

Table I. Radiolysis of 1,4-Cyclohexadiene

Dose rate × 10 ⁻¹⁹ , e.v./ g. hr.	Irradiation period, hr.	G(D)	G(B)	G(C)	G(80) ^a	C:B	A:B
5.3	2	1.12	0.64	2.54	0.45	4.0	3.0
5.3	5	1.23	0.61	2.33	0.35	3.83	2.83
5.3	10	1.22	0.56	2.06	0.46	3.7	2.7
1.1	22	1.34	0.61	2.16	0.43	3.55	2.55
1.1	48	1.15	0.53	1.91	0.42	3.6	2.6
Av. = 2.74 ± 0.14							

^a Unidentified product with mass spectrometric parent mass of 80.

The results with 0.11 mole % CH₃I (Table II) also show a very high yield of isomerization of 1,4-cyclohexadiene to 1,3-cyclohexadiene which is presumably the result of a chain process. As expected from a radical chain reaction, a significant amount of isomerization takes place only at low dose rates in the ⁶⁰Co source, but not with 2.8-Mev. electrons at 10⁻⁶ amp. At low temperature (-50 to -15°) the G(B) is considerably decreased. This temperature effect shows that the isomerization requires some activation energy. We propose a mechanism involving the production of iodine atoms by the (indirect) dissociation of the methyl iodide followed by an iodine atom catalyzed isomerization of the cyclohexadiene similar to that indicated in studies with molecular iodine.⁶ With increasing dose rates, the chain-terminating steps be-

(6) M. K. Eberhardt, to be published:

Table II. Radiolysis of 1,4-Cyclohexadiene-¹⁴CH₃I^a

Irradiation period, ^b hr.	G(D)	G(B)	G(C)	G(80) ^c	I:II
2	1.76	58.7	4.84	0.44	1.73
2	1.77	54.7	3.73	0.43	1.15
2 ^d	1.76	4.45	2.54	0.37	1.28
5	1.61	41.8	4.65	0.43	1.85
10	1.51	26.4	2.96	0.41	2.04
Av. = 1.61 ± 0.3					

^a Amount of ¹⁴CH₃I, 0.11 mole % ± 10%. ^b At a dose rate of 5.3 × 10¹⁹ e.v./g. hr. ^c Unidentified product with mass spectrometric parent mass of 80. ^d Temperature -50 to -15°.

come more important and thus decrease the amount of isomerization. In the studies with iodine,⁶ the disproportionation of 1,4-cyclohexadiene in the presence of small amounts of iodine (0.5 M) gives in quantitative yield cyclohexene, benzene, and some 1,3-cyclohexadiene and 4-iodocyclohexene. The yield of 1,3-cyclohexadiene was found to increase with decreasing iodine concentration. The results observed in the present study can be explained as a continuation of the effect of decreasing iodine concentration, which favors chain propagation over the chain-terminating steps. We have also observed⁶ that the photolysis of CH₃I in 1,4-cyclohexadiene leads to a large amount of isomerization.

The yields of the unknown compound of mass 80 are listed in Tables I and II as G(80). The yield of this compound is not affected by added CH₃I and must therefore be formed by a nonradical process.

Acid-Base Equilibria in Benzene. I. A Colligative Property and Infrared Study of the Reactions of Some Carboxylic Acids and Nitrogen Bases

Stanley Bruckenstein and Atsuoshi Saito

Contribution from the Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455. Received August 14, 1964

The reaction of primary, secondary, and tertiary amines (B) with carboxylic acids (HX) in benzene as solvent was studied at a base concentration of 0.01 M. A dynamic differential vapor pressure technique and infrared spectroscopy were used to establish the stoichiometry of the acid-base reactions. The principal species identified were ion pairs and other uncharged ionic aggregates. Three types of ion pairs are postulated: (1) BH⁺X⁻, (2) BH⁺HX₂⁻, and (3) BH⁺X(HX)₂⁻. These ion pairs tend to form oligomers; the stronger the acid or base, the greater the oligomer formation. Reaction of mixtures of two bases with an acid indicates that specific, strong interactions can occur between ion pairs containing different cations.

Introduction

Relatively few quantitative equilibrium studies have been made in benzene. Early indicator studies by LaMer and Downes,¹ involving both indicator acids and bases with colorless acids and bases, demonstrated that aqueous equilibrium concepts could not adequately account for their experimental results. They interpreted their data semiquantitatively by assuming equilibrium constants of the form

$$K_I' = \frac{K_{HA}^n}{K_{H,I}} = \frac{(H_n I)(A)^n}{(I)(HA)^n}$$

(1) V. K. LaMer and H. C. Downes, *J. Am. Chem. Soc.*, **55**, 1840 (1933).

to describe the reaction between indicators and colorless acids or bases, e.g., between dimethyl yellow (H_nI) and trichloroacetic acid (HA). LaMer and co-workers also demonstrated the feasibility of potentiometric titrations in benzene.¹ Again, complex equilibrium behavior differing considerably from aqueous behavior was noted.

Davis^{2a-i} examined acid-base indicator properties in benzene using spectrophotometric techniques. Their results demonstrate that specific interactions between different acids and bases can be extremely important; e.g., the color of bromophthalein magenta E in the presence of excess amine depends on whether the amine is a primary, secondary, or tertiary amine.^{2a}

The association of carboxylic acid in benzene has been studied by various methods. The principal approach has involved using colligative properties,³⁻⁶ though infrared spectroscopy^{7,8} and solvent extraction⁹ have also been employed.

In recent years, a better understanding of equilibria in nonaqueous solvents has developed. The dissociation of ionic compounds in a solvent is governed both by the solvent's dielectric constant and its solvation ability. A detailed treatment of acid-base equilibria in a low dielectric constant, but good solvating solvent has been given,^{10a-e} as have quantitative treatments in solvents of intermediate dielectric constant.¹¹⁻¹³

The solvent benzene represents an extreme example of a low dielectric constant, low solvating ability solvent. Elementary facts such as the stoichiometry of acid-base reactions and the extent of aggregation of acid-base adducts have never been studied systematically in benzene, and we believe that such information is fundamental in order to obtain a quantitative understanding of solution equilibria in benzene.

One of the simplest, and least ambiguous, methods for obtaining this kind of data involves using a colligative property. The method originally described by Hill^{14a} has been developed considerably in recent years

(2) (a) M. M. Davis and P. J. Schuhmann, *J. Res. Natl. Bur. Std.*, **39**, 221 (1947); (b) M. M. Davis, P. J. Schuhmann, and M. E. Lovelace, *ibid.*, **41**, 27 (1948); (c) M. M. Davis and E. A. McDonald, *ibid.*, **42**, 595 (1949); (d) M. M. Davis and H. B. Hetzer, *ibid.*, **46**, 496 (1951); (e) *ibid.*, **48**, 381 (1952); (f) *ibid.*, **54**, 309 (1955); (g) *J. Am. Chem. Soc.*, **76**, 4247 (1954); (h) *J. Res. Natl. Bur. Std.*, **60**, 569 (1958); (i) M. M. Davis and M. Paabo, *J. Am. Chem. Soc.*, **82**, 5081 (1960).

(3) B. C. Burton and C. A. Kraus, *ibid.*, **73**, 4561 (1951).
 (4) G. Allen and E. H. Caldin, *Trans. Faraday Soc.*, **49**, 895 (1953).
 (5) K. L. Wolf and G. Metzger, *Ann. Chem.*, **563**, 157 (1949).
 (6) H. J. Wall and H. W. Banes, *J. Am. Chem. Soc.*, **67**, 898 (1945).
 (7) H. Dunken and K. Palm, *Z. Chem.*, **53** (1961).
 (8) H. Dunken and G. Rudakoff, *ibid.*, **54** (1961).
 (9) M. Davies and D. M. L. Griffiths, *J. Chem. Soc.*, **132** (1955).
 (10) (a) I. M. Kolthoff and S. Bruckenstein, *J. Am. Chem. Soc.*, **78**, 1 (1956); (b) S. Bruckenstein and I. M. Kolthoff, *ibid.*, **78**, 10 (1956); (c) *ibid.*, **78**, 2974 (1956); (d) *ibid.*, **79**, 5915 (1957); (e) I. M. Kolthoff and S. Bruckenstein, *ibid.*, **79**, 1 (1957).

(11) H. Van Looy and L. P. Hammett, *ibid.*, **81**, 3872 (1959).
 (12) (a) I. M. Kolthoff, S. Bruckenstein, and M. K. Chantooni, Jr., *ibid.*, **83**, 3927 (1961); (b) I. M. Kolthoff and M. K. Chantooni, Jr., *J. Phys. Chem.*, **66**, 1675 (1962); (c) *J. Am. Chem. Soc.*, **85**, 426 (1963); (d) *ibid.*, **85**, 2195 (1963).

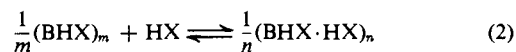
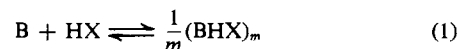
(13) (a) J. F. Coetzee and W. S. Muney, *J. Phys. Chem.*, **66**, 89 (1962); (b) J. F. Coetzee and G. R. Padmanabhan, *ibid.*, **66**, 1708 (1962); (c) J. F. Coetzee, G. R. Padmanabhan, and G. P. Cunningham, *Talanta*, **11**, 93 (1964).

(14) (a) A. U. Hill, *Proc. Roy. Soc. (London)*, **A127**, 9 (1930); (b) E. J. Baldes, *Biodynamica*, No. 46 (1939); (c) R. J. Muller and H. J. Stolten, *Anal. Chem.*, **25**, 1103 (1953); (d) W. Simon, C. Tomlinson, and C. Chylewski, "Proceedings of the International Symposium on Microchemical Techniques," Interscience Publishers, Inc., New York, N. Y., 1961, part III; (e) W. I. Higuchi, M. A. Schwartz, E. G. Rippie, and T. Higuchi, *J. Phys. Chem.*, **63**, 996 (1959); (f) J. J. Neumayer, *Anal. Chim. Acta*, **20**, 519 (1959); (g) A. P. Brady, H. Huff, and J. W. Mc-

as a result of the development of thermistors and modern instrumentation.^{14b-g} Such devices, often erroneously called osmometers, provide a simple, rapid way to obtain the temperature difference between a pure solvent and a solution, both of which have the same equilibrium partial pressure of solvent. This experimental technique, which we will call the "differential vapor pressure (DVP) method" is advantageous as compared to classical cryoscopy and ebulliometry, since the temperature of the experiment can be adjusted as needed, and has been employed by us to study acid-base equilibria in benzene. The results we have obtained with the DVP method have been corroborated by infrared spectrophotometry of the appropriate benzene solutions.

