drierite for two days and then distilled through a packed five-foot vacuum-jacketed column. Boiling point, 55.0°C.

Lithium perchlorate

Lithium perchlorate ($LiClO_4 \cdot 3H_2O$ - G.F. Smith Co.) was dehydrated *in vacuo* for ten hours at 145°C. An aqueous lithium perchlorate solution was made up in a one-liter volumetric flask to 0.479 M. by dissolving 51.0 g. of the anhydrous salt.

Potassium nitrate

Potassium nitrate (KNO_3 - Baker and Adamson, reagent grade) was used without further purification.

p-Toluenesulfonyl chloride

p-Toluenesulfonyl chloride (Eastman Kodak, reagent grade) was redistilled *in vacuo*. Boiling point, 124-125°C. at 7-8 mm. Melting point, 69.5-70.5°C.

Triethylamine

Triethylamine (Eastman Kodak, reagent grade) was refluxed over sodium shavings for one-half hour and then distilled through the helix packed column. From a 100 ml. sample, a 25 ml. forerun was separated. Thirty milliliters boiling at 88.0°C., was collected.

Indicator

A 0.1% solution of brom cresol green (Harleco) and 0.2% solution of methyl red (Harleco) were prepared in acetone as solvent. A slight amount of water (16% by volume) was necessary to dissolve the methyl red indicator. These two solutions were mixed in equal volumes before use. Eight drops of the mixed indicator was added to each run.

Hydrochloric acid

A standard aqueous hydrochloric acid solution, approximately 0.02 N., was made up in the usual manner. Its concentration was checked periodically by titration with sodium hydroxide standardized with potassium acid phthalate.

The benzyl alcohols

Benzyl alcohol (Eastman Kodak, chlorine-free) was redistilled *in vacuo*. Boiling point, 86.8-88.0°C. at 7 mm.

p-Nitrobenzyl alcohol was prepared by hydrolysis of *p*-nitrobenzyl chloride according to the method of Soderbaum and Widman[115]. Yield - 37%.

m-Bromobenzyl alcohol was obtained by the lithium aluminum hydride reduction of *m*-bromobenzoic acid. Boiling point, 255-257°C. at 738 mm. Yield - 76%.

p-Methoxybenzyl alcohol was also obtained by the lithium aluminum hydride reduction of *p*-methoxybenzaldehyde. Boiling point, 106°C. at 22 mm. Yield - 40%.

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[115] S. Soderbaum and Widman, *Ber.*, *25*, 3290 (1892).

p-Methylbenzyl alcohol was obtained from p-methylbenzoic acid via the lithium aluminum hydride reduction. The oil on recrystallization from water yielded fine white crystals melting at 61.0-62.1°C. Yield - 89%. In a previous attempt to prepare this compound, p-methylbenzaldehyde (Matheson, reagent grade) was reduced with lithium aluminum hydride. The oil resulting from this synthesis did not crystallize after repeated freezings. It showed a wide range in melting from -13 to -4°C., although the liquid distilled at a constant temperature of 216-217°C. at 721 mm. Derivatization of the parent aldehyde with p-nitrophenylhydrazine and oxidation of the aldehyde to the corresponding p-methylbenzoic acid indicated that the aldehyde was a mixture of the ortho and para compounds.*

m-Methylbenzyl alcohol was prepared by the reduction of m-methylbenzoic acid. Boiling point, 217.5-219.5°C. at 743 mm. Yield - 78%.

m-Methoxybenzyl alcohol was obtained from the lithium aluminum hydride reduction of the corresponding acid. Boiling point, 243-244°C. at 734 mm. Yield - 74%.

The unsaturated alcohols

The unsaturated alcohols, 3- and 4-hydroxymethylstilbene and 3- and 4-hydromethyltolane were used as such.

Preparation of substituted benzyl tosylates - general procedures

Method A: Benzyl tosylate. To 10 ml. (0.0966 moles) benzyl alcohol, dissolved in 100 ml. of anhydrous ether, was added 2.4 g. (0.10

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*Work performed by Dr. G. Hammond.

moles) of sodium hydride. The mixture was stirred and refluxed for twelve hours. The use of 6 mm. glass beads in conjunction with a paddle-type stirrer was found to be helpful in crushing the sodium hydride in situ. The suspension of the sodium alcoholate was cooled to -20°C. with a dry ice bath and a solution of 19.5 g. (0.0974 moles) of p-toluenesulfonyl chloride in 100 ml. of anhydrous ether was then added dropwise to the suspension. In all operations caution was taken to exclude moist air from the solutions. After the tosyl chloride solution was added, the reaction mixture was stirred for two hours at -10°C. and then at room temperature for one additional hour. The suspension was then repeatedly filtered with a minimum exposure to air until a clear solution was obtained. It was found helpful to use a medium grade sintered glass funnel for the last filtration. When the clear ethereal solution was cooled in a dry ice bath, a copious precipitate of fine white needles was obtained. The crystals were quickly filtered and recrystallized several times from dry Skelly B. Yield - 20 g. (80%). The amount of tosylate isolated depends greatly on the anhydrous nature of the reagents used and the extent of their exposure to the air. Pure benzyl tosylate under Skelly B has been kept in a tightly corked flask in a refrigerator for periods of over three months without apparent decomposition.

p-Methoxybenzyltosylate. The reactivity of p-methoxybenzyl tosylate is much greater than that of the unsubstituted compound. The preparation of this particular compound required extremely anhydrous conditions and facile manipulation. The sodio salt of the alcohol was prepared in the usual manner, caution being taken to exclude all possibilities of moist air entering the reaction. An anhydrous solution of tosyl chloride was added to the salt suspension maintained at -70°C. within five minutes. The reaction was then allowed to rise to -30°C. in one-half hour. A siphon arrangement was quickly attached to the system, and a vacuum applied at the lower end. The filtration was carried out through a pressure filter into a filter flask maintained at -70°C. in a dry ice bath. It was necessary to execute this process in a few minutes. After several minutes the p-methoxybenzyl tosylate began to crystallize as fine white needles. Subsequent rates of solvolysis of this compound were made directly with the crude material. Its isolation involved filtration in the absence of moist air on a sintered glass plate and rapid removal to the solvolysis cell. The polymerization of the p-methoxybenzyl tosylate proceeds even at -70°C; the rate of the process, however, depends greatly on the extent of its exposure to moisture. It has kept at this temperature for a period of one hour without noticeable degeneration. Previous attempts to recrystallize the material in a variety of solvents were futile. Even attempts to procure melting points were unsuccessful. In every case the fine crystals polymerized into a redmass after a few minutes in its new environment.

Method B: p-Nitrobenzyl tosylate. Method A was found to be not applicable to p-nitrobenzyl tosylate. This compound was made by the method of Tipson[116]. Five grams tosyl chloride was dissolved in dry pyridine (25 ml.) and cooled to -10°C. To this solution was added 317 g. p-nitrobenzyl alcohol and the temperature maintained. After twenty

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[116] J. Tipson, J. Org. Chem., 9, 239 (1944).

minutes fine crystals began to appear; ten minutes later 60 ml. 5 N. sulfuric acid at -10°C. was added. The temperature rose to 26°C. and an amorphous yellow solid separated. The mixture was cooled to 5°C. and filtered. The hard crystals were washed three times with 50 ml. portions of Skelly D. The crude tosylate was recrystallized five times from Skelly D, yielding finally white leaflets melting at 103-104°C.

With the exception of p-nitrobenzyl tosylate all the alcohols were treated by Method A. The variations in experimental conditions for the various alcohols were: length of heating the alcohol with sodium hydride, temperature and length of time in which the alkoxide was mixed with tosyl chloride, and the temperature and length of time in which the two were stirred. For convenience these experimental conditions are listed in tabular form in Table 17.

Every tosylate, with the exception of p-methoxybenzyl tosylate and 4-hydroxymethylstilbene, was recrystallized from Skelly D. It was found that the temperature of the recrystallizing solvent should never be above 50°C. Higher temperature led to the rapid polymerization of most of the tosylates, especially the more reactive ones. The tosylate of 4-hydroxymethylstilbene was always contaminated with the alcohol and could only be isolated 85% pure. The partial purification procedure for this compound consisted of dissolving the solid obtained from the chilled ether solution (-70°C.) in anhydrous benzene (approximately 5 ml. benzene for 2 g. crude solid). The solution was filtered to remove the unreacted alcohol. The clear benzene solution was then evaporated under vacuum, without heating. The residual solid was then washed with Skelly D twice and used as such. The sole contaminant of the tosylate was the alcohol. This was determined by hydrolyzing the tosylate in a medium consisting of 50 volume-percent aqueous acetone. The solution was then titrated with standard base to assay the tosylate. The acetone was evaporated, and the resulting aqueous mixture treated with ether. The ether solution was washed with water and the ether removed _in vacuo_. A melting point of the residual solid was taken and in all cases, despite the assay of the tosylate (which was sometimes as low as 35%), the residue melted within a few degrees of 4-hydromethylstilbene. Its melting point was not depressed by mixture with the authentic alcohol, indicating that it was fairly pure 4-hydroxymethylstilbene.

The identity of _p_-methoxybenzyl tosylate was confirmed in a similar manner. Although the assay was useless (because of the presence of tosyl chloride) the material obtained from the ether solution was subjected to an infra-red analysis. The spectrum of this material was identical in all respects with that of an authentic sample of _p_-methoxybenzyl alcohol.

The yields from the various preparations of the substituted benzyl tosylates are tabulated in Table 18. The solvolysis equivalents were determined by hydroyzing a weighed amount of tosylate in a medium of 50 volume percent acetone in water. The liberated acid was titrated with standard hydrochloric acid solution. The quantitative sulfur analyses were made on a semimicro scale (100 mg. sample) with a Parr

Table 17

Preparation of Substituted Benzyl Tosylates

Alcohol	Time Reaction With NaH (hours)	Reaction TsCl With Alkoxide				Wt. Alcohol (g.)
		Mix		Stir		
		Temp.	Time	Temp.	Time (hr.)	
Benzyl alcohol	12	-30	0.5	-10	2	10.5
p-Bromobenzyl alcohol	36	0	0.5	10	3	7.6
m-Bromobenzyl alcohol	16	-30	1	25	3.4	9.4
p-Methylbenzyl alcohol	12	-30	0.5	-20	2	4.1
m-Methylbenzyl alcohol	17	-30	0.5	00	2	4.1
p-Methoxybenzyl alcohol	8	-70	0.2	-30	0.5	6.7
m-Methoxybenzyl alcohol	10	-20	1	15	2.5	4.4
4-Hydroxymethylstilbene	60	-60	1	15	2	1.8
3-Hydroxymethylstilbene	36	-30	2	25	3	2.1
4-Hydroxymethyltolane	38	-30	1	20	3	1.7
3-Hydroxymethyltolane	26	-30	1	30	3	2.1

Table 18

Physical Constants of Substituted Benzyl Tosylates

Tosylate	Mol. Wt.	Yield	M.P.[a]	Sulfur Analysis Calc.	Sulfur Analysis Found	S.E.[b]
Benzyl	262.3	80%	58.5- 58.8	--	--	262
p-Nitrobenzyl	307.3	70%	105.0-105.5	10.39	10.43	308
p-Bromobenzyl	341.2	59%	76.8- 77.5	9.40	9.41	340
m-Bromobenzyl	341.2	63%	105.2-105.6	9.40	9.40	341
p-Methoxybenzyl	292.4	--	---	--	--	--
m-Methoxybenzyl	292.4	58%	83.7- 84.0	10.97	11.07	293
p-Methylbenzyl	276.3	41%	57.9- 58.5	--	--	276
m-(-Styryl)-benzyl	364.5	44%	104.0-104.3	8.80	8.67	362
p-(-Styryl)-benzyl	364.5	30%	150	--	--	--
m-(Phenyl-acetylenyl)-benzyl	364.4	57%	79.0- 79.5	8.85	9.45	358
p-(Phenyl-acetylenyl)-benzyl	362.4	61%	115.2-115.9	8.85	9.38	362

[a] Melting points are uncorrected.

[b] Solvolysis equivalent.

bomb[117]. The precipitated barium sulfate was filtered and weighed on a fine grade sintered glass crucible. All determinations were made in duplicate and the listed values represent the average sulfur contents.

The kinetics of the tosylate solvolysis

The rate of solvolysis was investigated using the rapid intermittent titration method[118]. The arrangement was modified slightly by the insertion of a glass and a calomel electrode into the cell to supplement the visual indicator. Preliminary comparison studies with visual indicators showed that the response of the glass electrode was sufficiently sensitive in the medium to measure pH changes of the order of one unit per second. The advantages of the glass electrode over the visual indicator for detecting end-points lie in its convenience and in the freedom from personal factors. The pH change caused by dilution during the run, can be minimized by adjusting the ratio of the titrant to the solvolysis solution to a minimum. In most cases the total volume of the titrant added was approximately 4 ml. This represents a dilution of four percent at the end of the run.

The following procedure was used. A weighed amount of tosylate (0.5-1.0 meq.) was transferred to the reaction cell and washed down with 50 ml. (pipet) of anhydrous acetone. The cell was fitted with the electrodes, thermometer, burette and stirrer, then equilibrated in a constant temperature bath maintained at 25° ± 0.03°C. In the meantime 40 ml. of

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[117] Parr Instrumental Manual No. 121, Parr Instrument Co., Moline, Ill.

[118] P. Bartlett and C. Swain, J. Am. Chem. Soc., 71, 1406 (1949).
W. Peters and S. Walker, Biochem. J., 17, 260 (1923).

0.478 M. lithium perchlorate was pipetted into a modified fast delivery separatory funnel equipped with a thermometer. This cylinder was immersed in an ice bath until the temperature of the solution cooled to 13°C., a value which had been calculated to give no temperature rise due to heat of solution when the salt solution was added to the acetone solution. The delivery from the cylinder was reproducible to within 0.03 ml. The addition of the lithium perchlorate solution was followed by the addition of eight drops of the indicator solution. The titrant consisted of a solution of triethylamine in the solvolysis medium, 55.6% aqueous acetone. The base maintained its strength for several days after standardization with aqueous hydrochloric acid to the indicator end-point. The remainder of the procedure is similar to the method of Bartlett and Swain, except for the use of the potentiometric determination of the end-points.

Since the majority of the tosylates could not be kept for prolonged periods (a few days), it was necessary to prepare and identify the compounds immediately before use. In order to maintain reproducible experimental conditions, benzyl tosylate was used as a control standard. It was solvolyzed at various times to be sure that the conditions were the same in all cases.

The unimolecular rate constants were obtained from the integrated form of the rate equation:

$$k_1(t_2 - t_1) = \ln \frac{a - x_1}{a - x_2} \quad .$$

A typical run is shown in Table 19. In Table 20 are listed the rates of

Table 19

The Solvolysis of Benzyl Tosylate in 76.6 Mole Percent Water in Acetone at 25.3°C. and Constant Ionic Strength

Vol. Titrant Added[a] (ml.)	Time Increment (sec.)	10^3k_1 (sec.$^{-1}$)
1.066	113.5	102.1
1.275	161	105.9
1.480	163	106.6
1.705	184	108.2
1.896	165	106.9
2.094	179	106.6
2.306	198	107.7
2.509	198	108.8
2.704	200	109.7
2.904	216	108.8
3.119	241	111.2
3.301	222	108.1
	Average -	108.4

[a] Weight of sample solvolyzed - 225.2 mg.
Normality of triethylamine solution - 0.1351.

