formula weight. The actual freezing point lowering (at 0.021 N) amounts to only 0.0096°, which is barely within the limits of sensitivity of ordinary freezing point methods.

Bearing in mind the fact that the solutions with which we are here dealing are extremely dilute with respect to ions, it seems that the deviations from the ideal curve can be due only to interactions between the ion pairs as has been suggested by Fuoss and Kraus.[4] When the ions are symmetrical, the pairs readily build up to higher aggregates—quadrupoles and multipoles. At very low concentrations, the observed molecular weight should approach the formula weight as a limit; which is the case, except with salts having large symmetrical ions, like tetraisoamylammonium thiocyanate, where the limiting curve is not approached even at concentrations as low as 10^{-3} N. The other three electrolytes exist largely as ion pairs below 10^{-3} N.

The difference between the behavior of electrolytes having symmetrical and unsymmetrical ions is likewise exhibited in other of their properties as, for example, their conductance and their dielectric constant effects. As was shown by Fuoss and Kraus, conductance curves of electrolytes having symmetrical ions exhibit two inflection points at concentrations above the minimum. In other words, there is a region in which the conductance increases only slowly with increasing concentration. This corresponds to the region in which dipoles are disappearing from the solution and multipoles are being formed. The conductance curve of electrolytes with asymmetrical ions is everywhere convex toward the concentration axis at higher concentration.

As Kraus and Hooper have shown, the dielectric constant of solutions of electrolytes with asymmetrical ions increases approximately linearly with concentration. On the other hand, in the case of electrolytes with symmetrical ions, the dielectric constant increase falls off rapidly with increasing concentration, the curves being strongly concave toward the axis of concentration.

Our results would seem to show that, at concentrations between 10^{-3} and 10^{-4} N, electrolytes in solution exist largely in the form of ion pairs, which form more complex aggregates at higher concentrations, the complexity increasing the more rapidly the greater the electrical symmetry of the ions.

V. Summary

Improvements are described in an apparatus for determining the freezing point of solutions in benzene at low concentrations.

The freezing point constant of benzene has been redetermined and found to be 5.075°.

The freezing points of solutions of triisoamylammonium picrate, silver perchlorate, tetraisoamylammonium picrate and tetraisoamylammonium thiocyanate have been determined.

At very low concentrations, the freezing point curves approach the ideal linear slope, based on the formula weight of the electrolyte. At higher concentrations, the deviations increase and are greatest for electrolytes having electrically symmetrical ions, and smallest for electrolytes having asymmetrical ions.

PROVIDENCE, R. I. RECEIVED JUNE 8, 1934

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY AT PRINCETON]

Activation Energies of Reactions Involving Oxygen. I. The Reaction $O + H_2 = H_2O$

BY RICHARD S. BEAR[1] AND HENRY EYRING

For several years one of us,[2] in collaboration with others, has been interested in developing quantum mechanical methods of calculating activation energies for chemical reactions. Hitherto no satisfactory procedure has been devised whereby systems containing oxygen can be studied in this manner. This paper discusses the reaction $O + H_2 = H_2O$, determining activation energies of excited and normal oxygen atoms with hydrogen molecules.

The results obtained herein seem of general importance in that they demonstrate a method for handling a system in which polar forces are important and indicate the treatment of a reaction during which a change in multiplicity takes place.

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[1] National Research Fellow in Chemistry.

[2] Eyring and Polanyi, *Z. physik. Chem.*, **B12**, 279 (1931); Eyring, THIS JOURNAL, **53**, 2537 (1931); Sherman and Eyring, *ibid.*, **54**, 2661 (1932); Kimball and Eyring, *ibid.*, **54**, 3876 (1932); Eyring, Sherman and Kimball, *J. Chem. Phys.*, **1**, 586 (1933).

The H_2O Molecule

Figure 1 illustrates the designation of orbitals and of interatomic distances and angles which will be employed throughout this discussion. Only the *s* orbitals of the hydrogen atoms and the *p* orbitals of the two oxygen valence electrons will be specifically mentioned in these considerations. The effects of the other oxygen electrons are to be thought of as included in the additive terms of the energy equations.

