From the measurements a value for the molal potential for the half cell reaction $4H^+ + MnO_2(s) + 2e^- = Mn^{++} + 2H_2O$ of 1.230 volts at 25° has been calculated.

This value is 6 mv. less than that computed by Brown and Liebhafsky[1] from data obtained in a similar study.

STATE COLLEGE, PA.   RECEIVED MAY 12, 1947

Theory and Kinetics of Specific Oxidation. II. The Periodate–Glycol Reaction
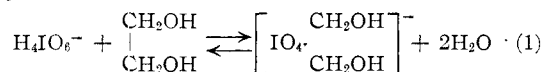
BY FREDERICK R. DUKE

Trivalent manganese has been shown to oxidize oxalate through the disproportionation of oxalate manganate complexes.[1] In order to further test the postulate that specific oxidations of glycols and related compounds generally proceed through the disproportionation of coördination complexes,[1] it was considered desirable to study as different an oxidation as possible which fits into the same category of specificity. The oxidation of glycol by periodate fulfills these conditions.

Previous work on the kinetics of the periodate oxidation of glycol[2,3] is very sketchy, presumably because of the rapidity of the reaction at ordinary temperatures. Price[3] concluded that the reaction is second order in periodate and glycol and suggested a cyclic ester as intermediate, the slow reaction being taken as the ester formation.

Theory

The coördination intermediate should be formed by the reaction

$$H_4IO_6^- + \begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix} \rightleftharpoons \left[IO_4 \cdot \begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix} \right]^- + 2H_2O \cdot (1)$$

The kinetics, according to the theory,[1] would be expressed by the equation

$$\frac{d[A]}{dt} = \left[\frac{kK[C]}{K[C] + 1} \right] [A] \qquad (2)$$

where [A] is total periodate, k the rate constant and K the equilibrium constant for reaction (1) as written ([H$_2$O] taken as unity), and [C] is the concentration of uncoördinated glycol. Equation (2) may be subjected to experimental verification by measuring the rate of disappearance of periodate from solutions containing sufficient glycol to validate the assumption that [C] remains constant throughout the portion of the reaction studied.[4] Under these conditions, a series of first-order (in oxidant) pseudo-constants may be obtained, the pseudo-constant k being identified with the bracketed portion of equation (3).

(1) Duke, THIS JOURNAL, **69**, 2885 (1947).

(2) Criegee, Kraft and Rank, Ann., **507**, 159 (1933).

(3) Price and Kroll, THIS JOURNAL, **60**, 2726 (1938).

(4) The stoichiometry of the oxidation is the same as that of equation (1). Thus, "sufficient glycol" concentration depends upon the magnitude of K. If K is very large, the uncoördinated glycol concentration will remain essentially constant even though [C] is of the same order of magnitude as [A]. If K is small [C] should exceed [A] by ten-fold or more.

Experimental

The constant temperature baths used in the study were melting ice and melting benzene to obtain temperatures of $0 \pm 0.05°$ and $5.1 \pm 0.05°$, respectively. The solid phase in each case was placed into the corresponding liquid in a 2-liter wide-mouth Dewar flask, and the contents stirred. The temperature of the melting benzene is somewhat below the reported value for the melting point (5.48°) presumably because the benzene was saturated with water.

Fifty-ml. volumetric flasks with an additional 48 ml. calibration line were used for reaction vessels. The amount of 1.0 M glycol to give the desired final concentration, and 5.0 ml. of 2 M potassium nitrate were placed in the volumetric flask and the contents diluted to 48 ml. After half an hour in the constant temperature bath, 2.0 ml. of 0.20 M H$_5$IO$_6$ at the bath temperature were added and the timer started during the mixing. Five-ml. samples were removed at known times and quenched in 5 ml. of a solution saturated with sodium bicarbonate and containing 5% potassium iodide to which 1.0 ml. of 0.100 N arsenite had been added. The excess arsenite was titrated with 0.01 N I$_2$.

The pH was varied by including in the original mixture in the reaction vessel 1 ml. of 0.2 M sodium hydroxide, thereby cutting the acidity in half.

Results and Discussion

Pseudo-constants obtained at 0 and at 5.1° with various concentrations of glycol, taken from the slope of plots of log [A] vs. t are recorded in Table I. The value of uncoördinated glycol concentration, [C], was obtained by assuming that the periodate is completely converted to the glycol complex when the glycol concentration is 0.2 M or greater; then the amount of coördinated glycol at any concentration is the ratio of the rate at that concentration to the rate at 0.2 M multiplied by the periodate concentration. The selection of the rate at 0.2 M glycol concentration as the rate corresponding to complete coördination seems justified by the fact that the rate is nearly independent of glycol concentration in this range.

