in finite difference approximation, and one illustration has been given previously (for the case depicted in Fig. 3c) in differential form.[3]

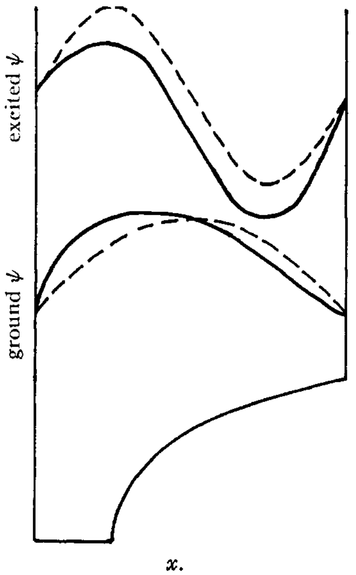
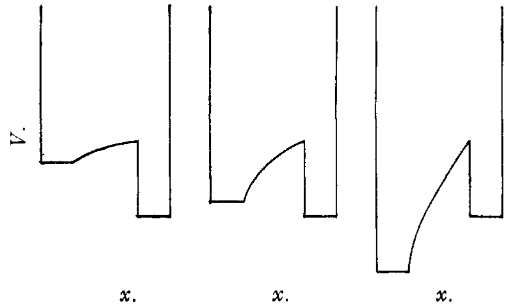


Fig. 4.—Changes in ψ as a result of charge separation.

It is now possible very simply to investigate the effect, neglected in Part I, of departures from the assumption $Q_{\rm N} = Q_{\rm C} = Q_{\rm O}$. For if a stabilizing ΔQ on the right is introduced, Fig. 3a say, can be converted in essence into Fig. 2b. Moreover, depending upon the dielectric constant, a single substance can be altered in the remarkable fashion demonstrated by Brooker[1] (Fig. 5). As D is *decreased* (5*a* to 5*b*) it is seen that $\lambda_{\max.}$ moves to longer wave lengths, an inversion of the "normal" behavior. Continued decrease in D (5*b* to 5*c*) finally gives the normal effect, a shift of $\lambda_{\max.}$ to shorter wave lengths.



a, high D, inverted behavior.
b, intermediate D, symmetrical behavior.
c, low D normal behavior.

Fig. 5.—Changing dielectric constant in a model substance which is considered to represent a strongly polar merocyanine.

The writer wishes to thank Dr. L. S. Brooker for the opportunity of studying the interesting experiments on the merocyanine dyes prior to publication.

SEATTLE, WASHINGTON RECEIVED APRIL 11, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF WASHINGTON]

Internal Dispersion Forces. The Polyenes

BY WILLIAM T. SIMPSON

Internal dispersion forces in polyenes (butadiene, hexatriene, etc.) are sufficient to account qualitatively for observed alternations in bond lengths, positions of first singlet–singlet absorption bands, and resonance energies. The question of the relative importance of conjugative interaction and internal dispersion effects is therefore raised. Configurational interaction in unsaturated compounds may be explainable in part as arising from internal dispersion forces.

Introduction

Bond distances in molecules can be considered to represent a compromise between attractive and repulsive forces of various sorts. Included in the effects which counterbalance the bonding tendency of the center carbon–carbon link in *n*-butane are exchange repulsions[1] between perfectly paired electrons in the bonds centering on the 2- and 3-carbon atoms. This repulsion is analogous to the repulsions encountered in the close approach of "closed shell" atoms or molecules.

Part of the attraction between the left and right region of the molecule is undoubtedly due to dispersion forces, *i.e.*, to the tendency for instantaneous dipoles in the two regions to be in phase. A change in the polarizability of the regions such as is brought about in the abstraction of four hydrogens to produce butadiene still leaves the same number of electron pair bonds on each of the center carbons, and so may be considered to affect the attractive force, with only a second order influence on the repulsion. Thus some of the observed shortening of the middle link in butadiene may be attributed to an *internal* dispersion force.