The quantum mechanical treatment of four electrons arranged in the symmetry of Fig. 1 results in the following equations for the singlet and triplet energies of the H_2O molecule. Throughout this paper the subscripts 1, 2 and 3 on E's and Q's refer, respectively, to the systems singlet H_2O, doublet OH, and triplet H_2O.

$$E_1 = Q_1 + \sqrt{\frac{1}{2}\left[(2\gamma - \alpha - \delta)^2 + (\alpha + \delta - 2\beta)^2 + (2\beta - 2\gamma)^2\right]} \qquad (1)$$

$$E_3 = Q_3 - \beta - \gamma + \sqrt{(\alpha - \delta)^2 + (\beta - \gamma)^2} \qquad (2)$$

Here E_1 and E_3, the total energies, are expressed in terms of Q's, which include coulombic, ionic, and all other additive terms, and of exchange integrals defined by

$$(ab) = \alpha \qquad (ac) = \beta = (bd)$$
$$(ad) = \gamma = (bc) \qquad (cd) = \delta$$

The three-electron equation applicable to the OH molecule is

$$E_2 = Q_2 + \sqrt{\frac{1}{2}[(\beta - \gamma)^2 + (\gamma - \delta)^2 + (\delta - \beta)^2} \qquad (3)$$

In order to avoid the frequent use of negative numbers, we take positive energies to represent stable configurations, hence the α, β, γ and δ are actually the negative of the corresponding exchange integrals. The energy calculated from equations (1), (2) or (3) is that referred to a hypothetical system in which r_1 and r_2 are infinite while δ is zero. Consequently, $Ei - \delta$ (i = 1, 2 or 3) is the actual "binding energy" of a given system according to the usual definition of this term.

Certain experimental facts of importance in determining the various interactions can be briefly summarized as follows.

(1) The optical constants of the OH molecule are: r_0 = 0.964 Å., ω_0 = 3735 cm.$^{-1}$, D = 114.8, D' = 120.1 kg. cal. Here r_0 is the equilibrium separation, ω_0 the vibration frequency, D the observable dissociation energy, and D' the same quantity with the half quantum of zero-point energy added. These are constants determined by Johnston, Dawson and Walker,[3] whose results have been used to calculate also D and D'. The H_2 constants[4] are: r_0 = 0.74 Å., ω_0 = 4375 cm.$^{-1}$, D = 102.4, D' = 108.6 kg. cal. These values can be used to calculate potential energy (Morse) curves for OH and H_2 molecules by substituting them into the expression (in the units given)

$$E = D'[2e^{-a(r-r_0)} - e^{-2a(r-r_0)}]$$

where

$$a = 0.1227\,\omega_0\sqrt{m_1m_2/[(m_1 + m_2)352\,D']}$$

Here m_1 and m_2 are the masses of the two atoms.

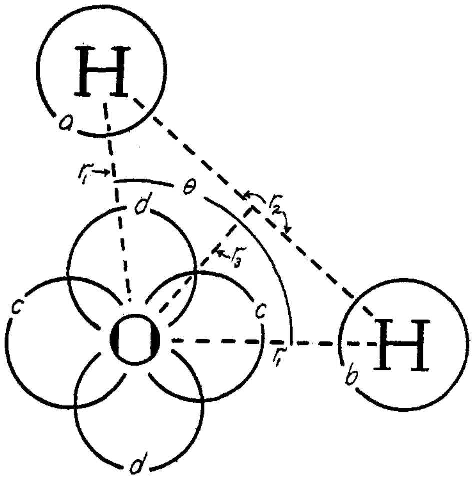

Fig. 1.—Important orbitals, distances and angles of the water molecule.

(2) The binding energy of H_2O is 218.9 kg. cal.,[5] and with a zero-point energy of 12.7 the total energy of the water molecule is 231.6 kg. cal.

