

JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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VOLUME 86, NUMBER 21

NOVEMBER 5, 1964

PHYSICAL AND INORGANIC CHEMISTRY

[CONTRIBUTION FROM THE BELL TELEPHONE LABORATORIES, INCORPORATED, MURRAY HILL, NEW JERSEY]

Relative Strength of Picric, Acetic, and Trichloroacetic Acids in Various Environments. Dispersion Effects in Acid-Base Equilibria

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RECEIVED MAY 25, 1964

London dispersion interactions of a solute molecule with the surrounding medium are especially strong if some of the virtual electronic oscillators that represent the solute molecule are delocalized. Thus, in acid dissociation, the dispersion energy contribution to ΔF° should be relatively large if either the acid or the conjugate base absorbs light in the visible, that is, for one-color indicators. An example is picric acid. The visible color of picrate ion can be ascribed to delocalized dipole oscillators that have one monopole located in the O^- atom and the other in a nitro group. The relative acid strength, K^0 , of picric acid relative to acetic acid increases by almost two orders of magnitude in the solvent series HOH , CH_3OH , C_2H_5OH , while that of trichloroacetic acid remains nearly constant. These results are qualitatively consistent with a dispersion effect. The dominant dispersion term comes from the interaction of the delocalized oscillators of picrate ion with dispersion centers in nearby solvent molecules. The latter are localized, and their effective density increases in the sequence $HOH < CH_3OH < C_2H_5OH$. A system permitting actual calculation of the dispersion energy is the reaction $HOPic + BH^+ \cdot OAc^- = BH^+ \cdot OPic^- + HOAc$. The relevant equilibrium constant, K^{BH^+} , was measured in glacial acetic acid for $BH^+ = NH_4^+$ and for $BH^+ = (CH_3)_3NH^+$. K^{BH^+} increases by almost an order of magnitude as a result of the methyl substitution. The corresponding equilibrium constants for trichloroacetic acid are insensitive to the change in BH^+ . Electrostatic interactions within the ion pairs should largely cancel out in these comparisons. Calculation using a model in which BH^+ is hydrogen-bonded to the O^- atom in the ion pairs leads to an increment in dispersion energy of 1.6 kcal./mole, which is quite consistent with the observed increase in K^{BH^+} . The hypothesis of strong dispersion effects can also account for the well-known differences in the relative base strength of the aliphatic amines as obtained from measurements in dilute solution in water or with color indicators in solvents of low dielectric constant. In mixed water-organic solvents, the dispersion effects oppose and sometimes overcome the preferential solvation of ions by water that would result from purely electrostatic interactions.

Dispersion forces are van der Waals forces resulting from the interaction of the same virtual electronic oscillators that enter into the description of the optical dispersion of molecules.^{1,2} It is well known that the dispersion forces make a major or even dominant contribution to the van der Waals forces in liquids.¹⁻³ Yet in the theory of medium effects on ionic organic reactions, emphasis is usually placed on the electrostatic interactions of permanent molecular charge distributions,⁴ and it is not unusual for dispersion effects to be neglected entirely. The assumption is, of course, that dispersion interactions with solvent molecules are about the same for reactants and products and cancel each other in their effect on ΔF° . It is difficult either to prove or to disprove this assumption. Although the calculation of dispersion energy quantities is understood in principle, actual calculations for neighboring complex organic molecules cannot be carried out exactly because the enormous amount of microscopic information that is needed is not available.

There are special cases, however, where we can predict qualitatively that dispersion effects on ΔF° should be maximal even though we cannot calculate them quantitatively. These cases are of interest not only for their own sake, but also because they set a rough upper limit to the magnitude of dispersion effects on ΔF° in general.

In this paper we shall be concerned with dispersion effects due to the solvent environment in acid-base reactions. Analysis of data for reactions in which such effects are expected to be relatively large reveals very substantial specific effects that vary with molecular structure in precisely the way expected qualitatively for a dispersion effect. New measurements are reported for the relative strength of picric, acetic, and trichloroacetic acid under conditions where enough is known about the molecular environments so that the dispersion effects can be roughly calculated. The medium effects observed under these conditions are highly specific, yet agree both qualitatively and semi-quantitatively with the calculated dispersion effects. Our conclusion is that the contribution of the dispersion effect to the medium effect on ΔF° can range up to several kilocalories per mole.

- (1) F. London, *Z. physik. Chem. (Leipzig)*, **B11**, 222 (1930).
- (2) F. London, *J. Phys. Chem.*, **46**, 305 (1942).
- (3) B. Linder, *J. Chem. Phys.*, **37**, 963 (1962); B. Linder and D. Hoernschemeyer, *ibid.*, **40**, 622 (1964).
- (4) See, for example, C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 345-350.

Localized vs. Delocalized Electronic Oscillators

In this section we wish to obtain some macroscopic criteria for predicting the relative magnitude of the dispersion effects on ΔF° for acid dissociation. Our discussion will closely follow the methods for treating complex organic molecules that have been suggested by London,² but will not go beyond the approximation represented by second-order perturbation theory. A brief review of the basic ideas will be helpful.

1. Each optical transition of the molecule is represented as a virtual electronic oscillator, and the transition moment is identified with the dipole moment of the oscillator.⁵ The dispersion effect of the molecule is a sum of independent terms assignable to the individual oscillators. The effect of an individual oscillator depends on the properties of that oscillator and is proportional to the oscillator strength, f . Weakly allowed transitions ($f < 0.01$, say), which are of considerable interest in spectroscopy and photochemistry, play only a minor role.

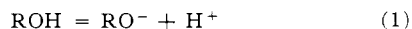
2. If the electrons are localized in a given part-structure, the transition moment of any *strongly allowed* transition must also be localized in that part-structure. Hence the monopoles, q , in the expression $\mu = qr$ for the dipole moment of the corresponding oscillator are localized in the same region of space in which the electrons are localized.

The proof of this important theorem is almost self-evident. When we say that an electron is localized in a given part-structure, we mean that its wave function in the ground state of the molecule is negligible except in that part-structure. Hence, the transition moment integral for excitation of the electron to an electronic level k in an arbitrary direction x , $\int \psi_0 \cdot x \psi_k^* d\tau$, cannot be large unless $x \psi_k^*$ is large in the same region of space in which ψ_0 is localized.

3. The interaction of two adjacent molecules can be represented as a double sum of pairwise interaction terms, each virtual oscillator in one molecule interacting independently with every virtual oscillator in the other molecule.

4. Dispersion effects attenuate rapidly with the distance between the interacting oscillators.

Let us now apply these concepts specifically to the dissociation of an oxygen acid (eq. 1). It is convenient



to subdivide the oscillators representing ROH and RO⁻ into three sets, those that are localized in R, those that are localized in OH or O⁻, and those that are delocalized. The latter are oscillators that have one monopole located in R and the other in OH or O⁻.⁶

Delocalization results in a marked increase of the dispersion energy. For definiteness, consider a solvent molecule adjacent to the O⁻ atom in RO⁻. Such a solvent molecule will interact relatively strongly with the electronic oscillators assignable to the O⁻ atom, but, because of the greater distance, only relatively weakly with those localized in R. We shall neglect interaction with the latter in first approximation.

(5) See, for example, W. Kauzmann, "Quantum Chemistry," Academic Press, New York, N. Y., 1957.

(6) The status of oscillators representing the electron pair that is localized in the R-O bond is ambiguous in this scheme but causes no problem in making predictions. We shall arbitrarily regard one electron as localized in O, the other as localized in R.

According to the Kuhn-Thomas sum rule,⁵ the total strength of all oscillators assignable to a structure is just equal to the number of electrons. Hence the total oscillator strength formally assignable to the O⁻ atom is equal for all RO⁻ species. We shall now compare two species. In i, all oscillators assignable to the O⁻ atom are localized. In ii, one of the localized oscillators of species i becomes delocalized while the others remain localized.

