

be hexafluorobenzene. The effect of pressure would be to drive the reaction to the left but again the rapidity of the bromine removal could be expected to overcome the opposing effect of pressure.

The residues (b.p. $> 115^{\circ}$) of all the pressure runs in the platinum tube were combined and subjected to a steam distillation. The volatile fraction (79%) was dried and pyrolyzed again under the optimum conditions listed above. The material recovery was essentially quantitative. The weight of bromine removed amounted to 34% by weight of the recovered products. A partial analysis of the remaining fraction was as follows: 4.6% by weight hexafluorobenzene, 15.5% bromopentafluorobenzene, and small amounts of some C_7F_7Br product.

From these results it is quite evident, then, that the residues obtained from the initial pyrolysis of $CFBr_3$ still contain intermediates, such as $CFBr=CFBr$ and $CFBr_2-CFBr_2$, which are capable of producing more hexafluorobenzene by further concentration and pyrolysis. This, however, improves the net yield of C_6F_6 by only a few per cent.

Experimental

Tribromofluoromethane.—This compound was prepared essentially by the method of Rathsburg⁶ using stoichiometric amounts of tetrabromomethane and antimony trifluoride in the presence of a small amount of bromine. Standard glass equipment was used. By refluxing for 4–6 hours from a bath kept at 120 to 140° and subsequent distillation, yields of 60 to 70% were obtained, which contribute a substantial improvement over the 19% yield reported by Rathsburg. The product was purified by washing with sodium bisulfite and sodium hydroxide. After drying over calcium chloride the product was fractionated in a four-foot column. Some of the tribromofluoromethane used in subsequent experiments was obtained from the Columbia Chemical Company, Columbia, South Carolina.

Hexafluorobenzene.—Pyrolysis of tribromofluoromethane was performed in a platinum tube 80 cm. long, 1 cm. wide and about 1 mm. thick. An electrically heated furnace was wound around this tube and the temperature of this

furnace was controlled by an automatic relay. The entrance and exit of the tube were cooled by water-cooled brass condensers. Tribromofluoromethane was introduced from a reservoir by means of a solenoid pump. The outlet of the pyrolysis tube was connected to an ice-cooled trap followed by Dry Ice traps. For the runs performed at higher pressures a capillary tube was inserted between the traps. This proved to be adequate for keeping the system under pressure and ensure a slow and even flow rate. In a typical run tribromofluoromethane was introduced into the reservoir, and a slow stream of dry nitrogen was passed through the system while the furnace was brought to the desired temperature. The relay controlling the addition of tribromofluoromethane was then activated and the reagent added at a constant rate. After completion of the addition the product in the receiver and traps was carefully washed with sodium bisulfite and dilute sodium hydroxide. The loss of bromine was determined by weighing the product before and after washing. After drying, the washed product was fractionated to recover hexafluorobenzene (b.p. 79 to 81°) and unreacted tribromofluoromethane (b.p. 106 to 108°). The residues were saved for further purification.

The experiments in graphite and Vycor tubes were performed in a similar but cruder apparatus. The tubes were inserted vertically into a ceramic furnace with the inlet and outlet cooled by brass condensers. The dimensions of the tubes were 86 cm. long, 1.3 cm. wide and 2 mm. thick. The heated length of the tubes was 60 cm. The graphite tube was inserted into a tight fitting iron tube to ensure even heating and to protect the tube from breaking. At the top of the tube a dropping funnel with a bypass tube was inserted by means of a rubber stopper. The outlet of the pyrolysis tube was connected to two traps, one cooled in ice, the other in Dry Ice. Again dry nitrogen was passed through the system during the run. The rate of addition was controlled by setting the stopcock of the dropping funnel. The product was worked up as described above, with the additional step of combining all residues and fractionating them under reduced pressure to obtain samples for mass spectrometer analysis.

Acknowledgments.—The authors wish to express their deep appreciation to Miss Y. Desirant for making her results available prior to publication. Acknowledgment is also made of the aid given by Miss Edith I. Quinn in the interpretation of the mass spectra.

WASHINGTON 25, D. C.

(6) M. Rathsburg, *Ber.*, **51**, 669 (1918).

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

Solvolysis of Alkyl Borates. Catalysis by Amines and Phenols¹

By CLINTON L. DENSON AND THOMAS I. CROWELL

RECEIVED JULY 1, 1957

The ethanolsis of *sec*-butyl borate is subject to general catalysis by amines and phenols. The catalytic constants of the amines obey the Brønsted catalysis law except for negative deviations ascribed to steric effects.

