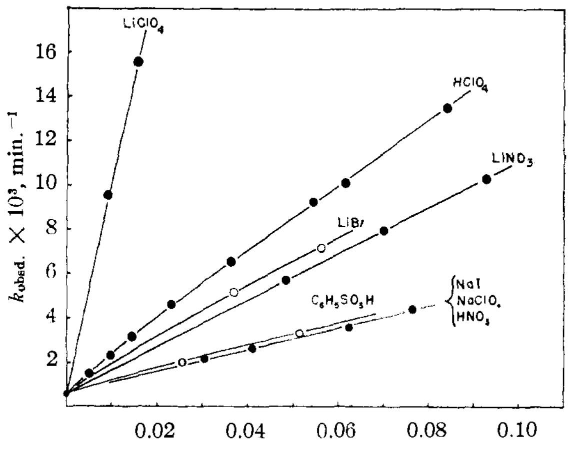

Fig. 4.—Effect of salts on the rate of mutarotation of tetramethylglucose.

ent that the dependence upon acid strength is qualitatively similar to but less pronounced than that observed in the ethylene oxide reaction.

The methyl and acetyl sugars show similar but by no means identical reactions with the electrolytes. The sodium salts are much more effective catalysts with the acetyl than with the methyl sugar while the opposite seems to be true for pyridinium perchlorate. The greater sensitivity of the methyl sugar to acid may perhaps be related to its very low value for k_1.

There is no obvious relationship between the dissociation constants of the salts in pyridine and their effectiveness as catalysts. The highly ionized silver salts[2] are the least effective but sodium iodide is more effective than the slightly dissociated lithium chloride. However, dissociation constants measured in pure pyridine are not necessarily the same as those in pyridine containing a relatively large amount of sugar.

Above about 0.02 *M*, the rates show a linear dependence upon electrolyte concentration. The slopes in this region are listed in Table I.

TABLE I

RELATIVE RATES OF MUTAROTATION OF TETRAACETYLGLUCOSE IN THE PRESENCE OF VARIOUS SALTS

	Lithium	Sodium	Pyridinium	Silver
Perchlorate	1.09	0.177	0.058	0.012
Iodide	1.09	.192	.053	
Picrate	0.235	.078	.036	
Bromide	.268		.022	
Nitrate	.194		.022	0.010
Benzenesulfonate			.022	
Chloride	.125			

In general the results suggest that the effectiveness of the cations varies inversely with the size of the ion while that of the anions, with the exception of the picrate, is in the order of the acid strengths.

Discussion of these results has been reserved for the following paper, in which the mutarotation of tetramethylglucose in nitromethane is described.[7]

OTTAWA, CANADA

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[7] E. L. Blackall and A. M. Eastham, THIS JOURNAL, **77**, 2184 (1955).

[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, NATIONAL RESEARCH COUNCIL]

Electrolyte Catalysis. II. The Mutarotation of Tetramethylglucose in Nitromethane

BY E. L. BLACKALL AND A. M. EASTHAM

RECEIVED NOVEMBER 11, 1954

The rate of mutarotation of tetramethylglucose in nitromethane has been studied. The reaction is strongly catalyzed by carboxylic acids and by ionic bases but not by phenols or by un-ionized bases. Un-ionized bases become powerful catalysts in the presence of electrolytes. A mechanism is suggested to account for the kinetics in both pyridine and nitromethane.

The pronounced catalytic activity of electrolytes toward the mutarotation of tetramethyl- and tetraacetylglucose in anhydrous pyridine[1] suggested that the reaction should be studied in other aprotic solvents. Nitromethane was chosen for the present work because of its high dielectric constant, good solvent properties and relatively acidic character.

Experimental

Materials.—A good grade of nitromethane was dried over P_2O_5, fractionated from P_2O_5 and stored under $CaCl_2$. All acids, phenols and salts were recrystallized where necessary, thoroughly dried in a vacuum oven and stored over P_2O_5. Tetramethylammonium hydroxide was used as the 10% solution in water.

