order rate constants, listed in the last column, are based upon the equation

$$k = \frac{\ln 2}{([G] + [G'])\tau_{1/2}}$$

although it must be admitted that the only experimental justification for its use is in the case of chlorophyll-*b* in benzene. It is suggestive that in all cases the calculated values of *k* do not differ by more than a factor of 2.5 from the limiting (maximum) rate constants for a diffusion-controlled process estimated from the approximate equation[12]

$$k\,(\text{diff.}) = \frac{8RT}{3 \times 10^3\eta}$$

MINNEAPOLIS, MINN.

(12) J. Umberger and V. LaMer, THIS JOURNAL, **67**, 1099 (1945).

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

Electrolyte Catalysis. I. The Mutarotation of Glucose in Pyridine

BY A. M. EASTHAM, E. L. BLACKALL AND G. A. LATREMOUILLE

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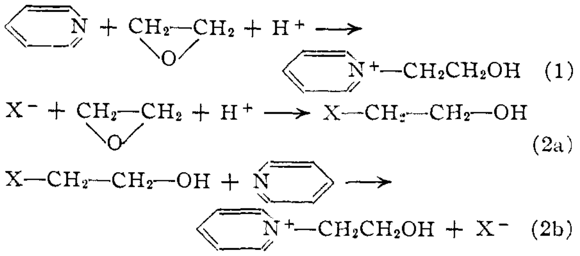
The rates of mutarotation of tetraacetyl- and tetramethylglucoses in anhydrous pyridine and the effect of electrolytes upon the rates have been determined. Lithium iodide and perchlorate are the most effective catalysts; other salts follow in the order $Li^+ > Na^+ > C_5H_5NH^+ > Ag^+$ and $ClO_4^- = I^- > Br^- >$ picrate $> NO_3^- > Cl^-$. The effect of the electrolytes on the two sugars is similar but not identical.

Kinetic studies of the acid-catalyzed reaction of ethylene oxide with anhydrous pyridine show the reaction rate to be markedly dependent upon the acid anion, *i.e.*, $HIO_4 \geqslant HClO_4 > H_2SO_4 > C_6H_5SO_3H > HNO_3$.[1] In a solvent as basic as pyridine, where complete ionization of the acids may be assumed, the proton source in all cases must be the pyridinium ion, but there is no simple explanation for the manner in which the anion influences the proton transfer. The effect is surprising because neutral salts have no apparent effect upon the rate, and because the dependence upon acid concentration is linear between 0.005 and 0.5 *M*.

In catalysis by halogen acids[1] this reaction (1) is complicated by a second mechanism (2)



in which step (a) is essentially similar in type to reaction (1). In the case of hydrogen iodide the kinetics of step (2a) appear experimentally as a transition from third order to second order with increasing concentration of iodide ion but can be interpreted as a simple second-order process if one assumes that reaction occurs almost entirely between ethylene oxide and an ion pair of pyridinium iodide and only slightly through the stepwise (third order) addition of hydrogen and iodide ions. A rough estimate of the dissociation constant of pyridinium iodide ion pairs in pyridine can be obtained from the data of Kraus and co-workers[2] and when this value is used to obtain the actual concentration of ion pairs good agreement with the kinetic data is obtained.

If the addition of hydrogen iodide occurs through ion pairs, then in all probability the dependence of reaction (1) upon the nature of the anion is also due to the presence of an ion pair in the active complex. The effect may be particularly marked in this case because the product is itself an ion and its formation may depend upon immediate stabilization. There seems, however, to be no reason to suppose that the more acidic anions would be the most effective stabilizers—ion size should perhaps be a more important factor.

In an effort to obtain more information about these effects a study of the mutarotation of glucose was undertaken. This reaction has been studied extensively in aqueous solution, but has received little attention in aprotic solvents. Lowery and Faulkner[3] found that it took place very slowly in either pyridine or cresol alone but rapidly in a mixture of the two. They suggested that both an acid and a base were necessary for catalysis, a conclusion also reached by Swain and Brown[4] in their recent studies of the mutarotation of tetramethylglucose in benzene solution using pyridine–phenol mixtures as catalyst.

In preliminary experiments glucose proved an unsatisfactory sugar for this work because of its low solubility and rate of solution. Tetra-acetyl-β-*d*-glucose and tetra-methyl-α-*d*-glucose were therefore selected for further study.

