

interest to carry out a complete oxygen exchange study for a carboxylic acid derivative in which the Arrhenius activation energy for hydrolysis and/or oxygen exchange is a sufficiently sensitive function of temperature to allow an experimental test of the theory that the temperature variation of the hydrolytic activation energy can be quantitatively accounted for on the basis of the mechanism proposed.

The Equivalence of the Intermediate in the Acidic and Alkaline Hydrolysis of Ethyl Benzoate.—In a previous investigation it was pointed out that the ratio k_h/k_e was identical for the hydrolysis of ethyl benzoate in either acidic or basic solution.^{3a} The equivalence of this ratio has been cited by Taft¹⁷ to indicate the existence of a common intermediate in acid and base-catalyzed ester hydrolysis. The previously reported values k_h/k_e for acidic and alkaline hydrolysis of ethyl benzoate were not performed at the same temperature. Therefore it was thought desirable to redetermine these values under exactly identical conditions of temperature and solvent composition. The results are given in Table III.

(17) R. W. Taft, Jr., *THIS JOURNAL*, **74**, 3120 (1952); R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 538.

TABLE III

THE HYDROLYSIS AND OXYGEN EXCHANGE OF ETHYL BENZOATE IN ACIDIC AND ALKALINE SOLUTION^a

Catalysis	k_h , l./mole sec.	k_h/k_e
Acidic	3.3×10^{-7}	5.3
Basic	8.4×10^{-8}	11.3

^a 25.0°, 33% dioxane-water solution, initial concentrations of ester and catalyst were approximately 0.01 *N*.

It is seen that the values of k_h/k_e for acidic and basic catalysis differ by a factor of approximately two. However, in view of the fact that the rates of hydrolysis differ by a factor of roughly 10^4 , the difference in the values of k_h/k_e is relatively insignificant. It therefore can be affirmed with substantial probability that in both the basic and acidic catalyses, a similar intermediate is formed, the most likely possibility in both cases being the unionized hydrate of the ester.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

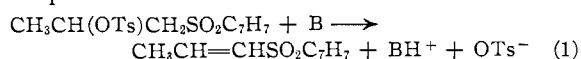
The Effect of Solvent on the Catalytic Activity of Aliphatic Amines in Elimination Reactions¹

By R. G. PEARSON AND D. C. VOGELSONG²

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Triethylamine, di-*n*-butylamine and *n*-hexylamine have been used as catalysts to study the rate of elimination of *p*-toluenesulfonic acid from 1-(*p*-toluenesulfonyl)-2-propyl *p*-toluenesulfonate in several non-aqueous solvents. By changing the solvent one can make either the primary, secondary or tertiary amine the strongest catalytic base.

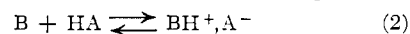
Weinstock, Pearson and Bordwell³ have shown that the elimination of *p*-toluenesulfonic acid from 1-(*p*-toluenesulfonyl)-2-propyl *p*-toluenesulfonate (hereafter called tosylate compound) is general base catalyzed in 50% dioxane-water mixtures. The kinetics indicate that the reaction follows the simple bimolecular mechanism



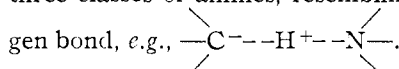
where B is the base, and OTs⁻ the *p*-toluenesulfonate anion. Because of this, it was thought that this reaction might be used in the study of the effects of solvents on the relative base strengths of primary, secondary and tertiary amines. Triethylamine, di-*n*-butylamine and *n*-hexylamine were chosen as representative amines because of the ease of purification. In previous studies⁴ the equilibrium constants for the reactions of these three

bases with the reference acid 2,4-dinitrophenol have been determined in several solvents.

The observed reaction in solvents of low dielectric constant was the formation of an ion-pair



where HA is 2,4-dinitrophenol. A possible complication in the case of a primary or secondary amine compared to a tertiary amine, is that a double or triple hydrogen bond might hold the ion-pair together in the first two cases. This would cause these amines to appear stronger than the tertiary amine. In a kinetic process involving a proton removal, the transition state should be similar for all three classes of amines, resembling a single hydro-



In studies of the rate of proton abstraction from nitroethane in water by various alkylamines,⁵ it was found that tertiary amines reacted more rapidly than their basic ionization constants in water would have predicted. This was considered evidence for a high electron density, or potential basicity, on nitrogen for these amines. It is of in-

(1) Taken in part from a dissertation submitted by D. C. Vogelsong to the graduate school of Northwestern University in partial fulfillment of the requirements for the Ph.D. degree, August, 1956.