Measurements.—Rotations were followed as previously described; the runs showed excellent first-order dependence over two or three half-lives. All solutions were about 0.08 *M* in tetramethylglucose and gave final specific rotations which, with few exceptions, agreed well within themselves ($[\alpha]^{25}D = 73.8°$). Sodium iodide and perchlorate tended to raise, tetramethylammonium benzoate to lower, the final rotation.

Results

The dependence of the rate of mutarotation upon acid concentration for a series of carboxylic acids is shown in Fig. 1; the relationship is very nearly linear over this concentration range but seems to show a slight decrease in slope with increasing concentration of acid. The decrease could be due to association of the acid. The relationship between rate and acid strength (Brönsted relation) is shown in Fig. 2 where the specific rates are plotted against the dissociation constants of the corresponding acids.[2] The correspondence is about as good as

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[1] A. M. Eastham, E. L. Blackall and G. A. Latremouille, THIS JOURNAL, **77**, 2182 (1955).

[2] R. P. Bell and W. C. E. Higginson, *Proc. Roy. Soc.* (*London*), **A197**, 141 (1949).

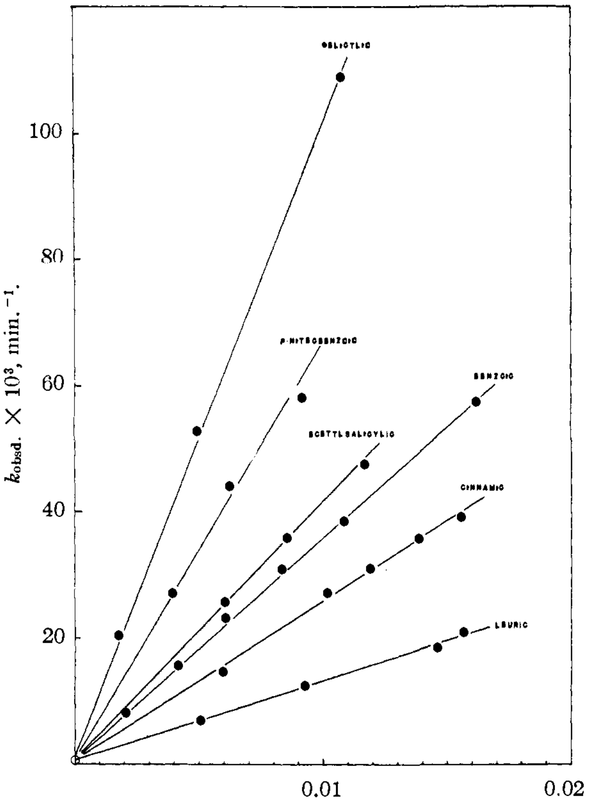


Fig. 1.—Catalysis of the mutarotation of tetramethylglucose in nitromethane by carboxylic acids.

that usually obtained in aqueous solutions and the slope of the line (α) is about 0.5. However, in distinct contrast to the behavior in aqueous solutions, phenols of equivalent acid strength have very little catalytic activity. Thus $k_{obsd.}$ for 0.01 M 2,4-dinitrophenol or pentachlorophenol is about 10^{-4} min.$^{-1}$.