Theory

Considering the existing understanding of low dielectric constant solvents and solvents with poor solvating ability, it was apparent that the principal species in solutions ($C > 10^{-3} M$) of acids and bases would carry no net charge. Furthermore, charged species resulting from the slight dissociation of acids, bases, or their adducts, would probably consist of a significant fraction of ion triplets and/or homoconjugate ions.^{12d} These considerations lead to the expectation that the differential vapor pressure data should be interpretable in terms of equilibria such as



where n and m are integers, B is the base, and HX the acid which is reacting with B. The species $(BHX \cdot HX)_n$ may react with additional HX to form more complex compounds.

Suppose that at constant analytical concentration of base, various amounts of acid are added to the base solution. The total equilibrium concentration of B, associated forms of B, associated forms of HX, and all acid-base adducts can be determined from the van't Hoff i value obtained using the DVP technique. In this work we define i as

$$i = \frac{\text{temperature rise for mixtures of B and HX, } (C_B)_t = aM}{\text{temperature rise for } aM \text{ naphthalene solution}}$$

where $(C_B)_t$ is the analytical concentration of base. If i is plotted vs. the ratio of total acid concentration to total base concentration, the extent of acid-base interaction, the stoichiometry of the acid-base interaction, and the degree of association of the acid-base adduct all can be determined simultaneously.

Figure 1 represents some hypothetical examples. The line ABC corresponds to the reaction given in eq. 1, where $m = 1$, B and HX interact quantitatively and are both monomeric, and where no further reaction between B·HX and HX occur. Line ABC' will be obtained if reaction 2 occurs to a small extent. Line A'BC corresponds to the situation where B is partially dimerized. Line ABDE represents the reaction scheme given by eq. 1 and 2 where $m = 1$, $n = 1$, HX and B are monomers, and where no more HX can react with $BHX \cdot HX$. If $m = 2$, the line AFDE will be found.

Bain, *J. Phys. Colloid Chem.*, **55**, 304 (1951); (h) M. Davies and D. K. Thomas, *J. Phys. Chem.*, **60**, 763 (1956).

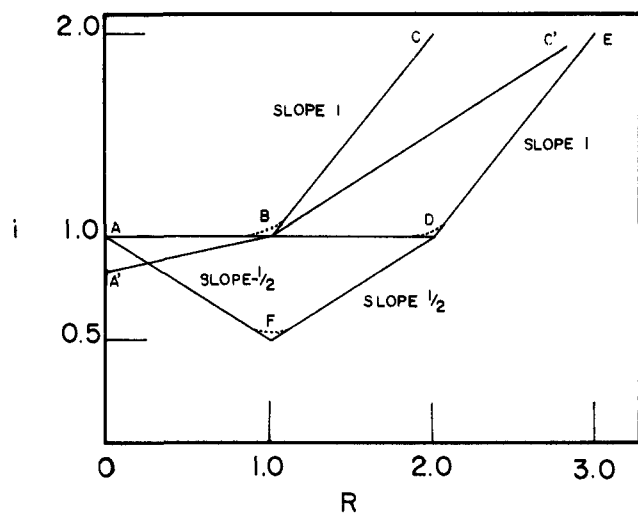


Figure 1. Hypothetical titration curves (see text for explanation).

Dotted, curved portions in Figure 1 correspond to reactions which do not proceed quantitatively to the right. Thus, the stoichiometry of the acid-base reaction, the state of aggregation of the adducts which form, and the quantitative extent of the reaction (or reaction equilibrium constant) can be determined readily from plots such as shown in Figure 1.

Experimental

Differential Vapor Pressure Measurement. The apparatus used was constructed in these laboratories and is described in detail elsewhere.¹⁵ Briefly, it consists of an all-glass apparatus which has a thermostated chamber containing pure benzene at the bottom and a glass fiber wick to saturate the rest of the chamber volume with benzene vapor. Four long glass droppers containing three different solutions and pure benzene separately can be introduced into the chamber and allowed to reach thermal equilibrium. Two glass-covered thermistors (VECO A 59) are also present in the chamber, and the ratio of the resistances of these two thermistors is monitored using a Wheatstone bridge circuit. A Keithley Model 150 AR microvolt amplifier is used to amplify the unbalance Wheatstone bridge voltage, and this unbalance voltage (E) is then recorded using a potentiometric strip-chart recorder. An experimental measurement is performed as follows. With solvent on both thermistors, the Wheatstone bridge circuit is balanced. A base line is obtained by adding fresh benzene to both thermistors and recording E -time curve. After about 5 min. the unbalance voltage becomes constant. Then, several drops of a solution are added to one of the thermistor beads and the E -time curve recorded. An idealized recording is shown in Figure 2. Depending upon the solution temperature, one or the other of the curves shown in Figure 2 is obtained. Usually within 5 min. a linear region is attained. For each experiment a 15-min. recording is made and the linear region extrapolated back to the time solution was added ($t = 0$). The linear portion has a negative slope because the solution is continuously being diluted by condensing solvent vapor. The difference between the base line and the intersection of the extrapolated line with

(15) R. J. Farm, M.S. Thesis, University of Minnesota, 1963.

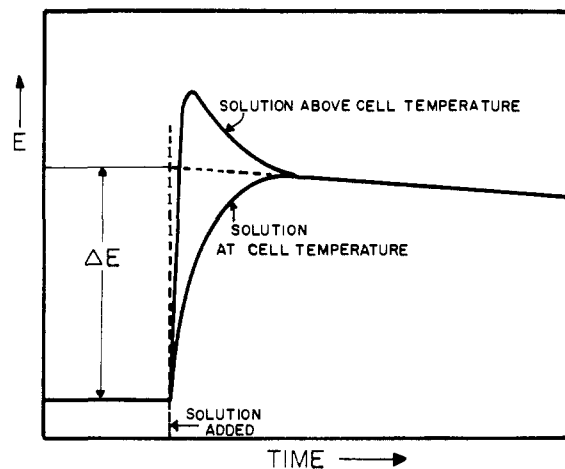


Figure 2. Time variation of temperature of solution thermistor; increasing E corresponds to lower temperature.

$t = 0$ is taken as the voltage difference (ΔE) arising because of the difference in solution and solvent vapor pressures.

Using naphthalene as a standard, ΔE -concentration curves were constructed in the range 0.001 to 0.1 M . This calibration curve is *linear*. The reproducibility of a measurement corresponded to $\pm 2.5 \times 10^{-5}$ M monomer solute or $\pm 0.3\%$ relative, whichever was larger. In an experiment involving solutions of acids and/or bases the observed ΔE was divided by the ΔE for the same concentrations of naphthalene. This ratio is the experimental definition of the van't Hoff i value.

Infrared Spectroscopy. A Perkin-Elmer Model 521 instrument was used with a 455- μ thick cell with sodium chloride windows as the sample cell. A variable path cell was used to compensate for benzene absorption. Substantially the same results were obtained with AGC or the 2X slit program. No data were used unless 10% transmission was possible at the wave length, and in most cases at least 30% transmission was available.

Chemicals. *Benzene.* Mallinckrodt or Merck A.R. benzene, thiophene-free, was stored for at least 3 days over Linde Molecular Sieves, Type 4A ($1/16$ -in. pellets), filtered, and then fractionally distilled. The water content was determined by Karl Fischer titration and was less than 5×10^{-3} M .

Bases. *n*-Dodecylamine and didodecylamine were obtained from the General Mills Research Laboratories, while all other bases were Eastman Kodak White Label products. All bases were used as supplied. The purities of the bases were confirmed during the differential vapor pressure titrations reported below. It was found possible to obtain precise stoichiometric ratios of 1 mole of base:1 mole of acid at the first end point to within several tenths of a per cent.

Acids. Trichloroacetic acid (Merck A.R.) and dichloroacetic acid (Eastman Kodak White Label) were dried by dissolving in a 25% excess of dry benzene and distilling off 25% of the solvent. Absence of water was established by Karl Fischer titration. Titration with aqueous sodium hydroxide established the actual acid concentration. Trifluoroacetic acid (Eastman Kodak) was titrated with sodium hydroxide and

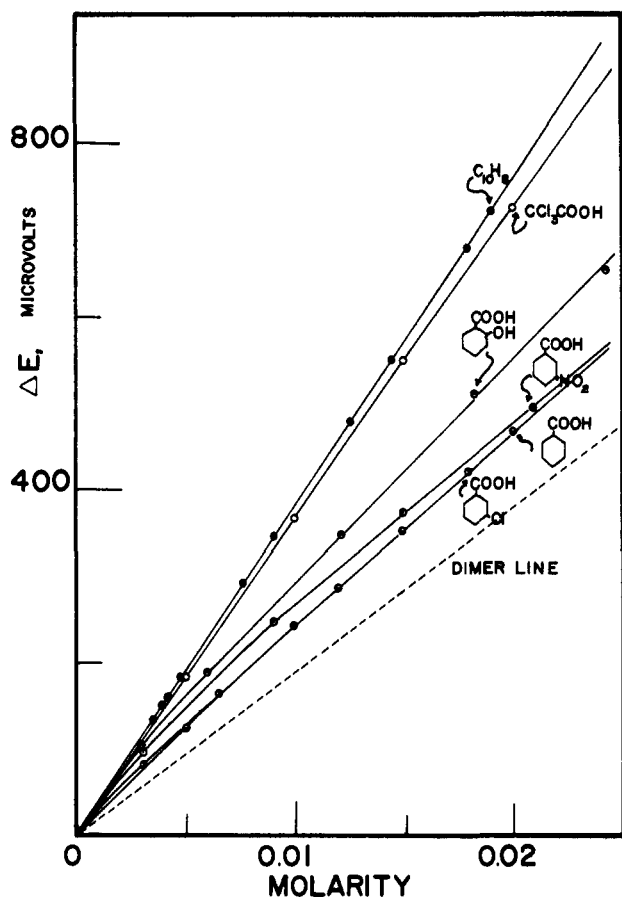


Figure 3. Association of carboxylic acids in benzene. Monomer and dimer lines are shown; i values of various acids are given in the format: name of acid, $1/i$ at 0.005 M , i at 0.01 M , i at 0.02 M , and i at 0.025 M . Trichloroacetic: 1.03, 1.03, 1.05, 1.06; dichloroacetic: 1.20, 1.20, 1.24, 1.24; benzoic: 1.45, 1.58, 1.62, 1.66; phenylacetic: 1.42, 1.57, 1.62, 1.64; m -chlorobenzoic: 1.45, 1.58, 1.62, 1.63; m -nitrobenzoic: 1.26, 1.42, 1.60, 1.63; salicylic: 1.17, 1.31, 1.38, 1.40; trifluoroacetic acid is volatile (dichloroacetic and phenylacetic acid lines are omitted to avoid crowding figure).

