417. *Kinetic Salt Effects on the Decomposition of Diacetone Alcohol in Solutions of Tetra-alkylammonium Hydroxides.*

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The rate of decomposition of diacetone alcohol has been studied in solutions of tetramethyl-, tetraethyl-, tetra-*n*-propyl-, tetra-*n*-butyl-, and tetra-*n*-amyl-ammonium hydroxides. The catalytic constants for the hydroxyl ion increase with the concentration, the effect being greatest with tetrapropylammonium hydroxide. The origin of these effects is discussed.

THE activity coefficients and conductances of tetra-alkylammonium salts (Ebert and Lange, *Z. physikal. Chem.*, 1928, **139**, *A*, 584) are abnormal, and it seemed of interest to investigate whether they display correspondingly abnormal kinetic salt effects. Brady and Jakobovits (*J.*, 1950, 767) have noted the specific influences of tetra-alkylammonium cations on the rate and even the products of some reactions involving the hydroxyl ion. We selected for study the hydroxyl-ion catalysed depolymerisation of diacetone alcohol. In a recent paper (Bell and Prue, *J.*, 1949, 362) the negative specific kinetic salt effects observed for this reaction in solutions of various metallic hydroxides were successfully interpreted in terms of the incomplete dissociation of some of the hydroxides. The salt effects observed for potassium and rubidium hydroxides were extremely small and these hydroxides may be considered as providing a standard of normal behaviour.

EXPERIMENTAL

The tetra-alkylammonium hydroxides were prepared from the corresponding iodides by shaking them with silver oxide and then filtering the mixtures. Commercial samples of tetramethyl- and tetraethyl-ammonium iodide were purified by repeated crystallisation from water. Tetrapropyl-, tetrabutyl-, and tetra-amyl-ammonium iodide were made by refluxing the tertiary amine and the alkyl iodide in acetonitrile and precipitating the salts with ether; this seems to provide a very satisfactory general method for the preparation of these salts. All hydroxide solutions were standardised against constant-boiling hydrochloric acid, and carbon dioxide was rigidly excluded.

The kinetic measurements were made at 24·77°±0·01° in a bath, of which the temperature variations during an experiment were not greater than ±0·002°. A simple dilatometer similar to that described by Halberstadt, Hughes, and Ingold (*J.*, 1950, 2441) was employed. The concentration of diacetone alcohol was about 4%. Velocity constants were calculated by Guggenheim's method (*Phil. Mag.*, 1926, **7**, 538), and their accuracy is estimated as about ±0·5%. It may be noted that no reaction was observed in acid solution in the presence of tetra-alkylammonium salts.

TABLE 1.

Potassium hydroxide.

$[OH^-]$	0·038	0·075	0·150	0·188	0·226	0·263	0·338	0·376
$10k/[OH^-]$	4·86	4·90	4·83	4·82	4·81	4·82	4·75	4·70

Tetramethylammonium hydroxide.

$[OH]^-$	0·040	0·080	0·120	0·160	0·200	0·239	0·279	0·319	0·359
$10k/[OH^-]$	5·05	5·16	5·29	5·36	5·48	5·58	5·68	5·77	5·94

Tetraethylammonium hydroxide.

$[OH^-]$	0·072	0·109	0·145	0·181	0·218	0·254	0·290	0·326	0·363
$10k/[OH^-]$	5·25	5·41	5·59	5·69	5·86	6·03	6·12	6·34	6·42

*Tetra-*n*-propylammonium hydroxide.*

$[OH^-]$	0·056	0·111	0·167	0·222	0·277
$10k/[OH^-]$	5·28	5·49	5·77	5·96	6·24

*Tetra-*n*-butylammonium hydroxide.*

$[OH^-]$	0·065	0·130	0·162	0·195	0·259	0·324
$10k/[OH^-]$	5·26	5·52	5·63	5·76	6·02	6·23

*Tetra-*n*-amylammonium hydroxide.*

$[OH^-]$	0·112	0·140	0·168	0·224	0·280
$10k/[OH^-]$	5·36	5·45	5·53	5·77	5·87

Results.—Table 1 gives values of the catalytic constants where k is the first-order velocity constant in terms of natural logarithms and minutes and $[OH^-]$ is the concentration of hydroxyl ion in moles/litre.

DISCUSSION

In Fig. 1 the observed catalytic constants $k/[OH^-]$ are plotted against the hydroxyl-ion concentration. For clarity only three of the series of results given in Table 1 have been plotted. A summary of the results for all the tetra-alkylammonium salts quoted in Table 1 may be found in Fig. 2, where slopes of all the lines as in Fig. 1 are shown for each alkyl group.

The catalytic constants converge to a mean value at infinite dilution of $0{\cdot}496_9$, within the estimated experimental error. The soap-like character of the solutions of the higher tetra-alkylammonium salts gave rise to difficulty in pipette drainage. This may explain the slight scatter of the limiting values of the catalytic constants in Fig. 1. Taking La Mer and Miller's data for the temperature coefficient at 25° (*J. Amer. Chem. Soc.*, 1935, **57**, 2674) we calculate the limiting value of our catalytic constant at 25° to be $0{\cdot}508_3$. This is between $0{\cdot}502_5$ recorded by Bell and Prue (*loc. cit.*) and $0{\cdot}511_0$ reported by La Mer and Miller.

FIG. 1.