(3) Mecke and Baumann[6] have found from an analysis of the infra-red spectrum of water that the equilibrium configuration of the H_2O molecule is that with r_1 = 0.97 Å., θ = 104°. We shall consider that the equilibrium value of r_1 is equal to r_0 for the OH molecule.

(4) The separation between ^3P and ^1D terms of the oxygen atom is 45.1 kg. cal.[7]

(5) The electric moment[8] of water vapor is 1.85 × 10^{-18}.

In considering the Q's of equations (1), (2) and (3) one might expect Q_1 and Q_3 to be equal and

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[3] Johnston, Dawson and Walker, *Phys. Rev.*, **43**, 473 (1933).

[4] Mulliken, "Interpretation of Band Spectra, Part III," *Rev. Mod. Phys.*, **4**, 1 (1932).

[5] See Pauling, THIS JOURNAL, **54**, 3574 (1932).

[6] Mecke and Baumann, *Physik. Z.*, **33**, 833 (1932); Mecke, *Naturwissenschaften*, **20**, 657 (1932).

[7] Bacher and Goudsmit, "Atomic Energy States," McGraw-Hill Book Co., Inc., New York, 1932.

[8] C. P. Smyth, "Dielectric Constant and Molecular Structure," A. C. S. Monograph, 1931, p. 192.

twice Q_2. This will not be true for the following reasons:

(1) Q_1 and Q_3 will differ in the amount of ionic interaction, which is probably pretty small in Q_3, the triplet term. The non-ionic parts will be approximately the same in both.

(2) Q_1 will be approximately twice Q_2, but the following corrections will be made.

(a) Homopolar and ionic H to H interactions will enter Q_1 but not Q_2.

(b) Van Vleck and Cross[9] point out that, since the O atom of H_2O is counted twice in doubling the OH energy, excitation into the valence state $({}^3/_4{}^3P + {}^1/_4{}^1D)$ will be included once too often. To correct for this one adds $V = 11.3$ kg. cal. to Q_1, an amount equal to one quarter of the ${}^3P$–${}^1D$ separation of the oxygen atom.

(c) It is probable that the ionic interactions of O to H are different in OH and H_2O, since the conditions are so different in the two molecules. The oxygen atom of H_2O is being furnished with negative charge by two hydrogen atoms, while that of OH interacts with one only.

The above statements are summarized in

$$\begin{aligned} Q_2 &= C_{OH} + I_{OH} \\ Q_1 &= 2C_{OH} + 2I_{O-H} + C_{HH} + I_{HH} + V \\ Q_3 &= 2C_{OH} + C_{HH} + V \end{aligned}$$

Here C_{OH} is the coulombic contribution of an OH group to the energy, I_{OH} and I_{O-H} are the corresponding ionic quantities for the OH molecule and radical, respectively, C_{HH} the coulombic H to H attraction, and I_{HH} the ionic H–H repulsion.

That the ionic interactions are the largest single factors for the H_2O and OH molecules at their equilibrium configurations becomes evident when one considers the high electric moment of the water molecule. "Effective charges," e, of 1.57×10^{-10} e. s. u. on each hydrogen atom and $-2e$ on the oxygen are necessary to calculate the correct electric moment when the atoms are regarded as charged points at the separations determined by Mecke and Baumann. The potential energies of such a charge distribution are given by

$$I_{HH} = -\frac{e^2}{r_2} = -\frac{35.5}{r_2}\ \text{kg. cal.}$$

$$I_{O-H} = \frac{2e^2}{r_1} = \frac{71.0}{r_1}\ \text{kg. cal.}$$

These interactions, when r_1 and r_2 have the values of the equilibrium separation for the H_2O molecule, are $I_{HH} = -24.0$ and $I_{O-H} = 74.0$ kg. cal., resulting in a net ionic energy of 124.0 kg. cal., or 53% of the total.