(2) Predoctoral fellow, E. I. du Pont de Nemours and Co., 1955-1956.

(3) J. Weinstock, R. G. Pearson and F. G. Bordwell, *THIS JOURNAL*, **78**, 3473 (1956).

(4) R. G. Pearson and D. C. Vogelsong, *ibid.*, **80**, 1038 (1958).

(5) R. G. Pearson and F. V. Williams, *ibid.*, **76**, 258 (1954).

terest to see if this unusual large catalytic effect of tertiary amines persists in non-aqueous solvents.

Experimental

Triethylamine, Di-*n*-butylamine and *n*-Hexylamine.—Each amine was dried over and distilled from fresh potassium hydroxide immediately before use. Small, constant boiling center cuts were taken.

Acetonitrile.—Matheson, Coleman and Bell 99% pure acetonitrile was distilled from phosphorus pentoxide. It was then refluxed over potassium carbonate for several hours, and finally fractionated from phosphorus pentoxide again.

Methyl Alcohol.—Carbide and Carbon C.P. methyl alcohol was refluxed over and distilled from calcium oxide.

Other solvents: Described elsewhere.⁴

1-(*p*-Toluenesulfonyl)-2-propyl *p*-toluenesulfonate was obtained as previously described.⁶

Kinetic Procedure.—For solvents of dielectric constant below ten and acetonitrile, pseudo-first-order rate constants were obtained by using a large excess of tosylate compound. Stock solutions of amine and tosylate compound were made up by weighing each into volumetric flasks containing the appropriate solvent. After diluting each, these solutions were placed in a water-bath thermostated at 25.0° for a period of at least 15 minutes before mixing. After mixing and diluting to the proper concentrations, the decrease in base concentration was followed by abstracting 2-ml. aliquots of the reaction mixture, and stopping the reaction by pouring the aliquot into benzene solution containing enough picric acid to react completely with the amine. Picric acid was used because it is sufficiently strong to react completely with the amines, but not strong enough to remove amine from the alkylammonium *p*-toluenesulfonate ion-pair formed as a product in the kinetic reaction. The benzene solutions were diluted to 25 ml. and the absorbancy measured at 400 m μ on a Beckman Quartz Spectrophotometer, from which the amine concentration of the reaction mixture readily could be calculated. Extinction coefficients of picric acid and the amine-picric ion-pairs were obtained in benzene with 2 ml. of the reaction solvent added. At least two different concentrations of tosylate were used for the determination of each second-order rate constant, the results checking within a few per cent. for a doubling of the tosylate concentration.

Rate constants in methanol and 50% dioxane-water (by volume) were followed conductometrically with the amine in large excess. The amine stock solutions were buffered with the salts di-*n*-butylammonium- and *n*-hexylammonium *p*-toluenesulfonate and triethylammonium hydrochloride (the hydrochloride being used because of the inability to prepare the *p*-toluenesulfonate salt of the tertiary amine) in about one-tenth the concentration of the amine.

Resistances were measured on a direct reading Jones conductivity bridge in connection with a cathode ray oscilloscope as a null indicator. The conductance cell was in the shape of a Y tube so that the amine-buffer solution could be placed in the leg with the platinized platinum electrodes, and the solution of tosylate compound in the other leg. After the cell with the two solutions had come to bath temperature, 25.0°, the solutions were mixed by inverting the cell several times, and the resistance of the solution measured as quickly as possible. The first-order rate constants were obtained by plotting $\log [R/(R - R_{\infty})]$ vs. time. Second-order rate constants were obtained from the slopes of plots of observed first-order rate constants vs. amine concentration. In all cases at least four first-order rate constants were determined for the second-order plots.