The ethanolsis of *sec*-butyl borate, an ester interchange producing ethyl borate, recently was found to be subject to general acid and base catalysis.² The catalytic constants obtained, together with the existence of a solvent-catalyzed reaction, indicated that the solvolysis rate was only moderately sensitive to the acid or base strength of the catalyst, so that the effect of structure on reactivity of a greater variety of catalysts might easily be determined. We have now extended our previous results to include two phenols and a series

of amines covering a fairly wide range of basicity and steric requirements.

Experimental

Materials.—*sec*-Butyl borate and dry ethanol were prepared as before.² Reagent grade pyridine was used. Other liquid amines were redistilled; aniline was distilled from zinc dust. Solid amines and *p*-nitrophenol were recrystallized from methanol-water and dried in a vacuum desiccator. Phenol was recrystallized from petroleum ether.

Procedure.—Solvolysis rates were determined dilatometrically in ethanol, at 25°, as previously described except that the time intervals were adapted to the method of Guggenheim and the data plotted accordingly, to give the first-order rate constants.³

(1) From the M.S. thesis of Clinton L. Denson, University of Virginia, 1957.

(2) G. T. Perkins and T. I. Crowell, *This Journal*, **78**, 6013 (1956).

(3) E. A. Guggenheim, *Phil. Mag.*, **1**, 538 (1926).

Results

The rate constants, k , from the kinetic runs, plotted against the catalyst concentration in Fig. 1,

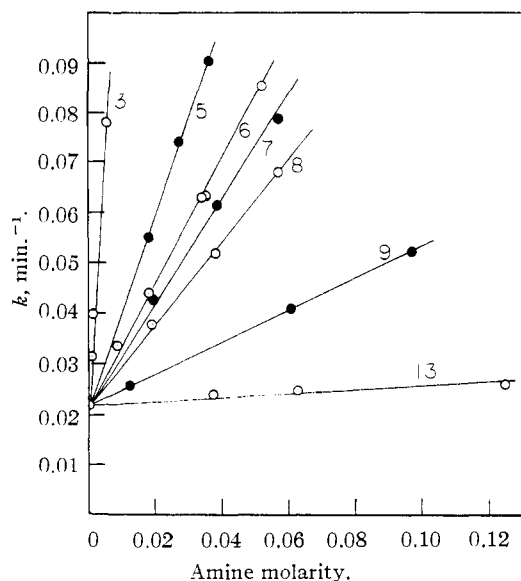


Fig. 1.—Rate constant as function of amine concentration. Compounds numbered as in Table I.

show the linear relation, $k = k_0 + k_c[C]$, where k_c is the catalytic constant of C, the acid or basic catalyst, and $k_0 = 0.0226 \text{ min.}^{-1}$. Table I summarizes the values of k_c . The first two amines and the phenols were omitted from Fig. 1 for clarity; the values for acetate ion and for water were calculated from the data of Perkins and Crowell.² The dissociation constants of the bases also are given in Table I; those in the last column, pK_b in ethanol, are based on the value 19.5 for the autoprotolysis constant of this solvent.⁴ The uncertainty in k_c , given in the second column, was estimated by assuming a 1.8% error in k , and calculating the corresponding error in k_c at the highest concentration of C actually used. When the observed k was not much larger than k_0 , the uncertainty was relatively high (12% in the case of *p*-nitroaniline).

Table II gives the results of adding both phenol and aniline to the reaction mixture. The values of k calculated by the equation, $k = 0.0226 + 0.043[\text{phenol}] + 1.23[\text{aniline}]$, are in fair agreement with those observed. Although there are some discrepancies which might be attributed to interaction between phenol and aniline, we believe them to be experimentally insignificant and consider that Table II shows the solvolysis to be independently catalyzed by phenol and aniline.

Discussion

The amines evidently function as general basic catalysts in borate solvolysis: the rate is linear in the amine concentration and not explicitly in the ethoxide ion concentration. This is apparent in Fig. 1; if specific ethoxide ion catalysis obtained, the rate would be linear in the square root of the amine concentration. The calculated ethoxide ion

concentrations are, moreover, much too small to account for the observed rates. Table II gives further confirmation of general catalysis.