We expect that C_{OH} will be 10% of the total energy of the OH molecule, or 12.0 kg. cal. This actually is a larger fraction of the homopolar energy than is usually assumed for the coulombic integral, since a large part of the OH molecule's energy is of ionic origin. This value has the experimental justification that it leads to agreement between the calculated and observed total energies for the water molecule.

The coulombic term, C_{HH}, can be taken, as in previous investigations,[2] to be one-tenth of the binding energy of the H_2 molecule as determined from the H_2 Morse curve at the given H–H separation. The remaining nine-tenths are then included in the exchange integral α.

The integral δ is determinable directly from the energy levels of the oxygen atom. It is equal to one-half the difference between the ${}^3P$ and ${}^1D$ levels and has a minus sign since the ${}^3P$ term is the lower one. Consequently, $\delta = -22.5$ kg. cal. The value of this integral is to be kept constant under all conditions of the three-atom system. Remembering that $Ei - \delta$, where $i = 1$, 2 or 3, is the actual binding energy in each case, it is evident in equations (1), (2) and (3) that any variation in δ will be of only minor importance.

The interesting calculation of Coolidge[10] gave values for β, γ and δ of -14, 53, and -30 kg. cal., respectively, for the water molecule. Coolidge's determination of the total H_2O energy was notably low, however, and until such time as the results of the variation method are improved it seems necessary to use experimental facts for the estimation of the desired quantities.

The magnitudes of the integrals β and γ are dependent upon the angle θ between O-H bonds and the distance r_1. At any definite value of r_1, β and γ vary with θ according to the following relations, which are determined by the properties of exchange integrals and the p eigenfunctions involved

$$\begin{aligned} \beta &= \beta_0 \cos^2({}^1/_2\theta - \pi/4) + \gamma_0 \sin^2({}^1/_2\theta - \pi/4) \\ \gamma &= \gamma_0 \cos^2({}^1/_2\theta - \pi/4) + \beta_0 \sin^2({}^1/_2\theta - \pi/4) \end{aligned}$$

The β_0 and γ_0 are the values of the integrals when $\theta = \pi/2$.

Van Vleck and Cross[9] were able to calculate a good value for the ω_3 vibration frequency of water. This vibration is essentially a bending one, with θ varying while r_1 remains practically constant.

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(9) Van Vleck and Cross, *J. Chem. Phys.*, **1**, 357 (1933).

(10) Coolidge, *Phys. Rev.*, **42**, 189 (1932).

The important assumption upon which their results for ω_3 depended was that $\gamma_0 - \beta_0 = 60$ kg. cal. Inclusion of ionic H-H repulsion, which they neglected, modifies the calculations in such a way as to require a smaller value of this difference, *i. e.*, $\gamma_0 - \beta_0 = 50$ kg. cal. This requirement can be regarded as an experimentally determined limitation upon the values of the exchange integrals.

One other relation is needed to fix β_0 and γ_0. When one chooses them in such a way that the proper equilibrium value for θ can be calculated from equation (1), with the other interactions that have been found, one finds that $\beta_0 = 0$, $\gamma_0 = 50$ kg. cal.[11] In such a calculation δ, C_{OH}, and $I_{\text{O-H}}$ are independent of θ, while C_{HH}, I_{HH}, and α depend on $r_2 = r_1\sqrt{2(1 - \cos\theta)}$ and β and γ vary with θ. With r_1 constant at 0.96 Å. we have the results:

θ	90°	100°	105°	110°	120°
$E_1 - \delta$, kg. cal.	229.8	231.3	231.8	231.7	229.5

The interactions that have been chosen are thereby demonstrated to give a sufficiently close approach to the proper binding energy and equilibrium angle for the water molecule. Since the OH Morse curve determines how the interactions depend on r_1, the proper equilibrium value of this coördinate is obtained automatically in calculations using these interactions.

Calculation of Activation Energies

In Fig. 2 we have plotted potential energy curves for entirely ionic and homopolar OH molecules as well as the experimentally determined Morse curve. The experimental curve may be thought of as resulting from "resonance" between the pure ionic and pure homopolar states.

