

effects for several reactions with the probable change in extent of solvation of the reactants on going to the transition state.

The data in Table III on alkyl halides and sulfides appear to support the suggestion that increased solvation for the transition state leads to a smaller value of the rate ratio k_{D_2O}/k_{H_2O} . The data for the base-catalyzed hydrolysis of epoxides are also consistent with this. For the water reaction of epoxides, mechanisms III(a) and (c)

both involve increased solvation upon reaction but the increase should be much more for the latter. The observed low value of k_{D_2O}/k_{H_2O} is hence consistent with the proposal that III(c) may contribute at least to some extent. However, a decision on the relative contributions of mechanisms III(a) and (c) must await the results of other types of experiments since the differences of Table III are not large enough to be more than suggestive. ITHACA, N. Y.

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

Kinetics of the Solvolysis of Alkyl Borates^{1a}

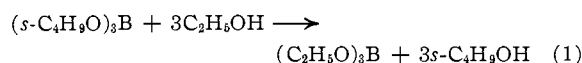
BY GILBERT T. PERKINS^{1b} AND THOMAS I. CROWELL

RECEIVED JULY 5, 1956

The rate of ethanolysis of *sec*-butyl borate has been measured dilatometrically at 0 and 25°. The first-order rate constants are linear in the concentrations of hydrogen ion and acetic acid, and are increased in a more complex manner by ethoxide ion and acetate ion, indicating general acid-base catalysis. The reaction is markedly accelerated by small amounts of water, except that water inhibits oxonium-ion catalysis. Uncatalyzed methanolysis is faster than ethanolysis and has a lower apparent activation energy. The order of reactivity of several alkyl borates with ethanol at 25° is *n*- and iso-Bu >> iso-Pr > *sec*-Bu >> *t*-Bu.

The *n*-alkyl borates (tris-*n*-alkoxyboranes) are liquids which hydrolyze rapidly in water. Branched chain borates such as neopentyl, isopropyl² and *t*-butyl,³ react much more slowly, a generalization which has been verified in a recent, more comprehensive study of hydrolysis rates.⁴ No careful consideration has been given to the possibility of acid or base catalysis.

We have investigated the kinetics of alcoholysis of several alkyl borates, especially the reaction of *sec*-butyl borate with ethanol



The stoichiometry of this type of ester interchange has been established in the preparation of many alkyl borates.⁵ The rate was most conveniently measured dilatometrically; a few cases in which titrations were used are described in the Experimental section.

Experimental

Reagents.—*sec*-Butyl borate was prepared by the methods of Bannister⁶ and Lippenscott.⁷ Analysis by titration with standard aqueous sodium hydroxide, in the presence of mannitol and phenolphthalein, gave 100.4% of the theoretical titer. *t*-Butyl, isobutyl and isopropyl borates were prepared according to Lippenscott, *n*-butyl borate according to Bannister, and methyl borate obtained from Anderson Laboratories. All were purified by distillation and protected from the atmosphere.

(1) (a) From the Dissertation of Gilbert T. Perkins, University of Virginia, 1956. Presented in part at the Southeastern Regional Meeting of the American Chemical Society, Columbia, South Carolina, November 1955. (b) Du Pont Fellow, 1955-1956.

(2) A. Scattergood, W. H. Miller and J. J. Gammon, *THIS JOURNAL*, **67**, 2150 (1945).

(3) P. D. George and J. R. Ladd, *ibid.*, **77**, 1900 (1955).

(4) H. Steinberg and D. L. Hunter, Abstracts of Papers, American Chemical Society, Minneapolis, Minn., September, 1955, p. 36-O.

(5) H. Wuyts and A. Duquesne, *Bull. soc. chim. Belg.*, **48**, 77 (1939).

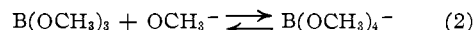
(6) See J. R. Johnson and S. W. Thompkins, *Org. Syntheses*, **13**, 16 (1933).

(7) S. B. Lippenscott, U. S. Patent 2,642,453 (1954).

