Oxidation of Formaldehyde by Cerium(IV) Sulphate in Aqueous Sulphuric Acid

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Summary Kinetic evidence for the complex formation between cerium(IV) and formaldehyde is obtained and the rate of the reaction is found to be inversely proportional to [H_2SO_4].

THE kinetics of the oxidation of aqueous formaldehyde by cerium(IV) ions in sulphuric and perchloric acid medium was first investigated by Hargreaves and Sutcliffe,[1] who reported a third-order dependence of the reaction on sulphuric acid. A perusal of the recent review[2] on the oxidation of organic compounds by cerium(IV) ions indicates this type of rate dependence to be anomalous. I report here the results of a re-investigation.

TABLE 1

The dependence of the rate on formaldehyde concentration

[Cerium(IV)] = 0·005M; [H_2SO_4] = 0·5M; Temp. 35°.

[HCHO](M)	0·1	0·2	0·32	0·63	1·26	1·90	2·53
10^4k_1 (sec.$^{-1}$)	0·28	0·52	0·78	1·41	2·40	3·20	3·70
10^4k_2	2·8	2·6	2·50	2·24	1·90	1·70	1·46

{where k_2(l./mole sec.) is the second-order rate constant and is equal to k_1/[HCHO]}.

TABLE 2

The effect of variation of sulphuric acid concentration on the reaction rate

[Cerium(IV)] = 0·005M; [HCHO] = 0·32M; Temp. 35°

[H_2SO_4] (M)	0·25	0·5	1·0	2·0	2·5	3·0	3·5	4·0
10^5k_1 (sec.$^{-1}$)	14·0	7·83	4·50	2·0	1·40	1·10	0·83	0·58

The reaction rate was measured by estimating the amount of cerium(IV) that had reacted at any time by the titrimetric method described earlier.[3] The titrimetric method is more reliable than the spectrophotometric, especially in the present case where coloured cerium(IV) complexes of sulphuric acid are involved.

The order of the reaction with respect to cerium(IV) ions is one. The value of the first-order rate constant, k_1, measured in the presence of an excess of formaldehyde, is obtained from the slope of the straight line plot of the log of titre changes against time.

The results (Table) show a deviation in the rate constant k_1, which is consistent with the formation of a transient cerium(IV)–formaldehyde complex prior to the rate-limiting step. The correlation of the rate constant k_1 with the formaldehyde concentration is consistent with equation 1, where a and b are the constants.

$$1/k_1 = a + b/[\mathrm{HCHO}] \qquad (1)$$

The effect of variation of sulphuric acid concentration on the reaction rate is found to be just opposite to that reported by Hargreaves and Sutcliffe.[1] The reaction rate is retarded by the increase in sulphuric acid concentration. The correlation of the rate constant k_1 with the sulphuric acid concentration can be expressed by the following equation (2).

$$k_1 = A + B/[\mathrm{H_2SO_4}] \qquad (2)$$

where A and B are constants.

The linear plot of the rate against [H_2SO_4]$^{-1}$ could also be interpreted to mean that the rate is linearly dependent either on (i) the inverse hydrogen ion concentration or (ii) the inverse hydrogen sulphate ion concentration. The former possibility seems to be supported by the fact that the rate in the presence of perchloric acid has exhibited this type of dependence.[1]

(Received, August 26th, 1969; Com. 1307.)

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[1] G. Hargreaves and L. H. Sutcliffe, *Trans. Faraday Soc.*, 1955, **51**, 1105.

[2] W. H. Richardson in "Oxidation in Organic Chemistry," ed. K. B. Wiberg, Academic Press, London, Part A, 1965, p. 243.

[3] Raj N. Mehrotra and S. Ghosh, *Z. phys. Chem.*, (*Leipzig*), 1963, **224**, 57.