The ionic curve was calculated by a well known method[12] according to the equation

$$E = A/r_1 - B/r_1^9$$

A is proportional to ϵ^2, the charge of a proton, while B is chosen so that the equilibrium point will come in the neighborhood of the correct r_0 for the OH molecule.[13]

Definite relative location of the ionic and experimental curves is impossible because of the fact that the affinity of an oxygen atom for *one* electron is unknown. In any case, there is a separation of the order of 10 volts (230 kg. cal.) or perhaps more between the two curves at large values of r_1.

Since the experimental Morse curve and the homopolar one separate the OH molecule into normal atoms we expect both to be identical for large values of r_1. That the actual point where they become indistinguishable is at fairly small OH separations is evident from the shape of the ionic curve. It rises extremely rapidly from the minimum point, and for this reason interaction with the non-polar level will decrease rapidly.

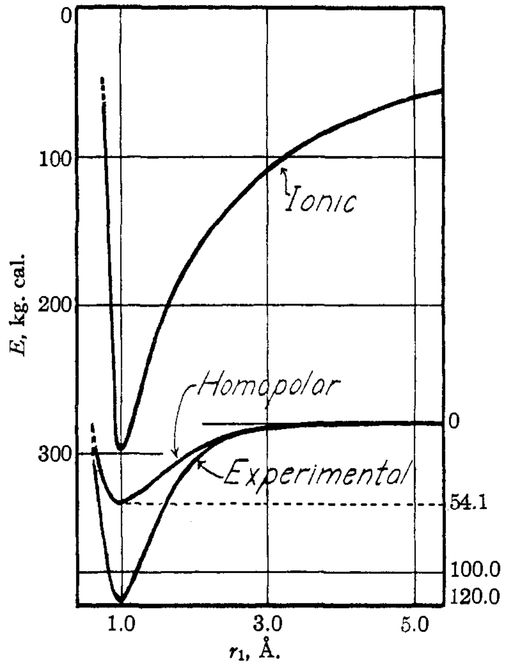

Fig. 2.—Potential energy curves for the OH molecule.

In order to determine the actual form and location of the homopolar curve we must have quantities corresponding to D′ and ω_0 for a hypothetical OH molecule in which only non-ionic forces are operative. We have for the desired D' the equation

$$D' = E_2 - I_{\text{OH}} - \delta \qquad (4)$$

To find the value of $E_2 - I_{\text{OH}}$ to be used in (4) one inserts the known values of C_{OH} and the exchange integrals into equation (3). This gives $D' = 54.1$ kg. cal.[14]

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[11] Actually a small negative value of β_0 would be more satisfactory, but the difference is not important enough to require any greater exactness.

[12] See Pauling, THIS JOURNAL, **54**, 988 (1932).

[13] Though the ionic curve is not actually used in the activation calculations, for completeness we give the values of A and B expressed in units which give the energy in kg. cal. when r_1 is in Å.: $A = 329$, $B = 36.7$.

[14] Introducing the experimental values of E_2 and δ in equation (4) we obtain $I_{\text{OH}} = 66.0$ kg. cal. Though too much importance is not to be attached to the exact figures, it is interesting to point out the reasonableness of this value. It corresponds to an "effective charge" per atom of 2.09×10^{-10} e. s. u., to an electric moment of 2.01×10^{-18} for the OH molecule, and to 55% of the total energy being of ionic origin.

A comparison of the ω_0's for all hydrides, except those in which strong polar forces are present (particularly the hydrides of several of the alkali metals and halogens), discloses the fact that most of the vibration frequencies fall within the range 1300 to 2300 cm.$^{-1}$. Though the relation between the polar nature of an element and its position in an arrangement according to the ω_0's of the hydrides is not always a simple one, generally hydrides of electropositive elements have low vibration frequencies, while the electronegative elements form hydrides of higher frequencies. The non-importance of the atomic weight of the element with which the hydrogen is united is, of course, an effect of the disparity between the masses of the two vibrating particles in each case. This results in a fairly constant reduced mass.