Experimental

Materials.—Pyridine and pyridinium salts were prepared as previously described.[1] Moisture determination by the Karl Fischer method indicated less than 0.005% water in the pyridine. Picrates were prepared from the acid and the corresponding hydroxides and recrystallized several times before use. The remaining salts were thoroughly dried but not otherwise purified. Where necessary the salts were handled in a dry-box.

2,3,4,6-Tetra-acetyl-β-*d*-glucose was prepared by the method of Fischer and Hess[5] and recrystallized to a melting point of 135–136° (Pyrex tubes) and a specific rotation $[\alpha]^{25}\text{D}$ $-2°$ (ethanol). 2,3,4,6-Tetra-methyl-α-*d*-glucose

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(1) A. M. Eastham and B. deB. Darwent, *Can. J. Chem.*, **29**, 585 (1951); A. M. Eastham, *J. Chem. Soc.*, 1936 (1952).

(2) D. S. Burgess and C. A. Kraus, THIS JOURNAL, **70**, 706 (1948); C. J. Carnigan and C. A. Kraus, *ibid.*, **71**, 2983 (1949).

(3) T. M. Lowery and I. J. Faulkner, *J. Chem. Soc.*, 2883 (1925).

(4) C. G. Swain and J. F. Brown, Jr., THIS JOURNAL, **74**, 2534 (1952).

(5) E. Fischer and K. Hess, *Ber.*, **45**, 912 (1912).

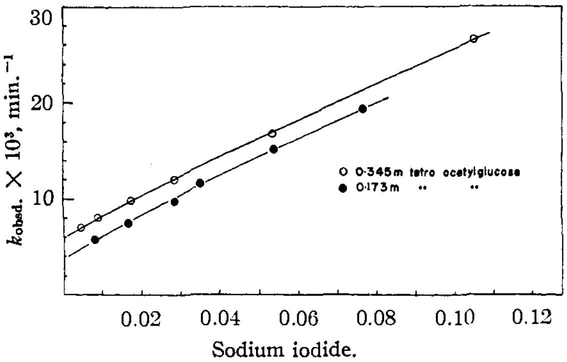

Fig. 1.—The mutarotation of tetraacetylglucose in pyridine solutions of sodium iodide.

was prepared by the method of West and Holden[6] and recrystallized from petroleum ether to a melting point of 94–96° and a specific rotation $[\alpha]^{25}\text{D}$ +112° (water).

Measurements.—Rotations were determined with a Rudolph Model 75 precision polarimeter operating from a sodium vapor lamp. Water was circulated through 20 and 40 cm. tubes from a bath controlled to ±0.002° to give a temperature at the tube of 25.0°.

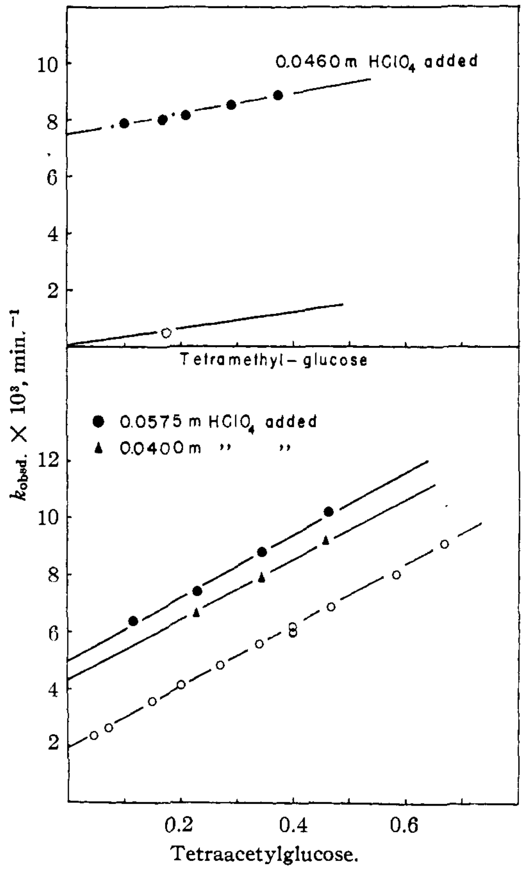

Fig. 2.—Rate of mutarotation in pyridine at 25°: upper, tetramethylglucose; lower, tetraacetylglucose.

All experiments with tetramethylglucose showed excellent unimolecular characteristics in the individual runs when followed for at least two half-lives. Results with tetraacetylglucose were usually equally good but in some cases, notably in the presence of sodium iodide, the observed rate constants showed a decline of 1–2% per half-life. Accordingly the results reported here are the average values of the constant during the second half-life of the reaction. The final rotations of the solutions were in all cases sufficiently similar to indicate the absence of side reactions or shifts in equilibrium.