In order for such a force to exist, it is necessary that the individual double bonds be polarized. If the bonds are compared with isolated double bonds, this polarization implies a mixing with excited states. It is seen that if the excited states of a double bond are considered to represent a weakening in binding energy, then a natural result of the dispersion force shortening of the 2,3-bond in butadiene is a lengthening of the double bonds. The question as to the relative importance of conjugation effects and internal dispersion forces then arises.

A Procedure for Calculating Energies

It might be thought that a comparison of the importance of conjugation and internal dispersion forces could be made by an appeal to π-electron spectra, which in the case of so-called conjugated polyenes are considered to be fairly well understood on the basis of a pure conjugation model.[2] In

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[1] J. H. Van Vleck and A. Sherman, *Rev. Mod. Phys.*, **7**, 167 (1935) eqn. (40) *et seq.*

[2] *E.g.*, the valence bond method or the simple LCAO molecular orbital method.

order to investigate this point, a simplified calculation of energy levels for polyenes[3] will be made on the basis of a pure dispersion force model. This calculation is in some ways comparable to a valence bond calculation. In the latter, the individual CH radicals from which polyenes are built are removed to infinity while the molecular symmetry is kept constant, and wave functions are constructed which are quite accurate at large inter-nuclear distances. These wave functions are then used to describe molecular properties at the true internuclear distance in terms of an *atomic* parameter Q and an interaction parameter α, and with the neglect of other interaction parameters which may, in fact, be not quite negligible. In the present calculation the individual *double bonds* are considered as pulled away from one another, wave functions are constructed which again are, in principle, accurate at large distances of separation, and these functions are then used at the true distances.

As a consequence of this choice of the functions, overlap between wave functions describing the loosely bound or π-electrons belonging to individual double bonds is neglected. The elimination of these overlap effects is equivalent to the prevention of electron exchange between the double bonds. It can perhaps be described as elimination of conjugative interaction or of conjugation.

From the standpoint of time-dependent perturbation theory, an individual double bond in a polyene is in a non-stationary state such that an allowed optical transition is considered to be in the process of taking place. This tends to raise the energy but produces a large separation of charge which fluctuates with the excitation frequency. A similar fluctuation in adjacent double bonds, characterized by the same frequency, leads to an *interaction* between the bonds, and brings about a net lowering of the ground state energy for a polyene molecule. The stabilization of the ground state is a maximum for some particular value of the degree of excitation of a double bond, to be determined in a variation calculation.

The sth trial function ψ_s for a polyene is written as a product of terms each of which refers to the state of a double bond. For example, for three double bonds, as in hexatriene, a typical function is

$$\psi_s = \psi_{s,12}{}^\dagger\ \psi_{s,34}\ \psi_{s,56}$$

The description of a particular double bond is arbitrarily restricted to two states: ground and excited, corresponding to the 1630 Å. transition in ethylene[4] and represented by the absence or presence of a dagger.[5] Thus, in the example, the double bond between carbons 1 and 2 is considered to be excited. Then the mathematical statement of the interaction described qualitatively above is that two functions ψ_s and ψ_t interact if at adjacent double bonds, ij and kl, one and only one of the bond functions $\psi_{s,ij}$ and $\psi_{t,ij}$, and also of $\psi_{s,kl}$ and $\psi_{t,kl}$, are marked with a dagger. For example, ψ_s above interacts with

$$\psi_t = \psi_{t,12}\ \psi_{t,34}{}^\dagger\ \psi_{t,56}$$

because the 1,2-bond is marked with a dagger in one and only one of the interacting functions (giving rise to a transition electric moment) while at the same time an adjacent bond, the 3,4-bond, is also undergoing transition.