Commercial absolute ethanol was dried by distillation from magnesium ethoxide. Karl Fischer titration indicated a maximum water content of 0.02%. Methanol was dried by the same procedure. Sodium ethoxide solutions were prepared from clean sodium and ethanol, then standardized against aqueous hydrochloric acid. Ethanolic hydrogen chloride solutions were prepared by passing the gas through concentrated sulfuric acid and into ethanol; the solutions were standardized against aqueous sodium hydroxide.

Reagent grade sodium acetate and lithium chloride were oven-dried. Lithium acetate was prepared by adding excess acetic acid to a solution of lithium carbonate, evaporating to dryness, and fusing the residue. Acetic acid was dried by distillation with benzene in a fractionating column. Standard ethanol solutions of acetic acid appeared to esterify to the extent of nearly 1% per day, and consequently were always freshly prepared.

Rate by Titration.—Meerwein⁸ reported that methyl borate in methanol could be titrated to a sharp end-point with sodium methoxide, using thymolphthalein indicator, but that larger alkyl groups reversed the reaction. Accordingly, we attempted to determine ethyl borate in the presence



of *sec*-butyl borate by titration and thus follow the kinetics of ethanolysis. Although Meerwein's results were qualitatively confirmed, the end-points faded badly due to ester interchange, catalyzed by the titrant. The rough values of k so obtained for ethanolysis of *sec*-butyl borate at 0° are 0.003, 0.005 and 0.007 min.⁻¹.

The uncatalyzed solvolysis of *t*-butyl borate was followed by pipetting samples of the reaction mixtures into cold water. While *t*-butyl borate (m.p. 18°) separated as a solid, primary borates were quickly hydrolyzed and titrated as boric acid with sodium hydroxide in the presence of mannitol. The titer at complete reaction was obtained by hydrolyzing a sample overnight in aqueous hydrochloric acid.

Rate by Dilatometer.—The dilatometer consisted of a Pyrex bulb (capacity 20 ml.) bearing a 12-cm. length of 0.5 mm. precision-bore capillary tubing with etched millimeter scale. A stopcock and funnel were also attached to the bulb.

In the kinetic runs, the reaction mixtures were quickly made up at the temperature of the thermostat and poured into the dilatometer, which was immersed in the thermostat. Zero time was taken as the time of mixing. The decrease in volume with time was observed until the reading became constant. The exact borate concentration was determined after the run by hydrolyzing a sample and titrating for boric

(8) H. Meerwein and T. Bersin, *Ann.*, **476**, 122 (1929).

acid. The variation in thermostat temperature was kept within 0.002° at 25° and 0.01° at 0°.

Results and Discussion

"Uncatalyzed" Solvolysis.—A plot of $\log(V_t - V_\infty)$ vs. t , where V_t is the volume at time t , is shown in Fig. 1 (curve A) for the ethanolsis of *sec*-butyl borate at 0°. The first-order course after a short period of temperature change is typical of all the reactions except those catalyzed by sodium ethoxide. The rate constant, k , is defined as -2.303 times the slope of the linear portion of the curve. An eightfold variation in the borate concentration (0.035 to 0.280 *M*) caused no significant change in k . The total volume change, obtained by linear extrapolation of the curve of Fig. 1 back to zero time, was proportional to the borate concentration. The solvolysis is therefore a first-order reaction which proceeds practically to completion at these concentrations.

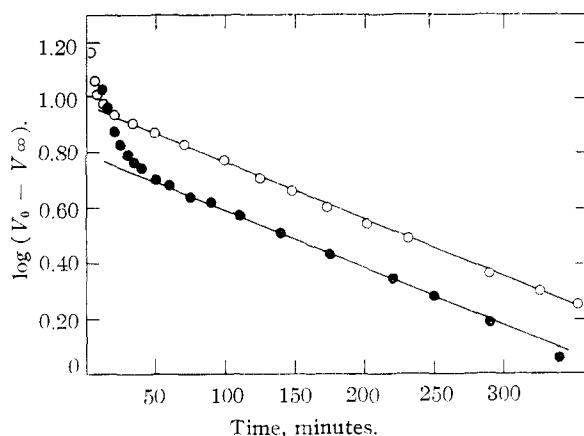


Fig. 1.—Dilatometer curves for ethanolsis: A (open circles), *sec*-butyl borate; B (dark circles), mixed ethyl-*sec*-butyl borates. Volume in arbitrary units which are different for A and B.