The rate of mutarotation of tetraacetylglucose (G) in pure pyridine is given by the equation

$$-\mathrm{d}G/\mathrm{d}t = k_1(\mathrm{G}) + k_2(\mathrm{G})^2$$

where the first term represents a "spontaneous" or solvent catalyzed rearrangement and the second term a self-catalyzed rearrangement (Fig. 2). For tetraacetylglucose k_1 and k_2 have the values 0.0019 min.$^{-1}$ and 0.0108 l. mole^{-1} min.$^{-1}$, respectively; the corresponding values were not determined for the tetramethylglucose because of the low rates but were estimated to be about 0.0001 min.$^{-1}$ and 0.003 l. mole^{-1} min.$^{-1}$

Since the effect of electrolytes upon the reaction rate appears to be independent of the sugar concentration (Fig. 1) all runs were made with either 0.345 M tetraacetylglucose or 0.170 M tetramethylglucose.

Results

The mutarotation is markedly accelerated by small amounts of certain electrolytes. From the data in Fig. 2 it is clear that no part of this acceleration is due to a salt effect associated with k_2. It is due either to an increase in k_1 (salt effect) or to a new term in the rate expression (specific electrolyte catalysis) or to both and there appears to be no way of distinguishing between the two possibilities. However, the magnitude of the acceleration and the absence of salt effects associated with k_2 suggests that the effect should be regarded as electrolyte catalysis.

The effect of various electrolytes upon the rate of mutarotation is shown in Figs. 3 and 4. It is appar-

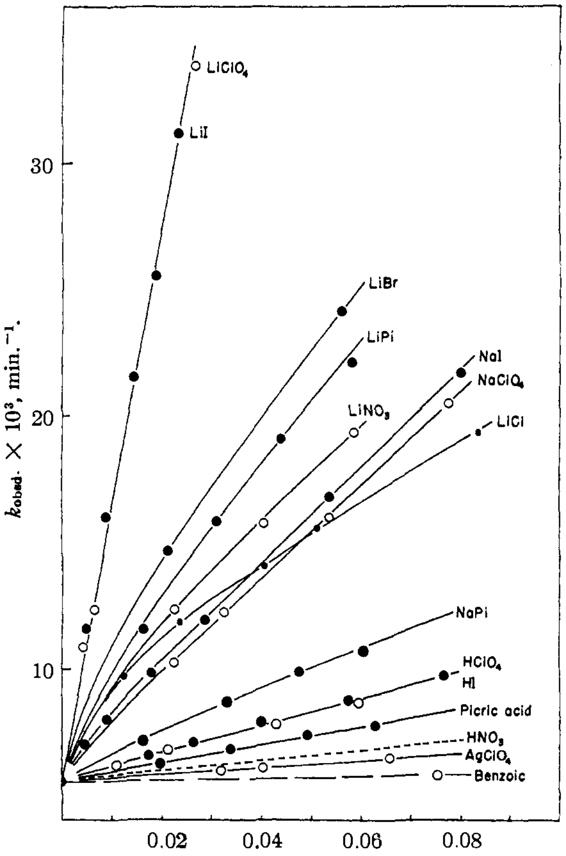

Fig. 3.—Effect of salts on the rate of mutarotation of tetraacetylglucose.

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[6] E. S. West and R. F. Holden, *Org. Syntheses*, **20**, 97 (1940).

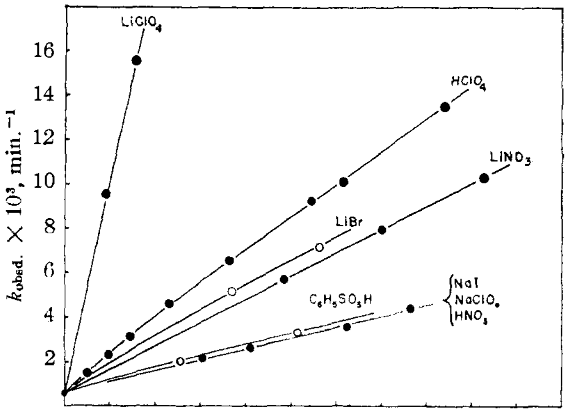

Fig. 4.—Effect of salts on the rate of mutarotation of tetramethylglucose.

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

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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 ($[\alpha]^{25}\text{D} = 73.8°$). 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).