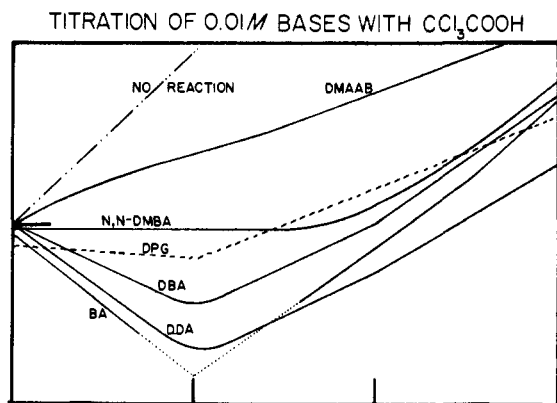


Figure 4. Titration of 0.01 M bases with trichloroacetic acid. Values of $1/i$ for different R are given in the format: name of base, $1/i$ actually observed at $R = 1$, $1/i$ at $R = 1$ obtained by linear extrapolation, $1/i$ observed at $R = 2$, $1/i$ observed at $R = 3$. BA: 9.05 (ppt.), 5.85, 1.16, 0.59; DDA: 3.33, 4.03, 1.37, 0.76; DBA: 1.79, 1.90, 0.99, 0.56; DPG: 1.25, 1.25, 0.84, 0.63; NNDMBA: 1.04, 1.04, 0.90, 0.56; DMAAB: 0.72, 0.72, 0.58, 0.48.

found to be 99.9% pure. N.B.S. benzoic acid was used without further purification. All other acids were Eastman Kodak White Label grade and used

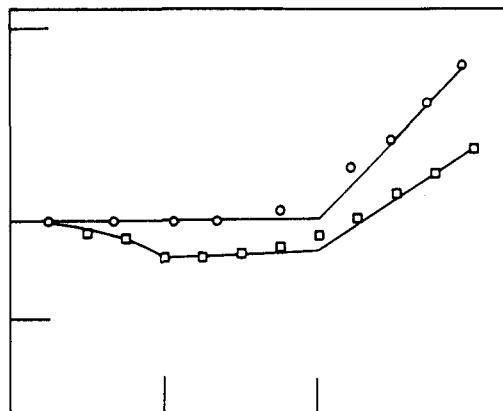


Figure 5. Titration of 0.01 and 0.05 M NNDMBA with trichloroacetic acid: \circ , 0.01 M base; \square , 0.05 M base. In 0.05 M base solutions, at $R = 1$, $1/i = 1.23$, while at $R = 2$, $1/i = 1.06$ actually observed, $1/i = 1.18$ obtained by linear extrapolation.

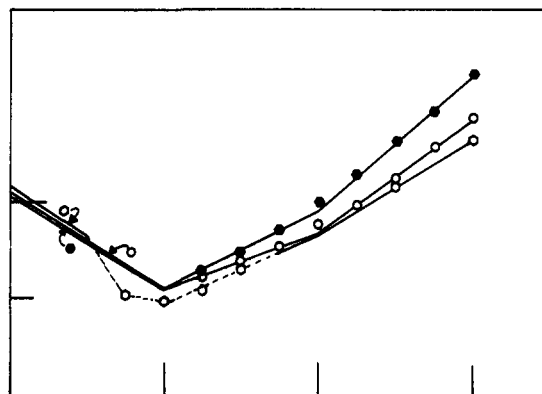


Figure 6. Titration of 0.01, 0.05, and 0.1 M DBA with trichloroacetic acid: \circ , 0.1 M base; \circ , 0.05 M base; \bullet , 0.01 M base. Dotted lines indicate precipitate was present. Observed value of $1/i$ at $R = 2$ was 1.12 for 0.05 M base and was 1.19 for 0.1 M base.

without further purification. Differential vapor pressure titration confirmed the purity of these acids.

Solution Preparation. All glassware was dried at 120° for at least 3 hr. and stored in a vacuum desiccator over calcium chloride until needed. Mixtures of acids and bases corresponding to various points on the titration curve were prepared by adding concentrated stock solutions of the requisite volume of acid and base to a 10-ml. volumetric flask and diluting to volume.

Results

A number of acids, trichloroacetic, dichloroacetic, benzoic, phenylacetic, m -nitrobenzoic, m -chlorobenzoic, and salicylic acids, were studied in benzene solution using the DVP method. Some of the results obtained are illustrated in Figure 3. Numerical values of the reciprocal of i are given for all acids at 0.005, 0.01, 0.020, and 0.025 M in the legend to Figure 3.

At 0.01 M concentrations all bases other than diphenylguanidine had i values differing no more than 5% from 1. For 0.01 M diphenylguanidine, $i = 0.87$.

Six bases—benzylamine (BA), dodecylamine (DDA), dibenzylamine (DBA), 1,3-diphenylguanidine (DPG), N,N -dimethylbenzylamine (NNDMBA), and dimethylaminoazobenzene (DMAAB)—at a concentra-

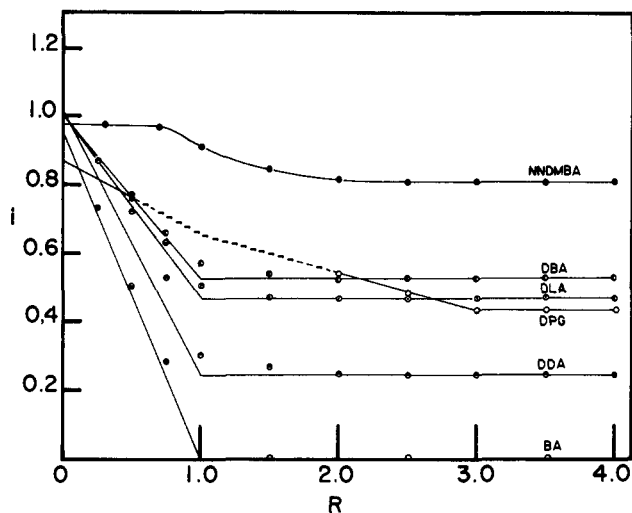


Figure 7. Titration of 0.01 *M* bases with trifluoroacetic acid.

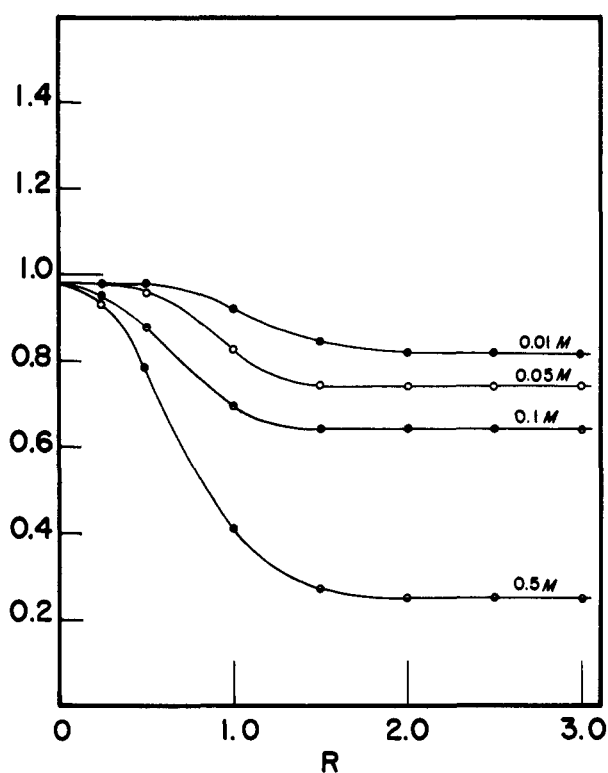


Figure 8. Effect of concentration on titration of NNDMBA with trifluoroacetic acid.

tion of 0.0100 *M* were allowed to react with various amounts of trichloroacetic acid at 25°. A plot of the *i* value vs. the ratio of the analytical concentrations of acid to base is given in Figure 4. Hereafter, the fore-mentioned ratio will be denoted by *R*. The effect of base concentration on the titration curve is shown in Figure 5 (0.01 and 0.05 *M* NNDMBA) and Figure 6 (0.01, 0.05, and 0.10 *M* DBA).

Solutions (0.01 *M*) of seven bases—the six titrated above using trichloroacetic acid and didodecylamine (DLA)—were titrated with trifluoroacetic acid at 25° and the results are shown in Figure 7. NNDMBA was treated at four different concentrations (0.01, 0.05, 0.1, and 0.5 *M*) using trifluoroacetic acid, and these results are shown in Figure 8.

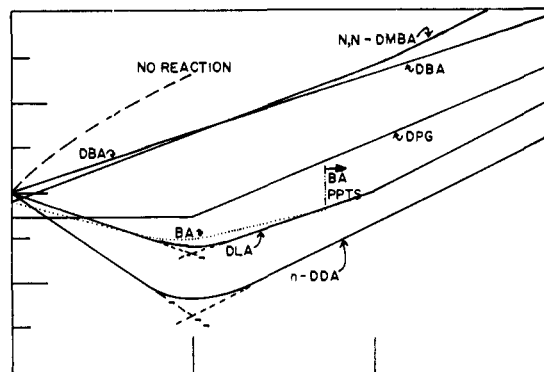


Figure 9. Titration of 0.01 *M* bases with benzoic acid. Values of $1/i$ for different *R* are given in the format: name of base, $1/i$ actually observed at $R = 1$, $1/i$ at $R = 1$ obtained by linear extrapolation, $1/i$ observed at $R = 2$. NNDMBA: 0.76, 0.76, 0.60; DBA: 0.75, 0.75, 0.61; DPG: 1.16, 1.16, 0.79; BA: 1.33, 1.33, ppt. at $R = 2$; DLA: 1.42, 1.55, 1.00; DDA: 2.40, 3.13, 1.23.