Plots of $\log k_b$ against $pK_b(\text{H}_2\text{O})$ and $pK_b(\text{C}_2\text{H}_5\text{OH})$ are given in Fig. 2. The only bases show-

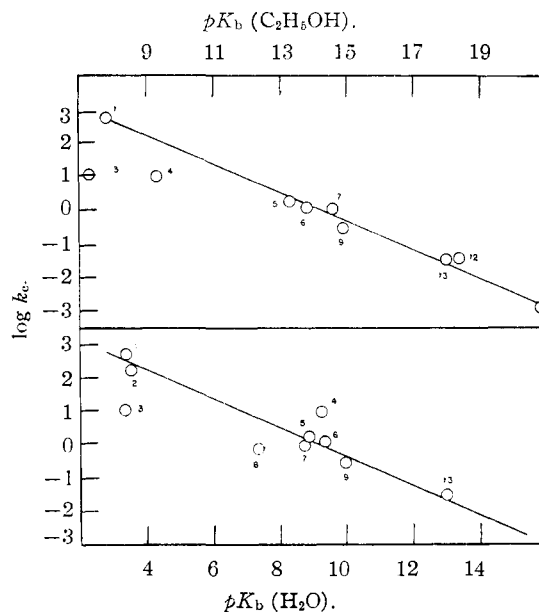


Fig. 2.—Upper curve, top scale: $\log k_c$ vs. $pK_b(\text{C}_2\text{H}_5\text{OH})$. Lower curve, bottom scale: $\log k_c$ vs. $pK_b(\text{H}_2\text{O})$. Compounds numbered as in Table I.

ing a deviation from linearity of more than 0.3 log unit are acetate ion, triethylamine and 2,6-dimethylpyridine. It may, therefore, be stated that the uncharged, relatively unhindered, bases studied conform approximately to the Brønsted catalysis law. The fact that lines of the same slope (-0.43) may be passed through both sets of points proves only that $pK_b(\text{C}_2\text{H}_5\text{OH}) - pK_b(\text{H}_2\text{O})$ is about the same for most of the amines. It is therefore of no great importance practically and possibly is no more correct fundamentally⁵ to refer to the basicities in ethanol, except that it permits H_2O (dilute solution in ethanol) and ethanol (the solvent itself) to be included in the correlation.

The negative rate deviation of triethylamine and 2,6-dimethylpyridine must be considered in the light of two opposite structural effects already well established for catalysis by tertiary amines⁶: while steric hindrance may decrease the rate (if there is a bulky group on the substrate molecule), tertiary amines as a class react more rapidly than expected on the basis of dissociation constants measured in hydroxylic solvents. The latter solvation effect is apparently outweighed by the steric effect (F-strain) for these two amines. The steric requirements of *sec*-butyl borate, with respect to basic catalysis, are therefore somewhat larger than those of nitroethane.⁶ On the other hand, our reaction is less sensitive to steric effects than several other types of reaction involving some of

(5) R. P. Bell, "Acid-Base Catalysis," Oxford Univ. Press, London, 1941, p. 108.

(6) For a pertinent discussion, see R. C. Pearson and F. V. Williams, THIS JOURNAL, **76**, 258 (1954).

(4) B. Gutbezahl and E. Grunwald, THIS JOURNAL, **75**, 563 (1953).

TABLE I
CATALYTIC CONSTANTS FOR SOLVOLYSIS OF *sec*-BUTYL BORATE

Catalyst	k_c , liters/mole-min.	$\frac{pK_b}{(H_2O)}$	$\frac{pK_b}{(C_2H_5OH)}$
<i>n</i> -Butylamine	517 ± 12	3.39 ^{a,b}	7.8 ^c
<i>t</i> -Butylamine	181 ± 7	3.55 ^d	...
Triethylamine	10.4 ± 0.2	3.35 ^e	7.3 ^f
Acetate ion	10.0 ± .2	9.25	9.3 ^g
<i>p</i> -Toluidine	1.88 ± .05	8.90 ^h	13.3 ⁱ
Aniline	1.23 ± .03	9.36 ^h	13.8 ⁱ
Pyridine	1.03 ± .03	8.75 ^j	14.6 ⁱ
2,6-Dimethylpyridine	0.80 ± .02	7.36 ^j	...
<i>p</i> -Chloroaniline	.305 ± .009	10.00 ^{a,k}	14.9 ^{i,l}
<i>p</i> -Nitrophenol	.083 ± .004
Phenol	.043 ± .003
Water	.040 ± .004	...	18.4 ^m
<i>p</i> -Nitroaniline	.033 ± .004	13.0 ^{k,l,n}	18.0 ^m
Ethanol	.00132	...	20.8 ^o
KSCN	.000