This interaction rule is accurate for a static van der Waals or internal dispersion force at large distances. To see this, we recall the form of the interaction term in the Hamiltonian: (the consideration of oscillators in a line simplifies the treatment)

$$H_{\text{int}} = -2X_LX_Re^2/R^3$$

where R is the distance between oscillator centers, and X_L and X_R are coördinates of the electrons undergoing transition in the left and right regions (the "optical electrons"). It is seen from the nature of the term which represents the interaction that the interacting electronic wave functions for the bond on the left have to be even and odd so that their product is an odd function (local symmetry); however, this condition fails to give a non-vanishing matrix element unless the interacting wave functions for the right bond are also one even, the other odd. The $1/R^3$ dependence gives a $1/R^6$ dependence for the potential energy, because the ground state stabilization energy is approximately proportional to the square of the matrix element. It is believed that although a $1/R^6$ proportionality no longer holds at comparatively short distances, still the rule for the interaction as stated in the preceding paragraph may have a larger region of validity.

Butadiene.—It is now possible to carry out a linear variation calculation for, say, any all s-*trans*-polyene,[6] for which the interaction parameter between adjacent (*e.g.*, 1,3) double bonds would be expected to be constant, and between non-adjacent double bonds, to be zero. This is done first for butadiene. The parameter is to be evaluated from the butadiene singlet–singlet absorption at 2090 Å.[7,8] The energies of the first two states of individual double bonds are E_1 and E_2 with $E_1 \rightarrow E_2$ leading to absorption at 1630 Å. Then if the interaction is δ, the secular equation minimizing the energy of

$$\psi = \sum_{i=1}^{4} c_i\psi_i$$

for butadiene is

$$\begin{vmatrix} 2E_1 - W & 0 & 0 & \delta \\ 0 & E_1 + E_2 - W & \delta & 0 \\ 0 & \delta & E_1 + E_2 - \mathrm{W} & 0 \\ \delta & 0 & 0 & 2E_2 - W \end{vmatrix} = 0$$

Here

$$\begin{aligned} \psi_1 &= \psi_{1,12}\quad \psi_{1,34} \\ \psi_2 &= \psi_{2,12}{}^\dagger\quad \psi_{2,34} \\ \psi_3 &= \psi_{3,12}\quad \psi_{3.34}{}^\dagger \\ \psi_4 &= \psi_{4,12}{}^\dagger\quad \psi_{4,34}{}^\dagger \end{aligned}$$

The middle block has the solution

$$W = E_1 + E_2 \pm \delta$$

and the remainder the solution

$$W = E_1 + E_2 \pm ((E_2 - E_1)^2 + \delta^2)^{1/2}$$

so that the long wave length band corresponds to

$$\Delta W = \delta + ((E_2 - E_1)^2 + \delta^2)^{1/2}$$

The experimental value (measurements refer to band maxima) $E_2 - E_1 = 7.60$ e.v. (1630 Å.) for ethylene, when combined with the experimental value 5.93 e.v. (2090 Å.) for butadiene, gives

$$\delta = -1.91 \text{ e.v.}$$

The "resonance energy" of butadiene is defined as the negative of the difference between the energy of the lowest level and an hypothetical energy obtained from it by setting $\delta = 0$

$$R.\ E. = 2E_1 - [E_1 + E_2 - ((E_2 - E_1)^2 + \delta^2)^{1/2}]$$

which is 0.24 e.v. (5.5 kcal./mole), a reasonable value.[9]

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[3] Related treatments have been given by W. Kuhn, *Helv. Chim. Acta*, **31**, 1780 (1948) (references to earlier work are given in this paper) and by G. N. Lewis and M. Calvin, *Chem. Revs.*, **25**, 273 (1939).

[4] W. C. Price and W. T. Tutte, *Proc. Roy. Soc.* (*London*), **A174**, 207 (1940).

[5] This restriction to two states introduces a *molecular* parameter, the energy difference, which may be considered to be analogous to the atomic parameter, the Coulomb integral Q, in the valence bond method.

[6] s-*trans* is Mulliken's notation for *trans* with respect to single bonds.