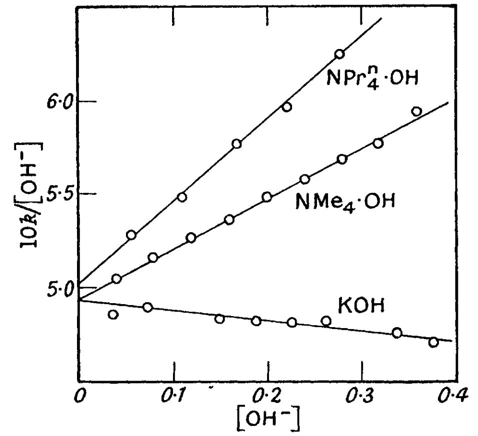
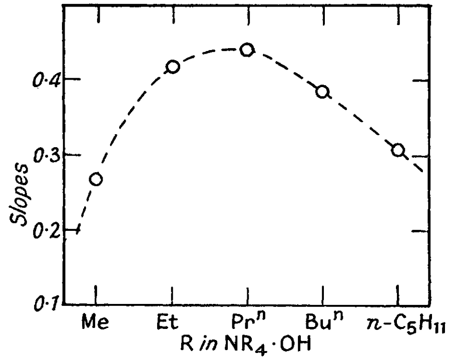


FIG. 2. *Slope of plots of catalytic constants against hydroxyl-ion concentration for tetra-alkylammonium hydroxides.*



The increases in catalytic constants observed for increasing concentration of the various tetra-alkylammonium hydroxides are surprisingly large, being comparable with the decreases observed for barium and thallium hydroxides due to the incomplete dissociation of these hydroxides (Bell and Prue, *loc. cit.*). The problem being stated in its most general form, the expression for the reaction velocity, irrespective of the detailed reaction mechanism, will contain the concentrations of diacetone alcohol and hydroxyl ion multiplied by an activity coefficient factor $f_A f_{OH^-}/f_{(AOH)^-}$, where f_A is the activity coefficient of the diacetone alcohol, f_{OH^-} that of the hydroxyl ion, and $f_{(AOH)^-}$ that of the transition state. If f_A is assumed to be effectively unity in fairly dilute solution, an increase in the catalytic constant may be ascribed to an increase in the factor $f_{OH^-}/f_{(AOH)^-}$ due, according to Brönsted's principle of specific interaction of ions (*J. Amer. Chem. Soc.*, 1922, **44**, 877), to short-range

TABLE 2. *The effect of added salts on the rate constant in* 0·273M-*potassium hydroxide.*

Addition of a single salt.

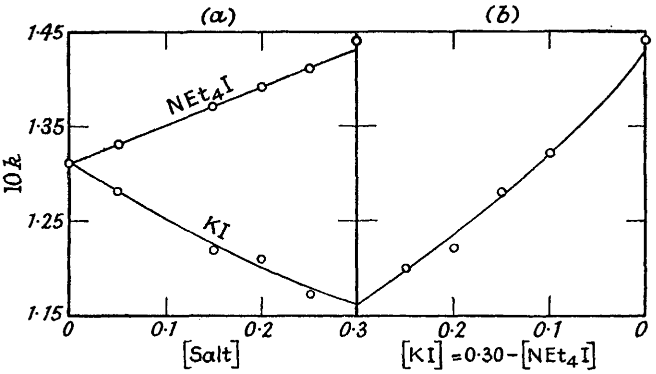
[KI]	—	0·050	0·150	0·200	0·250	0·300
$10k$	1·31	1·28	1·22	1·21	1·17	1·16
$[(C_2H_5)_4NI]$	—	0·050	0·150	0·200	0·250	0·300
$10k$	1·31	1·33	1·37	1·39	1·41	1·44

Replacement of potassium iodide by tetraethylammonium iodide, the total ionic strength being constant.

[KI]	0·300	0·250	0·200	0·150	0·100	0
$[(C_2H_5)_4NI]$	0	0·050	0·100	0·150	0·200	0·300
$10k$	1·16	1·20	1·22	1·28	1·32	1·44

interaction of the hydroxyl ion and/or the transition state with an oppositely charged tetra-alkylammonium ion. Some measurements by Harned and Robinson (*J. Amer. Chem. Soc.*, 1928, **50**, 3175) show that for sodium hydroxide (0·01m) and tetramethylammonium hydroxide (0·01m) in 0·5M-sodium chloride and above $f_{OH^-}(NMe_4{\cdot}OH)/f_{OH^-}(NaOH)$ is 1·05. The effect is in the right direction but more directly relevant data are required. There may also be a specific attraction between the large organic cations and the large organic transition state of opposite charge leading to a decrease of $f_{(AOH)^-}$ below the standard value. Bell, Gelles, and Möller (*Proc. Roy. Soc.*, 1949, *A*, **198**, 358) have postulated a similar effect to explain the abnormally high catalytic constants of the anions of higher aliphatic carboxylic acids in the base-catalysed halogenation of some ketones.

FIG. 3.



A specific primary kinetic salt effect of the type encountered here often shows a linear dependence on concentration. According to the usual derivation of the form of the expression (cf. Bell, "Acid–Base Catalysis," Oxford, 1941, p. 34), the linear term arises as the first term in the expansion of an exponential function. For the data in Table 1, however, a plot of the logarithm of the catalytic constant against [OH⁻] is curved.

Table 2 contains results and Fig. 3 plots of some additional data in mixed salt solutions. Fig. 3*a* represents the effect of the addition of potassium iodide and tetraethylammonium iodide to 0·273M-potassium hydroxide. In Fig. 3*b*, potassium iodide is being replaced by tetraethylammonium iodide in 0·273M-potassium hydroxide, the ionic strength being constant. Qualitatively the results agree with our other observations.

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