In Fig. 1 we depict the interaction of the oscillator that becomes delocalized with a fixed oscillator that is localized in the adjacent solvent molecule. The former is represented as a pair of monopoles $\pm q$ located at points P₁ and P₂, the latter as an isotropically oscillating dipole, μ_s , located at P₃. Let R_1 denote the distance P₁P₃, R_2 the distance P₂P₃, and φ the angle P₁P₃P₂. The dispersion energy, according to London,² is then given by eq. 2, where ν and ν_s are the characteristic frequencies of the oscillators. In Fig. 1a, which

$$E_{\text{disp}} = -\frac{q^2 \mu_s^2}{3 h(\nu + \nu_s)} \left(\frac{1}{R_1^4} + \frac{1}{R_2^4} - \frac{2 \cos \varphi}{R_1^2 R_2^2} \right) \quad (2)$$

represents species i, $R_1 \approx R_2$ and $\cos \varphi \approx 1$. Hence, $R_1^{-4} + R_2^{-4} \approx 2(\cos \varphi)/R_1^2 R_2^2$, and E_{disp} is the small difference of nearly equal quantities. In Fig. 1b, which represents ii, $R_2 \gg R_1$ and $2(\cos \varphi)/R_1^2 R_2^2 < R_1^{-4}$. Hence, E_{disp} is no longer the difference of nearly equal quantities and is therefore relatively large. Another way of putting it is that Fig. 1a represents essentially a dipole-dipole interaction, Fig. 1b a charge-dipole interaction. If we recall that the effect of a dipole is the small difference between the nearly equal but opposing effects of the monopoles, then it is obvious that delocalization, that is, removal of one monopole to a great distance, will result in a great enhancement of the effect.

Calculations reported in a later section for a particular model show that the enhancement in the dispersion energy resulting from the delocalization of a given oscillator can easily amount to a full order of magnitude. Compared to this large increase, any effect that the delocalization might have on the properties of the other oscillators, which remain localized, should be relatively insignificant. Of course, the other monopole of the delocalized oscillator, which is located in R (Fig. 1b), will also interact strongly with any solvent molecule near it.

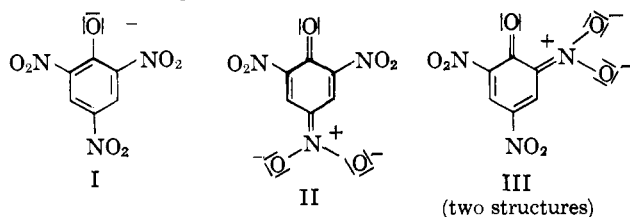
Returning to the equilibrium shown in eq. 1, we therefore expect a large dispersion energy contribution to ΔF° if a substantial oscillator strength that is localized in ROH becomes delocalized in RO⁻, or *vice versa*. Since delocalization of electronic oscillators can be recognized by the appearance of absorption bands in the visible or near-ultraviolet, we predict that dispersion effects on ΔF° will be relatively large if ROH is colorless while RO⁻ is intensely colored, or *vice versa*; that is, if the system ROH-RO⁻ is a one-color indicator.

In this paper we use picric acid as a typical one-color indicator for which dispersion effects on ΔF° should be relatively large. It is therefore instructive to analyze the relevant spectra. For picric acid and picrate ion we use some recent data obtained in chloroform solution.⁷ For other phenols and phenoxide ions we cite data for aqueous solution.⁸

(7) G. Briegleb, J. Czekalla, and A. Hauser, *Z. physik. Chem. (Frankfurt)*, **21**, 99 (1959).

In the region near 4000 Å. where neither picric acid nor phenoxide ion shows strong absorption, picrate ion shows strong absorption with two maxima. From the published graph⁷ we calculate the following wave lengths (λ_{\max}) and molar extinction coefficients (ϵ_{\max}) for the band maxima: (1) 4200 Å., 1.2×10^4 ; (2) 3670 Å., 2.0×10^4 . For comparison, *o*- and *p*-nitrophenoxide ions in water show analogous absorption at $\lambda_{\max} = 4160$ (*o*) and 4025 Å. (*p*), with $\epsilon_{\max} = 0.5 \times 10^4$ (*o*) and 1.9×10^4 (*p*).⁸

The well-known interpretation of these facts is that the characteristic absorption near 4000 Å. is the result of electronic coupling between the O⁻ atom and an *o*- or *p*-nitro group. The coupling is often described in terms of resonance among valence-bond structures such as I-III for the picrate ion.⁹



The ground state is described largely by I, with small contributions from II and III. We expect two excited states of nearly equal energy, a *para*-quinoid state that is described largely by II, and an *ortho*-quinoid state, with a statistical weight of 2, that is described largely by III. By analogy with the mononitrophenoxide ions, band 1 of picrate ion can be assigned to the transition to the *ortho*-quinoid state, band 2 to that to the *para*-quinoid state.

The properties of the virtual oscillators that represent these transitions are listed in Table I. The oscillator strength and μ^2 , the square of the transition moment, are derived from integrated band intensities by standard methods. The total oscillator strength of the two bands has the substantial value of 0.31. The valence-bond structures (I-III) suggest that the separation, r , of the monopoles, q , in the expression $\mu = qr$ is very close to the distance, d , from the O⁻ atom to the center of mass of the two oxygen atoms in the *o*- or *p*-nitro group. Values of d have been calculated from known interatomic distances¹⁰ and are listed in Table I. Assuming that $r = d$, we then obtain values of q^2 and of the fractional charge, q/e for each transition, as shown in Table I. Although this treatment is rather naive, its validity seems to be confirmed by the nearly identical values of q obtained for the monopoles located in the *o*- and *p*-nitro groups. In any case, there is little doubt that these oscillators are strongly delocalized.

Another useful, though less visual, macroscopic criterion for delocalization of electronic oscillators is the change in the molar refraction on acid dissociation. As is well known, the molar refraction is given accurately by an atom- or bond-additivity scheme^{11,12}

(8) L. Doub and J. M. Vandenberg, *J. Am. Chem. Soc.*, **69**, 2714 (1947); **71**, 2414 (1949).

(9) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, pp. 288-294.

(10) Based on data in L. Pauling, "Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960.

(11) N. Bauer and K. Fajans in "Physical Methods of Organic Chemistry," A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1949, Chapter 20.

(12) K. G. Denbigh, *Trans. Faraday Soc.*, **36**, 936 (1940).

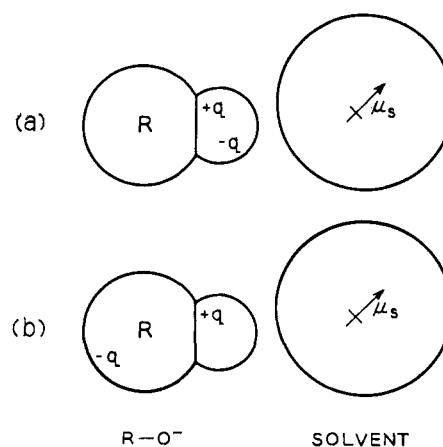


Fig. 1.—Model for calculating the dispersion energy: (a) the oscillator is localized in O⁻; and (b) the same oscillator is delocalized. Monopole $+q$ is located at P_1 , monopole $-q$ is located at P_2 , and dipole μ_s is located at P_3 .

if the electronic oscillators representing the dispersion of the molecule are all localized in atoms or bonds. Delocalization of electronic oscillators produces exaltation of the molar refraction above the value given by the additivity scheme. As a result, if in eq. 1 all oscillators assignable to the OH or O⁻ part-structures are localized, we expect a characteristic change of the molar refraction that is independent of R. The value of this change can be estimated as +1.34 cc. from molar refractions reported for the HOH-HO⁻ system.¹³

TABLE I
PROPERTIES OF VIRTUAL OSCILLATORS DERIVED FROM THE
ABSORPTION SPECTRUM OF PICRATE ION NEAR 4000 Å.

