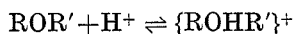


ACID-CATALYSED HYDROLYSIS OF *t*-BUTYL METHYL ETHER*

By P. S. HARRISON† and V. R. STIMSON†

Most ethers are rather resistant to hydrolysis by aqueous acids, and the reaction is not a very easy one to follow by chemical analysis. Consequently there have been few kinetic studies, and there is a dearth of information on which ideas concerning mechanism can be formed.¹ For this reason most investigations have been carried out in almost pure sulphuric acid or other strongly acid media.¹ However, if the ether ROR' contains an electron-releasing group R, the rate may be considerably increased, as greater basicity facilitates protonation, and also the unimolecular mechanism



may be followed. The above statement then no longer applies. The rate of acid-catalysed cleavage in aqueous solvents may be measurable, and the olefin produced affords a ready means of following the reaction. We have therefore studied the hydrolysis of *t*-butyl methyl ether in aqueous dioxan with up to 1M hydrochloric acid at 70–85°.

Experimental

Materials

t-Butyl methyl ether was prepared by the method of Norris and Rigby.² Chloroform and carbon tetrachloride were purified by washing with sulphuric acid and gave stable bromine solutions. Dioxan was B.D.H. AnalaR, treated with acid and alkali and distilled from sodium; 60% dioxan means 60 vol. of dioxan and 40 vol. of water. The rate is not sensitive to small changes of solvent composition.

Procedure

t-Butyl methyl ether (c. 1 g) was added to 95 ml of suitable solvent and brought to temperature in the thermostat. The reaction was started by addition of the necessary amount of 10N hydrochloric acid made up to 5 ml with water. The mixture was slowly aspirated with nitrogen saturated with dioxan. The emergent stream containing the isobutene passed through a water condenser fitted with a close-fitting cold finger and then through two traps each containing

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¹ Jaques, D., and Leisten, J. A., *J. chem. Soc.*, 1961, 4963; Burwell, R. L., *Chem. Rev.*, 1954, **54**, 618.

² Norris, J. F., and Rigby, G. W., *J. Am. chem. Soc.*, 1932, **54**, 2088.

20 ml of 1 : 1 carbon tetrachloride-chloroform mixture cooled to *c.* -15° . Satisfactory conditions were obtained by adjusting the nitrogen flow rate. Replacements for the traps were quickly attached at regular intervals and the isobutene collected estimated by the bromine method.

Kinetics

In order to keep the acid catalyst concentration reasonably low, temperatures of $70-80^{\circ}$ were necessary for the solvolysis. Isobutene production (measured in titres of sodium thiosulphate solution) increased smoothly with time. However, because of the method of collection, errors accumulated with progress of the reaction and sufficient accuracy in the final amount of isobutene could not be obtained for its use in the first-order rate equation. Rate constants were therefore obtained from first-order Guggenheim plots and these were satisfactory. For five runs at 85° with $0.445M$ hydrochloric acid in 60% dioxan the values $4.4, 4.3, 4.0, 4.6, 4.4 \text{ min}^{-1}$ for 10^3k_1 were obtained.

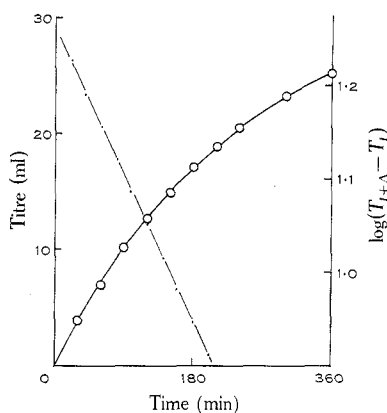


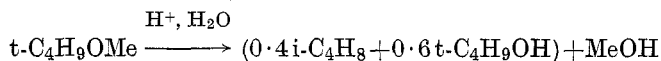
Fig. 1.—Production of isobutene (in titre of $0.3104N \text{ Na}_2\text{S}_2\text{O}_3$) from 0.981 g of *t*-butyl methyl ether in 60% dioxan at 84.3° with $0.44M$ acid and associated Guggenheim plot.

TABLE I
VARIATION OF RATE IN 60% DIOXAN WITH ACID CONCENTRATION AT 85°

c_{HCl} (mole l^{-1})	10^3k_1 (min^{-1})	$10^3k_1/c_{\text{HCl}}$ ($\text{min}^{-1} \text{ l. mole}^{-1}$)
0.103	1.1	11
0.227	2.1	9
0.445	4.3	10
0.556	5.0	9

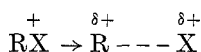
Results and Discussion

At $70-80^{\circ}$ in the presence of *c.* $0.5M$ hydrochloric acid in 60% aqueous dioxan, *t*-butyl methyl ether undergoes solvolysis yielding *c.* 40% isobutene and presumably 60% *t*-butanol and methanol.



The formation of isobutene in this proportion is indicative of the *t*-butyl carbonium ion and hence of the unimolecular mechanism above. The production of isobutene followed the first-order rate form (Fig. 1) and with various acid concentrations the rate constants were approximately proportional to the acid concentration (Table I).

For a reaction whose rate determining step is of the charge type



increase of solvent polarity leads to a small decrease in rate.³ In the present case the rate is also controlled by the acidity of the solution; however, this is likely to be approximately the same for 80 and 60% dioxan,⁴ so that a slight decrease in rate should occur with the more aqueous solvent. For solvolyses in 80 and 60% dioxan solutions of 0.76M hydrochloric acid at 84.3° the values of 10^3k_1 found were 14.0 and 5.0 min⁻¹ respectively.

To obtain an indication of the activation energy, runs in 60% dioxan with 0.486M acid were carried out at 70.8, 77.3, and 84.8° (a very short temperature range); the values of 10^3k_1 found were: 0.90, 1.38, and 4.21 min⁻¹ respectively, giving *E* c. 29 kcal mole⁻¹. Little accuracy can be attributed to this value, and constant acidity over the temperature range has been assumed; at higher concentrations acidity diverges significantly from acid concentration.⁵ A value of c. 30 kcal mole⁻¹ has been found for acid-catalysed Bu^t-O fission reactions in elimination from t-butanol^{6,7} and in the *A*_{AL}1 hydrolyses of t-butyl esters.⁸

³ Ingold, C. K. "Structure and Mechanism in Organic Chemistry." p. 347. (Bell: London 1953.)

⁴ Braude, A. E., and Stern, E. S., *J. chem. Soc.*, 1948, 1976.

⁵ Bunton, C. A., Ley, J. B., Rhind-Tutt, A. J., and Vernon, C. A., *J. chem. Soc.*, 1957, 2327.

⁶ Dostrovsky, I., and Klein, F. S., *J. chem. Soc.*, 1955, 791.

⁷ Boyd, R. H., Taft, R. W., Wolf, A. P., and Christman, R. D., *J. Am. chem. Soc.*, 1960, 82, 4729.

⁸ Stimson, V. R., and Watson, E. J., *J. chem. Soc.*, 1954, 2848.