Solvolysis of *sec*-butyl borate was more rapid in methanol than in ethanol. Small quantities of water accelerated the reaction without affecting the total volume change, the acceleration being

TABLE I

RATE CONSTANTS FOR SOLVOLYSIS OF <i>sec</i> -BUTYL BORATE					
Temp., °C.	Solvent	[H ₂ O], moles/l.	k , min. ⁻¹	$\log k$ _{25°}	$\log k$ (calcd.)
0	MeOH	0.00	0.056	-0.76	-0.65
		.11	.062	-.72 ^a	-.64
		.22	.067	-.68 ^a	-.61
		.32	.072	-.65 ^a	-.58
		.54	.083	-.59 ^a	-.54
		1.08	.118	-.44 ^a	-.44
		2.70	.187	-.24 ^a	-.21
25	EtOH	0.00	.0048		
		.00	.173		
	EtOH	.00	.0226	-1.65	-1.60
		.54	.0419	-1.38	-1.42
		1.08	.062	-1.21	-1.30
		1.62	.087	-1.06	-1.16
		2.70	.143	-0.85	-0.89
		3.78	.221	-.66	-.68
5.40	.329	-.48	-.37		

^a Calculated from data at 0°.

more marked in ethanol. In the rather limited series of solvents studied, the solvolysis rates were correlated, approximately and perhaps fortuitously, by the equation $\log k/k_0 = mY$, suggested by Grunwald and Winstein for the solvolysis of alkyl halides,⁹ with $\log k_0 = 0.43$ and $m = 1.03$. The solvolysis rates are shown in Table I. The apparent activation energies are 7.1 kcal./mole in methanol and 10.1 kcal./mole in ethanol.

Acid and Base Catalysis.—The ethanolsis of *sec*-butyl borate (1) was readily catalyzed by acids and bases. Figure 2 shows that 10^{-4} *M* hydrochloric acid causes a fivefold increase in k . The limiting slope gives $k = 0.0226 + 1050$ [EtOH₂⁺]. (The rate constant is more nearly linear in the activity of hydrochloric acid¹⁰: the equation becomes $k = 0.0226 + 1100a_{\text{HCl}}$.) The rate of the acid-catalyzed reaction is decreased by small amounts of water. This effect, which is opposite to that observed in the uncatalyzed reaction, must be due to the conversion of EtOH₂⁺ to the less reactive H₃O⁺. It has been previously noticed in other oxonium-ion catalyzed reactions.¹¹

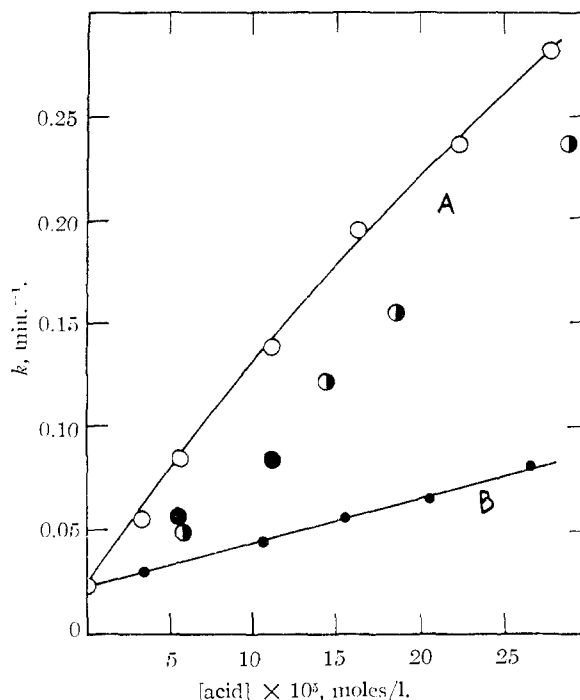


Fig. 2.—A, catalysis by hydrochloric acid; open circles, dry EtOH; shaded circles, undried EtOH; dark circles, dry EtOH + 0.2% H₂O; B, catalysis by acetic acid, electrolyte concentration 0.05 *M*.

