[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, STANFORD UNIVERSITY]

A Kinetic Study of the Oxidation of Glycerol by Vanadium(V)

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The kinetics of the oxidation of glycerol by vanadium(V) were found to be pseudo-first order with respect to both V(V) and to glycerol and appeared to be pseudo-second order with respect to H^+. These experimental findings are consistent with the postulate that the rate-determining step in the reaction involves the first-order disproportionation of a coördination complex between glycerol and vanadium(V).

An investigation of the applications of acidic vanadium(V) solutions to the volumetric analysis of organic compounds has shown that glycerol undergoes quantitative oxidation to formic acid

$$HOCH_2CHOHCH_2OH + 8VO_2^+ + 8H^+ \longrightarrow 3HCOOH + 8VO^{++} + 5H_2O$$

This reaction is complete in one hour at 100° in the presence of an excess of vanadate; analogous reactions have been observed for the vanadate oxidation of ethylene glycol and 1,3-propanediol.[1]

Elucidation of the kinetics of the glycerol oxidation was attempted with the aim of determining the manner in which vanadium(V) oxidizes this substance. The rate of the reaction was studied under two general conditions. In the one instance the concentration of oxidizing and reducing agent were comparable to those encountered in the procedure developed for the analysis, a moderate excess of vanadium(V) being employed. The effects of temperature and H_2SO_4 concentration were investigated. In the other case the concentration of glycerol was such that less than 1% of the amount available would be required to reduce all of the vanadium(V) present; only the effect of temperature was studied under these conditions.

A limited study of the rate of oxidation of *cis*- and *trans*-1,2-cyclohexanediol also was carried out in order to ascertain whether steric considerations are a factor in the reaction between vanadium(V) and polyhydric alcohols.

Experimental

Reagents and Solutions.—Vanadium(V) solutions were prepared by dissolving about 33 g. of C.P. NH_4VO_3 in sufficient 1.8 *F* H_2SO_4 to give a liter of solution; the solutions were filtered through fritted glass prior to use. Their concentrations were established by titration with freshly standardized Mohr salt solutions.

Commercial 95% glycerol was assayed for glycerol by specific gravity measurement and for water by Karl Fischer titration, concordant results for glycerol content being obtained between the two methods. Use was made of dilute aqueous solutions for runs involving approximately stoichiometric quantities of oxidizing and reducing agent. These were prepared by diluting carefully weighed amounts of glycerol to known volumes with distilled water. Weighed quantities of the 95% material were employed directly where the reaction was studied under conditions of large glycerol excess.

Samples of the two isomers of 1,2-cyclohexanediol were provided by Dr. William A. Bonner of Stanford University. The *trans*-isomer was found to have a melting point of 100–101°, in good agreement with the accepted value of 101.5–103°.[2] The *cis*-isomer was purified by recrystallization from ethyl acetate after treatment with decolorizing charcoal. The crystallized product melted at 97–98°, again in good agreement with the published value of 98°.[3] Dilute aqueous solutions containing identical quantities of the two glycols were employed for the rate studies.

Mohr salt solutions, approximately 0.02 *F* with respect to Fe(II), were employed for the titration of vanadate. These were made up in 10% H_2SO_4 and were standardized against $K_2Cr_2O_7$ at frequent intervals.

For each vanadate–ferrous titration 3 to 5 drops of 0.066 *F* N-phenylanthranilic acid were employed; this was prepared by dissolving 0.213 g. of the solid acid in 30 ml. of 5% Na_2CO_3 and diluting this solution to 150 ml. with distilled water.

Procedures.—The procedure employed throughout this study involved the experimental determination of the vanadium(V) concentration of samples withdrawn from reaction mixtures at suitable time intervals; where necessary, the concentration of glycerol was obtained by calculation. Reaction was effectively stopped by chilling the samples in an ice-bath immediately after removal.

Analytical Measurements.—In runs involving approximately stoichiometric quantities of vanadium(V) and glycerol, the samples were allowed to come to room temperature, at which time 10-ml. aliquots were taken; these were diluted with 80 ml. of distilled water, again chilled, twenty ml. of concentrated H_2SO_4 introduced, and further chilling carried out. Finally, as convenient, the samples again were brought to room temperature and the excess vanadate was immediately titrated with Mohr salt solution.