The above reasoning indicates that an intermediate value of 1800 cm.$^{-1}$ is a satisfactory frequency for a completely non-polar hydride. The Morse curve for $a = 1.55$, which follows from $\omega_0 = 1800$, $D' = 54.1$, is the one drawn in Fig. 2 for the completely homopolar OH molecule.

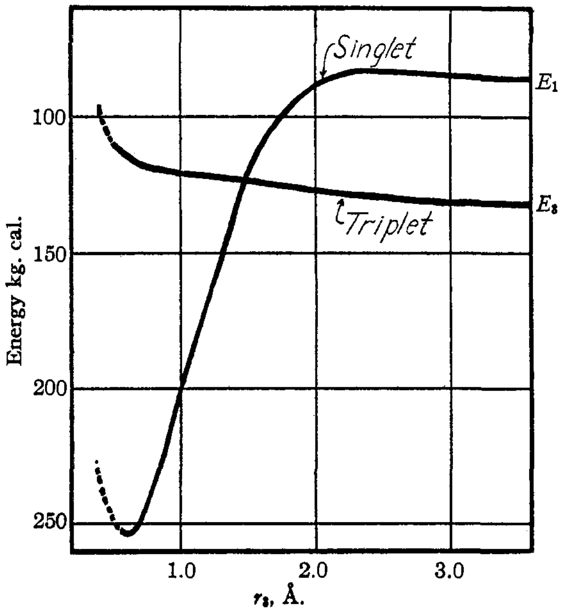

Fig. 3.—Singlet and triplet energies of the system H_2–O as a function of the distance H_2 to O. The H–H separation is constant at 0.74 Å. for $r_3 > 1.00$ Å.

For a given value of θ any O-H interaction (including the valence excitation correction) as calculated from the equations of the last section will depend upon r_1 in a way determined by the curves of Fig. 2. Each of the non-ionic quantities, C_{OH}, β, γ, and V, are as usual taken to be the same fraction of the total homopolar energy for the different values of r_1 used as they are at the equilibrium distance. The square of the effective charge of ionic interactions changes, of course, in such a way as to cause the ionic quantities to follow the difference between the experimental and homopolar potential energy curves. As expressed before, δ is constant, however, and α and C_{HH} are controlled by the H_2 Morse curve. The above procedure is the familiar one for determining interactions from potential energy curves, except that it has been adapted to the present more complex case.

Having thus determined how to calculate values for all quantities of equations (1) (2) and (3) at any configuration we can now investigate the activation energies for the reaction $O + H_2 = H_2O$. It can be shown that the path of least energy by which an oxygen atom can approach a hydrogen molecule is one on which the hydrogen atoms remain at nearly equilibrium distance for the H_2 molecule, while the O atom advances along a direction perpendicular to line at its midpoint. This is true for a wide range of the values of the parameters involved, but with the ones indicated previously the results are:

r_3, Å.	1.00	1.50	2.00	2.50	3.00	∞
E_1, kg. cal.	199.0	118.1	88.5	83.8	85.4	86.1
E_3	120.9	122.5	126.2	128.7	130.4	131.2

It should be noticed that the singlet-state equation dissociates water into a hydrogen molecule and an oxygen atom in the ^1D state. Also, somewhere near the point at which r_3 equals 1.50 Å. the singlet and triplet levels cross. A normal oxygen atom approaching a hydrogen molecule would follow the triplet energy curve up to this point, and sometime afterward the system could change to the more stable singlet multiplicity. These energy curves are sketched in Fig. 3.[15]

Conclusions

The results just obtained indicate a broad but low (about 2 or 3 kg. cal.) activation hump for a

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(15) If one considers the magnetic interaction terms in the Hamiltonian of the Schrödinger equation for the system, the intersection of the singlet and triplet curves disappears and the four branches recombine to form two non-crossing curves which are nearly tangent at the original point of intersection. However, for two curves so near each other transitions are fairly rapid, and one would be surprised to find a long life for molecules in the upper state. If a stable molecule of this sort were observed it would be necessary to assume sufficient polar contributions to the binding in the triplet state to introduce a minimum in the triplet curve of Fig. 3. Such an ionic interaction at the most could only reduce the activation energy of the normal atom reaction to about four kg. cal., though in doing so it would remove the sharpness of the barrier.