Figure 2 also shows the catalytic effect of acetic acid. Catalysis by EtOH₂⁺ accounts for less than 1% of the rate, as estimated using the value of Kilpatrick and Eanes¹² for the dissociation constant of acetic acid in ethanol containing 0.05 *M*

(9) E. Grunwald and S. Winstein, *THIS JOURNAL*, **70**, 846 (1948); S. Winstein, B. Grunwald and H. W. Jones, *ibid.*, **73**, 2700 (1951).

(10) J. W. Woolcock and H. Hartley, *Phil. Mag.*, **5**, 1133 (1928).

(11) A. J. Deyrup, *THIS JOURNAL*, **56**, 60 (1934); E. A. Brandle, *J. Chem. Soc.*, 443 (1944); P. F. Ritchie and L. F. McBurney, *THIS JOURNAL*, **71**, 3736 (1949).

(12) M. Kilpatrick and R. D. Eanes, *ibid.*, **75**, 586 (1953).

lithium chloride. Since the rate constants are linear in the concentration of undissociated acetic acid, the solvolysis is subject to general acid catalysis. There is no salt effect: the catalytic constant of 217 l./mole-min. agrees within 2% with the constant obtained in the absence of electrolytes.

The basic catalysts investigated were sodium ethoxide and lithium acetate. While showing the reaction to be catalyzed by ethoxide ion, the experiments involving sodium ethoxide showed certain deviations from the relatively simple results of the acid-catalyzed runs (see Table II). The variation in k with borate concentration, and a slight upward curvature of the first-order plots show that this reaction is not simply first order with respect to *sec*-butyl borate. This may be due to the known interaction of ethoxide ion with borates present, as in eq. 2.

TABLE II
ETHOXIDE-ION CATALYSIS OF THE ETHANOLYSIS OF *sec*-BUTYL BORATE

Initial borate, mole/l.	$10^3[\text{NaOEt}]$, moles/l.	k , min. ⁻¹
0.070	0.00	0.0226
	.14	.0309
	.72	.0483
	1.46	.0558
	2.16	.0657
	3.60	.0848
.036	7.20	.119
	0.00	.0226
	.73	.0523
	1.45	.0770
	2.15	.118

Concentrations of lithium acetate ranging from 0.0001 to 0.006 M accelerated the solvolysis as shown in Table III. The electrolyte concentration was maintained at 0.05 M by adding the requisite amount of lithium chloride. Obviously, k is not a linear function of the acetate ion concentration at low concentrations. The curve is approximately parabolic: Table III shows that the data fit the equation

$$k = 0.0226 + 7.03[\text{OAc}^-] + 0.355[\text{OAc}^-]^{1/2} \quad (3)$$

with an average deviation of 1.6%. Although this is the type of relationship expected if solvolysis of acetate ion produced enough acetic acid and ethoxide ion to catalyze the reaction, calculations using the best available figures yield a negligibly small coefficient of $[\text{OAc}^-]^{1/2}$. (The autoprotolysis constant of ethanol at 0.05 M electrolyte concentration was estimated to be 1.16×10^{-18} from the value of 3.16×10^{-20} for pure ethanol,¹³ assuming this constant subject to the same salt effect as the dissociation constant of acetic acid.¹²) It is possible that an alkyl borate might enhance the solvolysis of the acetate ion by combining with the ethoxide ion formed. It is also possible, of course, that the curvature is due to a more complex type of catalysis, or even to an impurity in the system. Although the question of the shape of the curve is left open, we may note that the slope attains a

(13) B. Guthezahl and E. Grunwald, *THIS JOURNAL*, **75**, 565 (1953).

nearly constant value above 0.0015 M , yielding a catalytic constant for the acetate ion of 10.0 l./mole-min.