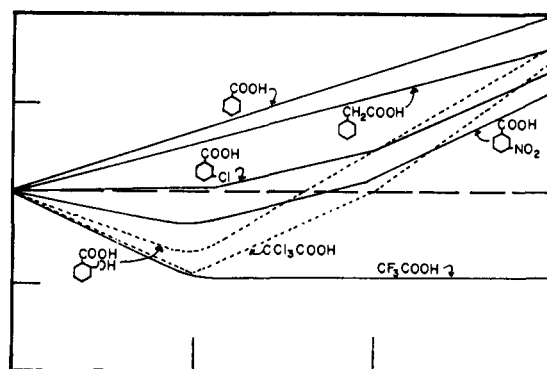


Figure 10. Titration of 0.01 *M* dibenzylamine with different acids. Values of $1/i$ for different *R* are given in the format: name of acid, $1/i$ actually observed at $R = 1$, $1/i$ at $R = 1$ obtained by linear extrapolation, $1/i$ observed at $R = 2$, $1/i$ observed at $R = 3$. Trifluoroacetic: 1.90, 1.70, . . . , . . . ; trichloroacetic: 1.81, 1.77, 1.00, 0.57; salicylic: 1.58, 1.49, 0.82, 0.55; *m*-nitrobenzoic: 1.23, 1.21, 0.93, 0.64; *m*-chlorobenzoic: 0.99, 0.98, 0.82, 0.60; phenylacetic: 0.79, 0.79, 0.65, 0.55; benzoic: 0.75, 0.75, 0.61, 0.51.

Figure 9 presents the results obtained in the titration of 0.01 *M* solutions of six bases—NNDMBA, DBA, DPG, BA, DLA, and DDA—with benzoic acid at 25°.

In Figure 10 the results of reacting 0.01 *M* DBA solutions with seven different acids—benzoic, phenylacetic, *m*-chlorobenzoic, *m*-nitrobenzoic, salicylic, trichloroacetic, and trifluoroacetic acids—are presented.

The effect of temperature on the titration of 0.01 *M* solutions of DMAAB, DDA, and NNDMBA with trichloroacetic acid was studied briefly. Figure 11 compares the titration curves obtained at 25 and 40°. Also included in Figure 11 are the results obtained for the identical titrations carried out in chlorobenzene as a solvent at 40°.

Titrations at 25° of solutions containing two bases (0.01 *M* in each base) are shown in Figures 12–15. In Figure 12 the results obtained using trifluoroacetic acid to titrate a DBA–DDA mixture and a NNDMBA–DDA mixture are shown, while Figure 13 presents the results obtained using trichloroacetic acid to titrate a DBA–DPG and a DDA–DPG mixture. Benzoic acid was used to titrate the following mixtures: DBA–

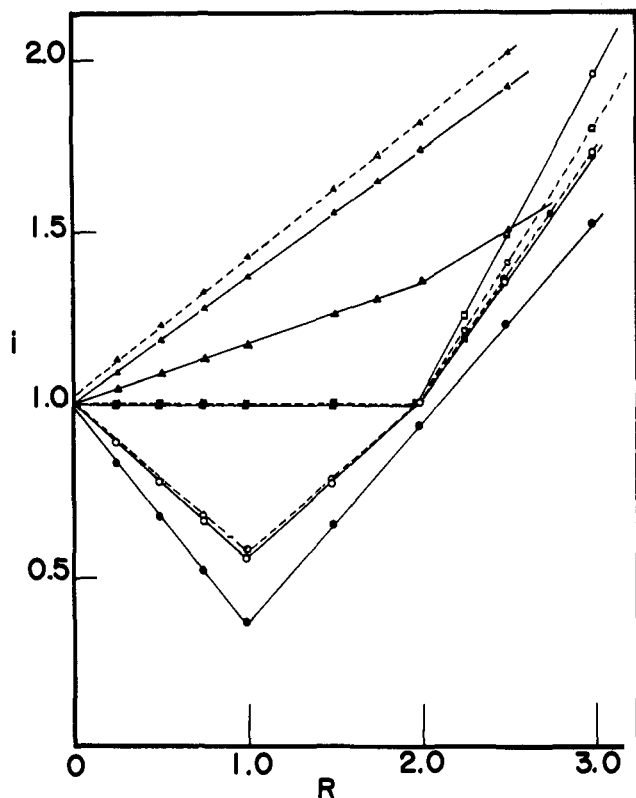


Figure 11. Effect of temperature and solvent on titration of some bases with trichloroacetic acid. DMAAB: Δ , benzene, 25°; \triangle (dotted lines), benzene, 40°; \blacktriangle , chlorobenzene, 40°; \circ , DDA, 25°; \circ (dotted lines), benzene, 40°; \bullet , chlorobenzene, 40°; NNDMBA: \square , benzene, 25°; \square (dotted line), benzene, 40°; \blacksquare , chlorobenzene.

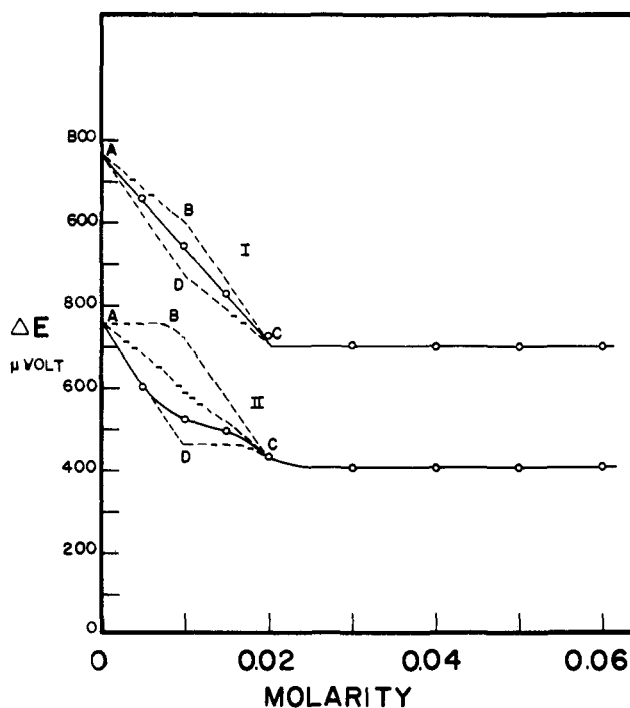


Figure 12. Titration of equimolar (0.01 *M*) solutions of two bases with trifluoroacetic acid. Dotted lines represent calculated curves. ABC assumes B reacts completely before B', ADC assumes *vice versa*, AC assumes simultaneous reaction. I: B = DDA, B' = DBA; II: B = NNDMBA, B' = DDA.

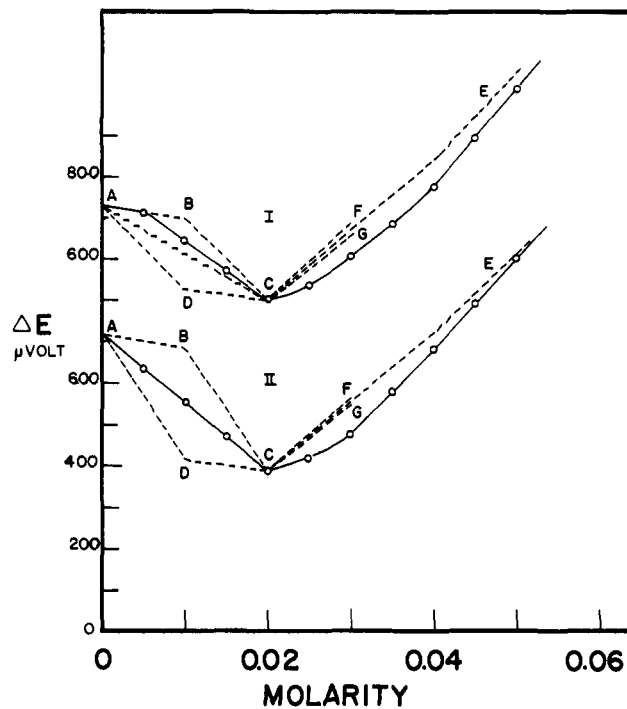


Figure 13. Titration of equimolar (0.01 *M*) solutions of two bases with trichloroacetic acid. Dotted lines represent calculated curves. ABC assumes B reacts completely before B', ADC assumes *vice versa*, AC assumes simultaneous reaction. I: B = DPG, B' = DBA; II: B = DPG, B' = DDA. CF assumes HX reacts with BHX before B'HX, CG assumes *vice versa*, and CE assumes simultaneous reaction of BHX and B'HX with HX. I: B = DBA, B' = DPG; II: B = DDA, B' = DPG.