Property	Position of excited nitro group—		
	<i>ortho</i> (total)	<i>ortho</i> (per NO ₂ group)	<i>para</i>
λ_{\max} , Å. ^a	4200	4200	3670
$\nu_{\max} \times 10^{-15}$, sec. ⁻¹	0.715	0.715	0.818
Oscillator strength ^a	0.083	0.042	0.229
$\mu^2 \times 10^{36}$, e.s.u. ² cm. ²	74	37	179
$d \times 10^8$, cm. ^b	3.17	3.17	6.27
$q^2 \times 10^{22}$, e.s.u. ²	7.4	3.7	4.5
q/e	...	0.40	0.44
$R_1 \times 10^8$, cm. ^b	...	3.3	3.3
$R_2 \times 10^8$, cm. ^b	...	5.3	9.6
$\cos \varphi$...	0.831	1.000
E_{disp} , kcal. ^c	0.96	0.48	0.86

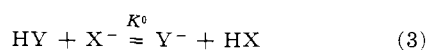
^a Based on data in ref. 7. ^b Based on data in ref. 10. ^c Equation 2.

For comparison, the value obtained for the CH₃COOH-CH₃COO⁻ system, in which we shall be interested in the next section, is +1.36 cc.,¹³ or essentially the same as for HOH-HO⁻. Thus, by this criterion, the contribution of the dispersion effect to ΔF° for the dissociation of acetic acid should have a value characteristic of localized oscillators and should therefore be relatively small.

Solvent Effects on Relative Acid Strength

The relative strength of two acids, HY and HX, is measured by the equilibrium constant for reaction 3 and is equal to the ratio of the acid dissociation constants (eq. 4). If Y⁻ + HX are stronger centers of dispersion than HY + X⁻, then the equilibrium in eq. 3 will shift to the right as the solvent is changed so

(13) K. Fajans, *Z. physik. Chem.* (Leipzig), **B24**, 141 (1934); K. Fajans and G. Joos, *Z. Physik*, **23**, 1 (1924).



$$K^0 = K_A^{\text{HY}}/K_A^{\text{HX}} \quad (4)$$

that the solvent molecules become stronger centers of dispersion. An actual example, to be considered in this section, is the relative strength of picric acid and acetic acid (HY = HOPic, HX = HOAc). In this example, the dispersion effect on K^0 is dominated by the interaction of solvent molecules with those delocalized oscillators of picrate ion that are responsible for its color.

Values of K^0 have been reported for the solvents HOH, CH₃OH, C₂H₅OH, and *n*-C₄H₉OH. These solvents have the property that the electronic oscillators representing the solvent molecules are all localized in atoms or bonds. To make a precise calculation of the dispersion energy of solvation for each solvent, we would have to know the geometry of the solvent shells around each solute species. This kind of information is simply not available for solutions of complex molecules. Fortunately, the information is not needed, because we can derive the relative effectiveness of these solvents as sources of dispersion energy by considering only (i) the density of localized oscillators in various solvent shells, and (ii) the short range of the dispersion effect.

The basic idea in this analysis is that matter can be packed more densely in the neighborhood of a solute molecule if the atoms in the adjacent solvent shell are separated by covalent bond distances rather than by van der Waals distances and if gaps corresponding to interstices between molecules are minimized. This means that a few large molecules will represent a higher density of oscillators around the solute molecule than will a larger number of smaller molecules. Consider, for example, the solvation shell around a solute molecule in liquid water. Much of the space in the solvation shell, and particularly the space between the first and the second hydration layer, is interstitial or is swept out by van der Waals radii, and the density of oscillators in that space is low. On the other hand, if *n*-butyl alcohol is substituted for water, the space that would have been near the boundary between the first and second hydration layer in water is now filled with CH₂ groups, and the density of oscillators within it is high. Of course, in *n*-butyl alcohol there is also a boundary between the first and the second solvation layer near which the density of oscillators is low. However, this boundary is at a greater distance from the solute molecule than it is in water, and if it lies outside the effective range of the dispersion effect, its adverse effect on the dispersion energy of solvation will be negligible.

Thus, in the series of solvents C_{*n*}H_{2*n*+1}OH, we expect the strength of picric acid relative to acetic acid to increase with *n* for small *n*. Furthermore, we expect that the effect will reach saturation when *n* is large enough so that the boundary between the first and second solvation layer is outside the effective range of the dispersion effect. This saturation value of *n* cannot be predicted without some *ad hoc* assumptions about the geometry of the solvation shells. If we assume that the OH groups are directed toward, and the alkyl groups away from, the solute molecules, the saturation value of *n* should be about 2 or 3.

TABLE II
EQUILIBRIUM CONSTANTS, K^0 , FOR RELATIVE ACID
STRENGTH AT 25°

Solvent	Acid pair				
	HOPic- HOAc 10 ⁻⁴ K ⁰	Cl ₃ CCO ₂ H- HOAc 10 ⁻⁴ K ⁰	HOPic- phenol 10 ⁻¹⁶ K ⁰	HOPic-2,4- (NO ₂) ₂ C ₆ H ₃ OH 10 ⁻⁴ K ⁰	
HOH	2.6	ca. 5	0.47	0.47	<i>a</i>
CH ₃ OH	78	6.0	3	1.3	<i>b</i>
C ₂ H ₅ OH	210	7.3	ca. 20	1.2	<i>c</i>
<i>n</i> -C ₄ H ₉ OH	170	0.9	<i>d</i>
<i>n</i> -C ₄ H ₉ OH, 0.05 <i>N</i> LiCl	28	1.4	...	0.3	<i>e</i>
CH ₃ CO ₂ H	...	1.7	<i>f</i>

^a K_A is known with good accuracy for picric acid,¹⁴ acetic acid, phenol, and 2,4-dinitrophenol.¹⁵ K_A for trichloroacetic acid is taken as 0.9 on the basis of kinetic, conductance, and spectrophotometric data and is uncertain by about a factor of two.¹⁶ The $\rho^*\sigma^*$ relationship predicts a K_A value of 1.1 for Cl₃CCO₂H.¹⁷ ^b Ref. 15, 18–20. ^c Ref. 15, 21, and 22. pK_A for phenol is taken as 15.3 ± 0.5 on the basis of data in ref. 20 and 23. Data in the latter reference were corrected to 100% ethanol. ^d See ref. 24. ^e See ref. 25. ^f $K^0 = K_{\text{molar}}/K_A^{\text{HX}}$ [HOAc]; data from ref. 26 and 27.

The results of our literature search are summarized in Table II. Although the data are taken from a variety of sources,^{14–27} results reported from different laboratories are mostly consistent and the values of K^0 should be accurate to 30% or better, except where noted in the table. It is seen that the relative strength, K^0 , of picric acid relative to acetic acid increases sharply with *n* for small *n*. However, the effect reaches saturation at about *n* = 2; further increase in the size of the alkyl group from ethyl to *n*-butyl produces no marked effect. This behavior is quite different from that of the dielectric constant in this series of solvents. The increase in 1/*D* is actually greater between ethanol and *n*-butyl alcohol than between methanol and ethanol.

Another revealing result in Table II is the large decrease of K^0 for picric acid in *n*-butyl alcohol (*D* = 17.4)²⁵ when 0.05 *N* LiCl is added. Under these conditions, a substantial fraction of the acetate and picrate ions form ion pairs with lithium ions, which are outstandingly poor centers of dispersion. (The molar refraction of Li⁺ ≈ 0.20 cc.¹³) Thus solvent molecules, which are good centers of dispersion, are displaced from the vicinity of the O⁻ atoms, and the extra dispersion energy of picrate ion is partially lost.