TABLE III
CATALYSIS BY LITHIUM ACETATE
Initial *sec*-butyl borate, 0.137 M ; total electrolyte, 0.05 M

LiOAc , $M \times 10^3$	Obsd. k , min. ⁻¹	Calcd.
0	0.0226	0.0226
0.092	.0258	.0266
.276	.0297	.0304
.459	.0329	.0334
.919	.0415	.0399
1.84	.0511	.0507
2.76	.0599	.0606
3.67	.0707	.0699
4.59	.0778	.0789
6.43	.0967	.0963

General acid and base catalysis was further demonstrated by measuring the rate of solvolysis of *sec*-butyl borate in acetic acid-lithium acetate buffers. Table IV shows the observed rate constants compared with the values calculated using the catalytic constants already given for acetic acid and acetate ion.

TABLE IV
SOLVOLYSIS RATES IN ACETATE BUFFERS
Initial *sec*-butyl borate, 0.137 M ; total electrolyte, 0.05 M

$10^3 [\text{LiOAc}]$, moles/l.	$10^4 [\text{HOAc}]$, moles/l.	Obsd. k , min. ⁻¹	Calcd.
0.53	0.41	0.0398	0.0368
1.05	.82	.0539	.0509
1.84	.89	.0643	.0603
1.84	1.12	.0693	.0653
1.58	1.25	.0675	.0655
1.84	1.75	.0781	.0790
1.84	1.76	.0788	.0792
2.11	1.64	.0795	.0793
2.63	2.07	.0949	.0938

Structural Effects.—The primary borates tested—methyl, *n*-butyl and isobutyl—apparently underwent complete ethanolysis before the dilatometer could be filled. Secondary borates reacted at a fast but measurable rate, and the single tertiary borate, very slowly. These results, which are summarized in Table V, are of course typical of reactions subject to steric hindrance.

TABLE V
ETHANOLYSIS RATES OF SEVERAL BORATES

Borate	Temp., °C.	k , min. ⁻¹	No. of runs av.
<i>n</i> -Butyl	0	Large	
Isobutyl		Large	
Methyl		Large	
Isopropyl		0.056 ± 0.002 ^a	2
Isopropyl	25	.28 ± .03	10
<i>sec</i> -Butyl	0	.0477 ± .0005	3
<i>sec</i> -Butyl	25	.0226 ± .0004	9
<i>t</i> -Butyl	25	.0000102	1

^a Average deviation from the mean.

The rate of solvolysis of *t*-butyl borate in ethanolic hydrochloric acid solutions followed the equation $k = 1.02 \times 10^{-5} + 2.70[\text{HCl}]$. This relation

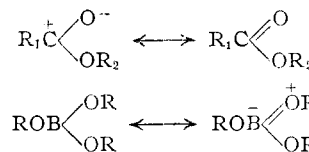
was obtained from the uncatalyzed reaction already cited, and from eleven runs involving acid concentrations between 0.0036 and 0.0421 *M*. The value of *k* in the latter case was 0.114 min.⁻¹.

The Reaction Mechanism.—The complete solvolysis of an alkyl borate obviously requires three steps, in which the alkoxy groups are successively replaced. We believe the first step to be practically rate-controlling. The structural studies show that a secondary borate reacts much more slowly than a primary one. The interpolation that ethyl di-*sec*-butyl borate¹⁴ (the first intermediate in the ethanolysis of *sec*-butyl borate) reacts faster than *sec*-butyl borate, seems safe enough. Separate evidence was obtained from a mixture of esters prepared by mixing 1.5 moles *sec*-butyl alcohol with 1.0 mole of ethyl borate and distilling off the ethanol formed. The expected product would consist of a preponderance of the two mixed esters (EtO)-(BuO)₂B and (EtO)₂(BuO)B with much smaller proportions of (EtO)₃B and (BuO)₃B. The behavior of this mixture in the dilatometer at 0° is shown in curve B, Fig. 1. The large initial volume change, prolonged to about 50 minutes, is probably due to fairly rapid solvolysis of the mixed esters. The final slope (0.00495 at 0°, 0.0230 at 25°), in close agreement with the ethanolysis rate of pure *sec*-butyl borate, probably represents the solvolysis