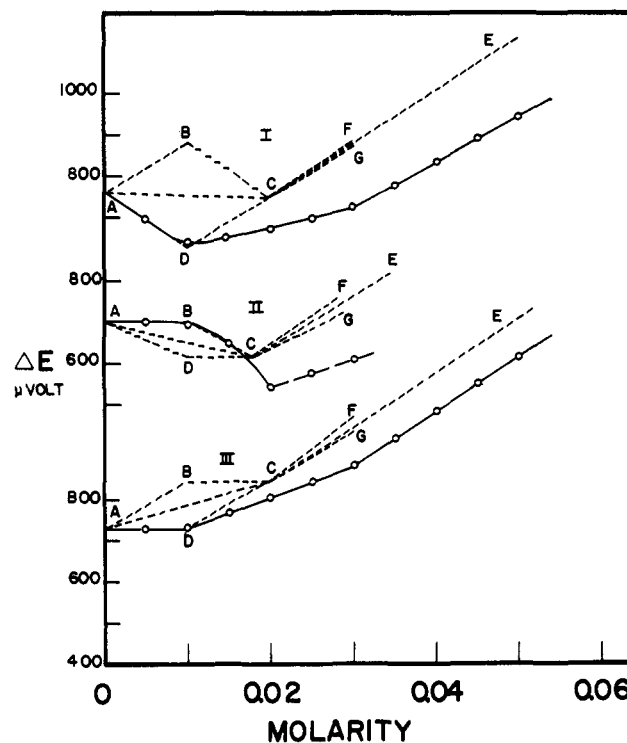


Figure 14. Titration of equimolar (0.01 *M*) solutions of two bases with benzoic acid. Dotted lines represent calculated curves. ABC assumes B reacts completely before B', ADC assumes *vice versa*, AC assumes simultaneous reaction. I: B = DBA, B' = DLA; II: B = DPG, B' = BA; III: B = DBA, B' = DPG. CF assumes HX reacts with BHX before B'HX, CG assumes *vice versa*, and CE assumes simultaneous reaction of BHX and B'HX with HX. I: B = DLA, B' = DBA; II: B = DPG, B' = BA; III: B = DPG, B' = DBA.

Table I. Infrared Studies of Reaction of Bases with Trichloroacetic Acid (HX)

Compound (molarity)	R^a	Frequency of principal absorption peaks in the range 1200–2000 cm^{-1} ^b							
HX (0.01)	...	1780 (0.22)	1762 (0.09)	1749 (0.05)				1223 (0.04)	
	(0.02)	1780 (0.40)	1762 (0.17)	1749 (0.12)				1223 (0.07)	
	(0.05)	1780 (1.47)	1762 (absent)	1749 (1.30)				1250 (0.49)	
DDA	0				No significant peaks				
	(0.01)	1.0			1680 (0.24)		1328 (0.20)		
	(0.02)	1.0			1680 (0.42)		1330 (0.34)		
		2.0	1780 (0.23)		1742 (0.32)	1665 (0.34)		1235 (0.24)	
		3.0	1780 (0.45)		1740 (0.51)	1650 (0.33)		1230 (0.37)	
	(0.03)	1.0			1680 (0.65)		1324 (0.58)	1209 (0.35)	
DBA	0				No significant peaks				
	(0.01)	1.0			1680 (0.36)		1318 (0.24)	1200 (0.10)	
		2.0	1774 (0.12)		1738 (0.14)	1664 (0.22)		1230 (0.12)	
		3.0	1774 (0.26)		1730 (0.23)	1651 (0.19)		1225 (0.18)	
	DLA	0				No significant peaks			
		(0.01)	1.0			1675 (0.35)	1605 (0.06)	1316 (0.23)	
		2.0	1770 (0.10)		1742 (0.14)	1665 (0.25)	1605 (0.10)	1319 (0.20)	
NNDMBA	0				No significant peaks				
	(0.01)	1.0			1680 (0.07)		1305 (0.12)	1290 (0.09)	
		2.0		1745 (0.14)	1650 (0.12)		1335 (0.12)	1290 (0.12)	
		3.0	1778 (0.19)		1745 (0.25)	1628 (0.18)	1335 (0.19)	1230 (0.20)	
	(0.05)	1.0			1670 (0.51)		1305 (0.83)	1250 (0.35)	
		2.0		1740 (0.78)	1645 (0.64)		1305 (0.53)	1230 (0.32)	
Piperidine	0						1330 (0.68)	1230 (0.70)	
	(0.01)	1.0			1745 (1.05)	1630 (0.79)	1330 (0.80)	1230 (0.85)	
		2.0	1775 (0.07)			1680 (0.34)	1610 (0.05)	1310 (0.04)	
		2.0		1720 (0.12)	1670 (0.22)	1610 (0.09)	1320 (0.24)	1325 (0.19)	
DPG	0				1658 (0.42)	1570 (0.35)	1335 (0.08)	1230 (0.14)	
	(0.01)	1.0			1680 (0.60)	1590 (0.29)	1325 (0.45)	1230 (0.08)	

^a R = analytical concentration of acid/analytical concentration of base. ^b Data are listed only if solvent has a transmittance greater than 10%.

Table II. Infrared Studies of Reaction of Bases with Trifluoroacetic Acid (HX)

Compound (molarity)	R^a	Frequency of principal absorption peaks in the range 730–2000 cm^{-1} ^{b,c}						
HX (0.01)	...	1780 (0.10)		1200 (0.17)		1160 (0.20)	1124 (0.27)	
DDA	0				No significant peaks			
	(0.01)	1.0		1685 (0.28)	1200 (0.34)		1130 (0.22)	
		2.0	1780 (0.13)		1675 (0.24)	1200 (0.45)	1150 (0.40)	
DBA		3.0	1780 (0.24)		1670 (0.21)	1210 (0.55)	1155 (0.58)	
	(0.01)	0			No significant peaks			
		1.0			1680 (0.31)	1210 (0.25)	1190 (0.37)	1125 (0.23)
		2.0	1780 (0.13)	1730 (0.16)	1660 (0.26)	1210 (0.46)	1190 (0.47)	1150 (0.38)
	3.0	1780 (0.24)	1730 (0.18)	1660 (0.25)	1210 (0.70)	1190 (0.60)	1150 (0.62)	

DLA (0.01)	0				No significant peaks				
	1.0			1672 (0.32)	1185 (0.37)		1120 (0.24)		
NNDMBA (0.01)	2.0	1770 (0.14)	1720 (0.12)	1660 (0.25)	1185 (0.42)	1145 (0.40)			
	0				No significant peaks				
(0.03)	1.0			1680 (0.15)	1185 (0.38)		1130 (0.34)		
	2.0	1770-1737 (0.15)		1647 (0.18)	1198 (0.46)	1150 (0.48)			
	0				No significant peaks				
	0.5			1680 (0.21)	1185 (0.52)		1130 (0.50)	820 (0.22)	790 (0.14)
	1.0			1675 (0.43)	1185 (0.92)		1130 (0.89)	820 (0.40)	790 (0.26)
	1.5		1735 (0.26)	1670 (0.45)	1185 (1.00)		1130 (0.77)	820 (0.30)	790 (0.27)
	2.0	1770 (0.41)	1737 (0.4)	1647 (0.5)	1198 (1.19)		1150 (1.00)	820 (0.19)	790 (0.29)
	3.0	1780 (0.79)		1647 (0.73)	1210 (1.52)		1150 (1.22)		740 (0.26)
CF ₃ COOH (0.09)		3385 (0.08)							790 (0.33)
		1780 (0.8)		1685 (0.16)	1210 (1.19)		1155 (1.04)		785 (0.13)
Piperidine (0.01)		3385 (0.41)					1128 (1.52)		770 (0.23)
	0				No significant peaks				
	0.5			1675 (0.23)	1200 (0.24)		1130 (0.15)		
	1.0			1675 (0.35)	1200 (0.39)		1130 (0.24)		
	2.0	1780 (0.11)		1675 (0.25)	1210 (0.44)	1200 (0.42)	1155 (0.31)		
	3.0	1780 (0.26)		1675 (0.20)	1210 (0.59)		1155 (0.59)		

^a *R* = analytical concentration of acid/analytical concentration of base. ^b Data are listed only if solvent has a transmittance greater than 10%. ^c Data to 740 cm⁻¹ are given for 0.03 *M* NNDMBA solutions. In these solutions intensity of peaks is sufficient to list quantitative data. Other 0.01 *M* base solutions show similar behavior at frequencies listed, but are too weak to be listed in a quantitative fashion.

Table III. Infrared Studies of Reaction of Bases with Benzoic Acid

Compound (molarity)	<i>R</i> ^a	Frequency of principal absorption peaks in the range 1000-2000 cm ⁻¹ ^b							
C ₆ H ₅ COOH (0.01) (0.02)	...	1730 (0.12)	1685 (0.32)	1595 (0.05)	1575 (0.04)	1410 (0.09)		1310 (0.11)	1280 (0.16)
	...	1730 (0.20)	1685 (0.69)	1595 (0.11)	1575 (0.10)	1410 (0.20)		1310 (0.24)	1280 (0.34)
DDA (0.01)	0				No significant peaks				
	1.0			1590 (0.15)	1550 (0.18)		1370 (0.34)		
NNDMBA (0.01)	2.0	1730 (0.11)	1690 (0.26)	1590 (0.17)	1550 (0.19)	1410 (0.10)	1370 (0.31)	1310 (0.12)	1280 (0.15)
	0				No significant peaks				
	1.0	1730 (0.10)	1690 (0.17)	1590 (0.06)	1575 (0.05)	1410 (0.05)		1310 (0.10)	1280 (0.11)
	2.0	1730 (0.18)	1690 (0.42)	1590 (0.11)	1575 (0.10)	1410 (0.12)		1310 (0.20)	1280 (0.24)
Piperidine (0.01)	0				No significant peaks				
	1.0			1620 (0.13)	1590 (0.09)	1540 (0.10)	1368 (0.31)	1310 (0.05)	1260 (0.05)
DPG (0.01)	2.0	1730 (0.10)	1690 (0.19)	1620 (0.13)	1590 (0.13)	1540 (0.14)	1368 (0.35)	1310 (0.14)	1260 (0.16)
	0			1658					
	1.0	1730 (0.11)	1685 (0.22)	1660 (0.21)	1595 (0.12)	1572 (0.13)	1410 (0.07)	1370 (0.17)	1310 (0.07)
	2.0	1730 (0.19)	1685 (0.54)	1660 (0.26)	1595 (0.17)	1572 (0.17)	1410 (0.19)	1370 (0.19)	1310 (0.19)
DBA (0.01)	0				No significant peaks				
	1.0	1730 (0.10)	1690 (0.19)	1590 (0.07)	1575 (0.05)	1410 (0.07)	1370 (0.08)	1310 (0.10)	1280 (0.12)
	2.0	1730 (0.17)	1690 (0.42)	1590 (0.12)	1575 (0.09)	1410 (0.14)	1370 (0.12)	1310 (0.19)	1280 (0.25)

^a *R* = analytical concentration of acid/analytical concentration of base. ^b Data are listed only if solvent has a transmittance greater than 10%.

