

## Hydrolysis of Methyl Methanetri-sulfonate

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An aqueous solution of methyl methane-trisulfonate reacts instantly with bromine<sup>1</sup>. The reaction is so rapid that the colour of an azo indicator such as methyl orange does not disappear before the trisulfonic ester has been brominated. This behaviour of the ester towards bromine calls to mind strongly that of the trisulfonylmethanes. A newly prepared solution of the ester in water requires a quantity of nearly two atoms (one mole) of bromine per mole ester, but the bromine consumption decreases with the time. The reason probably is the hydrolysis of the ester during which the negative ion  $\text{CH}(\text{SO}_2\text{O})_3^-$  is formed as the end product of consecutive stages. On the presumption that only the unhydrolyzed trisulfonic ester or its carbanion will react immediately with bromine, the concentration decrease of the ester can be followed by withdrawal of portions of its aqueous solution from time to time and direct titration with bromine in the presence of the indicator. It will be noted that the velocity of the reaction seems to increase with increasing hydronium ion concentration. Since the hydrolysis makes the solution still more acid, the reaction was studied in hydrochloric acid, where the hydronium ion concentration is approximately constant. Then the reaction is found to be pseudounimolecular.

It is of decided interest to note that the trisulfonic ester, in spite of its strongly acid properties, does not change the colour of ferric chloride in alcohol solution. The same behaviour is shown by tris-(ethylsulfonyl)-methane. As is well known, the ester  $\text{CH}(\text{COOC}_2\text{H}_5)_3$  will give an obvious colour change under similar circumstances, thus indicating a certain enolization.

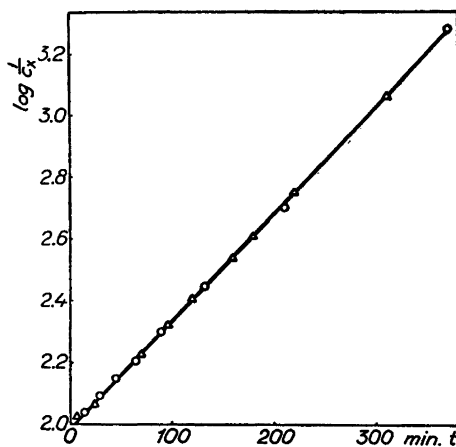


Fig. 1. Hydrolysis of methyl methanetri-sulfonate in 0.1 M HCl. Two parallel series, both with  $c_0 = 0.01 M$ .

*Experimental.* The potassium methane-trisulfonate was prepared according to Backer<sup>2</sup>. Instead of transforming the potassium salt to the barium salt and treating it with sulfuric acid, the author directly obtained the trisulfonic acid by using a cation exchanger, Amberlite I R-100 H. A solution of potassium salt was percolated through a layer of the  $\text{H}^+$ -exchanger. The methyl methane-trisulfonate was prepared by the action of methyl iodide on the silver salt in benzene<sup>1</sup>. After boiling for ten hours 1.2 g methyl ester was obtained from 6.8 g silver salt. A solution of the trisulfonic ester ( $c_0 = 0.01 M$ ) in 0.1 M hydrochloric acid was prepared and the reaction carried out at 25.0° C in a glass-stoppered flask from which samples were transferred with a four or five ml pipette into an Erlenmeyer flask. After addition of a few drops of 0.01 per cent solution of methyl orange the sample was immediately titrated with a solution of 0.5 M potassium bromide and 0.0025 M bromine until the indicator colour just disappeared. From this the actual ester concentration ( $c_x$ ) can be calculated. The indicator blank was negligibly small. By

## A Lithium Tungsten Bronze of Perovskite Type

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In a recent paper from this institute<sup>1</sup> the existence of a cubic lithium tungsten bronze of perovskite type was briefly mentioned. As the work on this subject must be postponed for some time, a few more of the details obtained so far will be given here.

The compound has been synthesized in two different ways: *a*) according to the method introduced by Brunner<sup>2</sup> by heating mixtures of lithium tungstate, tungsten trioxide, and tungsten dioxide *in vacuo* at about 850° C, and *b*) by cathodic reduction of fused acid lithium tungstate as was first done by Stavenhagen<sup>3</sup>. Attempts to prepare the compound by reducing acid lithium tungstate with hydrogen were not successful as inhomogeneous products were obtained. The products were purified

control experiments it was established that the generated methyl alcohol had no effect on the indicator blank. As an example, in Fig. 1, a curve for two parallel experiments is reproduced. The two series of points fall on the same straight line. If

$k = \frac{2.303}{t} \log c_0/c_x$ , the slope of the line gives a value of  $k$  of  $8.04 \cdot 10^{-3}$ . Another experiment ( $c_0 = 0.01 M$ ) with  $0.05 M$  hydrochloric acid at 25.0° C gives  $k = 4.25 \cdot 10^{-3}$ .

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2. Backer, H. J. *Rec. trav. chim.* **49** (1930) 1107.

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by repeated alternate boiling with concentrated potassium carbonate solution, concentrated hydrochloric acid, and aqua regia and finally with a mixture of concentrated nitric acid and a small amount of hydrofluoric acid. In this way a dark blue or bluish violet crystalline powder was obtained by the first method, while the electrolytic reduction gave dark blue crystals of irregular shape. The samples were tested for purity by means of X-ray powder photographs and microscopic examination.

The powder photographs were taken in focusing cameras using Cu-K radiation. All observed reflections are consistent with a cubic unit cell of perovskite type. This lithium bronze is evidently isomorphous with the cubic sodium tungsten bronze,  $Na_xWO_3$ , described by Hägg<sup>4</sup>. The length of the cube edge, being about 3.72 Å, is slightly different for various preparations, probably due to the lithium content of the compound not being constant. The formula may thus be written  $Li_xWO_3$ . Values and limits of  $x$  cannot be given for the present for lack of analytical data. However, if the relation between colour and average valency of the molybdenum or tungsten atoms shown to exist for a great number of oxides and bronzes<sup>1</sup> is also valid for this lithium bronze, the blue colour might indicate an  $x$  value of 0.3 or 0.4 for the investigated preparations.

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