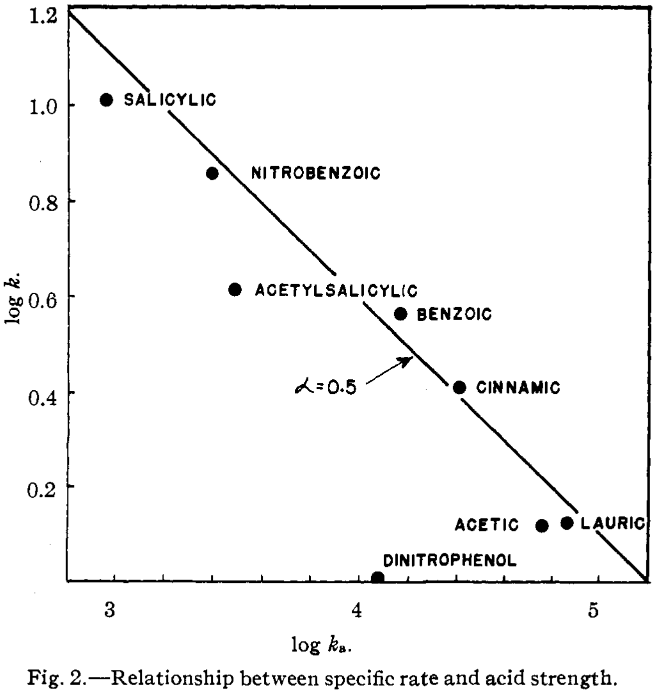


Fig. 2.—Relationship between specific rate and acid strength.

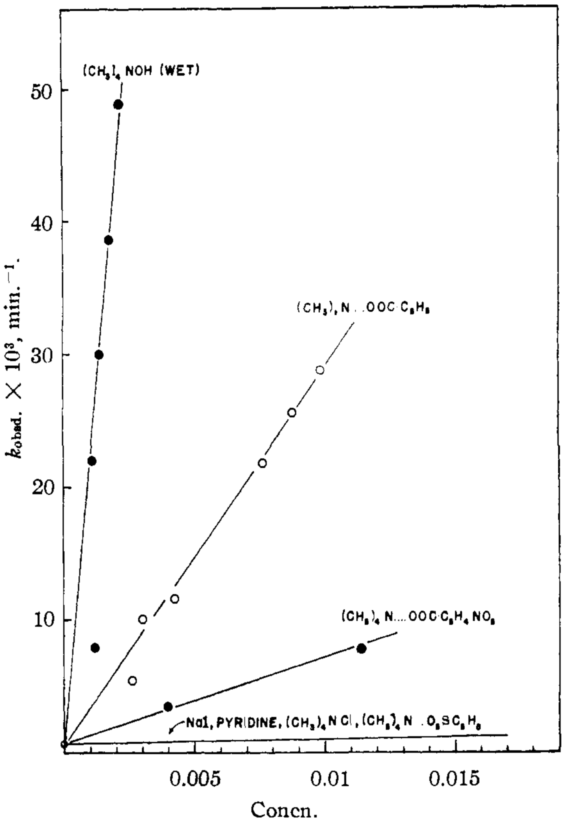


Fig. 3.—Base-catalyzed mutarotation of tetramethylglucose.

An attempt was made to determine the catalytic constant for hydrogen chloride but the rates were too high for satisfactory measurements. The specific rate constant appeared to have a value of about 100 l. mole^{-1} min.$^{-1}$.

The results in Fig. 3 are some evidence for the existence of a general basic catalysis since among the salts the rate increases with increasing basicity of the anion. However, this generalization must be confined to the ionic bases, since pyridine by itself has little catalytic activity.

Figure 4 shows the effect of adding 0.0047 M tetramethylammonium p-nitrobenzoate to solutions containing various concentrations of p-nitrobenzoic acid. The rates are not additive; the system behaves almost as if the salt had removed an equivalent amount of acid from the system. It is perhaps worth noting that the addition of 0.03 M tetramethylammonium chloride to 0.0025 M tetramethylammonium benzoate cuts the rate in half; since the chloride is itself inactive, the retardation may be due to a common ion effect but is probably more complex than this.

Of particular interest is the fact that a mixture of pyridine and sodium perchlorate is a much more effective catalyst than either component alone. The results of experiments with such mixtures are summarized in Table I.