(14) H. von Halban and M. Seiler, *Helv. Chim. Acta*, **21**, 385 (1938); R. G. Bates and G. Schwarzenbach, *Experientia*, **10**, 482 (1954).

(15) L. J. Minnick and M. Kilpatrick, *J. Phys. Chem.*, **43**, 259 (1939); C. M. Judson and M. Kilpatrick, *J. Am. Chem. Soc.*, **71**, 3110 (1949); M. Kilpatrick and C. A. Arenberg, *ibid.*, **75**, 3812 (1953).

(16) F. G. Ciapetta and M. Kilpatrick, *ibid.*, **70**, 639 (1948); G. H. Debus, *Can. J. Chem.*, **34**, 1358 (1956); J. E. B. Randles and J. M. Tedder, *J. Chem. Soc.*, 1218 (1955); K. N. Bascombe and R. P. Bell, *ibid.*, 1096 (1959).

(17) R. W. Taft, Jr., *J. Am. Chem. Soc.*, **75**, 4231 (1953).

(18) I. M. Kolthoff and L. S. Guss, *ibid.*, **60**, 2516 (1938); **61**, 330 (1939).

(19) H. Goldschmidt and H. Aarflot, *Z. physik. Chem. (Leipzig)*, **A117**, 317 (1925).

(20) B. D. England and D. A. House, *J. Chem. Soc.*, 4421 (1962). For pK_{AUTO} we used the value 16.92, which is appropriate for molar concentration units.

(21) E. Grunwald and B. J. Berkowitz, *J. Am. Chem. Soc.*, **73**, 4939 (1951).

(22) A. J. Deyrup, *ibid.*, **56**, 60 (1934).

(23) G. Schwarzenbach and H. Rudin, *Helv. Chim. Acta*, **22**, 360 (1939).

(24) R. B. Mason and M. Kilpatrick, *J. Am. Chem. Soc.*, **59**, 572 (1937).

(25) L. A. Wooten and L. P. Hammett, *ibid.*, **57**, 2289 (1935).

(26) S. Bruckenstein and I. M. Kolthoff, *ibid.*, **78**, 2974 (1956).

(27) A. M. Shkodin and N. A. Izmailov, *J. Gen. Chem. USSR*, **20**, 39 (1950).

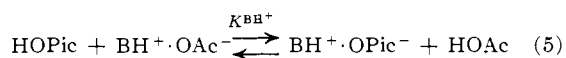
Other data in Table II serve as control experiments. Relative to acetic acid, the strength of trichloroacetic acid is quite insensitive to the solvent, in contrast to that of picric acid. This shows that the latter effect is not due to some peculiarity characteristic of acetic acid. The strength of picric acid relative to phenol varies with the solvent qualitatively in much the same way as that relative to acetic acid, showing that the effect is not due to a specific property of the carboxyl group. The solvent effect largely disappears in the comparison of picric acid with 2,4-dinitrophenol, a closely related one-color indicator.

Effect of Ion-Pair Formation with NH_4^+ and $(\text{CH}_3)_3\text{NH}^+$ on Relative Acid Strength

We have seen that the very striking medium effects on K^0 for picric acid relative to acetic acid are qualitatively consistent with dispersion effects. To complete the demonstration, we must also show that the effects are of the *correct magnitude* for a dispersion effect.

Attempts to calculate the dispersion energy among complex molecules in solution are always hampered by the incompleteness of our knowledge of the microscopic environments. At best, the introduction of arbitrary assumptions can be minimized—it can never be avoided entirely. In this section we report some measurements of relative acid strength under conditions where a good deal is known about the microscopic environments. Although some arbitrary assumptions are still needed to calculate the dispersion energy, we believe that they are mild enough so that at least semiquantitative agreement with experiment can be expected.

It is possible to change selectively the microscopic environment of an ionic species while keeping the overall solvent constant by taking advantage of ion-pair formation in a solvent of low dielectric constant. Accordingly, we have measured the equilibrium constant, K^{BH^+} , for reaction 5, where $\text{BH}^+ = \text{NH}_4^+$ or $(\text{CH}_3)_3\text{NH}^+$. The solvent is glacial acetic acid. As



might be expected on the basis of the low dielectric constant ($D = 6.2$ at 25°), the association of the free ions to ion pairs is nearly complete at the 0.01–0.1 M concentrations employed in these measurements.²⁸ The measurements of K^{BH^+} were made by a kinetic method and are based on an analysis of the rate of proton exchange between BH^+ and the carboxyl group of the solvent.²⁹ Details will be reported in the Experimental section, but we shall indicate here that the rates of exchange are almost exactly proportional to the concentrations of BH^+OAc^- in the equilibrium mixtures.

Results of our measurements are listed in Table III. K^{BH^+} is defined by eq. 6, where the brackets

$$K^{\text{BH}^+} = \frac{[\text{HOAc}][\text{BH}^+\text{OPic}^-]}{[\text{HOPic}][\text{BH}^+\text{OAc}^-]} \quad (6)$$

denote molar concentrations. The table shows that there is a large increase in K^{BH^+} for picric acid when BH^+ is $(\text{CH}_3)_3\text{NH}^+$ rather than NH_4^+ . The table

(28) See, for example, data in ref. 26 and 29.

(29) E. Grunwald and E. Price, *J. Am. Chem. Soc.*, **86**, 2965, 2970 (1964).

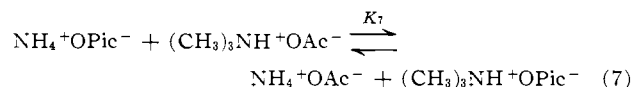
also lists our results for trichloroacetic acid, which serve as a control. The latter are quite insensitive to the change in BH^+ , the small difference being barely outside of experimental error. This pattern of K^{BH^+} (a high sensitivity to alkyl substitution in the cation in the case of picric acid, and a low one in the case of trichloroacetic acid) is completely analogous to the effect of alkyl substitution in the solvent on K^0 for these acids (see Table II).

TABLE III
ACID STRENGTH, K^{BH^+} , OF PICRIC ACID AND
TRICHLOROACETIC ACID RELATIVE TO ACETIC ACID AT 25° ^a

Acid	BH^+	$10^{-3}K^{\text{BH}^+}$	$10^{-3}k_{\text{BH}^+\text{OAc}^-}$ ^b sec. ⁻¹	$k_{\text{BH}^+\text{X}^-}$ ^c sec. ⁻¹
Picric	NH_4^+	0.69	6.08	30 ± 30
Picric	$(\text{CH}_3)_3\text{NH}^+$	3.4	0.945	$(0.3)^d$
$\text{Cl}_3\text{CCO}_2\text{H}$	NH_4^+	6.2	6.08	2 ± 2
$\text{Cl}_3\text{CCO}_2\text{H}$	$(\text{CH}_3)_3\text{NH}^+$	7.7	0.945	$(0.1)^d$

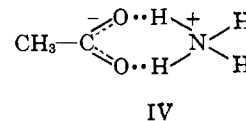
^a With glacial acetic acid as solvent and calculations based on eq. 14. ^b Taken from ref. 29. ^c $\text{X}^- = \text{OPic}^-$ or $\text{Cl}_3\text{CCO}_2^-$. ^d Calculated from data in columns 3 and 4 by means of the Brønsted relationship, assuming $\alpha = 1$; see text following eq. 14.

In analyzing the results, it simplifies matters to consider the *ratio* of K^{BH^+} , which is the equilibrium con-



stant for reaction 7. It is our thesis that the electrostatic free energy terms due to the interaction of the permanent charge distributions of the ions in the ion pairs nearly cancel in their effect on K_7 and that the observed effect is largely a dispersion effect, resulting from the replacement of H by CH_3 in the ammonium ion.