The oxidation of the cyclohexanediol isomers was carried out in the same manner as the foregoing.

A spectrophotometric determination of the blue vanadyl ion produced by the reaction was found to be a convenient and suitable method of measurement for runs in which glycerol was present in large excess; measurement of the absorbance due to this species was made at 760 mμ, at which wave length the absorbance of VO_2^+ could not be detected under the experimental conditions. A Beckman DU Quartz Spectrophotometer equipped with 1 cm. Corex cells was employed for these measurements.

All runs were carried out in round-bottomed flasks equipped with waterjacketed condensers. An insulated water-bath, equipped with stirrer, electric heating element and mercury thermoregulator, was effective in maintaining a constant temperature within ±0.1°.

Preparation of Reaction Mixtures.—Reaction mixtures were prepared by carefully measuring out volumes of the standardized reactant solutions. Where approximately stoichiometric quantities of glycerol and vanadate were involved, the VO_2^+ concentration of the freshly prepared reaction mixture was determined by titration; since it had been observed that the component volumes were not strictly additive the initial volume was calculated from this information. For runs wherein the reducing agent was present in large excess the reaction mixture remaining after sample collection was heated at 100° until the presence of vanadium(V) could no longer be detected by spot-test with N-phenylanthranilic acid. The initial vanadium(V) concentration then could be calculated from absorbance measurements upon this solution.

Results

The data from each run were tested for fit in the integrated form for the expression representing a simple first- or second-order reaction, as appropriate. Typical first-order plots are given in Fig. 1, which illustrate the effect of temperature upon the rate of oxidation in 0.9 *F* H_2SO_4 under conditions of large glycerol excess. Representative second-

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[1] D. M. West and D. A. Skoog, *Anal. Chem.*, **31**, 583, 586 (1959).

[2] H. Adkins and A. K. Roebuck, THIS JOURNAL, **70**, 4041 (1948).

[3] N. A. Milas and S. Sussman, *ibid.*, **59**, 2345 (1937).

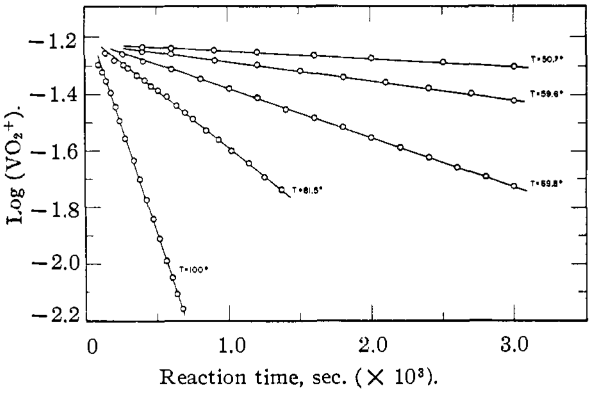

Fig. 1.—First-order plots for the V(V) oxidation of glycerol in 0.9 F H_2SO_4, effect of temperature: VO_2^+ concentration 0.05 N, glycerol concentration 5 N.

order plots are shown in Fig. 2 which illustrate the effect of temperature upon the reaction in 3.74 F H_2SO_4 when essentially stoichiometric quantities of oxidant and glycerol were employed. In these and all other instances, reactant concentrations were expressed in equivalents per liter, the equivalent weight of VO_2^+ being taken as its formula weight and that of glycerol as one eighth of its formula weight. Linear plots also were yielded by data from runs at 100° in media which ranged from approximately 1 to 4 formal in H_2SO_4 and from those relating to the oxidation of the isomeric cyclohexanediols.