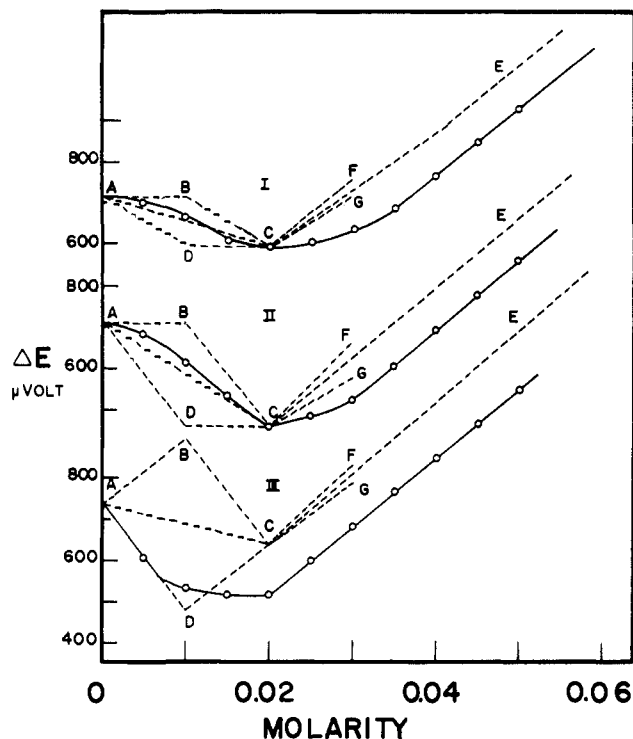


Figure 15. Titration of equimolar (0.01 *M*) solutions of two bases with benzoic acid. Dotted lines represent calculated curves. ABC assumes B reacts completely before B', ADC assumes *vice versa*, AC assumes simultaneous reaction. I: B = DPG, B' = DLA; II: B = DPG, B' = DDA; III: B = NNDMBA, B' = DDA. CF assumes HX reacts with BHX before B'HX, CG assumes *vice versa*, and CE assumes simultaneous reaction of BHX and B'HX with HX. I: B = DPG, B' = DLA; II: B = DDA, B' = DPG; III: B = DDA, B' = NNDMBA.

DLA, DPG-BA, DBA-DPG, DLA-DPG, DDA-DPG, and DDA-NNDMBA (Figures 14 and 15).

Tables I, II, and III present a summary of our infrared studies on various acid-base mixtures in benzene. Principal absorption peaks in the 1000- to 2000-cm.⁻¹ range are given, along with the observed absorbances.

Discussion

The data in Figure 3 indicate that the increasing order of association of carboxylic acids in benzene is trichloroacetic < dichloroacetic < salicylic < *m*-nitrobenzoic ~ benzoic ~ phenylacetic ~ *m*-chlorobenzoic acid. The DVP method has not proved to be a highly accurate technique for obtaining dimerization constants. For the reaction (RCOOH)₂ → 2RCOOH—defining the dissociation constant, $K_{2,1}$, of the dimers—we obtained $K_{2,1} = (2.0 \pm 0.1) \times 10^{-3}$ for benzoic acid over the concentration range 0.002 to 0.015 *M* and $K_{2,1} = 0.014 \pm 0.001$ for salicylic acid over the concentration range 0.006 to 0.03 *M*. Davis^{2b} has tabulated previously reported values and lists values of 1.76, 2.0, 1.61, and 1.9×10^{-3} at 25° for $K_{2,1}$. No value of $K_{2,1}$ at 25° for salicylic acid is available. In the case of all but one of the other acids we studied, $K_{2,1}$ values increased with the concentration of acid. The reasons for these variations are unknown and we report the value of $K_{2,1}$ for acids obtained by extrapolation of $K_{2,1}$ to zero concentration of acid: phenylacetic, 1.0×10^{-3} ; *m*-chlorobenzoic, 6×10^{-4} ; dichloroacetic, 0.02; trichloroacetic, 0.2. $K_{2,1}$ for *m*-nitrobenzoic

acid decreases with concentration. Extrapolation to zero concentration yields $K_{2,1} = 6 \times 10^{-3}$.

Figures 4, 9, and 10 show examples of acids which do not react appreciably with the base. All titration curves which rise above $i = 1$ for low values of R correspond to this situation, the weakest bases having the highest value of i at a given value of R .

The DVP curves for bases which were titrated with trifluoroacetic acid must be interpreted taking into account the volatility of trifluoroacetic acid. The vapor pressure of trifluoroacetic acid is so high at 25° that unreacted or weakly bound acid will rapidly evaporate from the liquid on the solution thermistor bead. Thus, the DVP curves in Figure 7 do not show an increase in i on adding acid in excess to the values of R greater than 1. The constant value obtained for i at R greater than 1 is solely due to the compound produced by the reaction between base and trifluoroacetic acid. From Figure 7 it is seen that DBA, DLA, DDA, and BA all form 1:1 compounds with trifluoroacetic acid and that this compound is progressively more associated in the order the bases are listed above. As is shown by the infrared data in Table I, these compounds are the trifluoroacetates of the protonated bases. The BA compound is insoluble and precipitates very early in the titration. The DPG titration indicates rapid precipitate formation between $\sim 0.5 < R < 2$. Extrapolation of data obtained in the absence of precipitate indicates the compounds BHX, BHX·HX, and BHX·2HX. The shape of the DPG curve is best explained by assuming the precipitate is BHX.

The effect of NNDMBA concentration on its reaction with trifluoroacetic acid is shown in Figure 8. The interpretation of this reaction is not clearcut and was supplemented by the infrared data in Table I. In the 1:1 mixtures a typical antisymmetric carboxylate band at 1680 cm.⁻¹ is present as are new bands at 1185 and 1130 cm.⁻¹. In addition, a band has appeared at 820 cm.⁻¹. When $R = 2$, the antisymmetric carboxylate band appears to have split into two bands, a broad flat band (1170 to 1137 cm.⁻¹) and a band at 1647 cm.⁻¹; in addition, two overlapping bands with peaks at 1198 and 1150 cm.⁻¹ have replaced the bands present in the 1:1 mixtures. Also the 820-cm.⁻¹ band has decreased considerably in intensity. These results clearly indicate the formation of BHX and BHX·HX. The formation of BHX·2HX is shown by the disappearance of the 820-cm.⁻¹ band and the weak absorption of the 3385-cm.⁻¹ band (OH stretching in the free acid). The shapes of the DVP curves in Figure 8 are difficult to interpret solely in terms of the three species suggested by the infrared data. The constancy of i for $R > 2$ suggests that the addition of the final HX is nonquantitative, and that loss of this last acid by volatilization must be occurring. The shapes of the E -time curves for $R > 2$ (Figure 1) confirm this conclusion, *i.e.*, a slow continuous drift down to the base line just as is observed in pure acid solutions. Similarly, the presence of the 3385-cm.⁻¹ absorption indicates that only ~ 0.01 *M* free trifluoroacetic acid exists in a mixture of 0.09 *M* trifluoroacetic acid and 0.03 *M* NNDMBA. The shapes of the DVP curves in Figure 8 suggest the formation of a compound between DBA and trifluoroacetic acid for which $R = 1.5$, but

Table IV. Acid-Base Adducts Identified in Benzene at 25°

Base	Reaction ratio of acid-base adduct [HX]/[B] for							
	Trifluoroacetic acid			Trichloroacetic acid			Benzoic acid	
DMAAB	Incomplete reaction							
NNDMBA	1:1	2:1	3:1	1:1	2:1	3:1	Incomplete reaction	
DBA	1:1	2:1	(No 3:1) ^a	1:1	2:1	3:1	Incomplete reaction	
DLA	1:1	2:1				1:1	2:1
DDA	1:1	2:1	(No 3:1) ^a	1:1	2:1	3:1	1:1	(2:1) ^b
BA	1:1 (ppt. forms)			1:1	2:1	(3:1) ^c	1:1	2:1
DPG	1:1	2:1	3:1	1:1	2:1	(3:1) ^c	1:1	2:1(?) ^d
Piperidine ^e	1:1	2:1 ^f		1:1	2:1		1:1	2:1

^a Infrared spectrum indicates no significant consumption of CF_3COOH by reaction with $\text{B} \cdot 2\text{HX}$ to form $\text{B} \cdot 3\text{HX}$. ^b Deduced on basis of broadening of the 1280-cm^{-1} band for $R = 2$ as compared to the 1280-cm^{-1} band in pure acid solutions. Other significant differences as compared to $R = 1$ mixture occur in band shapes in the $1600\text{--}1050\text{-cm}^{-1}$ region. ^c Deduced on basis of slope of line for $R > 2$. ^d DVP data indicate only incomplete formation of 2:1 species. Infrared data do not show any new bands. ^e Based primarily on infrared data. No conclusive DPG experiments possible because base vapor pressure is too high. ^f From DVP data of $0.01 M$ piperidine solution. DVP curve obtained rises from $i = 0$ at $R = 0$ to $i = 0.5$ at $R = 1$; the rise is linear from $R = 0.5$ to $R = 1.0$.

the infrared data are inconclusive and do not demonstrate the existence of such a species in $0.03 M$ NNDMBA solutions.

The conclusions we have reached concerning the species present in the various acid-base mixtures in benzene are summarized in Table IV. The manner in which we have interpreted our data will be illustrated again for two trichloroacetic acid experiments. Figure 5 shows that $0.01 M$ NNDMBA reacts quantitatively to form the monomeric compound BHX , which then reacts to form $\text{BHX} \cdot \text{HX}$. The slight rounding at $R = 2$ indicates less than quantitative reaction between BHX and HX . The $0.05 M$ titration of NNDMBA indicates the same stoichiometric reaction ratios and that significant association of both BHX and $\text{BHX} \cdot \text{HX}$ has occurred; m (eq. 1) is 1.23, while n (eq. 2) is 1.06. The decreased slope in the excess acid line for $R > 2$ in going from $0.01 M$ base to $0.05 M$ base suggests further reaction to form $\text{BHX} \cdot 2\text{HX}$. These conclusions are substantiated by the infrared spectra summarized in Table II. When $R = 1$ typical carboxylate stretching frequencies are observed at 1680 and 1305 cm^{-1} . When $R = 2$, the 1680-cm^{-1} band seems to have disappeared and split into two bands at 1745 and 1650-cm^{-1} . The 1305-cm^{-1} band in the 1:1 mixture appears to have decreased in intensity and a band at 1335-cm^{-1} has appeared. When $R = 3$, the intensity of the 1335-cm^{-1} band has increased considerably, and the 1650-cm^{-1} band present in the $R = 2$ mixture has shifted to 1628 cm^{-1} with considerable increase in intensity. The principal infrared spectral features do not appear to be concentration dependent for NNDMBA.