Results and Discussion

Tables I and II summarize the rate constants found. The reaction chosen supposedly takes place by a concerted mechanism whereby the amine abstracts a proton, and at the same time the *p*-toluenesulfonate group leaves. The ion-pair formed in the solvents of low dielectric constant as a product of the reaction should have no influence on the

rate determining step. The base strength of the amines as measured in this way should be independent of possible bi- and trifurcated hydrogen bond structures discussed in the equilibrium studies.⁴ The results of Table I, however, show the same general effects as observed in the equilibrium studies. The tertiary amine is the stronger catalytic base in chloroform and chlorobenzene, but in benzene the secondary amine is the stronger base. That specific solvation is an important factor to consider in these rates is also evidenced by the results in dioxane and ethyl acetate where the primary amine is the strongest catalytic base. It is probable, however, one must consider both solvation of the free amine and transition state as being important. For example, triethylamine reacts slower in ethyl acetate than it does in chlorobenzene despite the increased dielectric constant of ethyl acetate over chlorobenzene. Similarly, *n*-hexylamine reacts slightly slower in ethyl acetate than it does in dioxane. Thus ethyl acetate appears to be better at solvating the free amines than chlorobenzene and dioxane. Specific interaction of the amines with ethyl acetate may be attributed to the polar nature of the carbonyl bond of the ester. That such interaction does take place is shown by the results of Leonard, Fox, Ōki and Chiavarelli⁷ who measured infrared shifts of carbonyl bands in the presence of amines.

TABLE I

SECOND-ORDER RATE CONSTANTS OBSERVED SPECTROPHOTOMETRICALLY AT 25° FOR THE BASE CATALYZED ELIMINATION FROM 1-(*p*-TOLUENESULFONYL)-2-PROPYL *p*-TOLUENESULFONATE

	Benzene	Dioxane	Chloro- form	Chloro- benzene	Ethyl acetate	Aceto- nitrile
<i>n</i> -Hexylamine	2.19 ^a	14.0	0.33	1.11	12.9	48.8
Di- <i>n</i> -butyl- amine	4.64	10.4	3.30	4.52	11.7	143
Triethyl- amine	3.18	3.37	5.26	6.32	2.77	27.2
Dielectric constant	2.3	2.2	4.8	5.4	6.3	36.5

^a Rate constants are expressed in units molar⁻¹ hr.⁻¹.

TABLE II

SECOND-ORDER RATE CONSTANTS OBSERVED CONDUCTOMETRICALLY AT 25° FOR THE BASE-CATALYZED ELIMINATION FROM 1-(*p*-TOLUENESULFONYL)-2-PROPYL *p*-TOLUENESULFONATE

	50% (by vol.) Dioxane-water	Methyl alcohol
<i>n</i> -Hexylamine	460 ^a	294
Di- <i>n</i> -butylamine	845	259
Triethylamine	170 ^b	33.5
Dielectric constant	36	31.5

^a Rate constants expressed in units of molar⁻¹ hr.⁻¹.

^b Weinstock, Pearson and Bordwell, reference 8, report a value of 214. They used the *p*-toluenesulfonate salt in their studies instead of the hydrochloride.

The general trend is for all the rates to increase as the polarity of the solvent increases. This shows that the transition state is indeed polar as expected. However, the increase in rate is much less than the increase in equilibrium constant, in general, so that

(6) J. Weinstock, R. G. Pearson and F. G. Bordwell, THIS JOURNAL **78**, 3468 (1956).

(7) N. J. Leonard, R. C. Fox, M. Ōki and S. Chiavarelli, *ibid.*, **76**, 630 (1954).

the separation of charge in the activated complex is not great. This is confirmed very nicely by studying the effect of adding small amounts of polar substances and of salts on the rates in a non-polar solvent. Such addition has a very great influence on the equilibrium constant for primary amines and virtually none for tertiary amines presumably because of interaction with the excess acidic protons in the former case.⁴

Table III shows a comparison of the increases in rate in benzene caused by small additions of ethanol, or tosylate salts, and the corresponding changes in the equilibrium constants for reaction 2. The much smaller changes in the rates show that the transition state while polar is not strongly so.

In view of this it is surprising that triethylamine does not show up as a stronger catalytic base in all of the solvents and, particularly the more basic ones. In these cases the relative weakness of tertiary amines, as judged by equilibrium studies, was attributed to solvation of the excess acidic protons of the primary and secondary ammonium ions. Such effects should be smaller in the rate studies as demonstrated above.