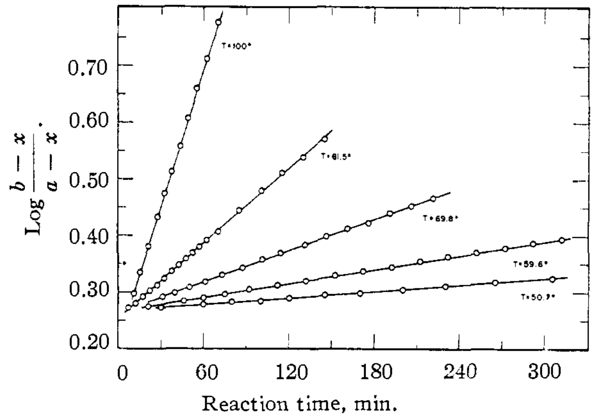

Fig. 2.—Second-order plots for the oxidation of glycerol (a) in 3.74 F H_2SO_4 in the presence of a moderate excess of VO_2^+(b); effect of temperature, VO_2^+ concentration 0.058 N, glycerol concentration 0.032 N.

Further corroboration was obtained by evaluating graphically the instantaneous rate for each experimental point on curves relating VO_2^+ concentration to reaction time. Assuming that the rate of the reaction under conditions of moderate vanadate excess was given by

$$\text{rate} = k[VO_2^+]^x[\text{Glycerol}]^y$$

the existing concentrations of V(V) and glycerol raised to various powers were divided into the appropriate slopes. It was found that the most constant values for k resulted when x and y were both 1.

TABLE I

GRAPHICAL ESTIMATION OF PSEUDO FIRST AND SECOND-ORDER RATE CONSTANTS

React. temp., °C.	Concn. H_2SO_4, F	$k' \times 10^5$, (sec.$^{-1}$)	$k \times 10^4$, (l. eq.$^{-1}$ sec.$^{-1}$)	$k'' \times 10^5$, (l. eq.$^{-2}$ sec.$^{-1}$)
		Glycerol		
100	0.91		8.98 ± 0.08	113
100	0.89	340 ± 12		70.6
100	1.84		25.5 ± 1.8	75.3
100	2.76		70.7 ± 4.2	92.8
100	3.74		113 ± 9	80.8
100	4.66		280 ± 32	129
81.5	3.74		31.7 ± 2.4	22.7
81.5	0.94	86.6 ± 4.4		16.8
69.8	3.74		13.5 ± 0.5	9.63
69.8	0.92	39.0 ± 1.0		7.60
59.6	3.74		6.05 ± 0.1	4.31
59.6	0.92	15.9 ± 0.7		3.40
50.7	3.74		2.79 ± 0.1	1.99
50.7	0.93	6.14 ± 0.3		1.35
		cis-1,2-Cyclohexanediol		
100	3.74		52 ± 3	
		trans-1,2-Cyclohexanediol		
100	3.74		21.7 ± 0.5	

Under conditions of large glycerol excess it was assumed that the rate was expressed by

$$\text{rate} = k'[VO_2^+]^x$$

Similar treatment of these data again showed the best agreement in values for k' when x was unity.

Numerical values for these pseudo first- and second-order rate constants are given in Table I.

The H^+ concentration in every instance was such as to constitute a 20- to 100-fold excess over that required for the oxidation. It was thus assumed that the pseudo second-order rate constant k was related to some power of the H^+ concentration

$$k = k''[H^+]^z$$

The pseudo first-order rate constant k' would then be related to k'' by

$$k' = k''[H^+]^z[\text{Glycerol}]$$

Figure 3 depicts the variation of log k with the log of $[H^+]$ for two temperatures. In computing $[H^+]$, estimates of the value of K_2 for H_2SO_4 were based upon an equation which closely pre-

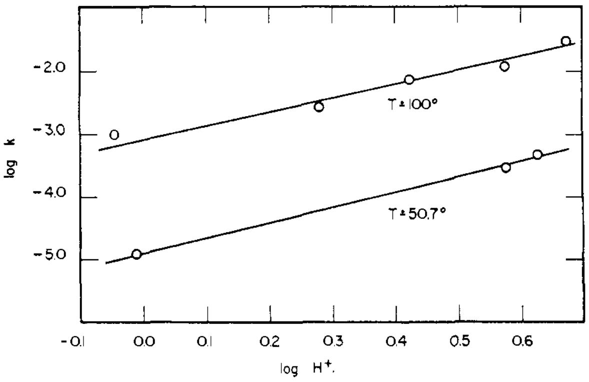

Fig. 3.—Logarithmic plot of pseudo second-order rate constants against the logarithm of the applicable H^+ concentration.