The structure of the ion pairs formed from aliphatic amines and excess acetic acid has been studied by infrared spectroscopic methods in carbon tetrachloride and in chloroform.³⁰ The data suggest that the ion pairs produced in acetic acid probably have the hydrogen-bonded structure, $\text{AcO}^- \cdot \text{HNR}_3^+$, with the acetyl group being further solvated by molecules of acetic acid. Cyclic structures such as IV, which are impossible for $(\text{CH}_3)_3\text{NH}^+$, appear to be unimportant even in the nonpolar solvents.^{30,31} We shall therefore



postulate that the ion pairs in our systems are represented by the formulas $\text{AcO}^- \cdot \text{HNR}_3^+$, $\text{AcO}^- \cdot \text{HN}(\text{CH}_3)_3^+$, $\text{PicO}^- \cdot \text{HNR}_3^+$, and $\text{PicO}^- \cdot \text{HN}(\text{CH}_3)_3^+$, which involve a single hydrogen bond between cation and anion. Molecular models then indicate that steric strains due to nonbonded repulsions between cation and anion are negligible in all ion pairs. Hence, the length of the $\text{O}^- \cdot \text{HN}$ hydrogen bond should not change when the cation is $(\text{CH}_3)_3\text{NH}^+$ instead of NH_4^+ . Since the ionic charge is formally located on the nitrogen

(30) E. A. Yeger and G. M. Barrow, *ibid.*, **77**, 4474, 6206 (1955).

(31) On the other hand, Davis and Paabo infer from the values of equilibrium constants that diphenylguanidinium benzoate in benzene has a cyclic structure analogous to IV: M. M. Davis and M. Paabo, *ibid.*, **82**, 5081 (1960).

atom in both species, and since the dipole moment of the permanent charge distribution is zero for one and very small for the other, NH_4^+ and $(\text{CH}_3)_3\text{NH}^+$ are nearly identical electrostatic systems. And because of the equal O^-HN bond lengths, the electrostatic free energies of interaction of NH_4^+ and $(\text{CH}_3)_3\text{NH}^+$ with a given anion should be almost exactly the same. Moreover, whatever small differences do exist should tend to cancel out in the comparison of electrostatic interactions with two anions, as in eq. 7.

On this basis, the considerable deviation of K_7 from unity could be largely a dispersion effect. To support this assignment, we shall now make a semi-quantitative calculation of the dispersion energy and show that it is of the same magnitude as $-RT \ln K_7$. Our model is essentially that shown in Fig. 1. The difference in the dispersion effect between $\text{HN}(\text{CH}_3)_3^+$ and HNH_3^+ will be represented as a single oscillator, equivalent to the dispersion effect of three CH_2 groups and located at the center of mass of the three carbon atoms. We shall assume that this oscillator is isotropic. The difference in the dispersion effect between picrate ion and acetate ion will be attributed to the delocalization in picrate ion of a certain fraction of the oscillator strength that is formally assignable to the O^- atom.

The properties of the oscillators that are delocalized in picrate ion have already been listed in Table I. The dispersion energy of these oscillators with the $(\text{CH}_2)_3$ equivalent oscillator can be calculated from eq. 2. The required value of μ_s^2 can be obtained from eq. 8, where ν_s is the characteristic frequency and α_s the

$$\mu_s^2 = 3h\nu_s\alpha_s/2 \quad (8)$$

polarizability. London assumed that $h\nu_s$ is equal to the ionization energy.¹² α_2 is equal to $3\alpha_{\text{CH}_2}$, which in turn is roughly equal to $3(3R_{\text{CH}_2})/4\pi N_0$, where R_{CH_2} is the additive contribution of a CH_2 group to the molar refraction and N_0 is Avogadro's number. We shall use $\alpha_{\text{CH}_2} = 1.82 \times 10^{-24} \text{ cm}^3$,¹¹ and $\nu_s = 2.4 \times 10^{15} \text{ sec}^{-1}$ (10 e.v.). Values of R_1 , R_2 , and $\cos \varphi$ were calculated from known interatomic distances¹⁰ for each delocalized transition. R_1 is the distance from the $(\text{CH}_2)_3$ equivalent oscillator to the O^- atom; R_2 is the distance to the NO_2 group. R_2 was calculated on the assumption that the O^-HN bond lies on the twofold axis of the picrate ion. ν was taken as ν_{max} . Numerical values, including those of the dispersion energy for each transition, are listed in Table I. The total dispersion energy for the two *ortho*- and the *para*-delocalized oscillators is -1.82 kcal./mole . These delocalized transitions represent a total oscillator strength of 0.31.

To be subtracted from this result is the dispersion energy ascribable to an equal oscillator strength that is localized on the O^- atom of acetate ion. We shall treat the localized oscillators as dipoles and obtain the relevant value of μ^2 from the polarizability (which is based on molar refraction data) and the ionization potential, as previously stated. The polarizability of acetate ion can be represented formally as the sum of the polarizability of the uncharged acetate group (which we deduce from that of acetic acid), and an additional term, $\delta\alpha$, due to the electron that is transferred to

the acetate group on ionization. Using molar and atomic refractions, $\delta\alpha$ is given by eq. 9. The value of

$$\delta\alpha = 3(R_{\text{OAc}^-} - R_{\text{HOAc}} + R_{\text{H}})/4\pi N_0 \quad (9a)$$

$$= 0.97 \times 10^{-24} \text{ cm}^3 \quad (9b)$$

$\delta\alpha$ (data of ref. 11 and 13) in eq. 9b refers to one electron and hence to an oscillator strength of 1.00. In the comparison with picrate ion, we must therefore use $0.31\delta\alpha$. We shall assume that the oscillator represented by $0.31\delta\alpha$ is isotropic, that it is localized at the oxygen nucleus, and that its characteristic frequency, ν , is $2.4 \times 10^{15} \text{ sec}^{-1}$ (10 e.v.). The dispersion energy of this oscillator with the $(\text{CH}_2)_3$ -equivalent oscillator is then given by eq. 10, which is based on London's papers.¹² The symbols α_s , ν_s , and R_1 have the same

$$E_{\text{disp}} = -\frac{3}{2} \frac{(0.31\delta\alpha)(\alpha_s)}{R_1^6} \frac{h\nu\nu_s}{(\nu + \nu_s)} \quad (10)$$

significance as before, and we shall use the same values. The result is $E_{\text{disp}} = -0.22 \text{ kcal./mole}$.

On the basis of this calculation, the dispersion energy contribution to ΔF° for reaction 7 is $-1.82 + 0.22$, or -1.60 kcal./mole . This value must be compared with the experimental value of $-RT \ln K_7$, which is -0.95 kcal./mole . It is clear that the experimental value is of the correct magnitude for a dispersion effect.

Some Applications

Base Strength of the Aliphatic Amines.—A problem of long standing concerning acid and base strength is the effect of alkyl substitution on the base strength of amines. In water, the observed effects are complex and cannot be rationalized on the basis of the inductive effect alone. Some examples showing this complexity are the following sequences of base dissociation constants in water: $\text{NH}_3 < \text{CH}_3\text{NH}_2 \approx (\text{CH}_3)_2\text{NH} > (\text{CH}_3)_3\text{N}$; and $\text{NH}_3 < n\text{-BuNH}_2 < (n\text{-Bu})_2\text{NH} >> (n\text{-Bu})_3\text{N}$.³² On the other hand, base strength has also been measured in aprotic solvents such as chlorobenzene or anisole, with color indicators such as 2,6-dinitrophenol, under conditions where the acid-base reaction produces an ion pair.^{33,34}



To quote Bell and Bayles,³³ "the values obtained (under these conditions) provide a more rational account of the effect of alkyl substitution on basic strength than do dissociation constants in water." For example, the base strength of the *n*-butylamines, measured with 2,4-dinitrophenol in chlorobenzene,³⁴ is in the sequence mono- < di- < tri-*n*-butylamine, which would be rational for an inductive effect. From the point of view of the present paper, however, the latter sequence is best characterized as a sequence of relative dispersion effects. In equilibrium 11, the ammonium ion, in contrast to the amine, exists adjacent to a molecule that indicates by its visible absorption of light that it is a strong center of dispersion. Hence, alkyl substitution on nitrogen should shift the equilibrium to the right because the dispersion energy of the product increases by more than that of the reactants. In water, where the dispersion effects on ΔF° are smaller, other

(32) N. F. Hall and M. R. Sprinkle, *J. Am. Chem. Soc.*, **54**, 3469 (1932).