Figure 6, which shows the DVP titration data for 0.01 , 0.05 , and $0.1 M$ DBA solutions with trichloroacetic acid, indicates the formation of $(\text{BHX})_2$ at 0.01 and $0.05 M$ followed by virtually quantitative formation of $\text{BHX} \cdot \text{HX}$, which is slightly associated at the higher concentrations. The $0.1 M$ DBA solution has precipitate present from $\sim 0.5 \leq R \leq \sim 1.75$. The precipitate is the 1:1 salt of DBA and trichloroacetic acid, which redissolves in excess acid to form $\text{BHX} \cdot \text{HX}$. The progressively decreasing slopes for $R > 2$, as the total concentration of base increases, indicates the formation of $\text{BHX} \cdot 2\text{HX}$. This reaction is nonquantitative. Again, the infrared spectral results show the stepwise addition of three acid molecules to one mole-

cule of DBA. The 1:1 adduct shows carboxylate frequencies at 1680 and 1318-cm^{-1} . The 2:1 adduct has new bands at 1738 and 1664 cm^{-1} ; the 1680-cm^{-1} band present in the 1:1 adduct has vanished. The 1318-cm^{-1} band of the 1:1 adduct has shifted to 1322 cm^{-1} and decreased in intensity. When $R = 3$, bands at 1730 and 1225 cm^{-1} have developed, and a broad band at 1651 cm^{-1} is present.

The infrared spectra of the 1:1 adducts demonstrate that these compounds contain carboxylate ions; however, while all the carboxylate spectra are qualitatively the same, quantitative differences exist. For example, the absorption of the 1680-cm^{-1} and the 1330-cm^{-1} carboxylate bands of the trichloroacetates of DBA, DLA, and piperidine are quantitatively the same within the experimental error. At these frequencies, the absorption is slightly less for DDA and considerably smaller for NNDMBA. In the case of the DPG salt, the interpretation of the 1680-cm^{-1} band is not clear-cut because of the presence of a DPG band in the absence of acid. However, the DPG 1:1 salt band at 1330 cm^{-1} seems to be due only to the trichloroacetate ion, and is twice the intensity in any of the other salts. This band is not associated with protonated DPG since it does not exist in 1:1 DPG-benzoic acid mixtures which are clearly benzoate salts.

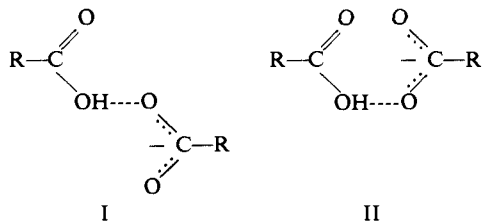
On the basis of the above evidence, we conclude that the monomeric 1:1 salts are ion pairs and that the spectral differences represent changes in the local environment resulting from the close proximity of the cation, BH^+ , to the anion, RCOO^- , in the ion pair. The absence of marked effect of oligomer formation on spectral features suggests that long-range electrostatic forces rather than hydrogen bonding are stabilizing such species in contrast to Yerger and Barrow's results^{16b,c} in carbon tetrachloride. We believe such species to be uncharged ion aggregates such as ion quadrupoles, etc.

Barrow's^{16a,b} infrared studies of the reaction of pyridine with various carboxylic acids in chloroform and carbon tetrachloride and of triethylamine and acetic acid demonstrate the formation of compounds at $R = 1$. The pyridine compounds appear to exist in a hydrogen-bonded form (proton not transferred to the

(16) (a) G. M. Barrow and E. A. Yerger, *J. Am. Chem. Soc.*, **76**, 5211 (1954); (b) E. A. Yerger and G. M. Barrow, *ibid.*, **77**, 4474 (1955); (c) *ibid.*, **77**, 6204 (1955); (d) G. M. Barrow, *ibid.*, **78**, 5802 (1956).

base) and an ion-pair form, with both forms existing in equilibrium. For the strongest acids only the ion-pair form was detected. Our results correspond to the case of virtually complete proton transfer and quantitative ion-pair formation, except perhaps in the case of NNDMBA and trichloroacetic acid.

The experimental evidence suggests the species found at $R = 2$ are ion pairs and uncharged ion aggregates consisting of the protonated base, BH^+ , and the homoconjugate ion of the carboxylic acid, HX_2^- . The ion pair $BH^+HX_2^-$ is conveniently designated a (homo)-conjugate ion pair. The absence of the OH stretch and change in the characteristic frequencies associated with COOH and COO^- can be accounted for by species such as I or II. I can be transformed into II by rota-



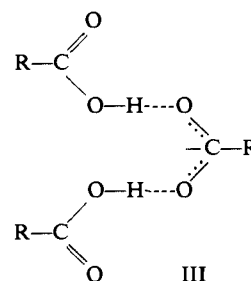
tion about the hydrogen bond, and it is apparent that stable configurations may exist in which the four oxygens are not coplanar. It is probable that the cation present in the conjugate ion pair plays a significant role in the actual configuration which is adopted by the conjugate ion. The smaller tendency to form ion aggregates by conjugate ion pairs, as compared to ion pairs, is explained most simply in terms of the larger size of the homoconjugate anion as compared to the simple anion.

Yerger and Barrow^{16a-d} have proposed anions similar to I and II and presented infrared evidence for these species in carbon tetrachloride and chloroform. Their work supports the view that hydrogen bonds exist between the protonated cation and the anion in such ion pairs. The spectral features observed by Yerger and Barrow are absent in the benzene systems we have studied. In particular at $R = 1$, no carbonyl-like groups are suggested by our infrared evidence, and no explanation involving approximately similar amounts of hydrogen bonding to both carboxylate oxygens, as proposed for chloroform solutions by Yerger and Barrow, seems possible in benzene. At $R = 2$, the ion pair with a hydrogen bond between the cation and the conjugate anion which they propose would require much more carboxylate character in the spectra than is observed.

Another significant difference between our results in benzene and their results in carbon tetrachloride and chloroform is the formation in benzene of salt oligomers at $R = 1$ with $m > 2$ (eq. 1); e.g., benzylamine yields 1:1 salts with m values of ~ 6 with trichloroacetic acid, ~ 3 with *m*-chlorobenzoic acid, and 2.3 with salicylic acid at 0.01 *M* base concentration. Other examples are to be found in the figures. This aggregation phenomenon cannot readily be explained in terms of hydrogen-bonded aggregates, as was the case of dimer formation in chloroform solution.

Table IV contains a number of examples of the formation of compounds at $R = 3$ ($BH^+X \cdot (HX)_2^-$). In all of these cases the conversion from $BH^+HX_2^-$ to $BH^+X \cdot (HX)_2^-$ is not quantitative. A possible

structure for the $X \cdot (HX)_2^-$ ion is III which has been written with both carboxylate oxygens hydrogen bonded to an acid hydrogen, in preference to the alternate structure involving one hydrogen bond between two acid molecules. The oxygen in the carboxylate ion is



more basic than in the parent acid and should be the preferred site for hydrogen bonding. Such a hydrogen bond will be much weaker than in HX_2^- because the formation of the first hydrogen bond decreases the basicity of the other oxygen in the carboxylate group.

In an ion pair, geometrical considerations such as shape and proximity of associated cations will play a more important role in influencing the stability of $X \cdot (HX)_2^-$ than of HX_2^- . The erratic formation of $X \cdot (HX)_2^-$ (Table IV) is interpreted on this basis.

Infrared studies of $CF_3COONa \cdot 2CF_3COOH$ by Klemperer and Pimentel¹⁷ in the solid state were interpreted in terms of species III. The same authors also studied CF_3COONa , observing carboxylate stretching motions at 1680 cm^{-1} .

It is convenient at this point to make use of a result given below which was obtained considering the DVP titration of solutions containing two bases; namely, assuming that there is no inversion in basic strength using different reference acids, the order of base strength deduced from the titration of base mixtures is $DPG > DDA \sim DLA > BA > DBA > NNDMBA$.

Excluding DPG from the discussion, the extent of association of the 1:1 trifluoroacetic acid-base salts (Figure 7) is directly related to the order of base strength—the stronger the base, the larger the association of the salt (*i* value). A similar order is observed for benzoic acid (Figure 9). For trichloroacetic acid, only BA falls out of the order predicted by base strength. Association is greatest at $R = 1$ and becomes less at higher integral values of R .

The relationship between association of an acid-base adduct and the strength of the acid-base interaction was investigated in a slightly different way by titrating a single base, DBA, with seven different acids (Figure 10). The strengths of these acids have the order of trifluoroacetic > trichloroacetic > salicylic > *m*-nitrobenzoic > *m*-chlorobenzoic > phenylacetic > benzoic acid. Again, the extent of association is closely related to the strength of the acid. The only inversion noted was for salicylic acid at a value of $R = 2$.

In the case of the reaction of DBA with different acids, it is possible that an appreciable concentration of the hydrogen-bonded adduct exists in equilibrium with the ion pair at $R = 1$. It seems likely that associated species present at $R = 1$ are principally ion aggregates in equilibrium with the ion pair. Assuming that the

(17) W. Klemperer and G. C. Pimentel, *J. Chem. Phys.*, 22, 1399 (1954).

tendency for ion-aggregate formation is approximately the same for all the ion pairs and reasoning by analogy with Barrow's observations,^{16d} it follows that the stronger the acid, the greater the ion-pair concentration, and thus the larger the extent of association.

Such an explanation cannot apply to the results obtained in trifluoroacetic and trichloroacetic acid experiments involving different bases, and the reason for correlation between extent of association and base strength is not clear.