dicts the temperature dependence of this constant to 60°.[4] The 50.7° plot is presented to lend support to the more extensive set of data. The slopes of these curves are 2.2 for the 100° set and 2.4 for that collected at the lower temperature; the integer value of 2.0 was taken for use in subsequent calculations.

According to the foregoing the pseudo second-order rate constant k should be related to k'' by

$$k = k''[\mathrm{H}^+]^2$$

Similarly, the pseudo first-order constant should be given by

$$k' = k''[\text{Glycerol}][\mathrm{H}^+]^2$$

Figure 4 is a plot of the log of k'' for each run against the reciprocal of the absolute temperature; according to this, the Arrhenius activation energy for the reaction is 19 kcal./mole, a figure which is considerably smaller than the energy of 60–70 kcal. estimated for the bond between hydroxyl-substituted carbon atoms.[5]

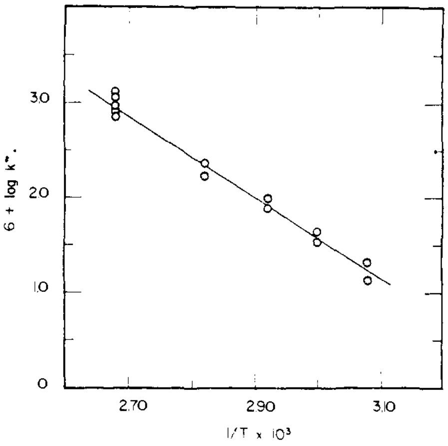

Fig. 4.—Effect of temperature upon the oxidation of glycerol with V(V). Plot of log k'' against the reciprocal of the reaction temperature, °K.

Discussion

The pseudo first-order dependence of the rate of oxidation upon V(V) and upon glycerol is clearly established by the foregoing data. Assumption of pseudo second-order dependence with respect to $[\mathrm{H}^+]$ led to the most consistent values for k''.

An explanation consistent with the experimental findings can be made by assuming the reactive vanadium(V) species to be the terpositive ion VO^{+3}, present in small amount and in equilibrium with the principal component VO_2^+

$$\mathrm{VO}_2^+ + 2\mathrm{H}^+ \rightleftharpoons \mathrm{VO}^{-3} + \mathrm{H}_2\mathrm{O} \qquad (1)$$

It is postulated that this ion is capable of forming a coördination complex with the glycol, equilibrium being established rapidly

$$\mathrm{VO}^{+3} + \mathrm{R(OH)}_2 \rightleftharpoons \mathrm{VOR(OH)}_2^{+3} \qquad (2)$$

The rate-determining step in the oxidation is postulated to involve the first-order disproportionation of this intermediate

$$\mathrm{VOR(OH)}_2^{+3} \longrightarrow \mathrm{VO}^{+2} + \text{products} \qquad (3)$$

The organic products are presumed to be rapidly oxidized in subsequent steps of the over-all reaction.

It is necessary to assume that the experimentally determined vanadate concentration C_T is the sum of the several quinquevalent vanadium-containing species present; thus

$$C_\mathrm{T} = C_1 + C_3 + C_4 \qquad (4)$$

where C_1 is the concentration of the terpositive ion, C_3 is the concentration of the coördination complex and C_4 represents the concentration of VO_2^+.

According to (3), then

$$-\frac{\mathrm{d}C_\mathrm{T}}{\mathrm{d}t} = k'''C_3 \qquad (5)$$

Denoting the equilibrium constant for the formation of the terpositive vanadium(V) ion as K_a, it is seen that

$$K_\mathrm{a} = \frac{C_1}{C_4[\mathrm{H}^+]^2} \qquad (6)$$

The equilibrium constant K_f for the formation of the coördination complex may be written as

$$K_\mathrm{f} = \frac{C_3}{C_1C_2} \qquad (7)$$

where C_2 represents the concentration of the uncomplexed glycol.