(33) R. P. Bell and J. W. Bayles, *J. Chem. Soc.*, 1518 (1952).

(34) J. W. Bayles and A. Chetwyn, *ibid.*, 2328 (1958).

mechanisms of interaction with the medium, such as hydrogen bonding, become relatively important and produce a more complex pattern for the observed overall substituent effects.

We might remark in this connection that the description of the substituent effect of alkyl groups as an *inductive* effect has always seemed a little unsatisfactory, especially since carbon is more electronegative than hydrogen.¹⁰ On the other hand, it could very well be that the substituent effect of alkyl groups is an intramolecular variety of the dispersion effect. In particular, the quantitative aspects of the effect, as measured for example by Taft's σ^* -parameters for alkyl and hydrogen,³⁵ are precisely in the sequence expected qualitatively for a dispersion effect.

Preferential Solvation.—If electrostatic interactions were dominant, an ionic solute in a binary solvent would tend to be solvated preferentially by the more polar solvent component, because such solvation would raise the local dielectric constant near the ions.^{36,37} If, however, the less polar solvent component happens to be the stronger center of dispersion, and if the ion is also a strong center of dispersion, then the electrostatic effect will be opposed by a sizable dispersion effect and the net result will be hard to predict. An example of a binary solvent in which the electrostatic and dispersion forces produce opposing patterns of preferential solvation is a mixture of water with an alcohol. We believe that when the ions are strong centers of dispersion, the dispersion effects will dominate.

Consider, for example, the data for the relative strength of 2,6-dinitrophenol and acetic acid in the system methanol-water,³⁸⁻⁴⁰ which are given in Table IV. K^0 is 11.5 in pure water and 87 in pure methanol. This increase is in the direction expected of a dispersion effect, since 2,6-dinitrophenoxide ion, in which some oscillators are delocalized, is a strong center of dispersion.

TABLE IV

ACID STRENGTH OF 2,6-DINITROPHENOL RELATIVE TO ACETIC ACID IN THE SYSTEM METHANOL-WATER AT 25°C

Mole % CH ₃ OH	log K^0	Mole % CH ₃ OH	log K^0
0.00	1.06	65.17	1.87
8.69	1.14	74.41	2.00
18.43	1.24	91.67	2.26
36.97	1.49	97.29	2.00
46.58	1.58	100.00	1.94

^a Based on data in ref. 38-40.

To analyze the data obtained in the mixed solvents, let us consider two extreme models: (i) very strong preferential hydration of the ions, and (ii) very strong preferential alcoholation of the ions. In model i the addition of small amounts of water to pure methanol will result in a large increase in K_A for both acids, partly because both conjugate bases are now stabilized by hydration. However, the stabilization by hydra-

tion is opposed more effectively by dispersion forces in the case of 2,6-dinitrophenoxide ion than of acetate ion. Hence K^0 , which is the *ratio* of the K_A values, should decrease appreciably as small amounts of water are added to methanol. On the other hand, small amounts of methanol added to water should exert only a small and possibly negligible effect on K^0 , largely owing to their effect on the macroscopic dielectric constant. In model ii this situation is reversed. Small amounts of water added to methanol should exert only a small effect on K^0 . Small amounts of methanol added to water should produce an appreciable increase in K^0 .

On examining the data in Table IV, we find much better agreement with model ii than with model i. The effect of adding water to methanol on log K^0 appears to be a small increase rather than a substantial decrease. In fact, if the point at 91.67 mole % can be neglected (experimental error is notoriously unpredictable in mixed solvents if results from different laboratories are compared), K^0 is substantially constant throughout the range from 100 to 70 mole % methanol. We conclude, therefore, that a model of strong preferential hydration for both conjugate bases is inconsistent with the facts. On the other hand, we cannot decide from the data whether solvation of the ions by water and by methanol are of coordinate importance or whether the strong preferential solvation by methanol assumed in model ii is the better description.

Experimental

Measurement of K^{BH^+} in Acetic Acid.—Consider a moderately dilute solution of the acid, HX, in glacial acetic acid. Suppose also that HX is a stronger acid than HOAc but weaker than H_2OAc^+ . When an aliphatic amine, B, is added at low concentration to such a solution, ionization of the amine is virtually complete, the products being the ion pairs, BH^+X^- and BH^+OAc^- , and a very small fraction of free ions, BH^+ . The ion pairs will be in equilibrium with their parent acids, as shown for $HX = HOPic$ in eq. 5.

We wish to deduce K^{BH^+} , defined for $HX = HOPic$ in eq. 6, from the *rate* of proton exchange of the NH protons with the COOH and XH protons of the medium. In the experiments reported here, this rate was measured conveniently by nuclear magnetic resonance techniques, as described previously.²⁹ Proton exchange between AcOH and HX is very fast, so that in the absence of B a sharp single COOH-HX proton resonance line results. In the presence of B this line is exchange broadened. Let R be the rate of exchange per liter per second of NH protons with AcOH and HX. On the basis of the kinetic analysis made previously,²⁹ R is proportional to the concentration of the ion pairs formed by BH^+ and is therefore given by eq. 12.⁴¹ It is

$$R = k_{BH^+OAc^-} [BH^+OAc^-] + k_{BH^+X^-} [BH^+X^-] \quad (12)$$

convenient to eliminate $[BH^+OAc^-]$ in eq. 12 by using the expression for K^{BH^+} . The result is eq. 13. In our experiments,

$$R = \left(\frac{k_{BH^+OAc^-}}{K^{BH^+}} \frac{[HOAc]}{[HX]} + k_{BH^+X^-} \right) [BH^+X^-] \quad (13)$$

$[BH^+OAc^-]$ was much smaller than $[BH^+X^-]$; hence $[BH^+X^-] \approx c_B$, the formal concentration of the added amine, and $[HX] = c_{HX} - c_B$. Thus eq. 13 reduces to 14. According to eq.

$$\frac{R}{c_B} = \frac{k_{BH^+OAc^-}}{K^{BH^+}} \frac{[HOAc]}{[HX]} + k_{BH^+X^-} \quad (14)$$

(41) Principles governing the rate laws for the reaction of pairs of rapidly interconverting subspecies are reviewed by J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, p. 119.

(35) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 13.

(36) P. Debye, *Z. physik. Chem.*, **130**, 56 (1927).

(37) G. Scatchard, *J. Chem. Phys.*, **9**, 34 (1941).

(38) G. Kortüm and M. Buck, *Z. Elektrochem.*, **62**, 1083 (1958).

(39) A. L. Bacarella, E. Grunwald, H. P. Marshall, and E. L. Purlee, *J. Org. Chem.*, **20**, 747 (1955); *J. Phys. Chem.*, **62**, 856 (1958).

(40) T. Shedlovsky and R. L. Kay, *ibid.*, **60**, 151 (1956).