Evidently in the experiments in pyridine so-

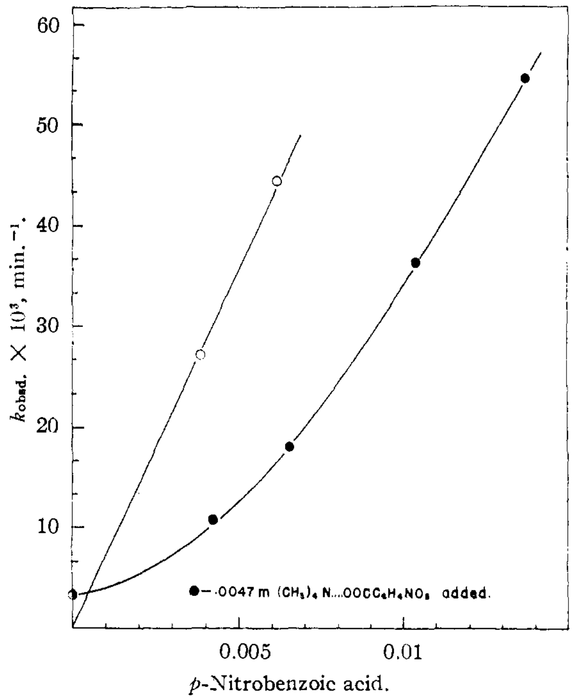


Fig. 4.—Effect of adding 0.0047 *M* tetramethylammonium *p*-nitrobenzoate to runs catalyzed by *p*-nitrobenzoic acid.

TABLE I

Salt	Pyridine	$10^3 k_{obsd.}$ (min.$^{-1}$)
....	....	<0.1
....	0.0410	0.7
0.0051 $NaClO_4$	....	~0.2
.0051 $NaClO_4$	.0615	4.6
.0051 $NaClO_4$	.0820	4.4
.0303 pyridinium perchlorate	....	0.5
.0217 pyridinium perchlorate	.0207	9.8
.0217 pyridinium perchlorate	.0410	14.0
.0217 pyridinium perchlorate	.0620	20.4

lution, the solvent was participating in the reaction.

The pyridinium salts are relatively poor catalysts for the reaction in nitromethane; the perchlorate has little effect while the nitrate and sulfonate give a weak catalysis which is not directly related to their concentrations. Slight dissociation into pyridine and free acid seems unlikely but could account for the results since there is an approximate square-root dependence upon salt concentration.

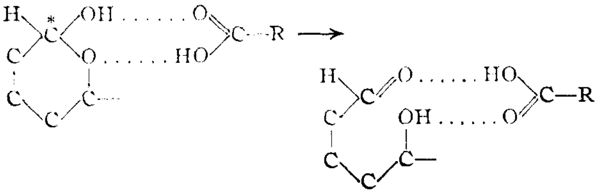
Discussion

The dependence of the rate of acid-catalyzed mutarotation upon the first power rather than the square root of the total acid concentration suggests that the catalyst is the undissociated acid molecule. It is true that similar results would be obtained if the rate expression involved both the hydrogen ion and acid anion, since $K(HA) = (H^+)(A^-)$, but this seems improbable because the ionic concentrations in these solutions must be very low. If the catalyst is in fact the un-ionized acid, then the correlation between rate and dissociation constant (Fig. 2) is to be expected and may properly be regarded as general acid catalysis.

The acid-catalyzed enolization of ketones which like the mutarotation is best explained through the addition and removal of a proton, probably takes place in the following steps

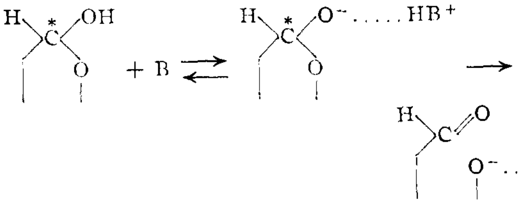
$$H'S + HA \rightleftarrows H'SH^+ + A^-$$
$$H'SH^+ + A^- \rightleftarrows SH + H'A$$

in which the second is rate controlling.[3] The general case with either or both steps rate-controlling has been discussed by Bell[4] and always leads to general acid catalysis. A mechanism of this type seems probable in the present case but must be modified to account for the fact that phenols are not catalytic. This is possible if reaction occurs through a complex of the type