Table 20

Solvolyses of Substituted Benzyl Tosylates

Tosylate	Wt. Used (mg.)	k x 10^5 ($sec.^{-1}$)	Reaction Followed %	Total Reaction %
p-Nitrobenzyl	162.0	.224	57	95.6
	174.5	.245	75	97.7
m-Bromobenzyl	174.8	.880	52	101
	170.7	.880	67	99.8
	215.4	.883	77	100
p-Bromobenzyl	201.1	4.30	96	100
	305.3	4.40	97	100
m-Methoxybenzyl	295.1	6.50	63	100
	220.0	6.48	67	99.7
	307.5	6.60	81	97.1
Benzyl	144.2	11.0	66	100
	303.7	10.7	70	100
	315.8	10.3	99	99.1
m-Methylbenzyl	273.9	18.7	91	98.4
	310.0	18.7	84	101
p-Methylbenzyl	266.6	318	97	98.6
	377.7	320	98	99.8
m- -Styrylbenzyl	113.2	5.33	81	97.8
	107.7	5.37	79	98.9
	108.1	5.38	83	97.2
p- -Styrylbenzyl	54.4	75.3[a]	98	31.2
	112.9	74.5[a]	51	85.1
	89.9	74.2[a]	49	63.0
	32.0	71.4[a]	92	91.3

[a] Values for rate constants are determined in 44.8 mole percent aqueous acetone solutions.

Table 20 (continued)

Tosylate	Wt. Used (mg.)	k x 10^5 (sec^{-1})	Reaction Followed %	Total Reaction %
m-Phenyl-acetylenylbenzyl	96.2	1.65	55	97.3
	102.0	1.56	71	98.3
	119.1	1.46	73	96.9
p-Phenyl-acetylenylbenzyl	84.5	15.1	93	99.6
	108.2	14.7	92	98.4
	84.0	14.1	48	96.5
	100.4	14.6	88	95.0
m-Methoxybenzyl	--	480[b]	--	--
	--	450[b]	--	--

[b] Values of the rate constant are determined in 13.5 mole percent aqueous acetone.

the solvolyses of the benzyl tosylates.

Rates of solvolysis of the very reactive tosylates in the bulk medium (76.6 mole percent water in acetone) were much too rapid to measure. In order to measure the rates of these compounds there were two feasible alternatives which could be followed. These two alternatives are:

(i) The solvolysis could be carried out at lower temperatures.

(ii) The rates could be measured in media of lower water concentration. The latter recourse was chosen.

The rates of solvolysis of benzyl and p-methylbenzyl tosylates were obtained as a function of the water concentration of the solvolyzing medium as follows:

To the weighed amount of tosylate dissolved in 50 ml. acetone was added an aliquot of lithium perchlorate solution at the prescribed time in the usual manner. The aqueous lithium perchlorate solution was calculated to be of such a concentration that when it was added to the acetone solution, the ionic strength of the resulting solution would be the same as that in the previous runs. An illustrative example is shown in Table 21 for a 10 ml. aliquot.

The data were recorded in the usual manner. When the desired number of points (5 or 6) had been recorded, another aliquot of aqueous solution of lower lithium perchlorate concentration, was added and several additional points obtained. This procedure was repeated until the desired final water concentration had been attained. In this manner, a series of rate constants could be obtained from one run. A typical series of such a run is shown in Table 22.

The solvolysis of the benzyl tosylates was found to be neither acid nor base catalyzed. This was determined by alternately allowing the solvolysis to proceed in basic and acidic solutions. In all cases, no correlation between the rate constant and presence of either acid or base could be found.

The rates of solvolysis of the reactive tosylates as a function of the water concentration of the solvolyzing medium are listed in Table 23. These tosylates included benzyl, p-methyl, p- -styrylbenzyl, p-phenylacetylenylbenzyl and p-methoxylbenzyl tosylates. In the case of p-methoxybenzyltosylate the rate constant was obtained in only one medium

Table 21

Adjustments of Ionic Strengths

Volume Acetone (ml.)	Volume Salt Soln. (ml.)	Total Vol. Solution (ml.)	Total Amt. Salt (meq.)	Molarity Salt Soln. (meq./liter)
50	10	58.5	10.44	1.04
50	15	63.0	11.24	0.16
50	20	67.6	12.08	0.16
50	25	72.2	12.90	0.17
50	30	76.9	13.74	0.16
50	35	81.7	14.62	0.16
50	40	86.5	15.5	0.16

Table 22

The Solvolysis of p-Methylbenzyl Tosylate in Aqueous Acetone Media of Various Water Concentrations at 25.3°C. and Constant Ionic Strength

Vol. Titrant[a] Added	Time Increment (sec.)	Vol. $LiClO_4$ Soln. Added (ml.)	Molarity $LiClO_4$ Soln. (M.)	k x 10 (sec.$^{-1}$)[b]
0.549	42	10.00	1.04	9.17
0.650	41.5			9.21
0.749	42			8.98
0.853	44.4			9.02
0.950	42.0			8.96

[a] Normality of basic titrant - 0.1567.

[b] Weight of sample solvolyzed - 518.5 mg.

Table 22 (continued)

Vol. Titrant[a] Added	Time Increment (sec.)	Vol. $LiClO_4$ Soln. Added (ml.)	Molarity $LiClO_4$ Soln. (M.)	k x 10 (sec.$^{-1}$)[b]
1.073	52.0			9.26
1.149	30.0			10.03
1.201	28.0			9.10
1.607	113.4			9.52
1.771	23.6	5.00	0.16	28.9
1.880	17.5			26.4
2.015	22.5			25.7
2.140	21.2			25.5
2.275	24.3			24.4
2.378	18.0			25.4
2.503	22.8			24.6
2.604	20.3			22.8
2.723	19.2			28.6
2.854	25.1			24.3
3.736	86	5.00	0.16	50.7
4.4416				55.3
4.594	19.4			52.5
4.716	13.9			51.2
4.987	30.5			53.3
Refill burette				
0.540	40.4			54.7
0.800	31.8			53.6
0.913	14.9			51.1
1.059	19.2			52.4
1.224	21.9			53.2
1.789	54	5.00	0.16	78.6
2.019	19.0			97.5
2.203	15.8			97.5
2.339	12.2			96.3
2.487	13.6			96.8
2.770	26.1			100.8
3.586				
4.001	36.8	5.00	0.16	140.0
4.254	21.8			158.3
4.480	21.0			160.1
4.656	18.6			157.7

Table 23

Rate Constants for the Solvolyses of Some Substituted Benzyl Tosylates as a Function of Water Concentration

Mole Percent[a] Water %			$k_1 \times 10^5$ (sec.$^{-1}$)		
	Benzyl	p-Methyl-benzyl	p- -Styryl-benzyl	p-Phenyl-acetylenyl-benzyl	p-Methoxy benzyl
13.5	--	--	--	--	465
29.0	0.103	1.98	--	--	--
44.8	0.415	9.40	74.7	--	--
55.0	1.02	25.1	189	--	--
62.0	1.93	54.1	356	2.38	--
67.0	3.05	98.2	--	--	--
71.1	4.81	154	--	6.66	--
74.1	7.50	230	--	10.1	--
76.6	10.7	319	--	14.7	--

[a] All runs were made at 25.3°C. and constant ionic strength (1.83 M. $LiClO_4$).

(13.5 mole percent water in acetone or 2.0 ml. water per 50 ml. acetone). Even in this medium the rate was much too fast to be followed by one operator. The coordinated efforts* of several persons were required.

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*The generous help by Dr. G. Hammond and Mr. G. Lucas in this and other rapid runs is acknowledged.

Since the reactivity of p-methoxybenzyl tosylate precluded careful technique, the rate constant for this compound represented in Table 23, is reliable only to within 0.0005 $sec.^{-1}$

The effect of added electrolyte on the solvolysis is tabulated in Table 24. In general, it appeared that the rate was fairly independent of the salt concentration when the salt was lithium perchlorate. In the case of potassium nitrate and lithium chloride, however, a pronounced salt effect was observed. This effect was retardation rather than acceleration as one might expect in a unimolecular solvolysis. It was noted that in every case where the abnormal salt effect was operative, the final titer of the base titrant after a suitable length of time did not correspond to complete reaction. This effect was later attributed to the mass effect described by Hammett and Beste[93]. Thus, for a particular potassium nitrate run the reaction may be formulated as the following:

$$\underset{a-(x-y)}{C_6H_5CH_2OTs} \xrightarrow[slow]{k_1} C_6H_5CH_2^+ + OTs^- \tag{a}$$

$$C_6H_5CH_2^+ + 2H_2O \xrightarrow[fast]{} \underset{(x)}{C_6H_5CH_2OH} + H_3O^+ \tag{b}$$

$$C_6H_5CH_2^+ + NO_3^- \xrightarrow[fast]{} \underset{(y)}{C_6H_5CH_2NO_3} \tag{c}$$

$$C_6H_5CH_2NO_3 + 2H_2O \xrightarrow[slow]{} C_6H_5CHO + C_6H_5CH_2OH + NO_3^- + HNO_2 + H_3O^+ \tag{d}$$

For this system

$$\frac{dx}{dt} = k_1\left[a - (x + y)\right] \tag{i}$$

Table 24

The Effect of Ionic Strength and Electrolyte on the Rate Constant of the Hydrolysis of Benzyl Tosylate at 25.3°C.

Mole Percent Water	Electrolyte (meq./ml.)	$k \times 10^4$ ($sec.^{-1}$)	Percent Reaction
76.5	2.21 $LiClO_4$	1.10	100
76.5	1.83 $LiClO_4$	1.07	100
76.5	no salt added	1.02	97.2
76.5	2.21 KNO_3	1.05[a]	85.7

[a] Calculated, see text.

If we assume step (d) to be negligibly slow as compared to (a), then the relative amounts of benzyl nitrate and benzyl alcohol formed may be approximated by the yields of each after a suitable length of time (compared with other runs using $LiClO_4$ solutions). Letting p equal the percent acid formed, on the basis that the added tosylate was pure, then

$$p \cdot x = (100 - p) \cdot y \qquad \text{or} \qquad (x + y) = \frac{100.x}{p} \quad . \qquad \text{(ii)}$$

The integration of equation (i) leads to,

$$\frac{p}{100} \ln \frac{p \cdot a - 100x_1}{p \cdot a - 100x_2} = k_1(t_2 - t_1) \quad . \qquad \text{(iii)}$$

This value of k_1 was found to be in good agreement with that obtained in lithium perchlorate solutions, as shown in Table 24.

The activation energies for the hydrolysis of the tosylates in 76.6 mole percent aqueous acetone were determined by the standard procedure. The rates were determined at 25.3°, 31.4° and 40.1°C. These values are listed in Table 25 for benzyl, p-bromobenzyl and m-bromobenzyl tosylates.

Table 25

The Activation Energies of Tosylate Solvolysis in 76.6 Mole Percent Aqueous Acetone

Tosylate	$k \times 10^4$ (sec.$^{-1}$) 25.3°	31.4°	40.1°	E (Kcal./Mole)
Benzyl	1.07	1.93	4.61	18.5
p-Bromobenzyl	0.435	--	2.05	19.6
m-Bromobenzyl	0.0881	--	0.395	17.9

The Ultraviolet Spectra

Ethanol used to make up the solutions was purified by treating 3.1 of 95% stockroom grade ethanol with 19 g. NaOH and 30 g. $AgNO_3$. The mixture was refluxed for three hours and then distilled through a 30 cm. Vigreux column; a 200 ml. forerun was discarded. The middle fraction boiling at 77.7°C. was collected.

Solutions of the compounds were prepared by dissolving the appropriate amounts of compounds in ethanol in 100 ml. volumetric flasks. The concentrations were adjusted on the basis of the extinction coefficients being approximately 20,000 liters/mole-cm.

The salient features of the spectra obtained from a Cary Model 12 Recording Spectrophotometer are recorded in Table 26. This table lists the maxima and extinction coefficients of the compounds.

Table 26

Ultraviolet Spectra Characteristics

	Band[b]							
	A		B		C		D	
Compound	λ_{max}	e_{max}[a]	λ_{max}	e_{max}	λ_{max}	e_{max}	λ_{max}	e_{max}
Tolane	2780	2.63	2845	2.10	2957	2.28	3024	0.817
4-Carboxytolane	2936	3.19	--	--	3107	2.79	--	--
3-Carboxytolane	2790	2.30	--	--	2936	2.03	--	--
	A		E				D	
Stilbene	2940	2.71	3070	2.62			3209	1.58
4-Carboxystilbene	3078	2.86	3186	3.04			3338	2.00
3-Carboxystilbene	2920	2.86	3044	2.54			3192	1.55

[a] Extinction coefficients, e_{max}, are measured in 10^4 liter/mole-cm; $e = D/md$, where D is the optical density, m is the molar concentration and d is in cm. λ_{max} values are recorded in Å.

[b] The assignment of the bands was arbitrary.

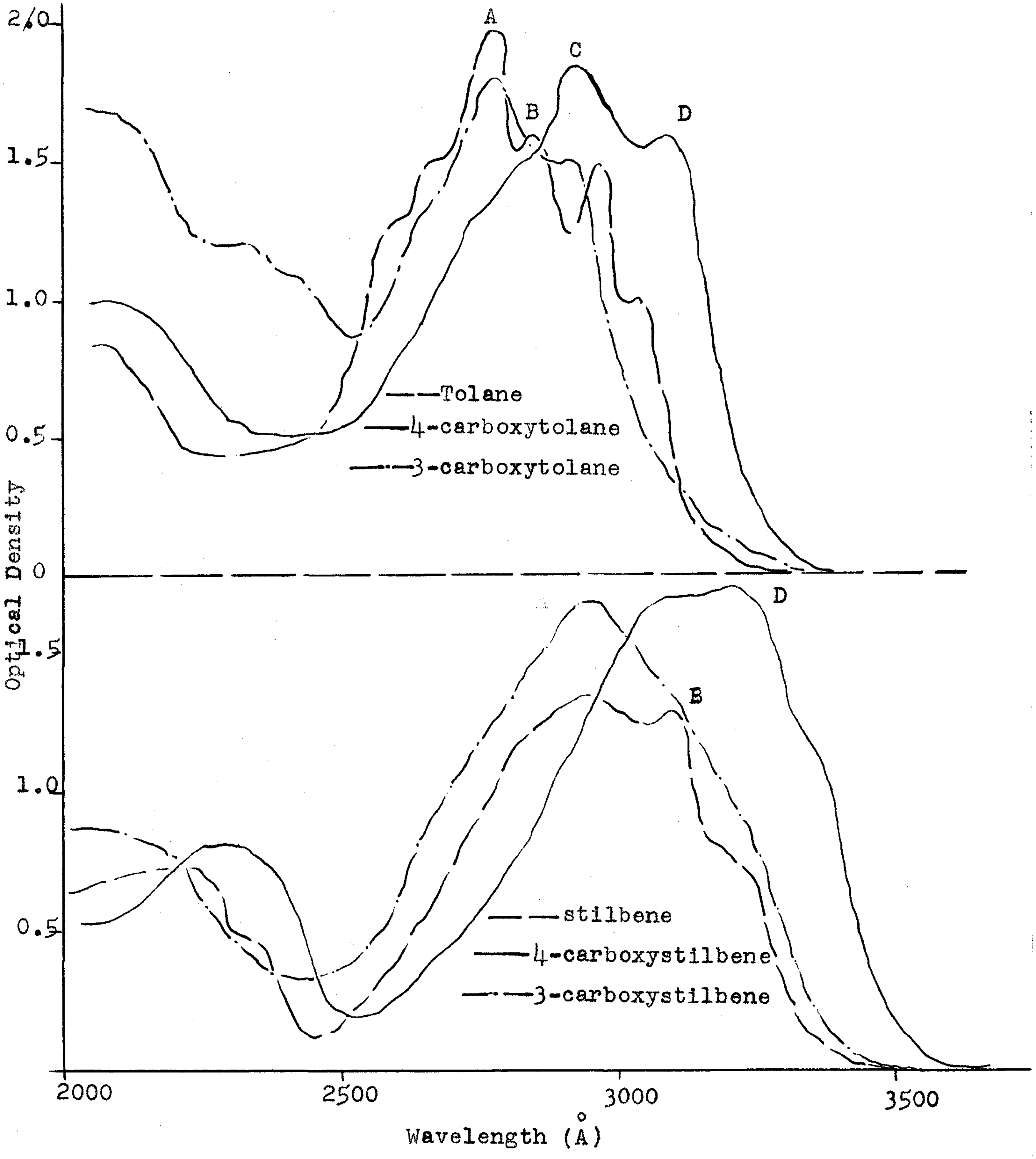

Figure II

Ultraviolet Absorption Spectra of Some Substituted Tolanes and Stilbenes

The Infra-red Spectra

A few representative infra-red spectra* of the derivatives of stilbene and tolane are shown in Figure 2. It is interesting to note that the stretching bands of the triple and double bonds are missing in the tolane and stilbene derivatives, respectively. This abnormal effect has been previously observed for nearly symmetrical alkynes[119] and octenes[120].