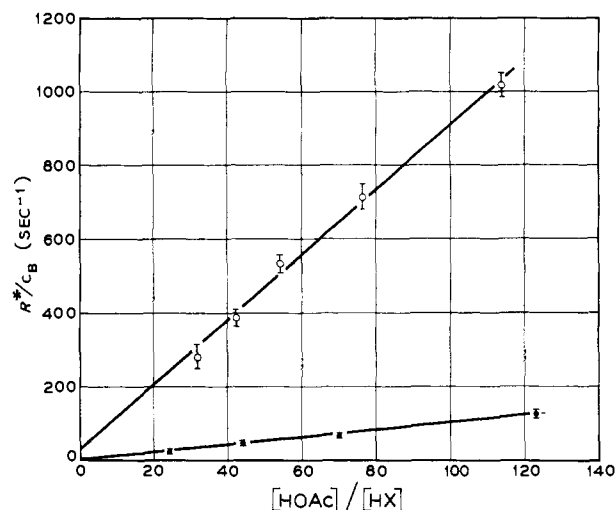


Fig. 2.—Kinetic plot for proton exchange of ammonium salts in glacial acetic acid at 25°: the open circles are for added picric acid, the closed circles for added trichloroacetic acid. $R^* = R(1 + [\text{HOAc}]/K^{\text{BH}^+}[\text{HX}])$; numerical results are listed in Table III.

14, a plot of R/c_B vs. $[\text{HOAc}]/[\text{HX}]$ is linear. Since $k_{\text{BH}^+\text{OAc}^-}$ is already known,²⁹ K^{BH^+} can be obtained from the slope.⁴²

Figure 2 shows kinetic plots according to this method for proton exchange of NH_4^+ at 25° when the added acid, HX, is picric acid or trichloroacetic acid. Good straight lines are obtained for both acids as required by the theory. The figure shows a striking difference between the two slopes and hence between the values of K^{BH^+} for the two acids.

In interpreting the kinetic data, the previously reported value, $k_{\text{NH}_4^+\text{OAc}^-} = 6.08 \times 10^3 \text{ sec.}^{-1}$ at 25°, was used. Results obtained for K^{BH^+} and for the intercepts, $k_{\text{BH}^+\text{X}^-}$, are given in Table III. The values of K^{BH^+} have already been discussed. The values of $k_{\text{BH}^+\text{X}^-}$ are very small, differing only by about one standard deviation from zero. According to the Brønsted relationship,⁴³ we expect that $\log(k_{\text{BH}^+\text{OAc}^-}/k_{\text{BH}^+\text{X}^-}) = \alpha \log K^{\text{BH}^+}$, where α is a constant, independent of HX. Within experimental error, the present data fit the Brønsted relationship with $\alpha \approx 0.9$. The uncertainty in α can be estimated from the standard deviation of $k_{\text{BH}^+\text{X}^-}$. Since the hypothesis that $k_{\text{BH}^+\text{X}^-} = 0$ cannot be definitely excluded, the upper limit to α is infinity. However, the lower limit to α is finite and is somewhat greater than 0.7. In a previous paper,²⁹ we found that for a series of aliphatic amines, $k_{\text{BH}^+\text{OAc}^-}$ in acetic acid is nearly proportional to the acid strength of BH^+ in water. The present data show that the rate constant for reaction of the ion pair in acetic acid is also nearly proportional to the base strength of the anion that accepts the proton.

Figure 3 shows kinetic plots for proton exchange of $(\text{CH}_3)_3\text{NH}^+$ in acetic acid at 49.7° when the added acid is picric acid or trichloroacetic acid. The slopes of the lines established by the data are defined with reasonable accuracy. However, the intercepts are not distinguishable from zero. In interpreting these data and those obtained at 25° (Table III), we assumed that the intercepts, $k_{\text{BH}^+\text{X}^-}$, actually have small positive values that are given by a Brønsted relationship with $\alpha = 1$. Values of $k_{\text{BH}^+\text{OAc}^-}$ for trimethylammonium acetate were 945 sec.^{-1} at 25°, as reported previously,²⁹ and $1.01 \times 10^4 \text{ sec.}^{-1}$, extrapolated on the basis of the previous work to 49.7°.

Materials.—Ammonia and trimethylamine were obtained as compressed gases from the Matheson Co. Trichloroacetic acid (Eastman) was recrystallized from benzene and dried over magnesium perchlorate for several days in a vacuum desiccator; m.p. 59.5–60.3 (lit.⁴⁴ m.p. 59.4°).

(42) A sufficient test of the assumed inequality, $[\text{BH}^+\text{OAc}^-] \ll [\text{BH}^+\text{X}^-]$, is that $R/c_B \ll k_{\text{BH}^+\text{OAc}^-}$. When this is not the case, an iterative method of calculation may be used. In first approximation, the data are plotted according to eq. 4 and an initial value, $K_1^{\text{BH}^+}$, is obtained. In second approximation, $\{R(1 + [\text{HOAc}]/K_1^{\text{BH}^+}[\text{HX}])\}/c_B$ is used in eq. 14 instead of R/c_B , and a second estimate, $K_2^{\text{BH}^+}$, is obtained from the slope. The procedure is iterated until the value obtained for K^{BH^+} converges.

(43) Reference 41, pp. 235–242.

(44) J. Kendall and P. M. Cross, *J. Am. Chem. Soc.*, **43**, 1429 (1921).

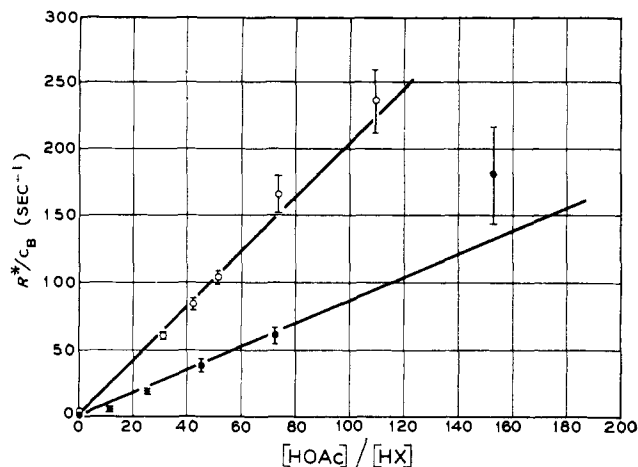


Fig. 3.—Kinetic plot for proton exchange of trimethylammonium salts in glacial acetic acid at 49.7°; symbols have the same significance as in Fig. 2. $k_{\text{BH}^+\text{OAc}^-} = 1.01 \times 10^4 \text{ sec.}^{-1}$, extrapolated to 49.7° from data at lower temperatures; $K^{\text{BH}^+} = 5.0 \times 10^3$ (picric acid) and 11.6×10^3 ($\text{Cl}_3\text{CCO}_2\text{H}$).

Picric acid (Baker) was recrystallized from absolute ethanol and dried over P_2O_5 at 80° in an Abderhalden pistol; m.p. 121.1–122.0°. Acetic acid was purified as described previously.²⁹

Solutions were prepared exactly as described previously.²⁹ However, weighed quantities of trichloroacetic acid were dried to constant weight *in vacuo* before using.

Rate Measurements.—Rates of exchange of NH protons with COOH protons were measured by n.m.r. techniques, as described previously.²⁹ We wish, however, to give the following additional information.

A. Trimethylammonium Salts.—In the experiments with added picric acid or trichloroacetic acid (Fig. 3 and Table III), rate measurements were based on the methyl-proton resonance of trimethylammonium ion, which was recorded in slow passage. Rates of exchange were calculated from the width or shape of the n.m.r. lines as described previously.⁴⁵ The CH–NH spin-coupling constant of trimethylammonium ion under the experimental conditions was found to be 32.2 radians/sec. The concentration of trimethylammonium salts was 0.1 to 0.2 M.

B. Ammonium Salts.—Rates of proton exchange were calculated from spin-echo measurements of the transverse relaxation time, T_2' or T_2 , of the carboxyl protons of acetic acid. In the experiments with added trichloroacetic acid, the COOH protons gave a single line. No detectable exchange broadening of this line was observed in the absence of ammonia. This shows that the rate of exchange of the two kinds of COOH protons is very fast. In the experiments with added picric acid, the OH–COOH proton line was slightly exchange broadened even in the absence of ammonia. This exchange broadening amounted to about 0.03 sec.^{-1} for 1 M picric acid and was not affected by the addition of sodium acetate.