(14) Mixed orthoborates of this type have not yet been isolated; see L. H. Thomas, *J. Chem. Soc.*, 820 (1946).

of this compound alone, for the molar volume change in the period of linearity is only 10% of the usual change.

The detailed mechanism of a single stage of ethanolysis was shown by Scattergood and co-workers² to involve fission of a boron-oxygen bond, presumably after addition of the solvent to the boron atom. Some additional evidence for such a mechanism, as opposed to a separation of a carbonium ion from the alkyl borate, is provided by our observation that the acid-catalyzed solvolysis of *t*-butyl borate produced no isobutylene; nor was ethyl *t*-butyl ether reported as a by-product of the preparation of *t*-butyl borate in boiling ethanol.³ The mechanism of ethanolysis of the borates may therefore proceed by addition of ethanol to the borate molecule followed by loss of an alkoxide ion, with suitable modification to accommodate acid or base catalysis. This mechanism is similar to the mechanism of carboxylic ester hydrolysis, the electron-deficient boron atom taking the role of the electron-deficient carbon atom of the carbonyl group



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Complexes of Biacetyldihydrazone and Pyridinalhydrazones with Iron(II), Cobalt(II) and Nickel(II)

BY R. CARL STOUFFER AND DARYLE H. BUSCH

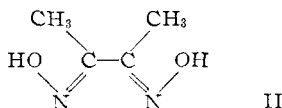
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Iron(II), cobalt(II) and nickel(II) complexes have been prepared and characterized with biacetyldihydrazone (BdH), 2-pyridinalhydrazone (PAH), 2,6-pyridindialdihydrazone (PdAdH) and 2-pyridinal-*p*-tolilimine (PAT). The compounds having a metal-ligand ratio of 1:3 were isolated in all cases and the compounds having a metal-ligand ratio of 1:2 were isolated in several instances. The magnetic susceptibilities have been measured and the corrected magnetic moments of the metal ions are reported. The iron(II) complexes which contain three molecules of ligand are diamagnetic; however, the metal atoms exhibit small residual paramagnetisms. The remaining complexes are all highly paramagnetic. The colors, solubilities, magnetic moments and chemical properties indicate that the complexes are closely related to the well-known complexes with such aromatic heterocyclic diamines as 2,2'-bipyridine.

Among the best known complexing agents for iron(II), cobalt(II) and nickel(II) are the aromatic heterocyclic diamines and triamines which may be exemplified by 2,2'-bipyridine (I)

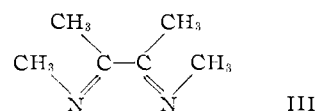


and the α -dioximes, of which dimethylglyoxime (II) is most familiar.

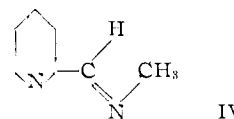


Krumholz¹ showed that the α -diimines, such as biacetylbis-(methylimine) (III), form iron(II) com-

plexes which are quite similar to those of the aromatic heterocyclic diamines.



Recently,² the preparation of compounds involving functional groups of both the cyclic amine type and the imine type have been reported. This



(1) P. Krumholz, *THIS JOURNAL*, **75**, 2163 (1953).
 (2) W. W. Brandt, F. P. Dwyer and E. C. Gyartas, *Chem. Revs.*, **54**, 980 (1954); D. H. Busch, thesis, University of Illinois, Aug., 1954; D. H. Busch and J. C. Bailar, Jr., *THIS JOURNAL*, **78**, 1137 (1956).

(1) P. Krumholz, *THIS JOURNAL*, **75**, 2163 (1953).