A number of solutions containing two different bases, 0.01 *M* in each base, were titrated with trichloroacetic, trifluoroacetic, and benzoic acids. The results of these titrations (Figures 12–15) indicate the complexity of acid–base equilibria in benzene. The simplest results were obtained using trifluoroacetic acid. In Figure 12 three theoretical titration lines have been constructed, *i.e.*, it was assumed that one base titrated quantitatively before the other, *vice versa*, or simultaneous titration occurred. The DDA–DBA titration corresponds to the simultaneous reaction of both bases, while 50% of the DDA in a DDA–NNDMBA mixture reacts first and then the remaining DDA and NNDMBA react simultaneously. The DVP curves yield no information about further reaction between the salt mixtures and trifluoroacetic acid.

The trichloroacetic acid titrations are more complex. While DPG and DDA titrate simultaneously to yield 1:1 salts, additional acid reacts with the mixture of salts more strongly than is predicted by simple additive considerations. In fact, a second end point at 0.03 *M* total acid suggests the formation of a compound having the stoichiometric composition DDA·DPG·3HX. The slope of the excess line indicates further reaction. At 0.04 *M* of added acid, the experimental curve for this mixture is significantly below the value predicted by simply adding the separate titration curves.

The reaction of trichloroacetic acid with DPG–DBA mixtures indicates that approximately one-half of the DPG reacts first, followed by simultaneous reaction of DPG and DBA. For concentrations of trichloroacetic acid in excess of 0.02 *M*, simple additivity of the single-solution data do not yield results in agreement with experiment. Again, interaction is occurring between the various species in solution and at least 0.02 *M* additional trichloroacetic acid reacts.

The results obtained using benzoic acid as titrant for a DBA–DLA mixture (Figure 14) are surprising. As expected, DLA titrates quantitatively and an end point is found at 0.01 *M* added benzoic acid. Unexpectedly, a distinct second end point is observed at 0.03 *M* added benzoic acid. The slope of the titration curve and the magnitude of ΔE suggest the formation of a compound DBA·DLA·3HX, *i.e.*, the titration of DBA with benzoic acid in the presence of DLA has radically enhanced the basicity of DBA. The formation of DBA·DLA·2HX is not precluded by the DVP data. Again, at higher concentrations, enhanced binding of benzoic acid is indicated in the DLA–DBA mixture as compared to the separate base solutions.

Similarly, the titration of a mixture of DDA and NNDMBA (Figure 15) shows a similar enhancement in the basic strength of the weak base, NNDMBA, by titration in the presence of the stronger base, DDA.

The titration of the DPG–DBA mixture (Figure 14) with benzoic acid shows that DPG is a much-stronger base than BA, while the formation of a precipitate just after the second end point demonstrates the interaction of the two salts as compared to the separate base solutions. No precipitate forms in DPG–benzoic acid mixtures, while a precipitate forms in 0.01 *M* BA only if the concentration of benzoic acid is between 0.015 and 0.017 *M*.

The titration of a mixture of DBA and DPG (Figure 14) again shows the enhancement of the basic strength of DBA by the prior titration of DPG, a stronger base.

The titration curves of mixtures of DPG–DLA and DPG–DDA with benzoic acid (Figure 15) have the same general features. DPG is partially titrated before the other base, and the first end point corresponds to the total analytical concentration of both bases. There is a good end point at 0.03 *M* added benzoic acid in the DPG–DDA mixture, while the corresponding end point in the DPG–DLA mixture is less well defined.

The order of base strengths given in the Discussion concerning the extent of association of 1:1 salts was deduced from Figures 12–15.

The effect of temperature on the DVP titration of bases of various strengths with trichloroacetic acid in benzene is shown in Figure 11. For NNDMBA and DDA increasing the temperature from 25 to 40° decreases the extent of association of the 1:1 salt significantly; the behavior of DMAAB suggests weaker acid–base interaction in benzene at 25 than at 40°. DBA was also studied in benzene at 25 and 40° and the results obtained with this compound follow the same general pattern as NNDMBA and DDA. The magnitude of this temperature effect is considerable and emphasizes the uncertainties involved in extrapolating oligomer formation data obtained by cryoscopy or ebulliometry to another temperature.

Data obtained in chlorobenzene at 40° for the reaction of the above-mentioned bases with trichloroacetic acid is also given in Figure 11. It is apparent that similar species exist in both chlorobenzene and benzene, and that for NNDMBA the behavior in chlorobenzene at 40° closely approximates their behavior in benzene at 25°. The extent of reaction of DMAAB and DDA with trichloroacetic acid is considerably greater in chlorobenzene than in benzene. These results are surprising, since it was thought that the larger dielectric constant of chlorobenzene (5.62) as compared to that of benzene (2.27), would produce a smaller tendency for oligomer formation. Indeed, the data in Figure 11 suggest that chlorobenzene is a more “inert” solvent than benzene.

It is apparent from these few comparisons between acid–base reactions in benzene and chlorobenzene that dielectric constant is not the sole governing factor—even for these two very similar solvents—and that specific solute–solvent interactions play a significant role in the so-called “inert” solvents.

Conclusions

The main features of the reaction of a number of amines and carboxylic acids in benzene can be explained in terms of the formation of ion pairs and other uncharged ionic aggregates. The cation in these ionic

aggregates is the protonated base, while the anion is the carboxylate ion, X^- , the simple homoconjugate ion, HX_2^- , or the more complex homoconjugate ion, $X(HX)_2^-$.

Infrared studies do not show evidence for hydrogen bonding between the protonated cation and the anion of the ion pair as has been noted in other solvents.^{16a-d} In mixtures of bases, strong interaction can occur between the ion pairs BH^+X^- and $B'H^+X^-$, suggesting

that ionic aggregates containing different cations are more stable than aggregates containing several identical cations.

Acknowledgments. This research has been financially supported by the U. S. Army Research Office (Durham). The authors wish to express their appreciation to Mr. John Belisle for his help in performing the preliminary DVP experiments.

Inhibition of the Oxidation and Polymerization of Methyl Methacrylate. II. Effect of Aromatic Amines¹

W. Ross Yates and Judson L. Ihrig

Contribution from the Department of Chemistry, University of Hawaii, Honolulu, Hawaii 96822. Received September 8, 1964

The action of aromatic amine retarders upon the polymerization of methyl methacrylate in the presence of air has been studied. Induction periods and polymerization rates have been determined dilatometrically. The results confirm and extend the conclusions of a previous study of the action of phenols under the same conditions. The amines display a wider range of reactivities than did the phenols. Of the 28 amines tested, 21 were amenable to the same kinetic treatment as used previously. This is an antioxidation scheme, from the success of which it is concluded that most of these terminators, like phenols, act by slowing down the depletion of oxygen in the system, thus extending the length of the inhibition period. Relative efficiencies have been determined for most of the amines. Highly reactive amines, however, appear to react directly with molecular oxygen in competition to their interaction with chain-carrying peroxy radicals.

Introduction

In an earlier study² (called part I) a report was made of the effect of phenols upon the polymerization of methyl methacrylate in the presence of air. It was demonstrated that the oxygen inhibition of methyl methacrylate is prolonged by the presence of phenolic substances which led to the conclusion that their action is one of retarding the initial autoxidation thus delaying the exhaustion of oxygen from the system. The importance of this mechanistic point has led us to extend our studies to an examination of the effect of aromatic amines under similar conditions to confirm the conclusion reached earlier and to extend the range of reactivities observed with the phenols.

Although aromatic amines as a class should be expected to be somewhat more reactive in autoxidation processes than phenols taken as a group, quantitative kinetic data bearing on this are considerably less

abundant in the literature for amines compared with phenols.

A third, and perhaps most important, rationale for this study is the continuing high degree of interest in the whole problem of autoxidation inhibition and its relation to polymerization retardation. Current efforts directed toward answering the central mechanism question, π -complex formation or labile hydrogen atom abstraction, seem to favor the latter hypothesis. Thus we have new studies of the kinetic isotope effect,³⁻⁷ transfer constant measurements,⁸⁻¹⁰ and solvent effects,¹¹ but certain of the problems posed by Hammond and co-workers¹²⁻¹⁴ remain unresolved. A very recent reminder by Lloyd and Lange¹⁵ points out that: "The state of the theory consequently lacks predictive power; we cannot be sure, for any new substrate-retarder system, which mechanism to invoke until we have obtained empirical knowledge of that particular system."

A direct, frontal attack upon the problem, that of measuring rate effects of phenols upon polymerization in the absence of oxygen, did not permit an unequivocal choice to be made because of the very small rate differences observed compared with those obtained for minute amounts of quinone impurities likely to be present.¹⁶ At the present moment it seems altogether

(1) Taken from a portion of the Ph.D. thesis of W. R. Y. Inquiries should be addressed to J. L. I. The financial support of the Research Corporation and of the University of Hawaii Research Committee is gratefully acknowledged.

(2) R. G. Caldwell and J. L. Ihrig, *J. Am. Chem. Soc.*, **84**, 2878 (1962).

(3) R. A. Bird, G. A. Harpell, and K. E. Russell, *Can. J. Chem.*, **40**, 701 (1962).

(4) J. A. Howard and K. U. Ingold, *ibid.*, **40**, 1851 (1962).

(5) J. A. Howard and K. U. Ingold, *ibid.*, **41**, 1744 (1963).

(6) K. U. Ingold, *ibid.*, **41**, 2807 (1963).

(7) J. R. Shelton and D. N. Vincent, *J. Am. Chem. Soc.*, **85**, 2433 (1963).

(8) M. P. Godsay, G. A. Harpell, and K. E. Russell, *J. Polymer Sci.*; **57**, 641 (1962).

(9) S. C. Barton, R. A. Bird, and K. E. Russell, *Can. J. Chem.*, **41**, 2737 (1963).

(10) L. R. Mahoney and F. C. Ferris, *J. Am. Chem. Soc.*, **85**, 2345 (1963).

(11) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **42**, 1044, 1250 (1964).

(12) C. E. Boozer and G. S. Hammond, *J. Am. Chem. Soc.*, **76**, 3861 (1954).

(13) G. S. Hammond, C. E. Boozer, C. E. Hamilton, and J. N. Sen, *ibid.*, **77**, 3238 (1955).

(14) G. S. Hammond and U. S. Nandi, *ibid.*, **83**, 1217 (1961).

(15) W. G. Lloyd and C. E. Lange, *ibid.*, **86**, 1491 (1964).