The hydrogen ion concentration was changed from 0.008 to 0.004 M without effect on the constants. Presumably, the lowering of the rate observed by Price[3] in alkaline solution may be explained by the greater difficulty in displacement of the hydroxyl by the glycol

$$H_3IO_6^= + \begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix} \rightleftharpoons \left[IO_4 \cdot \begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix} \right]^- + OH^- + H_2O$$
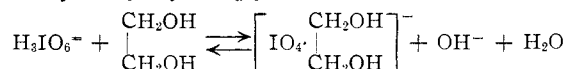
Fig. 1 is a plot of $1/k'$ vs. $1/[C]$. Reference to equation (2) shows that the slope of the straight line obtained is $1/Kk$, while the intercept is $1/k$. The large size of the constant K (130 at 0° and 80

at 5.1°) makes the latter difficult to determine accurately by the method used. The values of the rate constant k are more accurate, the intercept being confined to a small region by the proximity of points to the $1/k'$ axis. Although there is little doubt that K is larger at lower temperatures, it was not felt that the values were of sufficient accuracy to warrant calculation of the thermodynamic constants of the equilibrium. The activation energy, however, may be estimated from the variation in k with temperature to be 30 kcal. In view of the fact that the energy of the carbon-to-carbon bond in glycol is of the order of 60–70 kcal., coördination may be responsible for a lowering in the activation energy of 30 to 40 kcal per mole.

TABLE I

PSEUDO-CONSTANTS (TIME IN SECONDS); CONCENTRATIONS IN M./L.

[Glycol]	0° [H⁺] = 0.008 $k' \times 10^3$	[H⁺] = 0.004 $k' \times 10^3$	5.1° [Glycol]	[H⁺] = 0.008 $k' \times 10^3$
0.192	1.70	1.72	0.192	3.85
.0930	1.61	1.58	.0926	3.57
.0334	1.49	..	.0339	2.97
.0239	1.39	..	.0153	2.24
.0147	1.18	1.20		

Summary
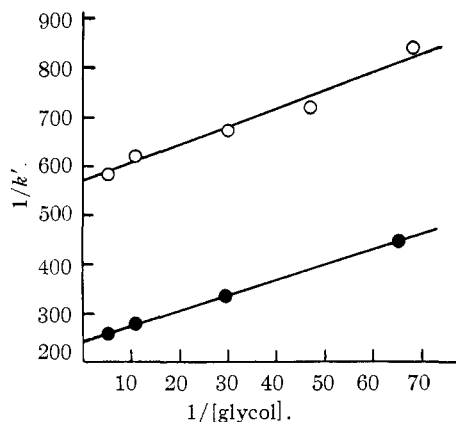
The oxidation of glycol by periodate is shown to

Fig. 1.—Plot of $1/k'$ vs. $1/C$: open circles, 0°: solid circles, 5.1°.

proceed through the disproportionation of a coördination compound intermediate involving the oxidizing and reducing agents.

The activation energy is some 30 to 40 kcal. less than one would predict on the basis of the energy necessary to break the carbon-to-carbon bond in glycol; coördination is necessary to the specificity of this type since it is responsible for the lowering of the activation energy.

EAST LANSING, MICHIGAN   RECEIVED JUNE 14, 1947

Ultraviolet Transmission Limits of Some Liquids and Solids[1a]

BY H. B. KLEVENS[1b] AND J. R. PLATT

In the course of some work on the spectra of solutions in the vacuum ultraviolet,[1,2,3] we have measured the transmission limits of a number of solids and liquids which were being considered for use as windows and solvents in this region. For the liquids, the limits are somewhat related to the position of the first strong absorption band maximum, and so are linked with the values of the first ionization potential. The limits have proved useful as partial criteria of the purity of the solvents.

Except for one small table[1] no previous reports have appeared on solvents suitable for the extreme ultraviolet below 1850 Å., but there have been

several reports[4–7] on types of solvents for the quartz ultraviolet. In particular, some recent work has aimed at attaining spectroscopic purity in the quartz region in solvents of the same type as those studied here. Maclean, Jencks and Acree[8] showed that the transmission limits of various saturated hydrocarbons and other solvents could be shifted to shorter wave lengths by the removal of small traces of mercaptans. Stepwise purification of these liquids resulted in final transmission limits near 2000 Å. for the saturated hydrocarbons in a 1-cm. cell. The method of purification used was that described by Mair and White,[9] and Mair

(1a) Presented before the Division of Physical and Inorganic Chemistry at the 110th meeting of the American Chemical Society at Chicago, Illinois, September 9–13, 1946.

(1b) Present address: The Firestone Tire and Rubber Company, Akron, Ohio.

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(9) B. J. Mair and J. D. White, ibid., 15, 51 (1935).