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*Kindly provided by Mr. R. Hedges of this Laboratory.

[119] V. Wotiz and F. Miller, J. Am. Chem. Soc., 71, 3442 (1949).

[120] T. Kletz and A. Summer, J. Chem. Soc., 1456 (1948).

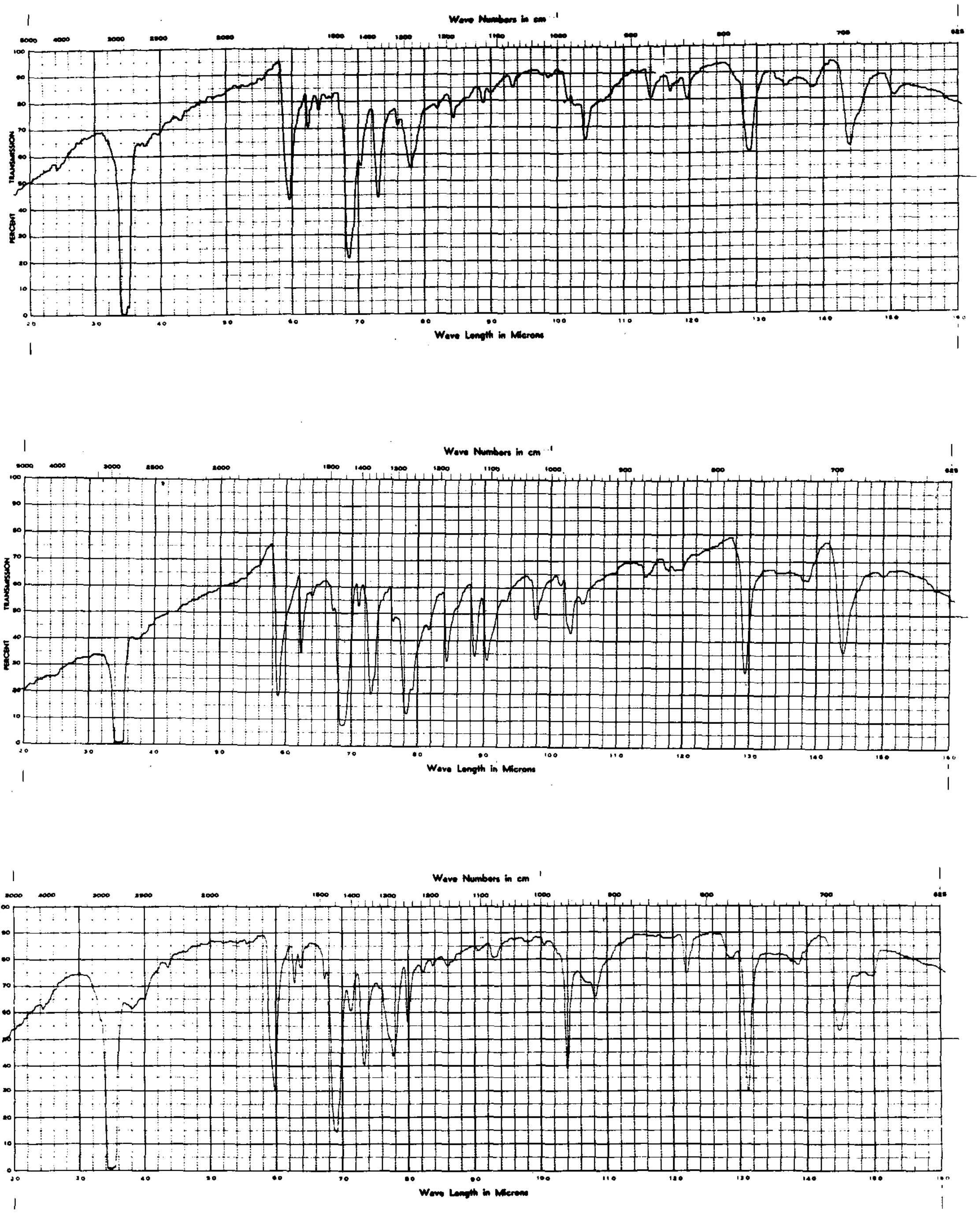

Figure IIIa. Infrared Spectra of Stilbene Derivatives: 4-Carboxystilbene, Ethyl 4-Carbethoxystilbene and 3-Carboxystilbene.

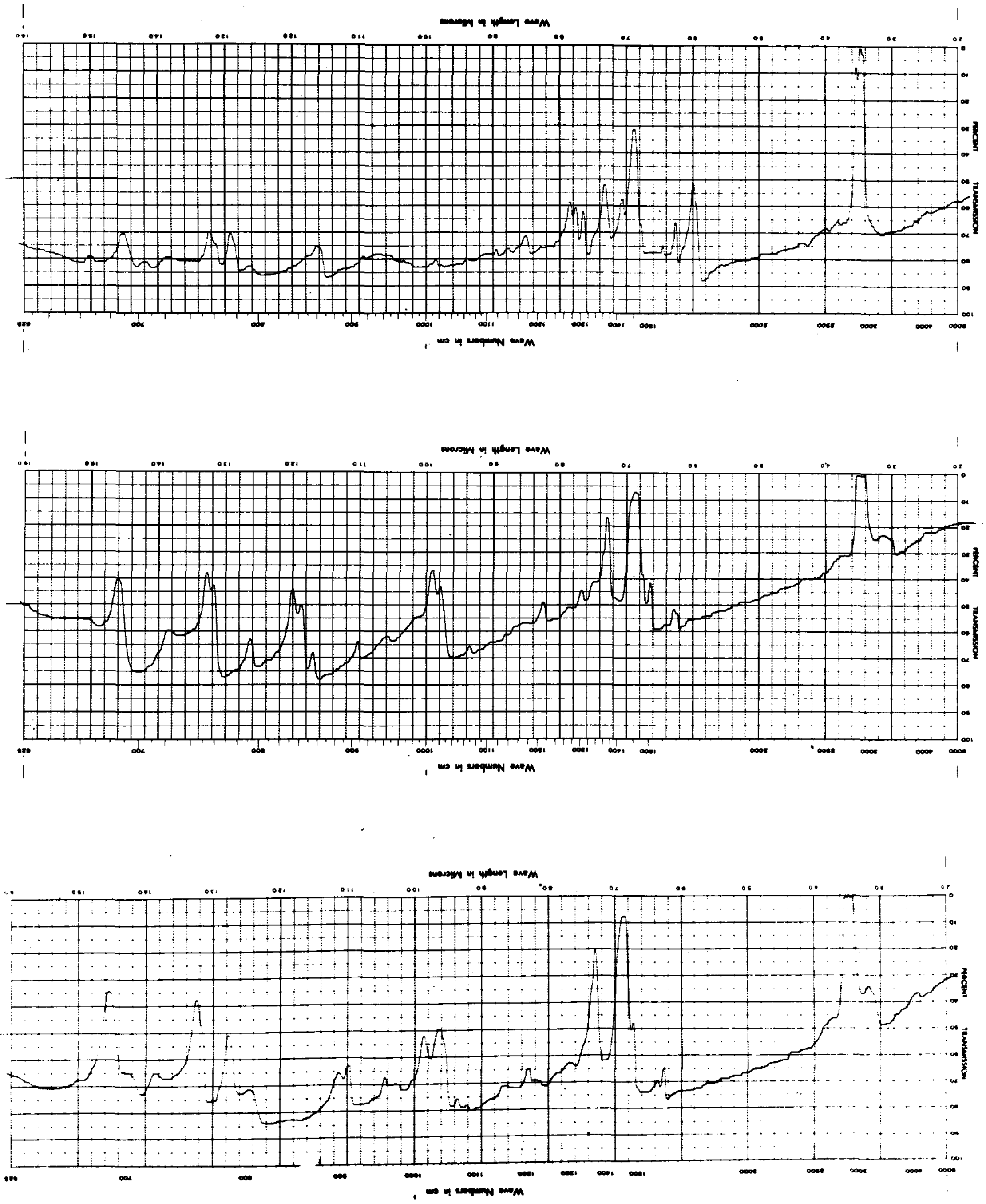

Figure IIIb. Infrared Spectra of Tolane Derivatives: 3-Hydroxymethyltolane, 4-Hydroxymethyltolane and 4-Carboxytolane.

RESULTS AND DISCUSSION

The apparent ionization constants of the substituted benzoic acids have been plotted against the respective *sigma* constants as shown in Figure IV. The value for the *rho* constant obtained from the slope by the method of least squares was 1.60 with a probable error, r, of 0.053 for seven points (n = 7).

A similar application of the data presented by Hinshelwood and Tommila[114], and Tommila[121], for the saponification of ethyl benzoates in aqueous acetone to the *sigma* constants gave *rho* equal to 2.373, r = 0.049, n = 19 as shown in Figure V. This result corresponds to *rho* equal to 2.373, r = 0.051, n = 7, obtained by Hammett[122] from a consideration of the data of Hinshelwood and Tommila alone.

The two determinations of the *sigma* values for *m*- and *p*-β-styryl and *m*- and *p*-phenylacetylenyl groups from these graphs are listed in Table 27.

The rate constants for the solvolyses of *p*-methoxy and *p*-β-styrylbenzyl tosylate were obtained by extrapolating values obtained in media containing lower water concentrations than that used for the other tosylates. In Figure VI the rate constants of the solvolyses of several tosylates have been plotted as a function of the water concentration of the solvolyzing medium. The apparent similarities in the series of curves can be readily seen. In fact it is possible to superimpose the curves on one another without too much show of discrepancies. The upper

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[121] E. Tommila, *Ann. Acad. Sci. Fennicae, Ser. A57*, No. 13, 3 (1941).

[122] L. Hammett, ref. 60, p. 191.

Table 27

<u>Sigma</u> Values for β-Styryl and Phenylacetylenyl

Substituent	σ_{ester}	σ_{pK}	$\sigma_{ave.}$
m-$C_6H_5CH{=}CH$-	0.020	0.030	0.025 ± 0.005
p-$C_6H_5CH{=}CH$-	-0.031	-0.070	-0.050 ± 0.020
m-$C_6H_5C{\equiv}C$-	0.180	0.140	0.160 ± 0.020
p-$C_6H_5C{\equiv}C$-	0.215	0.165	0.190 ± 0.025

and lower dashed curves for p-methoxy and p-β-styryl benzyl tosylate represent the greatest deviation of all the curves, and are probably a good indication of the error in the rate constants for these two compounds. That these extrapolations are valid is given further justification by the investigations of Winstein and Grunwald[123] and Braude[124].

Winstein and Grunwald have shown that the rate constant, (k_1), for the unimolecular solvolysis of alkyl halides, tosylates and brosylates can be correlated with the constitution of the medium by the equation,

$$\log k_1 = mY - \log k_o$$

where Y is a measure of the ionizing power of the solvent. Log k_o by an arbitrary designation is the rate of solvolysis in 80% ethanol-water

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[123] S. Winstein and E. Grunwald, J. Am. Chem. Soc., 70, 846 (1948).
S. Winstein, E. Grunwald and H. Hones, ibid., 73, 2700 (1951).

[124] E. Braude, J. Chem. Soc., 443 (1944).

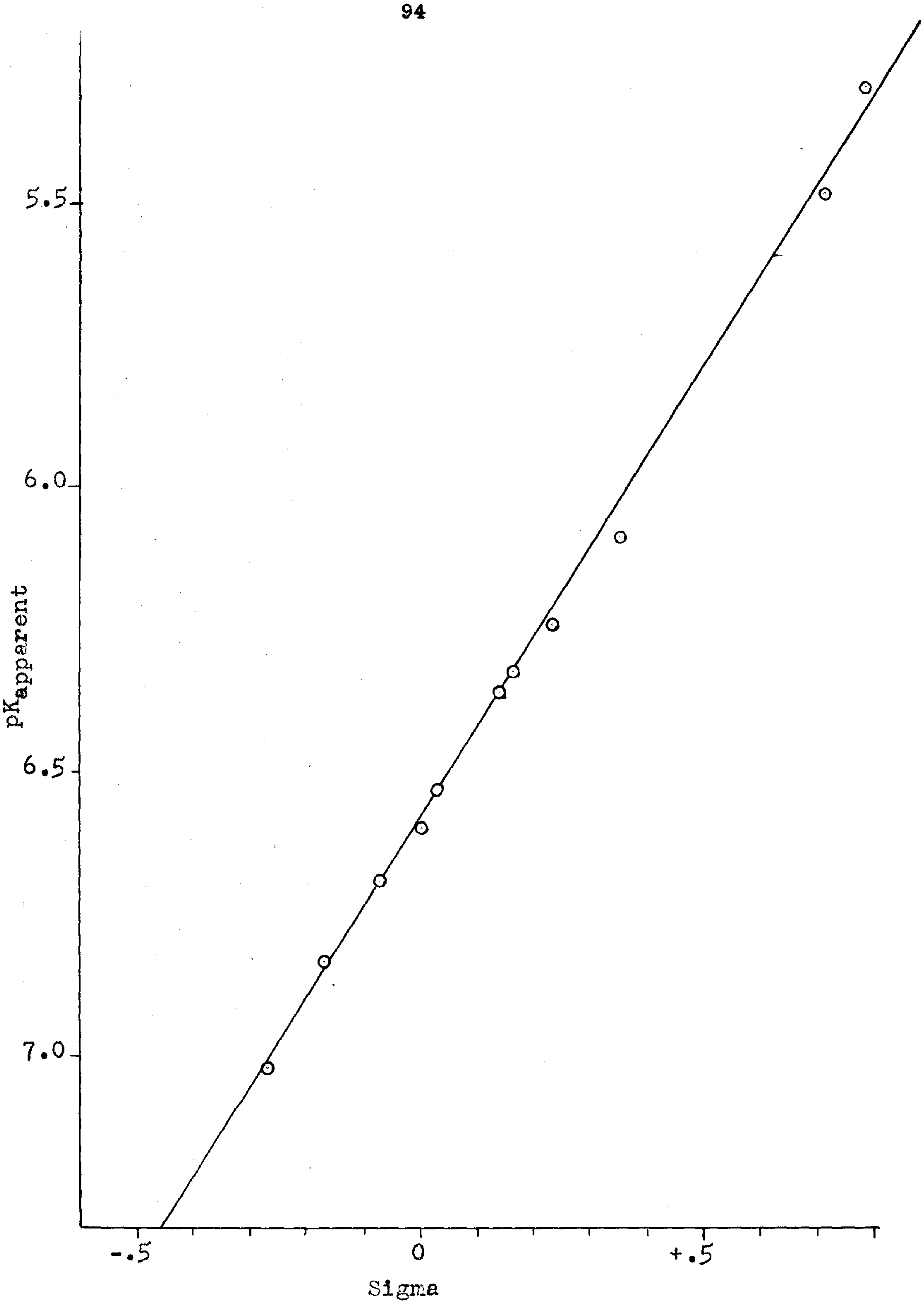

Figure IV

$pK_{apparent}$ vs. Hammett's Sigma

solution. The value of m is a function of the particular compound being solvolyzed and is a constant for various solvolyzing media. In the case of binary solvents there exists a smooth function of the Y-value with the water composition of the medium. This fact implies a correlation of log k with the water concentration.