[7] R. S. Mulliken, *Rev. Mod. Phys.*, **14**, 265 (1942). This paper contains a discussion of dienes based on a pure conjugation model, the LCAO, MO method.

[8] It is assumed, after Mulliken, that the 2090 Å. band is associated with the s-*trans* configuration. This assignment cannot be considered to be unequivocal.

[9] The estimated experimental resonance energy is 3.6 kcal./mole (G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith and W. E. Vaughan, THIS JOURNAL, **58**, 146 (1936)). The valence bond and LCAO values are somewhat higher, 11 and 6 kcal./mole, respectively. (See G. W. Wheland, *ibid.*, **63**, 2025 (1941), and references given there.)

The wave function (approximately normalized) for the ground state turns out to be $(-R.E./\delta = 0.125)$

$$\psi_g = \psi_1 + (-R.\ E./\delta)\ \psi_4$$

while that for the first excited state is

$$\psi_e = 2^{-1/2}\,(\psi_2 + \psi_3)$$

This excited state function implies correlations in the electronic motion (for s-*trans*-butadiene) of such a nature that the transition from the ground state is allowed.[10] The correlations in the lowest excited state of the s-*cis* isomer might reasonably be expected to be the same (same sign of δ), which leads to a predicted smaller intensity due to a partial cancellation of dipole moment vectors. The electric vector in the direction (z) in the plane of the molecule perpendicular to the 2,3-bond direction (x) is inactive in the s-*cis* compound while the perpendicular vector (x) is active to an extent approximately equal to $(\sin 30°)^2$ = one-fourth that for the s-*trans*-molecule. The higher energy transition to $\psi_{e'} = 2^{-1/2}\,(\psi_2 - \psi_3)$ is allowed (z) for the s-*cis* but completely forbidden for the s-*trans*.

These intensity predictions are similar to the ones which have been made on the basis of a conjugation model.[7] They can be stated more formally with the aid of group theory. The transformation properties of an excited double bond are taken to be given by the assignment of the upper state of ethylene to B_{3u} (D_{2h}). The electronic states of butadiene according to the present method are then, in order of increasing energy: (s-*trans*, C_{2h}) A_g, $B_u(x)$, A_g, A_g; and, (s-*cis*, C_{2v}) A_1, $B_1(x)$, $A_1(z)$, $A_1(z)$.

The position of the second transition is calculated to lie $-2.00\ \delta$ above the first (1270 Å.) and here LCAO theory with overlap considered may constitute a much better approximation (computed, 1530 Å.; probably observed, 1730 Å.).[7]

Hexatriene and Higher Members.—It is possible, using the same secular equation technique, and δ obtained from the butadiene spectrum, to predict energy levels for hexatriene. The eight solutions of the secular equation in e.v. are

$$W - 2E_1 - E_2 = \\ -8.08,\ -2.91,\ 0,\ 2.43,\ 5.17,\ 7.60,\ 10.52,\ 15.69$$

The longest wave length singlet–singlet absorption is calculated to occur at 2400 Å. (observed 2570 Å.)[11] and the resonance energy to be 11.1 kcal./mole.[12] The comparison between the calculated and observed values of the transition energies of polyenes has the undesirable feature that *cis–trans* isomerism equilibria have not been measured.[13] As an illustration, the comparatively long wave length absorption of cyclohexadiene (2490 Å.) indicates that the spectra of s-*cis* and s-*trans*-butadiene may be quite different.