Using these relationships, C_3 can be defined in terms of K_a, K_f, the total vanadium(V) concentration C_T, the uncomplexed glycol concentration C_2 and the H^+ concentration. The rate expression (5) then takes the form

$$-\frac{\mathrm{d}C_\mathrm{T}}{\mathrm{d}t} = \frac{k'''K_\mathrm{a}K_\mathrm{f}C_\mathrm{T}C_2[\mathrm{H}^+]^2}{1 + K_\mathrm{a}K_\mathrm{f}C_2[\mathrm{H}^+]^2 + K_\mathrm{a}[\mathrm{H}^+]^2} \qquad (8)$$

Provided that K_a and K_f are small, it is seen that the denominator in (8) should not vary significantly from unity. It follows, then, that the reaction should be pseudo first-order with respect to vanadium(V) under conditions of constant $[\mathrm{H}^+]$ and a large excess of glycol. Where both the glycol and V(V) concentrations are undergoing change pseudo second-order kinetics should be observed, $[\mathrm{H}^+]$ again being held essentially constant. Both of these predictions are in accord with the experimental findings. The expression also accounts for the apparent dependence of the rate upon the square of the H^+ concentration.

The several assumptions required for this argument are quite plausible. It is known that the principal species in acidic vanadium (V) solutions is the ion VO_2^+; it would thus be reasonable to expect that K_a, as defined in (6), would be numerically small. The occurrence of the terpositive VO^{+3} ion in aqueous solution has been reported.[6]

Independent evidence for the formation of an intermediate is available. A visible deepening of the color of vanadate solutions attends the addition of a polyhydric alcohol, particularly if the latter is introduced in large excess. A broad absorption of low magnitude appears in the region of 300 mμ; attempts to observe this effect spectrophotometrically under conditions of equimolar quantities of glycol and V(V) have not been suc-

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[4] C. W. Davies, H. W. Jones and C. S. Monk, *Trans. Faraday Soc.*, **48**, 921 (1952).

[5] F. R. Duke, This Journal, **69**, 3054 (1947).

[6] N. V. Sidgwick, "Chemical Elements and Their Compounds," Oxford University Press, London, 1950, p. 816.

cessful. This suggests that K_f, as defined in (7), is also a small number.

The assumption that the total vanadium(V) concentration is being measured analytically is plausible. This is particularly true in instances where large excesses of glycerol were employed; under these circumstances the V(V) concentration was obtained by difference, the V(IV) concentration actually being measured. That data obtained through the direct measurement of V(V) can be correlated to these tends to support the original assumption.

According to (8) the experimentally evaluated rate constant k'' is equal to the product of the three constants appearing in the numerator; it is thus dependent upon the equilibrium constant for the formation of the coördination complex. Of the three substances oxidized, it is reasonable to expect that the glycerol molecule, with relatively unhindered hydroxyl groups and effectively doubled sites for reaction, would enter into an equilibrium most favorable for complex formation, followed by *cis*-1,2-cyclohexanediol and then the *trans*-isomer. This order is in agreement with experimental fact; if the magnitude of the pseudo second-order rate constants for the oxidation of these substances is compared for the same set of reaction conditions, it is seen that they stand in a ratio of approximately 4:2:0.8, respectively.

While the numerical value of the Arrhenius activation energy is somewhat uncertain as measured, the magnitude is probably correctly indicated. The rate-determining step in the process thus does not appear to involve the direct cleavage of a carbon–carbon bond. The intermediate formation of some entity appears to reduce considerably the energy requirements for this process.