Braude has given a similar type of correlation for the unimolecular acid-catalyzed rearrangement of unsaturated alcohols as a function of the dielectric constant of the medium. In the case of acetone-water solutions, an examination of the date of Harned and Owen[125] for the variation in dielectric constant with water concentration reveals that a smooth monotonic function can be drawn for the plot of dielectric constant with the mole fraction of the water in solution.

From a consideration of the above investigations it appears that the extrapolation of the rate constants is justified in the case of the solvolysis of benzyl tosylates.

The logarithms of the rate constants for unimolecular solvolysis of benzyl tosylates have been plotted against the sigma values for the corresponding substituents in Figure VII. An examination of this graph reveals a rather indefinite linear relationship which characterizes a poor Hammett correlation. A close scrutiny of the data, however, discloses a fair linear relationship. If one excludes the following points: p-methoxy, p-methyl, p-β-styryl and to a certain extent p- and m-phenylacetylenyl and m-styryl, the values of the rho constant for the six

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[125] H. Harned and B. Owen, "The Physical Chemistry of Electrolytic Solutions", Reinhold Publishing Corp., New York, N.Y., 1943, p. 118.

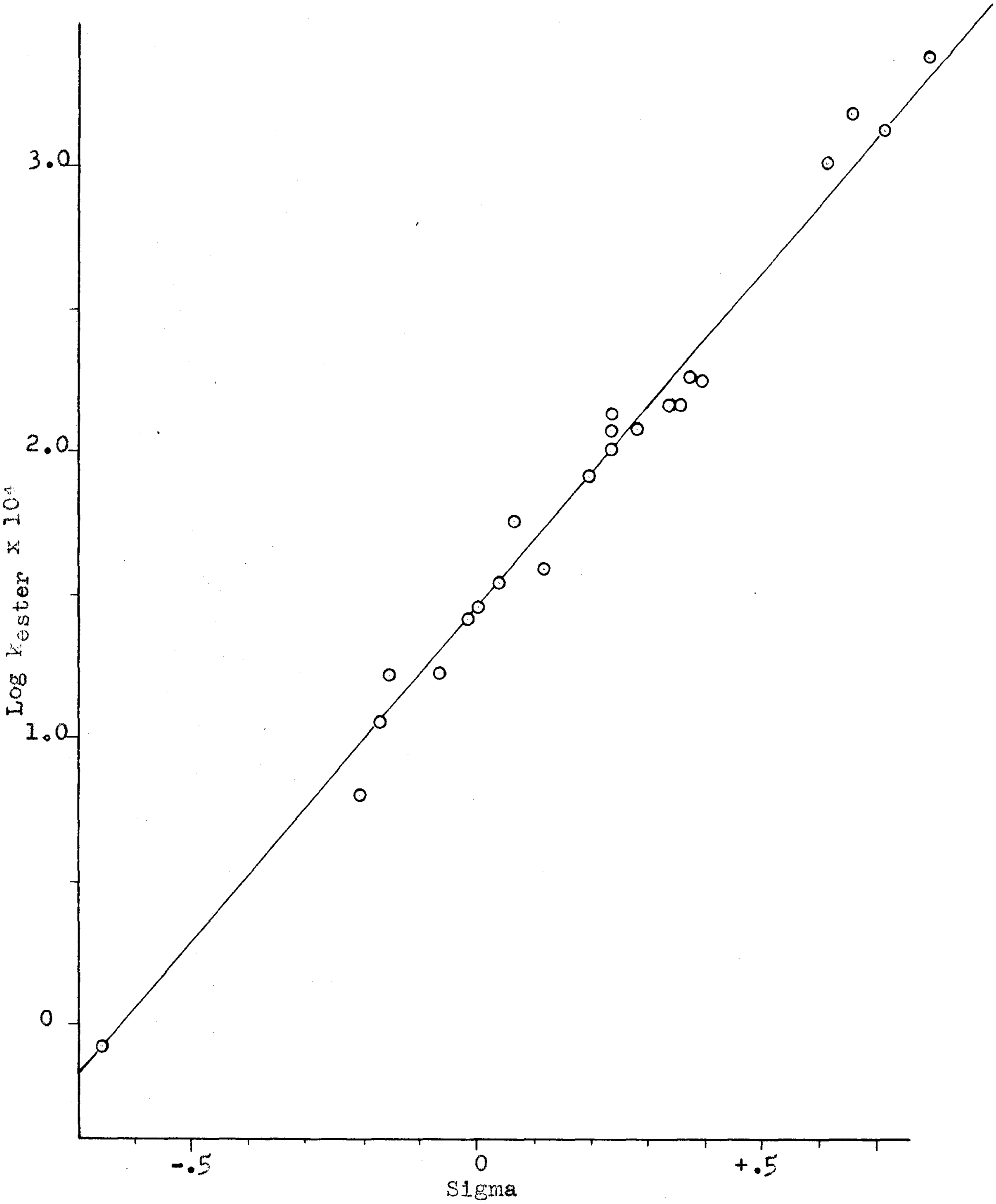

Figure V

Log k_{ester} vs. Hammett's Sigma Constant

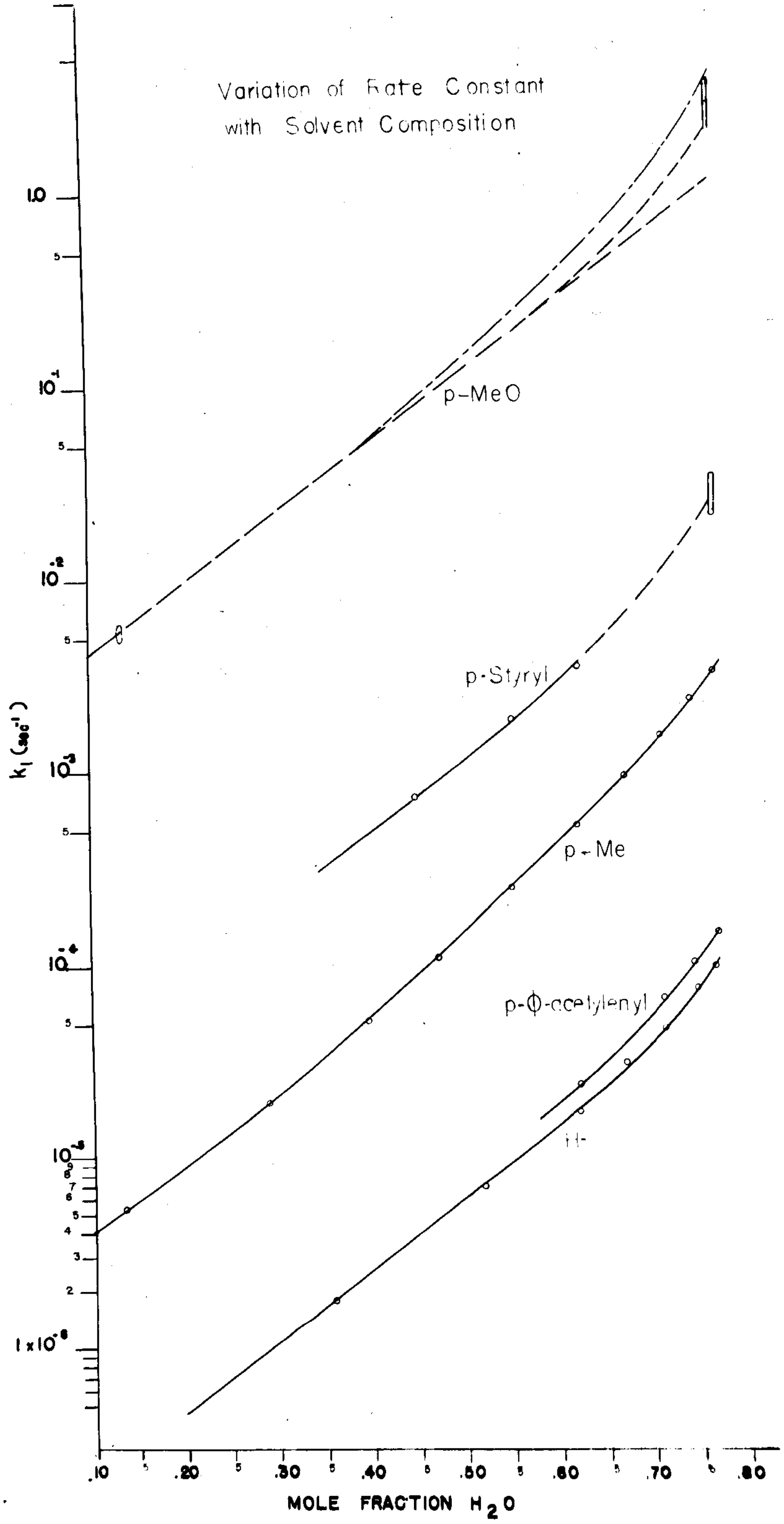

Figure VI. Variation of Rate Constant with Solvent Composition.

remaining points evaluated by the method of least squares is -2.20 with a probable error of 0.07 (n = 6). The inclusion of *m*- and *p*-phenylacetylenyl and *p*-β-styryl in the calculations of *rho* yields, = -2.19 and r = 0.27 (n = 9). The *rho* value, thus, is not changed by the inclusion of these latter points. It is the probable error for this value that suffers most. If one assumes a *rho* value of -2.19, the most reasonable figure, the values for *p*-methoxy, *p*-methyl and *p*-β-styryl all suffer from want of decent correlation.

The deviation from a linear relationship is shown up more clearly in Figure VIII in which the logarithm of the rate constant for the solvolysis has been plotted against the logarithm of the rate constant for the saponification of the ethyl ester of the corresponding acid. The least squares method (assuming an equal error in both variables)[127] was applied to all the points except *p*-methoxy, *p*-methyl and *p*-β-styryl to obtain the best straight line shown in the Figure.

That the value assumed for *rho* is a reasonable one is shown by examining the data of Olivier[126], and Bennett and Jones[87] for the solvolysis of substituted benzyl chlorides. The logarithms of the rate constants from these data have been plotted against the *sigma* constants in Figures IX and X. The data reported by Olivier appear to be more complete since he obtained rate constants in different media and at several temperatures as shown in Figure IX. A striking similarity in

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[126] S. Olivier, *Rec. trav. chim.*, *56*, 247 (1937).

[127] A. Worthing and J. Geffner, "Treatment of Experimental Data", J. Wiley and Sons, Inc., 1943, p. 258.