In working out the transition energies for octatetraene and higher homologs, the approximation is made that the mixing of multiply-excited states (states in which more than one bond is excited, as ψ_4 above) gives about the same increment of stabilization to the ground and first excited states, and so can be neglected. This leads to a zero ground state resonance energy; and, for the upper state, to a series of energies which are $E_2 - E_1$, added to a constant, β, times the lowest roots of successive members of a simple family of determinantal equations

$$\begin{vmatrix} x & 1 & 0 & \\ 1 & x & 1 & \\ 0 & 1 & x & \\ & & & \ddots \end{vmatrix} = 0$$

The first excited state energies are, starting with ethylene, respectively, $E_2 - E_1 - 0$, -1.000β, -1.414β, -1.618β, -1.732β, ..., -2.000β (limiting value).[14] If β is chosen so as to match the calculated transition energy for hexatriene, the absorptions are, respectively, (1630), 2110, (2400), 2580, 2690, . . ., 2990 Å. (limiting value). The characteristic convergence of absorptions in vinylogous polyene series is thus nicely accounted for.

Estimate of the Interaction Energy

It is necessary to treat the dispersion force not as an interaction between idealized point dipoles but rather as one between monopoles. The necessity of employing this approach has been discussed by London.[15] In order to obtain an estimate of the energy quantities involved, we shall adopt a particular description of the 1630 Å. transition in ethylene. The transition is pictured, after Mulliken, as involving an electron jumping between molecular orbitals described as linear combinations of $2p_\pi$ atomic orbitals. The first excited state wave function for butadiene serves conveniently to provide an estimate of the $2p_\pi$ electron charge distribution responsible for the interaction energy δ, because the energy of the state represented by $\psi_e = 2^{-1/2}(\psi_2 + \psi_3)$ is just $E_1 + E_2 + \delta$. As an example of the determination of the electronic distribution according to the LCAO description, ψ_2 is represented as

$$\psi_2 = \psi_{2,12}\dagger\quad \psi_{2,34} = \\ 2^{-5/2}\,[(\mathrm{I} + \mathrm{II})(1)(\mathrm{I} - \mathrm{II})(2) + (\mathrm{I} + \mathrm{II})(2)(\mathrm{I} - \mathrm{II})(1)] \times \\ [(\mathrm{III} + \mathrm{IV})(3)(\mathrm{III} + \mathrm{IV})(4)]$$

where I, say, is a normalized $2p_\pi$ atomic orbital on carbon atom one and the numbers in parentheses refer to electrons. The π-electron distribution given by ψ_e^2, with the neglect of the overlap is

$$\psi_e^2 = \tfrac{1}{2}\,[\tfrac{1}{2}\,(\bar{1}\,\bar{3} + \bar{2}\,\bar{4}) + \tfrac{1}{8}\,(\bar{3} + \bar{4})(\overline{12} + \overline{21}) + \\ \tfrac{1}{8}\,(\bar{1} + \bar{2})(\overline{34} + \overline{43})]$$

where $\bar{2}$, say, means $\mathrm{II}^2(\mu)\mathrm{II}^2(\nu)$ and $\overline{34}$ means $\mathrm{III}^2(\mu)\mathrm{IV}^2(\nu)$. It is seen from the $(\bar{1}\ \bar{3} + \bar{2}\ \bar{4})$ term that half of the time both optical electrons in each bond are polarized. Thus for one-fourth of the time the wave function squared is

$$\bar{1}\,\bar{3} = \mathrm{I}^2(1)\mathrm{I}^2(2)\mathrm{III}^2(3)\mathrm{III}^2(4)$$

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(10) It is helpful in deriving the selection rules to keep in mind an analogy with the spectra of molecular crystals, and to assume a model for the excitation process in a double bond, such as is given by the LCAO method.

(11) G. F. Woods and L. H. Schwartzmann, THIS JOURNAL, **70**, 3394 (1948).

(12) The resonance energy for polyene homologous series is approximately proportional to the number of double bonds (determined by a matrix iteration approximation method).

(13) *Cf.* R. S. Rasmussen, D. D. Tunnicliff and R. Robert Brattain, *J. Chem. Phys.*, **11**, 432 (1943).

(14) J. E. Lennard-Jones, *Proc. Roy. Soc.* (*London*), **A158**, 280 (1937).