^1D oxygen atom approaching a hydrogen molecule. A normal atom requires more activation (about 8 kg. cal.) and also has a barrier of high curvature at the maximum. Such barriers of very high curvature, which can arise with a change in multiplicity, may well be effective in the separation of isotopes by the tunnel effect. There is also an additional slowness of reaction resulting from transition between states of different multiplicities.

These results are in satisfactory agreement with the known experimental facts. Kistiakowsky[16] and Harteck and Kopsch[17] have studied this reaction. The results of the former seem to indicate that an excited ^1D atom will need a small activation, while a normal atom will require more. Actual temperature dependence of the reaction was used by Harteck and Kopsch to show an activation energy of 6 kg. cal. for the normal-atom reaction.

In the above calculation the activated state for the singlet system came at values of r_1 at which the ionic interactions had vanished. These results indicate that in reactions which convert polar into non-polar compounds, or *vice versa*, the activated state may occur at distances for which the polar forces are relatively unimportant. This rapid disappearance of the polar part of the bond is associated with the customary high ionization potential of atoms and molecules, which makes the polar level lie high above the homopolar one at activated state configurations. Most ionic reactions are rapid, though in solutions hydration effects are a complication and in oxidation–reduction reactions involving the approach of highly charged ions of like signs reaction is sometimes slow.

A completely satisfactory treatment of the problems here discussed must await the further development of the quantum mechanical variation method. In the meantime the use of all available experimental information, together with the perturbation theory, provides a less satisfying but apparently essentially correct picture of such reactions. It is hoped that the information provided by this study of the H_2O molecule will facilitate consideration of similar but more complicated systems.

PRINCETON, N. J. RECEIVED JUNE 23, 1934

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[16] Kistiakowsky, THIS JOURNAL, **52**, 1868 (1930).

[17] Harteck and Kopsch, *Z. physik. Chem.*, **B12**, 327 (1931).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Dielectric Properties of Acetylenic Compounds. IV. Arylhalogenoacetylenes. Positive Iodine

BY C. J. WILSON AND H. H. WENZKE

It has been shown by Pflaum and Wenzke[1] that there is a considerable reduction in the carbon to halogen moment in the alkyl halogenoacetylenes as compared to halogen derivatives of the paraffins, benzene and ethylenic compounds. The chemical behavior of the halogens attached to an acetylenic carbon indicates that they are "positive" in character. It would perhaps be more correct to say that chemical evidence indicates that the halogen atoms when attached to an acetylenic carbon are not as highly negative as when linked to more saturated carbon atoms. It is not the purpose of this article to discuss the chemical evidence that has been presented by various investigators. The electric moment data on arylhalogenoacetylenes should prove to be even of more interest than that on the alkylhalogenoacetylenes. This is true partly because the treatment of moments as vector quantities is more satisfactory in aryl derivatives on account of the rigidity of the structure of the benzene molecule. By the selection of appropriate derivatives one can then obtain more nearly quantitative data on the acetylenic carbon to halogen moment in aryl compounds than is possible in alkyl compounds. Chemical evidence also indicates that the halogens in the aryl acetylenic derivatives is even more "positive" than in the alkyl compounds.

Preparation of Compounds

All of the iodoacetylenes were made by the method of Vaughn and Nieuwland,[2] which is that of direct iodination in liquid ammonia as a solvent. Phenyl and tolyl iodoacetylenes were purified by repeated crystallization from the solvent heptane. In order to reduce the solubility the heptane was cooled by liquid ammonia. *p*-Chloro-

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[1] Pflaum and Wenzke, THIS JOURNAL, **56**, 1106 (1934).

[2] Vaughn and Nieuwland, *ibid.*, **55**, 2150 (1933).