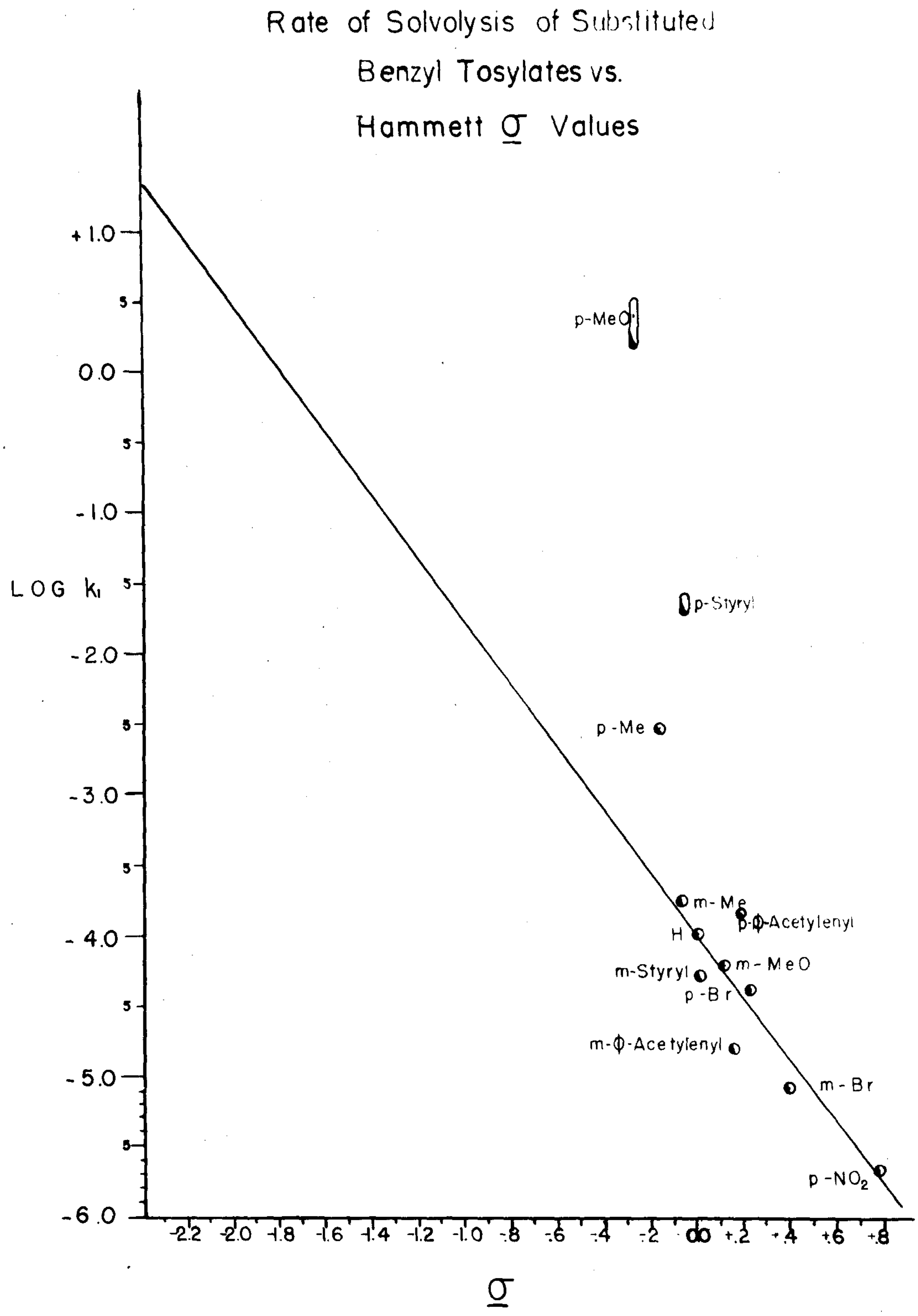
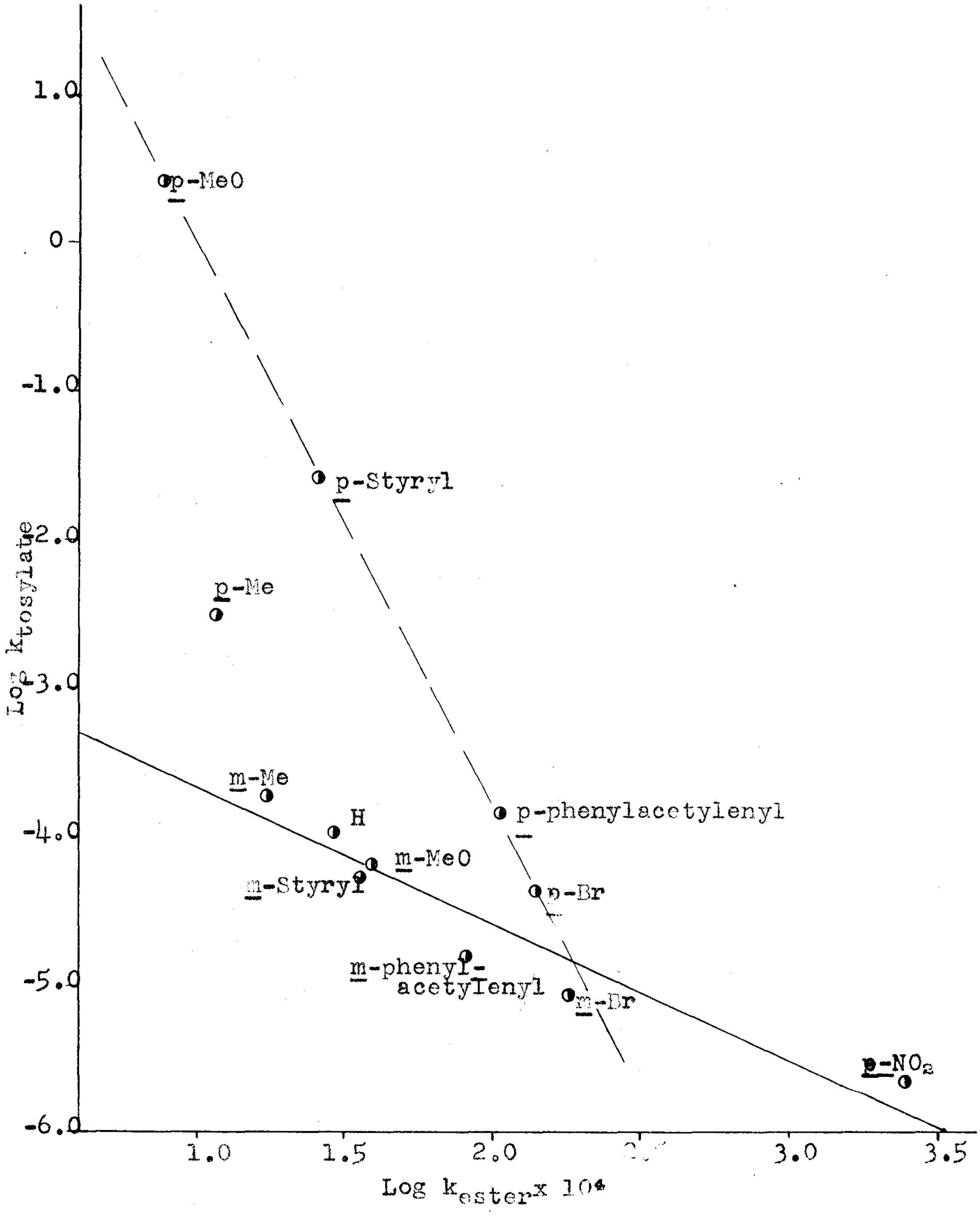
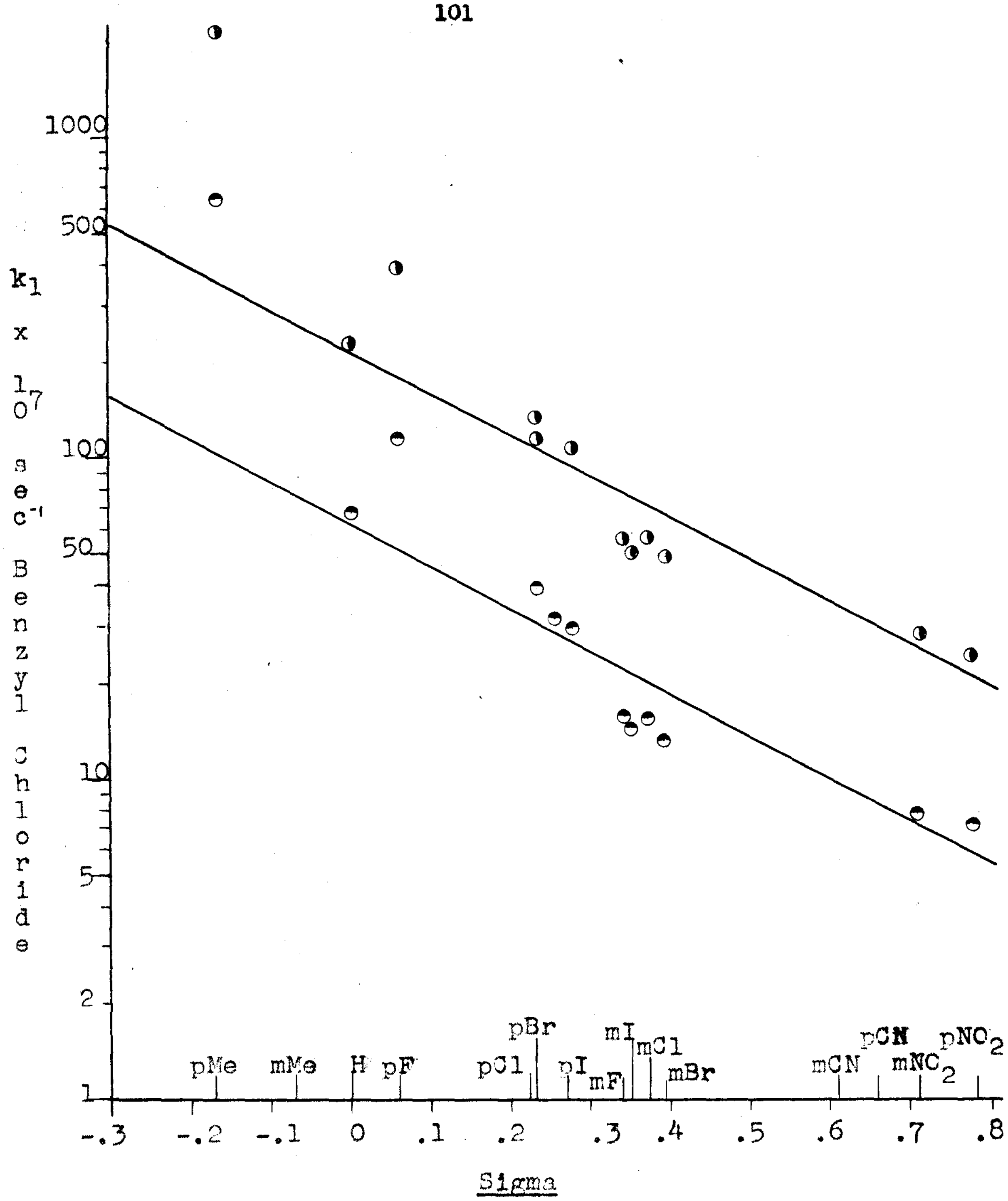


Figure VII. Rate of Solvolysis of Substituted Benzyl Tosylates vs. Hammett *Sigma* Values.



FigureVIII

Log k_{ester} vs. Log $k_{tosylate}$



Solvolysis of Benzyl Chloride vs. Sigma

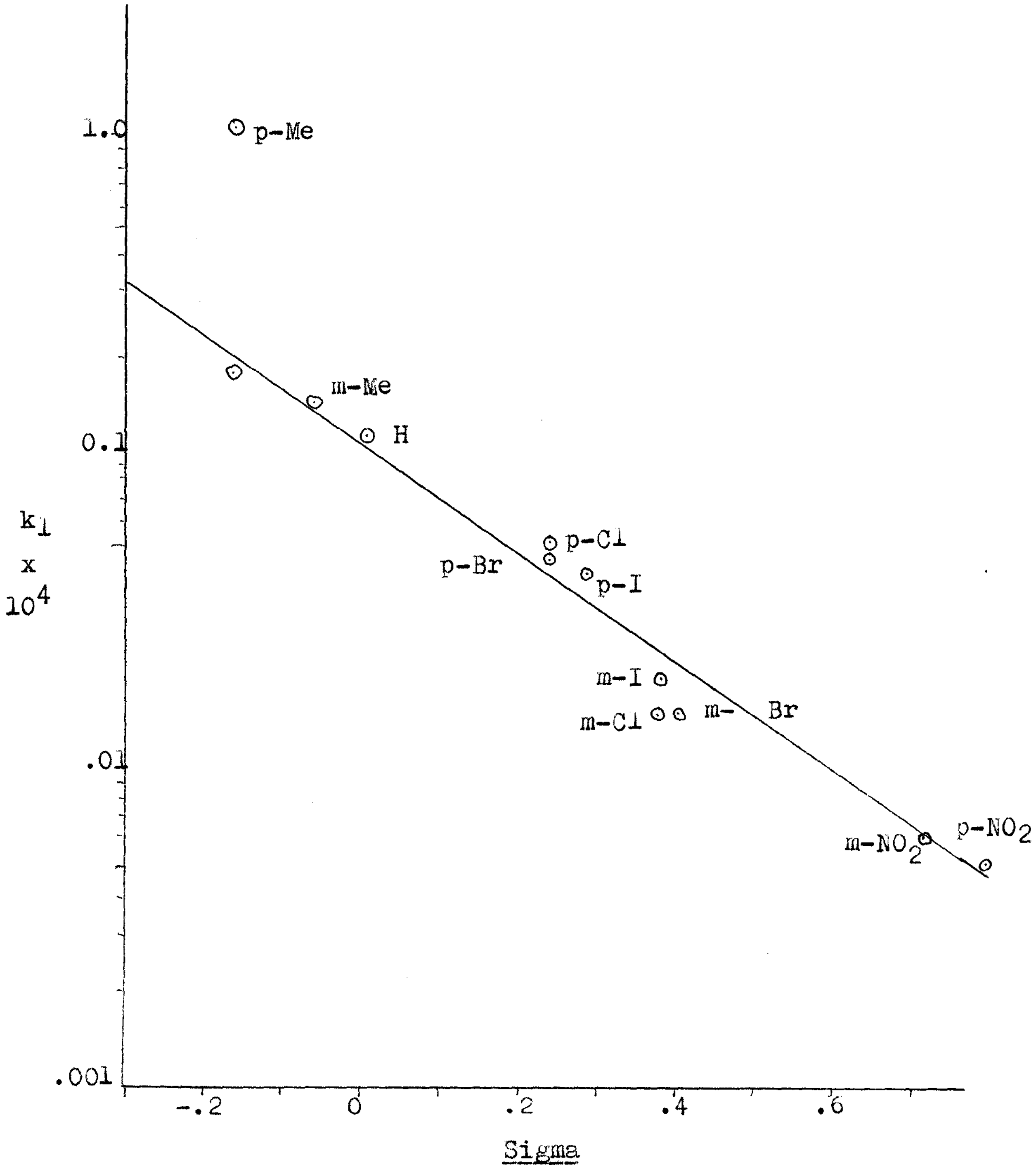
◑ 50 % aqueous acetone @ 69.8°

⊖ 50 % aqueous acetone @ 58.4°

Figure IX

the disposition of the points around the best straight line in each case is exhibited for all the curves of benzyl chlorides (Figures IX and X) as well as that of benzyl tosylates (Figure VII). It is apparent that in all the cases shown, the compound containing the p-methyl substituent deviates from the linear correlation of the logarithn of the rate constant and sigma shown by the others. A more apparent correspondence between the solvolysis of benzyl chlorides and the solvolysis of benzyl tosylates is shown in Figure XI, in which the logarithms of the rates of solvolysis of the chlorides have been plotted against the corresponding values for the tosylates. In the figure the values for the benzyl chlorides have been corrected to 25.3°C. using the activation energies listed by Olivier[126]. The slight difference in solvent composition in the two series (44 volume-percent for benzyl tosylate and 50 volume-percent for the benzyl chloride) should have little or no effect on the slopes of this curve. This is a result of the similarities in the curves obtained from the variation in the rate constants for several tosylates with water composition. It appears, thus, that whatever deviations do exist for the solvolysis of benzyl chlorides applicable to the tosylates as well, and are, therefore, a function of the benzyl system exclusively.