(15) F. London, *J. Phys. Chem.*, **46**, 305 (1942).

which, stated roughly, puts two electrons on the first carbon and two electrons on the third. Since the neutral molecule has one electron per carbon, the situation represented by $\bar{1}\ \bar{3}$ as well as the one represented by $\bar{2}\ \bar{4}$, is depicted approximately by a system of unit charges located at the sites of the carbon atoms, with alternating signs: $(\overset{-}{1}\ \overset{+}{2}\ \overset{-}{3}\ \overset{+}{4})$. The estimate of δ is one-half the electrostatic energy of such an arrangement, because the other terms in $\psi_e{}^2$ do not lead to electrostatic interaction between the right and left regions of the molecule. The 1,2- and 3,4-interactions (referring to numbered carbon atoms) must not be counted as part of the interaction, but are a sort of self-energy of the bonds, part of the excitation energy $E_2 - E_1$.

The attraction or repulsion of charge distributions is of course not adequately treated by considering the distributions as points. Nevertheless, it is believed that the electrostatic or estimated δ's may be considered *proportional* to more accurate ones such as might be determined empirically from spectra.

For a model of butadiene in which the bond distances are: 1,2- 1.35 Å.; 2,3- 1.46 Å.; and the 1,2,3-angle is 120°, the estimated values of δ turn out to be

$$-0.984 \text{ e.v. (s-}trans\text{)}$$
$$-1.577 \text{ e.v. (s-}cis\text{)}$$

The *s-trans* value is to be compared with the value obtained from the spectra of (presumably s-*trans*) butadiene and ethylene ($\delta = -1.91$ *e.v.*). It can be seen that dispersion forces may be of about the right order of magnitude, so that the computations made earlier in this paper can be considered less formal and more realistic.

An immediate use of the estimated interaction energies is in the computation of a δ for s-*cis*-butadiene, which is intended to be a quantity of the same rank as the spectroscopic δ for the s-*trans* isomer. The *cis* parameter is

$$(1.577/0.984)(-1.91) = -3.06$$

which gives 5.08 e.v. (2440 Å.) for the excitation energy. The comparatively long wave length absorptions of the cyclized dienes are in this range.

As pointed out by Parr and Mulliken[16] the implication of a larger resonance energy for s-*cis*-butadiene does not guarantee that the *cis*-compound shall have the lower free energy.

Bond Lengths

The lengthening in butadiene of the 1,2- and 3,4-bonds (which is probably only about 0.01 Å.,[17] a value not outside the limits of experimental error), can be estimated from the contribution to the ground state of ψ_4, the doubly excited trial function, and an estimated excited state equilibrium internuclear distance (1.65 Å.).[18] The lengthening is predicted to be (1.65 Å. − 1.35 Å.) $(0.125)^2$ or 0.005 Å. The shortening of the 2,3-bond can be estimated from the difference in resonance energy at 2,3-distances of 1.54 and 1.46 Å. The *R.E.* value at 1.46 Å. has already been given as 0.236 e.v. (5.5 kcal./mole). This value has to be recalculated for a new δ which is estimated from a ratio of electrostatic energies, as in the last section. The δ for 1.54 Å. (s-*trans*) turns out to be 1.67 e.v., so that *R.E.* (1.54) is 0.181 e.v. (4.2 kcal./mole). The work done in a displacement from 1.54 to 1.48 Å. against the assumed normal carbon–carbon single bond force constant, 5.0×10^5 dynes/cm., is just equal to $\Delta R.E.$ (0.055 e.v.); hence the predicted contraction is 0.06 Å. (observed, 0.08 ± 0.03).[17]

Conclusion

An attempt has been made to determine the relative importance of internal dispersion forces and conjugation in polyenes, by a consideration of certain spectroscopic and related properties. It has been shown that no decision presents itself on this basis, because the present interpretation (assuming no conjugation at all) is about as satisfactory as the one usually given.