In the presence of ammonia, there was appreciable exchange broadening due to exchange with NH protons. Under our conditions, the rate of this exchange could be calculated from eq. 15 for ‘lifetime broadening.’ Here $1/T_2'$ and $1/T_2$ are the values

$$\frac{1}{T_2'} - \frac{1}{T_2} = \Delta = \frac{R}{[\text{AcOH}] + [\text{HX}]} \quad (15)$$

of the transverse relaxation time at constant [HX], measured, respectively, with and without added ammonia.

The experiments with added trichloroacetic acid were done with degassed solutions. All other measurements were made on air-saturated solutions.

In connection with the trichloroacetic acid experiments, we had occasion to measure T_1 and T_2 of the carboxyl protons for degassed pure acetic acid. The results were (at 25°) $T_1 = 8.9$ and $T_2 = 7.8$ sec. for degassed acetic acid; and $T_1 = 3.13$ and $T_2 = 2.75$ sec. for air-saturated acetic acid.

Decarboxylation of Trichloroacetate Salts.—It is well known that trichloroacetate ion decarboxylates slowly in solution.⁴⁶

(45) E. Grunwald, *J. Phys. Chem.*, **67**, 2208 (1963).

(46) See, for example, J. Hine, ‘Physical Organic Chemistry,’ 2nd Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 491.

In order to find out whether decarboxylation was taking place in our systems, a solution consisting of 1.3 *M* $\text{Cl}_3\text{CCO}_2\text{H}$ and 0.2 *M* $(\text{CH}_3)_3\text{NH}\cdot\text{O}_2\text{CCl}_3$ in acetic acid was placed in a n.m.r. sample tube. The tube was then degassed, sealed, and heated at 100° for 1 hr. At the end of this treatment, the n.m.r. spectrum was compared with that of an unheated sample of the same solution at room temperature. The heat treatment resulted in the formation of a new n.m.r. line at 5.50 p.p.m. downfield from that of the CH_3 protons of acetic acid. This line could be assigned to chloroform. There was no trace of a chloroform n.m.r. line in the unheated sample.

If decarboxylation were taking place at a significant rate during the measurements of the relative acid strength of trichloroacetic acid, the result would be an increase in the ratio $[\text{HOAc}]/[\text{Cl}_3\text{CCO}_2\text{H}]$ with time, and hence, according to eq. 14, an increase of *R* with time. In order to test for this eventuality, we measured *R* immediately after the preparation of each solution, and then again after the lapse of a fixed interval of time. The changes in *R* were small enough so that extrapolation to zero time presented no problem. In the case of added ammonia, the values of *R*, measured immediately after the preparation of each solution, required no correction; in the case of added trimethylamine, the corrections amounted to less than 7%.

Special Techniques for Supersaturated Solutions of Ammonium Picrate.—When pure picric acid is added to a solution of

ammonium acetate in glacial acetic acid, a precipitate of ammonium picrate is formed immediately and the concentration, c_B , of ammonium salts remaining in solution is reduced to a small and undetermined value. On the other hand, when a solution of ammonium acetate in acetic acid is added to a solution of picric acid in acetic acid, a metastable liquid solution results. The lifetime of the metastable solution, before precipitation begins, seems to depend on c_B . At room temperature, when $c_B \approx 0.04$ *M*, the lifetime is too short to permit completion of the n.m.r. measurement of *R*, which takes about 20 min.; but when $c_B \approx 0.02$ *M*, the lifetime is greater than 12 hr. at the picric acid concentrations used in our experiments. Once precipitation has started, it proceeds rapidly, but prior to the onset of precipitation, there is no evidence for turbidity when the solution is examined under light with a magnifying glass. During their lifetime, the metastable solutions were handled just as if they were stable, and the measured values of *R* remained constant.⁴⁷

Acknowledgment—It is a pleasure to thank Drs. B. Linder, E. G. McRae, and S. Meiboom for helpful discussions.

(47) We are grateful to Dr. Z. Luz for doing the n.m.r. measurements immediately after the preparation of each solution; thus, *R* was obtained at the earliest possible time.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF OREGON, EUGENE, OREGON]

Diffusion Coefficients of Iodine Atoms in Carbon Tetrachloride by Photochemical Space Intermittency

By STUART A. LEVISON AND RICHARD M. NOYES

RECEIVED JUNE 22, 1964

The existence of the photochemical space intermittency effect has been confirmed, and the method has been used to measure the diffusion coefficients of iodine atoms in carbon tetrachloride at 25 and 38°. These results and less extensive previously reported studies by the same method constitute the first measurements of the diffusion coefficient of a reactive free radical in solution. Diffusion coefficients of iodine atoms are about five times larger than those of iodine molecules in the same solution; the difference is somewhat greater than had been expected.

Introduction

If photochemically produced radicals are destroyed in pairs, and if the medium is illuminated with a pattern of light and dark areas, the average steady-state concentration of radicals is dependent upon the size and shape of the illuminated regions as well as upon the total area illuminated. The theory of this photochemical space-intermittency effect was developed previously,¹ and the nonlinear differential equations were solved numerically for certain specific examples. Salmon and Noyes² subsequently demonstrated that the predicted effect did indeed exist for iodine atoms in hexane.

If quantum yields for radical production and rate constants for recombination are known independently, the effect can be used to determine diffusion coefficients of reactive free radicals; these quantities cannot be measured by any other known process. The present paper reports such a measurement for iodine atoms in carbon tetrachloride.

Experimental

Apparatus.—The apparatus was constructed by Dr. G. A. Salmon. It is shown schematically in Fig. 1. The light source, S, consisted of a medium pressure mercury arc (CH_5) surrounded by a jacket through which thermostated water was pumped. The light from the arc passed through a circular aperture, A, and the 4358-Å. line was isolated with an interference filter, F.

The beam was rendered parallel with the lens, L, and the mirror, M, was used to direct the beam vertically through a window in the bottom of the conventional water thermostat, T. This design was chosen so that the light path through the reaction cell would be vertical and the main component of convection would be parallel to the beam.

The beam was broken into light and dark areas by the pattern, P, mounted against the bottom face of the reaction cell, C. The beam was monitored by a conventional photometer detector, D, mounted in a tube with a window to eliminate distortion at the air-water interface of the thermostat.

The patterns, P, were mounted on glass plates 1 in. square. Each was a "leopard" pattern of circular spots arranged so that each spot had six nearest neighbors and so that the distance between centers of adjacent spots was exactly three times the spot diameter. The pattern was created as a photograph with a high-contrast, small-grain emulsion. The developed emulsion was then protected with a microscope cover glass, and the edges were sealed to keep out moisture. The first master design was prepared by drafting the approximately 10,000 spots by hand, and the individual patterns were then prepared by the Eastman Kodak Company by photographing this master. Because of the difficulty of getting sufficient uniformity with hand drafting, a new master having spot diameters of 0.179 cm. was prepared by Metal Marking Industries, Englewood, Colo., by a photographic process that involved repeated adjacent reproductions of the same small drafted design. The company then prepared individual patterns by photographing this master. Spot diameters in these patterns were measured with a microcomparator and ranged from 0.00796 to 0.1002 cm. The background of each pattern could be regarded as completely opaque, but the spots did not transmit the entire incident intensity. Lamp intensities were adjusted so that the same total amount of light was transmitted by the pattern used in every run.

(1) R. M. Noyes, *J. Am. Chem. Soc.*, **81**, 566 (1959).

(2) G. A. Salmon and R. M. Noyes, *ibid.*, **84**, 672 (1962).