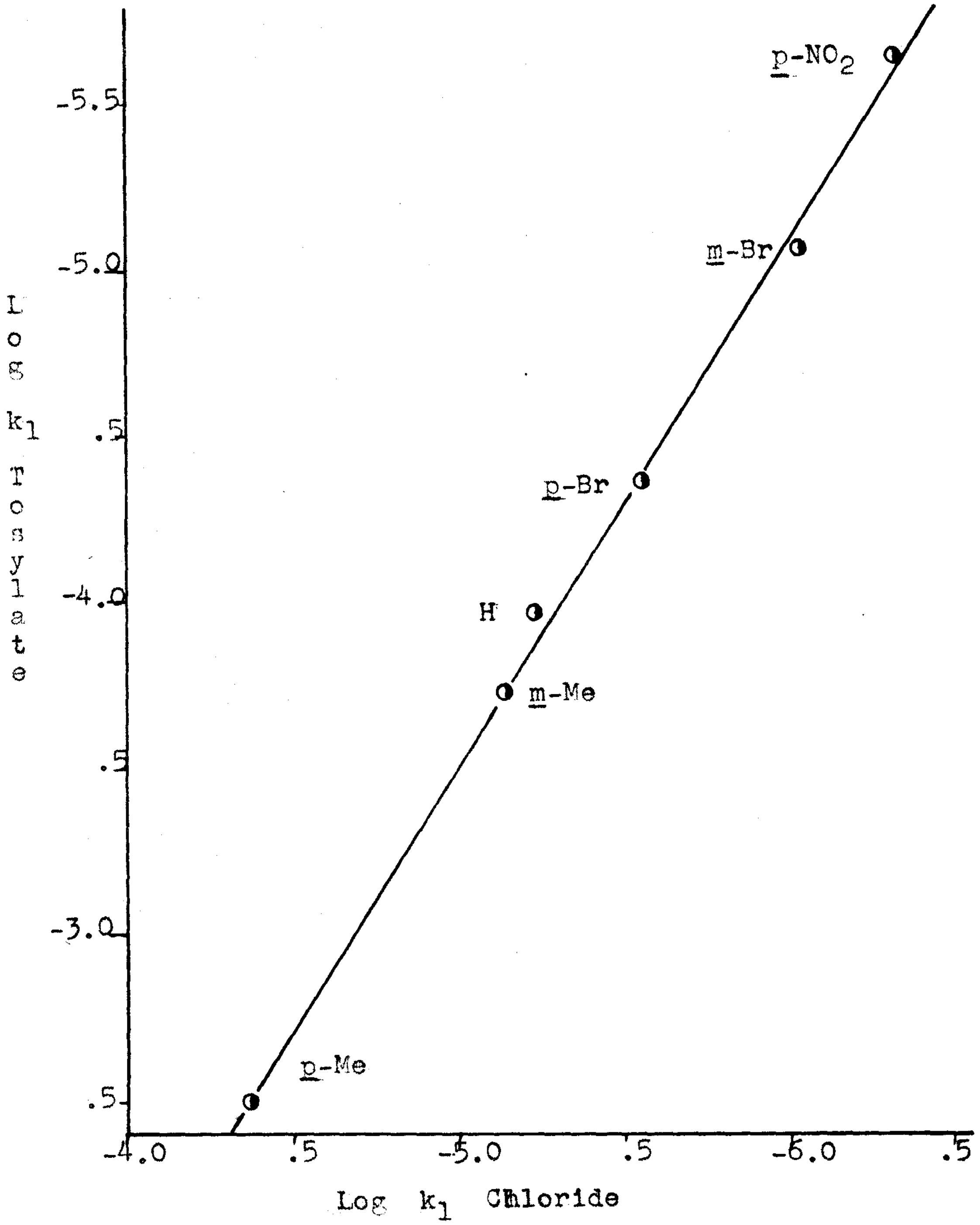
Deviations from the Hammett relationship were pointed out early in the studies of this equation. The most well-discussed case is the deviation of p-nitrophenol and p-nitroaniline in the relationship between the ionization constants of phenols and anilines, respectively, and the sigma constants for the substituent groups. In these compounds it was necessary to assign two values of sigma to the p-nitro function, one



Solvolysis of Benzyl Chlorides vs. Sigma

Figure X

104



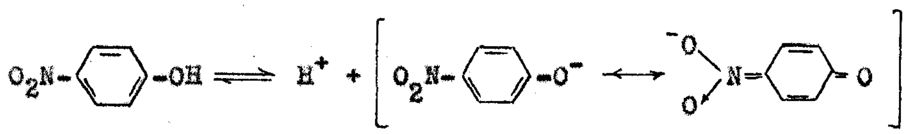
Solvolyzis of Benzyl Tosylates and Chlorides

Figure XI

value for anilines and phenol derivatives and another value for the other benzene derivatives. Branch and Calvin[128] have pointed out this anomaly, and have attributed the "abnormal" behavior of *p*-nitrophenol and *p*-nitroaniline to the strong resonance interaction of the subsitiuent, *p*-nitro, with the ring. They generalized by stating,

> ....Hammett equation.....is a fairly close approximation for *meta* and *para*-substitution, except when a *para*-substituted group resonates so as to put a positive charge in the ring. In such cases it is necessary to use two values of *sigma* for the group in the *para* position, one when the atom from which the proton dissociates resonates directly with the aromatic nucleus and the other for acids in which the benzene resonances are less directly concerned with the dissociation.

In addition, such substituents as *p*-COOR, *p*-CN, *p*-CH$_3$CO, *p*-CH$_3$SO and *p*-F$_3$C showed this abnormal behavior. Thus, in all these cases, it is believed that deviations from the Hammett equation (*i.e.*, assignment of two *sigma* values) in the case of phenols was due to the additional resonance stabilization of the anion. *Para*-nitrophenol may be used to typify the case as shown below.



The extraordinary resonance stabilization of the anion of *p*-nitrophenol is not exhibited in the case of the *meta*-isomer nor in the case of the other well-behaved *meta* and *para*-substituents.

The difference in the two *sigma* values assignable to these substituents

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[128] G. Branch and M. Calvin, Ref. 24, p. 249.

may give an indication of the extent of this additional stabilization in the anion. The *delta sigma* values are listed for several substituents in Table 28. These values are the differences between the *sigma's* of the phenols and the corresponding acids.

Table 28

Delta Sigma Values for Phenols

Substituent	σ_{phenol}	σ_{acid}	$\Delta\sigma$
p-Nitro	1.27	0.78	-0.49
p-Cyano	1.00	0.66	-0.34
p-Acetyl	0.87	0.43	0.44
p-Methylsulfonyl	0.98	0.72	0.26
p-Trifluoromethyl	0.73	0.53	0.20

It is not unreasonable to extend the interpretation of this abnormal behavior to other systems by stating that any substituent which may contribute stringly towards the stabilization of the products in an equilibrium process (or the stabilization of the transition state, in a rate process) as a result of the freeing of an electron-pair in that system, may lead to abnormal Hammett correlations.

A logical extension of this argument would lead one to state that a system in which the vacating of an orbital (formation of an open sextet) were important in stabilizing the product of an equilibrium process or stabilizing the transition state of a rate process would show a correspondingly abnormal behavior in the Hammett relationship. Moreover, those substituents which can donate an electron-pair to the ring (i.e., accommodate a positive charge) would be expected to deviate. In particular one might expect p-amino to show such a behavior because of the attractive resonance forms that may be important for this system as shown below.

In order to apply this interpretation to the solvolysis of benzyl tosylates and chlorides, it may be profitable to understand more completely the nature of the solvolytic process for this system. There is still some controversy[123] as to the exact nature of the unimolecular solvolytic process of tertiary and benzyl halides. The two mechanisms for this process can be formulated in the following manner:

I

$$RX_{aq} \rightleftharpoons R^{+}_{aq} + X^{-}_{aq}$$

$$R^{+}_{aq} + H_2O \xrightarrow{\text{fast}} ROH^{+}_{2aq}$$

II

$$RX_{aq} + H_2O \xrightarrow{\text{slow}} (H_2O \quad R_{aq})^{+} + X^{-}_{aq}$$

The first case is a two-step process involving a rate-controlling ionization of the solvated halide to form a solvated carbonium ion, which rapidly reacts in a follow-up process with the solvent to form the solvated first conjugate acid of the product. The second mechanism postulates an attack by a solvent molecule on the solvated halide molecule to form the protonated product directly. Recent work by Cram[129] and Winstein and co-workers [130,123] have given greater support to the former mechanism. A close examination of the rate-determining activation process (viz., the heterolytic severance of the old bond), however, shows that these two mechanisms differ only in degree and not in kind. For a critical analysis of the kinetics of the solvolysis we need consider only the nature of the transition state for the primary ionic dissociation process.

For the solvolysis of benzyl tosylates the rate-limiting process

$$ArCH_2OTs \longrightarrow ArCH_2^+ + OTs^-$$

would be expected to be aided by electron-repelling substituents on the aromatic system. The extent of this effect is indicated by the large negative value obtained for rho ($\rho = -2.19$). As it has been pointed out by Swain and Langsdorf[95], the large negative value of rho indicates that in the transition state for the solvolysis of benzyl tosylate, a large formal charge is place on the aromatic system (that is to say, there is a large amount of ionic character to the old bond).

The magnitude of the bond-breaking process in the transition state depends not only on the aromatic system, but also on the nature of the departing group. Since the rho constant for the solvolysis of benzyl

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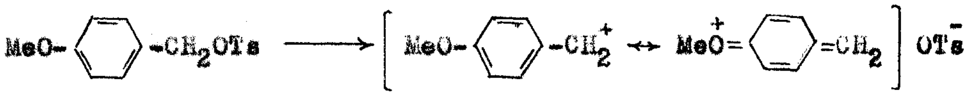
[129] D. Cram, J. Am. Chem. Soc., 74, 2159 (1952); and earlier papers.

[130] S. Winstein and K. Schreiber, ibid., 74, 2171 (1952); and earlier papers.

chlorides ($\rho = -1.33$) under similar conditions is found to be less than that of the tosylates ($\rho = -2.19$), the indication is that there is a more complete breaking of the old bond when tosylate is the departing group, and, therefore, a larger formal charge is placed on the aromatic system. The greater sensitivity of the tosylates to the bond-breaking process may be partly attributable to the more complete activation of the tosylate anion.

The deviation of such _para_-substituents as methoxy and methyl indicates that in addition to the large amount of ionic character to, and the normal resonance stabilization of, the transition state of the solvolysis of benzyl tosylates, there is an additional amount of ionic character (however small it may be) and resonance stabilization in the case of _p_-methoxy and _p_-methylbenzyl tosylate ascribable to the facile resonance interaction of these substituent groups with the electron-deficient aromatic system shown below.



The extent of this additional aid to the bond-breaking process (magnitude of _rho_) will depend greatly on the ability of the substituent group to form a π-molecular orbital with the aromatic ring. That the lowering of the activation energy and concomitant broadening of the plateau representing the transition state in the potential energy diagram for the system is due primarily to the type of _para_-substituents described is shown by the "normal" behavior of _m_-methoxy and _m_-methylbenzyl tosylate.

As pointed out by Swain and Langsdorf, there exists a continuously varying function of rho with each substituent. The value of rho for each substituent (or series of substituents) will depend greatly on the ability of each group to contribute to the stability of the ionic transition state.

The "abnormal" behavior of p-methoxy and p-methylbenzyl tosylate was predicted in part by the large mesomeric moment of p-nitroanisole[131], nucleophilic reactivity of anisole (toward bromine, for example[132]), and the large overlap integral of the O-C bond[133]. Hyperconjugation had been previously prescribed to account for the electron-releasing properties of the p-methyl-substituent by Baker and Nathan and others[134].

On the basis of the foregoing interpretation, it appears that there exists a large difference in the conjugative ability between the carbon - carbon double bond and triple bond. This difference may be deduced from the delta sigma values given in Table 29.

The much larger positive values of delta sigma for the p-styryl group than for the p-phenylacetylenyl group indicates that the conjugative ability of the double bond is much larger than that of the triple bond

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[131] R. Le Fevre, "Dipole Moments", Menthuen Co., Ltd., London, 1948; Trans. Faraday Soc., 30, Appendix IXX (1934).

[132] E. Huntress and S. Mulliken, "Identification of Pure Organic Compounds", J. Wiley and Sons, Inc., New York, N.Y., 1941, p. 526.

[133] R. Mulliken, J. Am. Chem. Soc., 72, 4493 (1950).

[134] V. Crawford, Quart. Revs., 3, 226 (1949).

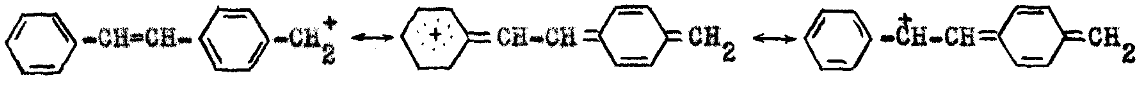
Table 29

Delta Sigma Values for Benzyl Tosylates

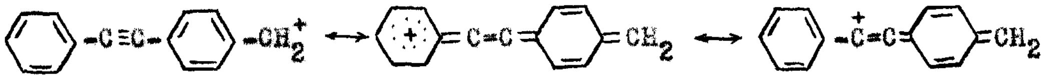
Substituent	$\sigma_{tosylate}$	σ_{acid}	$\Delta\sigma$
p-Methoxy	-2.0	-0.27	-1.7
p-Methyl	-0.63	-0.17	-0.46
p-β-Styryl	-1.0	-0.05	-1.0
p-Phenylacetylenyl	-0.03	+0.19	-0.22

with an electron-deficient aromatic system.

This effect shows up more clearly in the case of the ionization constants of the *para*-substituted acids previously listed in Table 27. The indication, then, is that the carbonium ion contributing to the transition state is more stable when it is ethylenic,



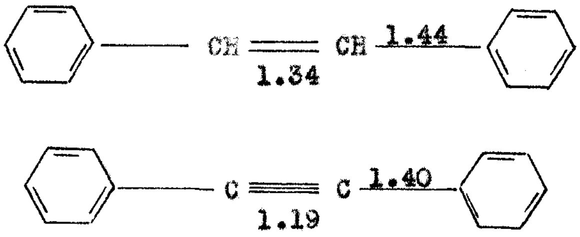
then when it is acetylenic,



This effect was predicted, in part, from the analysis of the photochemical excited states of the two systems by Walsh[105].

From a comparison of the π^{-1} ionization potentials of acetylene and ethylene (11.41 and 10.50 volts, respectively), it is evident that the *pi* electrons of acetylene are more firmly bound to the nucleus than the corresponding electrons of ethylene. The tighter binding of the *pi* electrons (*i.e.*, greater localization) of the triple bond can be attributed to the larger *s* character of the *sigma* bond (sp^2-sp) as compared to the *sigma* bond of the double bond (sp^2-sp^2). The larger localization of the *pi* bond in acetylenes is a direct result of the decreased "repulsion" between the *sigma* electrons and the *pi* electrons[105]. In particular the relative conjugative abilities of the triple bond and double bond would be expected to be manifested when the conjugation is at the expense of the delocalization of the *pi* electrons of the triple or double bond.

The preceding analysis of the conjugative aptitudes of the triple bond and double bond may also be made from a slightly different point of view. The bond distance in tolane and stilbene given below are reliable to within 0.01 A.[135]



Since the magnitude of the overlap of orbitals between adjacent atoms depends on the distance separating the atoms[136], one would expect from

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[135] J. Robertson, *Proc. Roy. Soc.*, *A164*, 436 (1938).
Y. Dyatkina and M. Syrkin, "Structure of Molecules and the Chemical Bond", Interscience Publishers, Inc., New York, N.Y., 1950, p. 180.

[136] A. Walsh, *J. Chem. Soc.*, 398 (1948).

only a consideration of the radial component of the orbitals that the *pi* bond of ethylenes will be weaker than that of acetylenes. The magnitude of this difference in energy may be calculated by the method recently published by Coulson and Altmann[137] for the compression energy required in the theoretical description of benzene.

The change in the character of the *sigma* bond may, thus, be invoked by both descriptions to account for the greater localization of the *pi* electrons in the triple bond than in the double bond. The decrease in *s* character of the *sigma* bond not only increases the delocalization of the *pi* electrons but also increases the bond lengths between the two atoms comprising the double and triple bonds. It is not entirely clear whether the two descriptions are equivalent, mutually dependent on one another or additive. The interdependence, equivalence or additivity of these effects is not explicit in the quantum mechanical formulation of the system.

The difference in the localization of the *pi* electrons in the double bond and triple bond is also apparent in the ionization constants of the *para*-substituted acids previously listed in Table 27.