A possibility for measuring the extent of conjugation lies in a careful examination of intensities of long wave length singlet–singlet transitions in a polyene series of known configuration, such as all s-*trans*. According to the dispersion force model, μ^2, the transition moment integral squared, and hence

$$\int \epsilon \, d \log \nu$$

(ϵ is the molar extinction coefficient) would be almost proportional to the first power of the number of double bonds (if $\mu_1{}^2$ is the ethylene intensity, the butadiene intensity becomes $2\mu_1{}^2(1 + 2(0.125))$ where 0.125 is the mixing coefficient of ψ_4 in ψ_g). The effect of conjugation is probably to produce a more rapid increase in intensity with increasing chain length. In fact, in the amidinium vinylogs,

$$Me_2\overset{\oplus}{N}{=}CH{-}(CH{=}CH)_n{-}NMe_2 \qquad \overset{\ominus}{X}$$

which may be considered a limiting case representing pure conjugation, the intensities for $n = 1, 2, 3$ are in the ratio of 2700: 4610: 6720, or, roughly, as the square of the number of unsaturation electron pairs.[19]

It is noteworthy that energy quantities involved in these dispersion force calculations can be regarded as correlation terms. The neglect of such quantities is almost the essence of a self-consistent field type calculation. Customarily, configurational interaction is invoked to offset this and other deficiencies in orbital calculations. In this connection it has recently been discovered that specifically in $2p_\pi$ anti-symmetrized molecular orbital computations, configurational interaction is large.[20] This has been interpreted as meaning that its inclusion leads to a better balance of ionic terms.

It is possible that internal dispersion forces, and hence correlation energies (involving ionic terms) may be of considerable importance, not only in polyenes but also in other unsaturated molecules. Thus the existence of configurational interaction in unsaturated molecules may depend on factors which rather prominently include internal dispersion forces.

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(16) R. G. Parr and R. S. Mulliken, *J. Chem. Phys.*, **18**, 1338 (1950).

(17) V. Schomaker and L. Pauling, THIS JOURNAL, **61**, 1769 (1939).

(18) D. P. Craig, *Proc. Roy. Soc.* (*London*), **A200**, 272 (1950).

(19) W. T. Simpson, *J. Chem. Phys.*, **16**, 1124 (1948).

(20) For example, D. P. Craig, *Proc. Roy. Soc.* (*London*), **A202**, 498 (1950).

It was learned while this research was being concluded that Davydov[21] had treated diphenyl by a method which makes explicit use of the dispersion force between the phenyls.

NOTE ADDED IN PROOF.—The interesting experimental results of Carmack and co-workers, in which interaction between nearby sulfur atoms in a molecule is demonstrated, seem to be capable of being nicely understood in terms of the discussion given in this paper.

Acknowledgment.—The writer wishes to thank Drs. D. S. McClure and Harvey Winston for reading the manuscript critically.

SEATTLE, WASH. RECEIVED APRIL 11, 1951

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[21] A. S. Davydov, *Zhur. Ekspil. Teoret. Fiz.*, **18**, 201 (1948).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE JOHNS HOPKINS UNIVERSITY]

The Kinetics of the Ethyl Alcohol–Acetic Anhydride Reaction Using a Dielectric Constant Method[1]

BY ROBERT C. AXTMANN[2]

A kinetic study of the esterification of ethyl alcohol by acetic anhydride in carbon tetrachloride has been made by a semi-automatic, electronic method which follows decrements in the dielectric constant of the solution as the reaction progresses. Data collected indicate that the dielectric constant of multi-component solutions of polar molecules in a non-polar solvent is directly proportional to the concentrations of the individual solutes.

I. Introduction

The first measurements of the rate of esterification of ethyl alcohol by acetic anhydride in carbon tetrachloride and other solvents were made by Soper and Williams[3] who found that in accordance with an earlier theory[4] the various solvents might be arranged in an order of increasingly deactivating influence on this reaction. This arrangement conforms fairly closely with one of increasing internal pressure of the solvents involved. The order is also one of increasing dielectric constants.