^a N. F. Hall and M. R. Sprinkle, *THIS JOURNAL*, **54**, 3469 (1932). ^b P. Rumpf, G. Girault-Vexlearschi and R. Schoal, *Bull. soc. chim. France*, 555 (1955). ^c L. C. Goodhue and R. M. Hixon, *THIS JOURNAL*, **57**, 1688 (1935). ^d G. Bredig, *Z. physik. Chem.*, **13**, 191 (1894). ^e J. Hansson, *Svensk. Kem. Tidskr.*, **67**, 256 (1955). ^f C. Li and T. D. Stewart, *THIS JOURNAL*, **59**, 2596 (1937). ^g M. Kilpatrick and R. D. Eanes, *ibid.*, **75**, 586 (1953). ^h M. Mizutani, *Z. physik. Chem.*, **113**, 318 (1925); J. N. Brønsted, A. Delbanco and A. Tovborg-Jensen, *ibid.*, **169A**, 361 (1934). ⁱ H. Goldschmidt and E. Mathiesen, *ibid.*, **119**, 439 (1926). ^j R. G. Pearson and F. V. Williams, *THIS JOURNAL*, **75**, 3073 (1953). ^k E. Sawicki and F. E. Ray, *J. Org. Chem.*, **19**, 1686 (1954). ^l M. Kilpatrick and C. A. Arenberg, *THIS JOURNAL*, **75**, 3815 (1953). ^m E. A. Braude and E. S. Stern, *J. Chem. Soc.*, 1976 (1948). ⁿ M. A. Paul, *THIS JOURNAL*, **76**, 3236 (1954). ^o Reference 5, p. 91.

the same amines. *t*-Butylamine, not notably unreactive here (Fig. 2), shows greatly decreased reactivity in Schiff base formation,⁷ displacement reactions⁸ and association with B(CH₃)₃.⁹ 2,6-Dimethylpyridine, a very unreactive amine in displacement and association reactions, shows a negative deviation of only 0.9 log unit in Fig. 2 and 0.4 log unit in the ionization of nitroethane, while

(7) R. L. Hill and T. I. Crowell, *THIS JOURNAL*, **78**, 2284 (1956).

(8) C. L. Brady and F. R. Cropper, *J. Chem. Soc.*, 507 (1950).

(9) H. C. Brown and G. K. Barbaras, *THIS JOURNAL*, **75**, 6 (1953).

TABLE II
CATALYSIS BY PHENOL-ANILINE MIXTURES

[Phenol], <i>M</i>	[Aniline], <i>M</i>	Obsd. k , min. ⁻¹	Calcd.
0.1360	0.0033	0.0295	0.0324
.0816	.0333	.0636	.0670
.1293	.0034	.0320	.0322
.0532	.0087	.0336	.0355
.1034	.0168	.0479	.0476
.0271	.0333	.0638	.0647
.0259	.0334	.0684	.0646

2,4,6-trimethylpyridine shows no negative deviation in the decomposition of nitramide.¹⁰

In the mechanism of base-catalyzed borate solvolysis, the function of the amine may be to remove a proton after addition of ethanol; it is also conceivable that the amine forms a bond with the boron atom, yielding an intermediate complex or even an aminodialkoxoborane. Bender¹¹ has found an analogous intermediate, *N*-acetylimidazole, in the imidazole-catalyzed hydrolysis of an acetate. No evidence for a long-lived intermediate has appeared in our experiments. The reactions are, dilatometrically at least, first order. The constancy of the total volume change indicates no important interaction between ethyl borate and amine at the end of the reaction. (The experiments of Horn and Gould¹² indicate compound formation between amines and methyl borate in liquid phase, but do not extend to dilute methanol solutions.) The slope of our linear free energy relation (Fig. 2) is, moreover, normal for reactions involving proton transfers, while Bender¹¹ found an unusually high value associated with the amine addition mechanism.

The acids studied, together with the corresponding k_c , are: EtOH₂⁺, 1050; acetic, 217; *p*-nitrophenol, 0.083; phenol, 0.043. Although the catalytic constants are in the order of acidity, no quantitative correlation is possible.

CHARLOTTESVILLE, VA.

(10) R. P. Bell and G. L. Wilson, *Trans. Faraday Soc.*, **46**, 407 (1950).

(11) M. L. Bender and B. W. Turnquest, *THIS JOURNAL*, **79**, 1652, 1656 (1957).

(12) H. Horn and E. S. Gould, *ibid.*, **78**, 5772 (1956).