In *p*-phenylacetylenylbenzoic acid the decreased repulsion between the *sigma* electrons and the *pi* electrons in the acetylenic acid has caused an increased ionization constant (with respect to benzoic acid) due to the increased *pi* bond order of the *alpha* bond (between substituted

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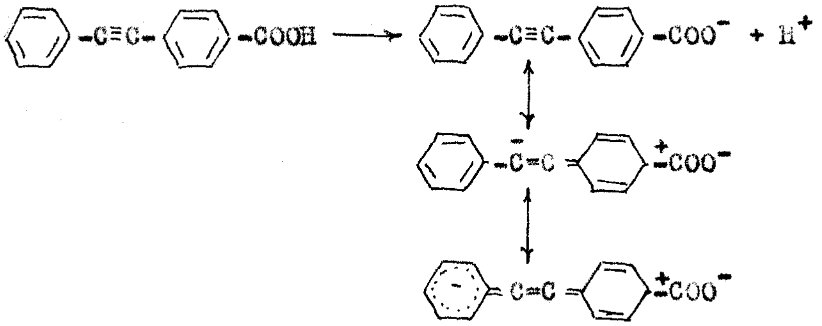
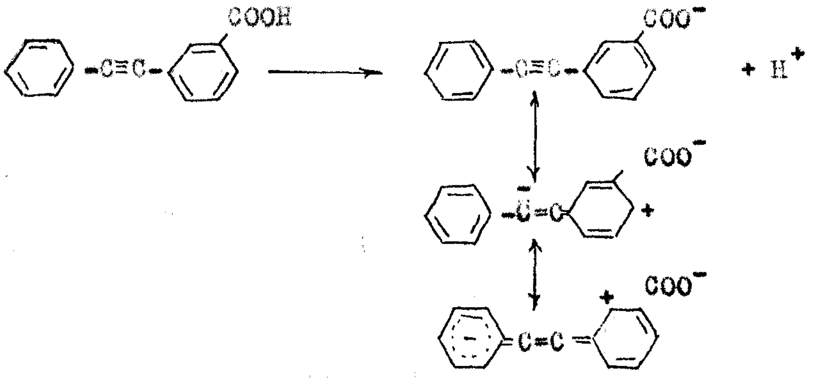
[137] C. Coulson and S. Altmann, *Trans. Faraday Soc.*, *48*, 293 (1952).

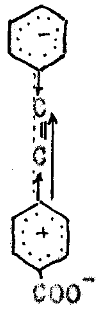
ring carbon and the substituent). It is to be noted that this increase in the bond order of the *alpha* bond is at the expense of the aromatic system. This type of interaction of the substituent with the ring is considered to be of a non-classical inductive effect operating on the *pi* bond system.

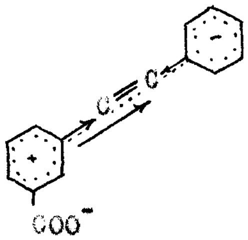


In *m*-phenylacetylenylbenzoic acid similar considerations as those proposed for the *para*-isomer lead to the description given below.



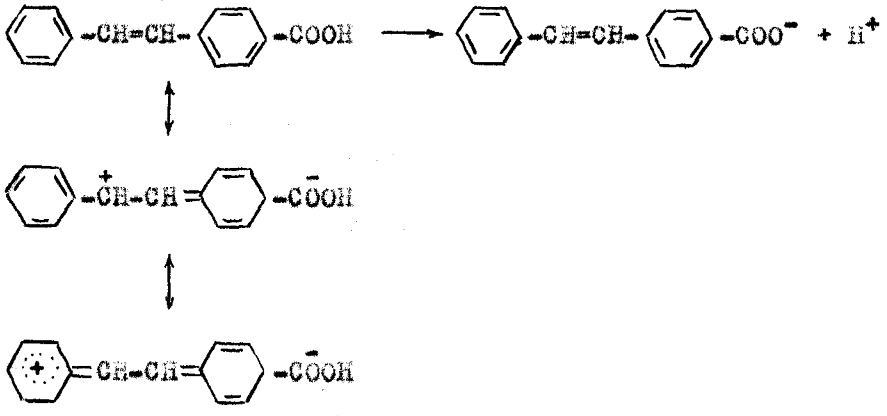
In addition to the *pi* bond perturbations that have been invoked for the interaction of an acetylenic substituent with the aromatic ring there is another factor which must be taken into account. If one considers the constitution of the *sigma* bond between the acetylenic side chain and the aromatic ring as consisting of an sp^2 orbital of benzene and an sp orbital of acetylene then the larger s character to the acetylene portion of the bond indicates the unsymmetrical distribution of the electrons in the bond, *i.e.*, the existence of a dipole oriented in the direction shown below.





The situation in acetylenic-substituted benzenes can be adequately described on the basis of a dipole compounded of two effects reinforcing one another. The effect of an acetylenic substituent, thus, appears to be similar to nitro or cyano function, which have been treated theoretically by Westheimer[29] and Sarmousakis[30].

In the case of the corresponding ethylenic compounds the repulsion between the *sigma* electrons and the *pi* electrons may cause a decrease in the *pi* bond order in the *beta* link (comprising the double bond) and, therefore, an increase in the order of the *alpha* bond. This effect will be felt especially when the aromatic system makes a demand for electrons, as is the case in the undissociated *p*-β-styrylbenzoic acid shown below.

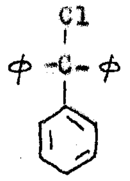


That this effect is real is apparent from the negative value of the *sigma* constant (which indicates that the acid is weaker than benzoic) for the *p*- -styryl group.

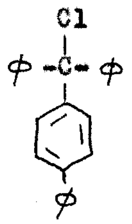
The difference in the ionization constants of the *para*-substituted acetylenic acid and the corresponding ethylenic analog may, thus, be partly attributed to the greater localization of the *pi*-electrons in the triple bond. It should be noted the *sigma* bond of the *alpha* link in the ethylenic compounds is considered not to be polarized since the component orbitals are equivalent (sp^2-sp^2).

The ionization constant of *m*-β-styrylbenzoic acid is shown to be larger than that of benzoic acid, indicating that the *sigma* constant of the β-styryl group has suffered a change in sign in going from the *para* position to the *meta* position. That the *m*-β-styryl group should have a positive *sigma* constant is not apparent from a consideration such as that given previously.

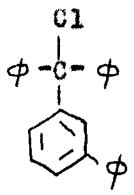
This situation is akin to that attributed to the *m*-phenyl group. It is not uncommon to find statements in the literature attributing a positive inductive effect to the *m*-phenyl group. Thus, the increasingly large ionization constants of acetic, phenylacetic and diphenylacetic have been rationalized on these grounds[99]. Recent investigations by Lichtin and Glazer[138] of the ionization constants of biphenylyldiphenylchloromethanes in sulfur dioxide yielded the following values for the equilibrium constants:



4.03×10^{-5}



23.2×10^{-5}



3.12×10^{-5}

Keiffer and Rumpf[139] have measured the basicity constants of substituted aniline and have reported them to be as follows,

aniline	4.57
m-phenylaniline	4.18
p-phenylaniline	4.29

The data on the saponification rates of phenyl-substituted ethyl benzoates is not complete. In the case of the saponification of ethyl *p*-phenylbenzoate in 50% aqueous ethanol[140], the value of the rate constant corresponds to a value of +0.015 for the *sigma* constant, using the *rho*

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[138] N. Lichtin and H. Glazer, *J. Am. Chem. Soc.*, *73*, 5537 (1951).

[139] F. Keiffer and P. Rumpf, *Compt. rend.*, *230*, 1874 (1950).

[140] K. Kindler, *Ann.*, *452*, 105 (1927).

constant evaluated by Hammett[122] to be 2.50. Similar studies by Tommila[141] in 50% aqueous acetone lead to a sigma value of -0.015 for the p-phenyl group. The average sigma value for p-phenyl is apparently zero. The corresponding sigma values for m-phenyl are, unfortunately, unavailable. Further work along these lines is contemplated.

An examination of the sigma values given by Hammett[122] reveals that the data are not completely reliable.[142]

From an inspection of the data of Lichtin and Glazer and Keiffer and Rumpf there appears to be an unresolvable anomaly. Thus, if we attribute to the p-phenyl group a large ability to stabilize the carbonium ion resulting from the ionization of the chloromethane, and attribute a positive inductive effect to the m-phenyl group to account for the smaller ionization constants of the m-biphenylylchloromethane as compared to trityl chloride, then the order in the basicity constants of the substituted anilines should be opposite to that reported above. A probable resolution of this difficulty may lie in the reexamination of the ionization constant of p-phenylaniline.

It appears, thus, from the preceding discussion that a conceivable rationalization of the effect of the m-phenyl or m-β-styryl group lies in attributing a certain amount of pi bond order to the bond linking the substituent to benzoate anion or aniline of the type prescribed for m- and p-phenylacetylenylbenzoic acid. In p-β-styryl benzoic acid this effect is apparently over-shadowed by the resonance stabilization of the

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[141] E. Tommila, L. Brehmer and H. Elo, Ann. Acad. Sci. Fennicae, Ser. A59, No. 9, 3 (1942).

[142] G. Burkhardt, D. Jenkins and C. Horrex, J. Chem. Soc., 1654 (1936).

free acid. The foregoing analysis is reasonable on the basis of the very small effects that are found experimentally (sigma constants of m-β-styryl and p-β-styryl are +0.025 and -0.050, respectively).

At this point we must pause and attempt to understand more fully the nature of the deviations from the Hammett equation that we have observed with respect to the solvolysis of benzyl tosylates and chlorides. In particular it is necessary that we deliberate on the limitations involved in the foregoing interpretations of the deviations which are exhibited by such substituents as p-methoxy, p-methyl and p-β-styryl on the solvolysis of benzyl tosylates. Thus, a discussion of the continuously varying rho function for these substituents and accompanying speculation as to the nature of the transition state for this reaction (with respect to the bond-breaking process) presumes fundamentally that the system in question obeys the Hammett relationship. That this is not always the case is pointed out subsequently. It is our desire to rationalize the anomalous behavior with the fundamental assumptions inherent in the Hammett equation.

The limitations of the Hammett equation have been explicitly enounced[143]. In brief, for the process,

$$\underbrace{RX_{aq} \xrightleftharpoons{K^*} RX^*_{aq} \longrightarrow}_{\xrightarrow[k_1]{}} R^+_{aq} + X^-_{aq}$$

the rate of the reaction is given by the rate-limiting step,

$$k_1 = \frac{kT}{h} K^*$$

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[143] L. Hammett, ref. 60, p. 194.

where the asterisk represents the transition state, and the term, K^*, is the constant for the equilibrium between the reactants and the activated complex. The free energy of activation is given by,

$$\Delta F^* = -RT \ln K^* = \Delta E_p^* + \Delta E_z^* - RT \ln f_{RX^*}/f_{RX} \qquad (1)$$

and the heat of activation by,

$$\Delta H^* = RT \frac{d \ln K^*}{dT} = \Delta E_p^* + \Delta E_z^* + RT^2 \frac{d \ln f_{RX^*}/f_{RX}}{dT} \qquad (2)$$

where ΔE_p^* and ΔE_z^* represent the difference in the potential energy and zero point energy of the reactants and the activated complex, respectively. The terms, f_{RX^*} and f_{RX}, represent the partition functions of the activated complex and the reactants. The other symbols have their usual thermodynamic significance.

As Hammett points out, the direct correlation of rates with structural properties of the system is feasible when an analysis can be made in terms of potential and kinetic energy changes implied in the equations above. Moreover, the interpretation of the effect of substituents on a molecule must be made with respect to the potential energy change (the quantity that measures the internal energy change of the molecule). The correspondence between the rate of the reaction and this potential energy change occurs only in limited cases.

If one considers the fundamental thermodynamic equation,

$$\Delta F^* = \Delta H^* - T\Delta S^* \qquad (3)$$

then a simplifying assumption $\Delta S^* = 0$ leads to $\Delta F^* = \Delta H^*$. From equations

(1) and (2) this result leads to $\ln f_{RX^*}/f_{RX} = 0$ and $\frac{d \ln f_{RX^*}/f_{RX}}{dT} = 0$ or $f_{RX^*} = f_{RX}$ at all temperatures. The constancy of the partition functions of the reactant and the activated complex implies the change in zero point energy is zero. Thus, the simplifying condition $\Delta S^* = 0$ leads to

$$\Delta F^* = \Delta H^* = \Delta E_p^* \quad . \tag{4}$$

For a series of similarly constituted compounds, a and b,

$$\Delta F_a^* - \Delta F_b^* = -RT \ln \frac{K_a^*}{K_b^*} = -RT \ln \frac{k_a}{k_b} = \Delta E_{pa}^* - \Delta E_{pb}^* \tag{5}$$

or

$$\ln k_a - \ln k_b = c\delta\Delta E_{pab}^* \quad , \tag{6}$$

which is in the form of the Hammett equation. The value of $c\delta\Delta E_{pab}^*$ was taken by Hammett to be measured by the variation in the ionization constant of benzoic acid with substituents.

The correlation of rates with the potential energy change was, then, made possible only by the simplifying assumption $\Delta S^* = 0$. In the reactions of <u>meta</u> and <u>para</u>-substituted benzene derivatives it has been found experimentally that the ΔS^* of many reactions is actually zero, very close to it, or constant.