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[CONTRIBUTION FROM THE CALIFORNIA RESEARCH CORPORATION]

Kinetics of Oxidation by Aqueous Polysulfide Solutions. II. Rate Dependence of the Oxidation of *m*-Toluic Acid on the Concentration and Chain Length of the Polysulfide Oxidant[1]

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The rate of oxidation of sodium *m*-toluate by aqueous sodium polysulfide solutions is proportional to the square root of the concentration of polysulfide molecules. This is true when the correlation is made at a constant value of *n*, the average chain length[1b] in $S_{n+1}^{=}$, over the range of values of *n* from 1.3 to 4.0. The correlation must be made at a constant value of *n* since the rate also depends approximately linearly on *n*. The concentrations of polysulfide used are corrected for sulfur disproportionation reactions which occur at reaction temperature and for the percentage of sulfide in the vapor as H_2S. Polysulfide is the only oxidant although several other sulfur species are present. Neither sodium thiosulfate nor sodium sulfate alone oxidizes sodium *m*-toluate, and sulfite and polythionate are believed not to be present. The kinetic data extrapolate to give zero rate of oxidation at zero concentration of polysulfide. The mechanism most consistent with these and earlier data[2] involves reversible fission of a polysulfide molecule to give two polysulfenyl radicals which then abstract a benzyl hydrogen in a slow step which has a rate constant proportional to the over-all rate of oxidation (equations 14, 15 and 16). The dependence on *n* arises from the fact that S–S bonds over the range $S_{2.3}^{=}$–$S_{5.0}^{=}$ are of similar energy and the rate of reaction 14 depends on the total number of S–S bonds.

Introduction

Aqueous solutions of sodium polysulfide quantitatively oxidize sodium *m*-toluate to sodium isophthalate at 250–350°. Part I of this series[2] presented evidence on the mechanism of this reaction which the present paper extends. It was shown that with polysulfide oxidant present in excess, the reaction rate is first order in *m*-toluic acid concentration. A mechanism which predicts the kinetic dependence to be first order in *m*-toluic acid and 0.5 order in polysulfide was presented. While the first work suggested that the order in polysulfide was 0.5, further work was necessary to substantiate this. Data now are presented which show that the dependence on the actual concentration of sodium polysulfide in solution at reaction temperature is 0.5 over the range of polysulfide chain lengths[1b] accessible in this study, $S_{2.5}^{=}$ to $S_5^{=}$. Since the rate is found to be dependent on chain length as well as concentration of polysulfide, one of these must be held constant while correlating the rate of oxidation with the other.

Experimental

Analysis.—The analytical techniques which use *m*-toluic acid-C^{14} and paper chromatography have been described.[2] The constant volume micro reactor also has been described.[3]

The most satisfactory analysis for sulfide, polysulfide-sulfur, sulfite, thiosulfate and sulfate together was taken from analyses conveniently summarized in the recent book by Kolthoff, Belcher, Stenger and Matsuyana.[4] The method chosen was found to be the most accurate on known solutions. It involves determining the number of sulfur atoms *n* in each polysulfide molecule $S_{n+1}^{=}$ using the procedure of Schulek.[2,4a,5,6] This polysulfide-sulfur, expressed in g. atoms/l., is symbolized (S^0) in the discussion below. Sulfide is precipitated with freshly prepared zinc carbonate; the zinc sulfide is filtered, redissolved in acidified iodine, and titrated with thiosulfate.[4b] An aliquot of the filtrate is

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[1] (a) Work supported by Oronite Chemical Company. Presented at the American Chemical Society Meeting, September 1959, Atlantic City, New Jersey. (b) Chain length refers to the number of sulfur atoms in the average polysulfide molecule, not to a kinetic chain length.

[2] W. A. Pryor, THIS JOURNAL, **80**, 6481 (1958).

[3] W. A. Pryor, V. C. Davis and M. Ausman, *Ind. Eng. Chem.*, **51**, 129 (1959).

[4] I. M. Kolthoff, R. Belcher, V. A. Stenger and G. Matsuyana, "Volumetric Analysis," Vol. III, Interscience Publishers, Inc., New York, N. Y., 1957: (a) pp. 292, 307, (b) pp. 295, 300, (c) p. 299 and references given there.

[5] E. Schulek and E. Koros, *Acta Chim. Acad. Sci. Hung.*, **3**, 111 (1953).

[6] E. Schulek, *Z. anal. Chem.*, **65**, 352 (1925).