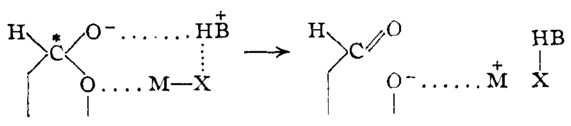


o that, effectively, both proton transfers occur simultaneously without ionic intermediates. Such a scheme is of course similar to the "concerted" mechanism of Swain and his co-workers.[5]

Catalysis by uncharged bases is very slow in both nitromethane and pyridine solutions and seems to require the presence of an electrolyte. If the reaction occurs in the following way



then the second step is probably the critical one since there is little evidence to suggest that electrolytes would have so great an influence on the acid-base equilibrium (an increase of at least 10^3 in the dissociation constant). The specificity of the electrolyte catalysis and its marked dependence upon concentration suggest that the electrolyte is present in the active complex; its role must be similar to that of water in aqueous solution. Since the catalytic activity of the cations is in the order of the stability of their oxonium salts[6] the active complex may have some such structure as



The mechanism is then similar to that proposed above for catalysis by carboxylic acids since essentially it is a means for transferring the ion charge from one oxygen to the other with a minimum of electrical disturbance. The first step need not even be an ionization; hydrogen bridging between the

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[3] L. Zucker and L. P. Hammett, THIS JOURNAL, **61**, 2791 (1939).

[4] R. P. Bell, "Acid-Base Catalysis," Oxford University Press, London, England, 1941.

[5] C. G. Swain and J. F. Brown, Jr., THIS JOURNAL, **74**, 2538 (1952).

[6] H. Rheinboldt, A. Luyken and H. Schmittmann, *J. prakt. Chem.*, **148**, 81 (1937).

sugar and the base would be sufficient. In the case of an ionic base such as tetramethylammonium benzoate the functions of base and electrolyte are combined and a simple second-order process results.

Implicit in the foregoing attempts to interpret the kinetics of these reactions is an assumption that ionic products or intermediates are difficult to form in inert solvents unless all charge transfers are balanced within the active complex itself. However, this conclusion is based only on reactions involving the cleavage of a carbon–oxygen bond in the solvents pyridine and nitromethane. The electrolyte effects are particularly marked in these cases but may in fact be merely an extreme example of a much more general phenomenon. For example, in the reaction of chloroacetate with thiosulfate ions in very dilute aqueous solution Kappana[7] observed a slight specific ion catalysis in addition to the normal salt effect. The order of catalytic activity was $K^+ > NH_4^+ > Na^+ > Li^+ >$ and $Cl^- > NO_3^- > SO_4^{=}$ or the opposite of that found in the present work. Since the reaction is a nucleophilic substitution carried out in dilute aqueous solution the electrolyte effect cannot be accounted for in the same way as was done for the mutarotation reaction. In other studies on the same reaction Ciapetta and Tomlinson[8] observed marked specific ion catalysis in propanol–water solution, especially with polyvalent cations; they suggested that the powerful catalytic activity of the La^{+3} ion was due to the clustering around it of the reactant ions. Scattered through the literature[9] are other examples of what appear to be specific ion effects but in most cases they are small and cannot be distinguished from normal salt effects. However, if these specific ion effects are in fact fairly general with respect to both solvent and reaction type, then they are probably of a physical rather than chemical nature and the above attempt to assign the ions a specific function within the active complex is not justified.

OTTAWA, CANADA

[7] A. N. Kappana, *J. Ind. Chem. Soc.*, **5**, 293 (1928).

[8] F. G. Ciapetta and H. M. Tomlinson, *J. Phys. Colloid Chem.*, **55**, 429 (1951).