The constant terms of the Arrhenius equation,

$$k = PZe^{-Ex/RT} \quad , \tag{7}$$

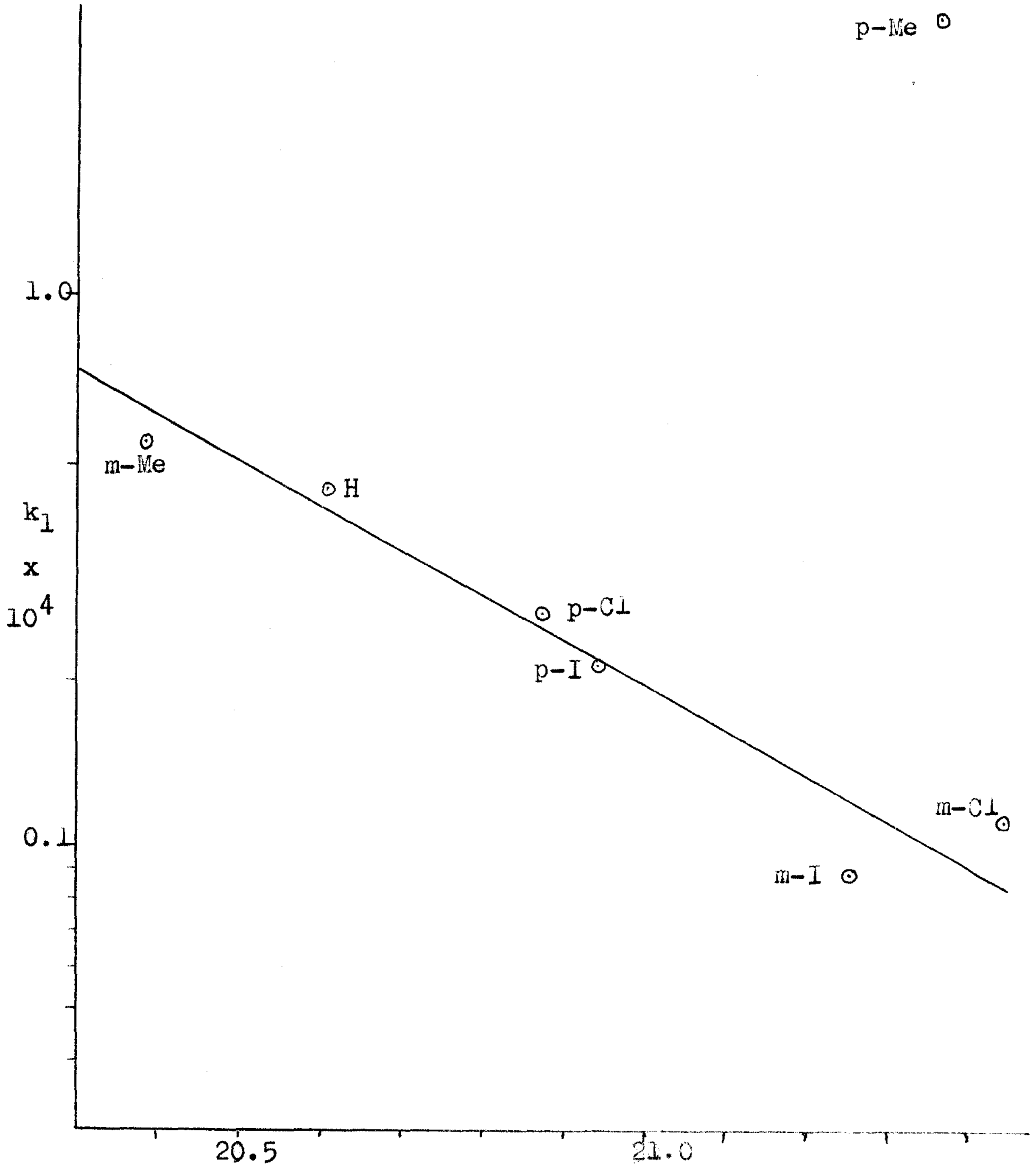
where E_x is the empirically determined activation energy, have been related to the entropy changes according to the formula,

$$\Delta S_a^* - \Delta S_b^* = R \ln \frac{P_a Z_a}{P_b Z_b} \quad . \tag{8}$$

Accurate measurements of E_x have shown that its variation with ln k is very nearly RT in many cases, as expected from equation (7). Hammett points out that it is in just such cases as this that the equation has been found to be most applicable.

The solvolysis of benzyl chlorides is one of the several reactions which have been reported to show nonconstant ΔS^* terms. However, a close examination of the data of Olivier, on the solvolysis of benzyl chlorides, shows that indeed there is a limited linear correlation between E_x and ln k as shown in Figure 12. This indicates a constancy in PZ terms for several members of the series. Since the activation energies were determined at only two temperatures, a small discrepancy in its value must be overlooked. A striking misbehavior is apparent in the case of p-methylbenzyl chloride, a misbehavior in the Hammett relationship. The large rate constant for the solvolysis of this compound appears not in the energy of activation but in the entropy terms. Thus, according to the basic hypothesis, it is not inexplicable to find p-methylbenzyl tosylate exhibiting an anomalous behavior.

In the previous discussions, the variation of the rho constant for the solvolysis of benzyl tosylates and chlorides with substituents, such as p-methyl and p-methoxy, was considered solely on the basis of the lowering of the activation energy due to the stabilization of the ionic



Activation Energy (kcal./mole)

Solvolysis of Benzyl Chlorides vs. Activation Energy

Figure XII

transition state. Since we know that S^* is no longer zero for the reactions of these particular compounds, it is necessary to determine to what extent the rho constant can be utilized to interpret the solvolytic processes for these compounds. As will be subsequently shown, a necessary condition for the qualitative discussion of the rates on the basis of activation energies alone is that there exists a correspondence between the resonance energy and the activation entropy.

If one considers the process,

$$\begin{tikzcd}
RX_{aq} \arrow[r, shift left, "K^*_{aq}"] \arrow[d, shift left] & RX^*_{aq} \arrow[l, shift left] \arrow[r] \arrow[d, shift left] & \text{products} \\
RX_g \arrow[u, shift left, "s_1"] \arrow[r, shift left, "K^*_g"] & RX^*_g \arrow[l, shift left] \arrow[u, shift left, "s_2"'] &
\end{tikzcd}$$

where aq, g and s represent the solution, gas and solvation process, respectively, then

$$F^*_{aq} = F^*_g + F_s$$

where $$F_s = F_{s_2} - F_{s_1}$$

and $$F^*_{aq} = H^*_g + H_s - T(S^*_g + S_s) .$$

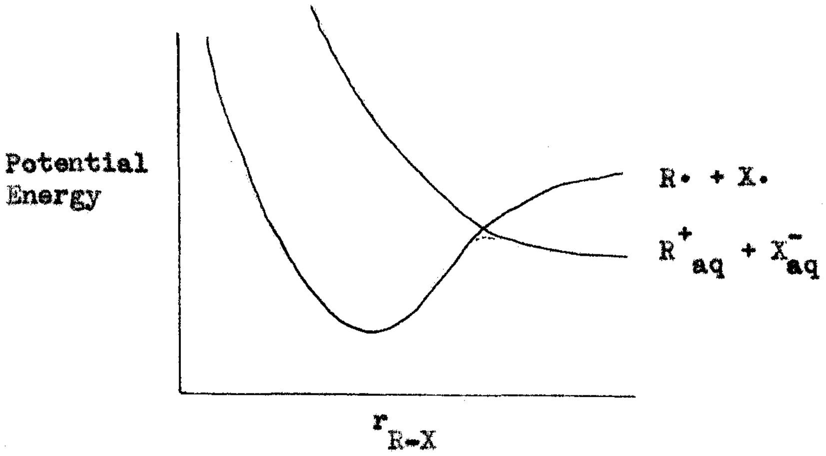
If one assumes that for a series of compounds, i and j, the difference in the heat of solvation between two unionized reactants is zero, i.e.,

$$H_{1_i} - H_{1_j} = 0$$

then $H^*_g + H_s$ is approximated by the heat of activation. The difference for a series is then,

$$(H_g^* + H_s) = E_x - (D + I - L),$$

where D is the heat of dissociation of R-X bond in the gaseous process. I is the ionization potential of R, and L is the heat of solvation of R^+. Diagramatically this is represented below.



For a series of similar compounds the values of (D + I) will depend to a large extent on the resonance stabilization of the corresponding free radical and carbonium ion[144]. In general, the greater the stabilization of the carbonium ion, the lower will be the energy for the overall dissociation process. The value of L for a series of compounds will depend on the geometrical configuration and also the distribution of the charge in the carbonium ion. Evans[145] has shown that the difference in the

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[144] R. Ogg and M. Polanyi, Trans. Faraday Soc., 31, 604 (1935); E. Baughan, M. Evans and M. Polanyi, ibid., 37, 377 (1941).

[145] A. Evans, ibid., 42, 719 (1946); "Reactions of Organic Halides in Solution", Manchester University Press, Manchester, Great Britain, 1946.

solvation energy of t-butyl carbonium ion and methyl carbonium ion (if one assumes the charge concentrated on the central carbon) lies in the distance of closest approach of the dipolar solvent molecules to the two ions, being larger for methyl carbonium ion than for t-butyl carbonium ion. The energy of the ion-dipole interaction, will, moreover, depend on the magnitude of the charge. If one assumes that the geometry of the substituted benzyl carbonium ions are approximately the same, the difference in the solvation energy of a series of these ions will vary inversely as the diffusion of charge on each species. From the concept of resonance, the ion possessing the greatest amount of resonance stabilization will be expected to show the largest diffusion of charge (attributable to the number of canonical forms that can be considered for the ion) and, therefore, the smallest energy of solvation.

The effect of the stabilization of the carbonium ion (in the transition state) on the activation energy is shown in two opposing manners. On the one hand, resonance stabilization of the ionic forms leads to the lowering of the internal energy and, on the other hand, leads to a smaller energy of solvation of the quasi-ion. The combined effects are not predicable. If one assumes that the internal energies in the ground states of all the species are the same (_i.e._, the absence of resonance interactions), the effects we have mentioned may be seen in the diagram below.

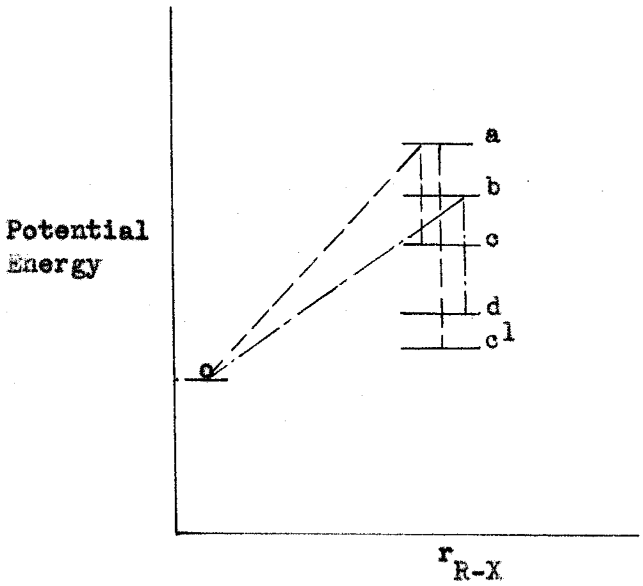
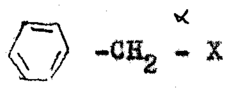


Figure XIII Potential Energy Diagram

The gaseous process oa or ob predicts that state a will be higher energy than state b, if B^+ represents the ion possessing a larger amount of resonance energy. There is at yet no reliable method of predicting the position of c or c^1, with respect to d, where oc (oc^1) and od represent the overall activation energies.

One may assume with a fair amount of confidence that the gas phase process will involve no difference or very little in the entropies of activation for a series of similar compounds. This assumption seems to be justified from a survey of the extensive correlations of the Hammett equation. This internal entropy of activation can arise from the differences in the change in the vibrational and the rotational partition functions between the activated state and the ground state for a series of compounds as the function of the alpha bond.



Thus, one would expect this difference, if present, to show up in the saponification rates of ethyl phenylacetates and in the ionization constants of phenylacetic acid. The adherence of these compounds to the Hammett relationship (r = 0.07 and 0.03, respectively) indicates that this difference is small. That the entropy terms consist for the most part of the solvation entropy was also considered by Evans[146]. The dependence of the entropy of solvation on the structure of R was discussed on the basis of following assumptions:

(i) In aqueous solvents the solvation entropy is due to the water molecules.

(ii) The change in entropy as a function of the size of the ion was determined by the extent of the "freezing" of these water molecules in the first solvation shell.

(iii) For an alpha substituent the amount of "freezing" of the water molecules will vary inversely as the size of the substituent. Calculations made on this basis, assuming reasonable values for the structural parameters, yielded results which were in qualitative agreement with the experimentally obtained entropies of activation. The values of the entropies of activation, consisting for the most part of solvation terms, may be obtained by studying the solvolysis of the benzyl tosylates in various aqueous media at different temperatures making the isodielectric

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[146] A. Evans and S. Hamann, Trans. Faraday Soc., 47, 25 (1951).

correction.

The dependence of the entropy of solvation on the nature of the intermediate carbonium ion is in the same sequence as the resonance stabilization of the gaseous quasi-ion and in opposite sequence to the energy of solvation of this ion. Thus, one would expect that in the most favorable case an increase in entropy of solvation on an ion would correspond to an overall decrease in the activation energy. It must be realized that all qualitative conclusions drawn are valid only in those cases in which solvation effects and resonance effects are considered in the overall solvolytic process. It has been assumed that internal kinetic energy differences for a series of compounds are negligible. A schematic representation of the entropy variation is shown below.

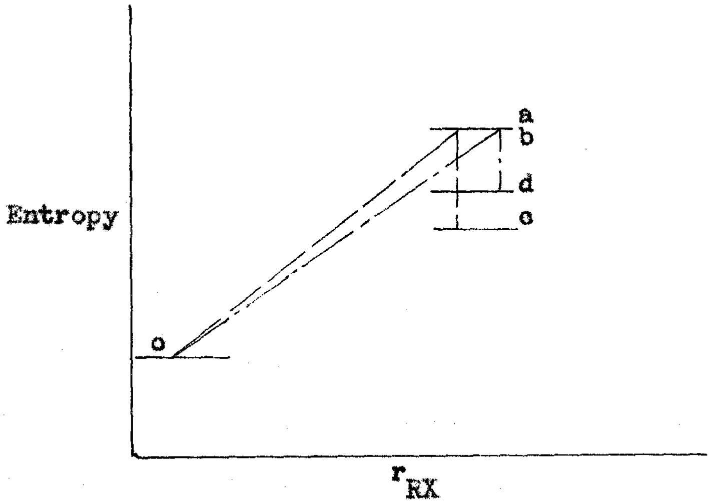

Figure XIV Entropy Diagram

The entropy of activation <u>oc</u> is considered to be smaller than <u>od</u> for all cases. The entropy of activation for the gaseous process is the same for both cases. The overall entropy of activation however, is not, oc being smaller in all cases than od.

The consideration of the above analysis indicates that the direct correlation between rates (and free energy of activation) and the experimental activation energy is not valid in the general case, because a direct correlation between activation energy and entropy, i.e., proportionality of ΔS^* with $-\Delta H^*$ (considered from $\Delta F^* = \Delta H^* - T\Delta S^*$), does not always exist. A more reasonable quantity which can be invoked is the resonance energy of the quasi-carbonium ion. Figures 13 and 14 show that an increase in resonance energy (ab in Figure 13) corresponds to a decrease in activation entropy (dc in Figure 14).

It is this qualitative correspondence between entropy terms and resonance terms that enables us to correlate rho with the configuration of the transition state in the cases in which the ΔS^* term is not a constant. Since the entropy and resonance energy terms vary in the opposite manner (i.e., the difference in the increase in the activation entropy and the difference in the decrease in resonance energy) the consideration of rates on the basis of one term, usually the resonance energy, is qualitatively valid.

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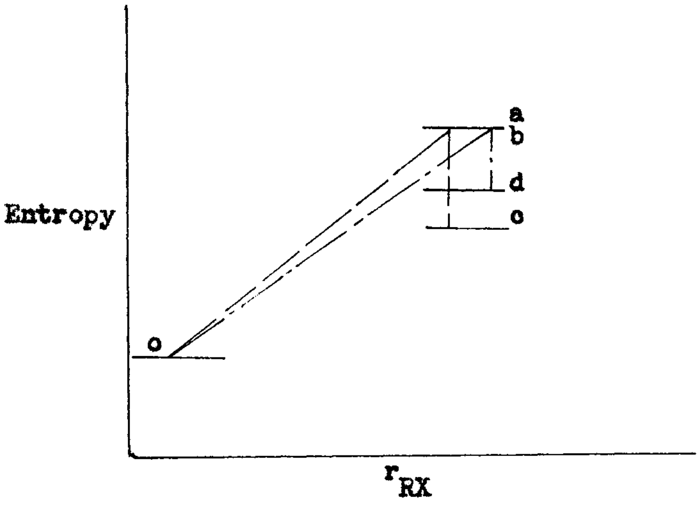

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