The reaction has also been studied by Moelwyn-Hughes and Hinshelwood who found a sharp dependence of *k* on the initial concentrations of reactants, *i.e.*, the higher the concentration, the slower the reaction.[5] Soper and Williams also observed this and consistently ascribed the phenomenon to a medium effect of the reactants which raises the internal pressure of the entire system.

Soper and Williams report an effect not found in the later work, namely, a slowing-down of the reaction as it proceeds to completion in carbon tetrachloride. They attribute this to a specific inhibitory effect of the acetic acid which is produced in the reaction. Their proof lies in experiments where they add acetic acid to the original solution and observe lower values of *k*. On the basis of their explanation for the dependence of *k* on initial concentration, however, the medium effect of additional acetic acid (or any other polar substance) would be to raise the internal pressure of the solution and slow down the reaction. The proof, then, is at best circumstantial. In the absence of other effects, however, one would expect the reaction velocity to increase slightly as it progresses, since the products are of lower dielectric constant than the reactants and hence the overall dielectric constant of the solution is decreasing.

The purpose of the following experiments, then, was to measure the velocity of the reaction by a method which would largely eliminate the possibility of systematic errors from an analytical procedure in an attempt to discover whether the slowing down of the reaction was real. A secondary aim was to demonstrate the usefulness of a new kinetic tool[6] which determines reaction velocities from dynamic measurements of the dielectric constant of the reacting solution.

II. Experimental

1. **Materials.**—The carbon tetrachloride was C.P. Reagent Grade which was fractionated in a 24-inch, lagged Vigreux column. Five-pound bottles were distilled collecting only the middle fraction which boiled within a 0.1° range. The anhydride was also C.P. Reagent Grade and was fractionated in the same apparatus, collecting over a 0.5° range. Weighed samples of anhydride hydrolyzed in water and titrated against standard base demonstrated that the substance was pure to well within 0.1%. The alcohol was anhydrous, prepared by a method described by Vogel.[7] Several standard solutions (about 0.1 *m*) were made up gravimetrically and stored in a cold room. The molarities of these solutions were in all cases known to 0.1%.

2. **Apparatus and Procedure.**—The instrument used for obtaining the kinetic data was a heterodyne beat assembly with an automatic timing circuit which will be described in another paper.[6] The power supplies for the oscillators and timing circuit were always turned on two hours before a run was started. The dielectric constant cell was also placed in the constant temperature bath at that time. Stability of the oscillators was checked by repeatedly resetting the micrometer capacitor to hear no beat in the loudspeaker of the receiver. When the same reading to ±0.002 mm. could be obtained at the beginning and end of a five-minute period, the circuits were judged to have come to a steady state.

150-ml. solutions of the two reactants in separate, stoppered erlenmeyer flasks were placed in the constant temperature bath one-half hour before the start of a run. When they had come up to temperature, they were poured simultaneously through a wide-mouthed funnel into the cell. To further ensure complete mixing of the two solutions, the magnetic stirrer in the bottom of the cell was allowed to run for five minutes.

No readings were taken until the mixing period was over.

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(1) This paper comprises a portion of the dissertation of R. C. Axtmann submitted to the School of Higher Studies of The Johns Hopkins University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Atomic Energy Division, E. I. du Pont de Nemours & Company, Inc., Argonne National Laboratory, Lemont, Illinois.

(3) F. G. Soper and E. Williams, *J. Chem. Soc.*, 2297 (1931).

(4) M. Richardson and F. G. Soper, *ibid.*, 1873 (1929).

(5) E. A. Moelwyn-Hughes and C. N. Hinshelwood, *ibid.*, 230 (1932).

(6) R. C. Axtmann, paper to be published soon.

(7) A. I. Vogel, "Textbook of Practical Organic Chemistry," Longmans, Green and Company, New York, N. Y., 1948, p. 166.