The additional complicating factor seems to be that of steric hindrance in the rate studies (of the F-strain type). The tosylate compound is much more blocked toward proton removal than nitroethane, for example. Thus in 50% dioxane-water trimethylamine reacts twice as rapidly with the tosylate compound as does triethylamine even

TABLE III
THE EFFECTS OF ADDING SMALL AMOUNTS OF ALCOHOL AND SALTS TO BENZENE AT 25° ON $B + RHOTs \xrightarrow{k} R + BH^+ + OTs^-$

B	Mole % ethyl alcohol	$k(M^{-1} \text{ hr.}^{-1})$	K^a
n-Hexylamine	0.00	2.19	53 ^b
	4.20	8.08	1600 ^b
Triethylamine	0.00	3.18	2700 ^b
	4.20	3.11	2700 ^b
Added n-hexylammonium p-toluenesulfonate, M			
n-Hexylamine	0.00	2.19	50
	3.06×10^{-3}	8.80	2300
Added di-n-butylammonium p-toluenesulfonate, M			
Di-n-butylamine	0.00	4.64	950
	4.80×10^{-3}	7.62	4500
	7.04×10^{-3}	7.88	..

^a Ion-pair formation constants using 2,4-dinitrophenol as reference acid. ^b In chloroform solvent. Very similar results would be expected in benzene.

though the latter is a ten times stronger base in water.³ With nitroethane as a substrate, triethylamine reacts 1.5 times as rapidly as trimethylamine. By this argument all of the rates for triethylamine in Tables I and II are low by roughly a constant factor because of steric strain in the transition state.

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Solubility, Entropy and Partial Molal Volumes in Solutions of Gases in Non-polar Solvents

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A critical review of such gas solubilities as appear to be sufficiently reliable for our purposes reveals the following relations. (a) For a given gas at 1 atmosphere and 25° dissolving in a series of solvents, $\log x_2$ ($x_2 \equiv$ mole fraction of gas) decreases with increasing solubility parameter, δ_1 , of the solvent. (b) For different gases in the same solvent, $\log x_2$ increases linearly with increasing Lennard-Jones force constant, ϵ/k , of the gas. (c) The entropies of solution of different gases in the same solvent vary linearly with $R \ln x_2$, and extrapolate at $x_2 = 1$ to the entropy of condensing to pure liquid the vapor of the solvent from a hypothetical pressure of 1 atmosphere. The temperature coefficient of solubility may thus be obtained from its isothermal value. Solubility increases with temperature for common solvents when x_2 is less than about 10^{-3} , and *vice versa*. (d) The partial molal entropy of solution of any one gas from 1 atmosphere to the same mole fraction (here 10^{-4}) is nearly the same in all solvents except fluorocarbons, where it is a little greater. In any one solvent, it increases in going to gases with smaller force constant. This is attributed mainly to increase in freedom of motion of the adjacent molecules of the solvent rather than to change in the behavior of the gas molecule in a "cage." Partial molal volumes of hydrogen, deuterium and argon have been determined in a variety of solvents. The results accord with the above interpretation.

Progress toward a satisfactory theory of gas solubility has been difficult because of the inaccuracy of much of the published data and the failure to cover a range of temperature sufficient to yield figures for the entropy of solution. An outstanding exception has been the broad work of Horiuti,¹ published in 1931. The need for precise, comprehensive data has recently been partly met by Cook and Hanson² and by Cook, Hanson and Alder³ for

hydrogen and deuterium, and by Reeves and Hildebrand⁴ for argon. Clever, Battino, Saylor and Gross⁵ have kindly put at our disposal in advance of publication their results for helium, neon, argon and krypton. We can utilize, further, data by Lannung⁶ for helium, neon and argon in two sol-

(1) J. Horiuti, *Sci. Papers, Inst. Phys. Chem. Research, Tokyo*, No. 341, **17**, 125 (1931).

(2) M. W. Cook and D. N. Hanson, University of California Radiation Laboratory Report, UCR-L 2459 (1954); *Rev. Sci. Instr.*, **28** (1957).

(3) M. W. Cook, D. N. Hanson and B. J. Alder, *J. Chem. Phys.*, **26**, 748 (1957).

(4) L. W. Reeves and J. H. Hildebrand, *THIS JOURNAL*, **79**, 1313 (1957).

(5) H. L. Clever, R. Battino, J. H. Saylor and P. N. Gross, *J. Phys. Chem.*, **61**, 1078 (1957).

(6) A. Lannung, *THIS JOURNAL*, **52**, 68 (1930).