[9] R. C. Anderson, G. W. Watt, *et al.*, THIS JOURNAL, **66**, 376 (1944); **67**, 2269 (1945); L. F. Audrieth, L. D. Scott and O. F. Hill, *ibid.*, **64**, 2498 (1942); F. A. Long, W. F. McDevit and F. B. Dunkle, *J. Phys. Colloid Chem.*, **55**, 813, 829 (1951); R. M. Schramm, W. Klapproth and F. H. Westheimer, *ibid.*, **55**, 843 (1951); L. C. Riesch and M. Kilpatrick, *J. Phys. Chem.*, **39**, 561 (1935).

NOTES

Formation of $Ce_2O_3 \cdot 2ZrO_2$ in the System $BaCl_2$–$CeCl_3$–$BaZrO_3$[1]

BY J. J. CASEY, LEWIS KATZ AND WILLIAM C. ORR

RECEIVED DECEMBER 13, 1954

The work reported in this paper has evolved from a study of ion distributions in solid–melt systems at high temperatures (about 1000°) in which the system principally studied has been $BaCl_2$–$CeCl_3$–$BaZrO_3$. Radiotracer experiments in which cerium ranged in concentration from 10^{-13} to 18.7 atom % of the cerium–zirconium content showed that essentially none of the cerium remained in the molten phase. At low cerium content (Ce:Zr atom ratio = 0.01 to 0.053) some of the barium ions in barium zirconium oxide are replaced by cerium(III) ions. As the cerium content of the system is increased the principal reaction becomes one resulting in the formation of the phase $Ce_2O_3 \cdot 2ZrO_2$. This is rapidly oxidized in air at elevated temperatures to $CeO_2 \cdot ZrO_2$.

Because recent interest in the solid solutions of zirconia with other metal oxides has been widespread,[2–11] arising in part from the desirability of obtaining systems in which the polymorphic inversion of zirconia from the high temperature tetragonal to the low temperature monoclinic form is suppressed, it was felt that the reaction described above merited further study.

Experimental

Materials.—Barium zirconium oxide was prepared by the solid state reaction of reagent grade zirconia and barium carbonate at 1300°. Barium carbonate was present in slight excess, and the excess barium oxide was leached from the product with acetic acid.

Cerium(III) chloride solution was prepared by reduction of cerium(IV) sulfate with hydrochloric acid in water solution. Cerium(III) hydroxide was precipitated, washed and redissolved in hydrochloric acid as many times as were necessary to remove all traces of sulfate ion.

[1] Based upon a dissertation submitted by J. J. Casey to the Graduate School of the University of Connecticut in partial fulfillment of the requirements for the degree of Doctor of Philosophy. The work was carried out under Contract No. AT(30-1)-1154 between the Atomic Energy Commission and the University of Connecticut.

[2] A. Dietzel and H. Tober, *Ber. deut. keram. Ges.*, **30**, No. 4, 71 (1953).

[3] J. Pierrey, *Ann. Chim.*, [12] **4**, 133 (1949).

[4] H. v. Wartenburg and W. Gurr, *Z. anorg. allgem. Chem.*, **196**, 374 (1931).

[5] A. Gambey and G. Chaudron, 14me Congr. chim. ind. Paris Oct., 1934, 5 pp.

[6] P. Duwez and F. Odell, *J. Am. Cer. Soc.*, **33**, 274 (1950).

[7] R. Schenck and H. Roters, *Z. anorg. allgem. Chem.*, **211**, 65 (1933).

[8] G. Braver and H. Gradinger, *Naturwiss.*, **38**, 559 (1951).

[9] P. Duwez, H. Brown, Jr., and F. Odell, *J. Electrochem. Soc.*, **98**, 356 (1951).

[10] F. Hund, *Z. Elektrochem.*, **55**, 363 (1951).

[11] F. Trombe and M. Foex, *Compt. rend.*, **233**, 254 (1951).