Kinetics of the Catalytic Hydrogen Peroxide Oxidation of Thiodiglycol in Aqueous Solutions

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In order to compare the catalytic activities of various inorganic compounds and to discover new catalysts in the aqueous hydrogen peroxide oxidation, the catalytic oxidation of thiodiglycol (TDG) was investigated.

$$(HOCH_2CH_2)_2S + H_2O_2 \rightarrow (HOCH_2CH_2)_2SO + H_2O \qquad (1)$$

The rate of the uncatalyzed hydrogen peroxide oxidation of TDG has been reported by Ross[1] to follow the second-order kinetics. We found that molybdate exhibited a stronger catalytic activity than well-known tungstates and selenous acid. The kinetics of sodium molybdate (SM)-catalyzed oxidation has also been investigated, since the mechanism of the catalysis of molybdates had not previously been clarified in detail.[2]

The present paper describes the rate data and a probable mechanism of the SM-catalyzed hydrogen peroxide oxidation of TDG in aqueous solution. In the course of this study, the rate of the oxidation of TDG by yellow sodium peroxymolybdate (YPM), together with the absorption spectra of the SM-hydrogen peroxide system, were measured.

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[1] S. D. Ross, *J. Am. Chem. Soc.*, **68**, 1484 (1946).

[2] Molybdates have been used in the hydrogen peroxide oxidation of organic compounds in the following experiments: a) I. D. Raacke-Fels, C. H. Wang, R. K. Robins and B. E. Christensen, *J. Org. Chem.*, **15**, 627 (1950); b) A. R. Bader, *J. Am. Chem. Soc.*, **73**, 3731 (1951); c) K. Kahr and C. Berther, *Chem. Ber.*, **93**, 132 (1960); d) G. Toennies and J. T. Kolb, *J. Biol. Chem.*, **140**, 131 (1941); e) J. C. Ghosh and B. C. Kar, *J. Indian Chem. Soc.*, **11**, 485 (1934).

Experimental

Materials.—TDG was purified by vacuum distillations; b. p. 131~134°C/3 mmHg. YPM was synthesized according to the Kobosev-Sokolov procedure.[3] All the catalysts used were commercial reagents of G. R. grade.

Typical Procedure for Kinetic Measurements.—A buffered aqueous solution containing TDG, a catalyst, sodium acetate and acetic acid was thermostated at the reaction temperature; the reaction was started by adding a known amount of aqueous hydrogen peroxide. Aliquots were taken out at appropriate intervals of time, and their peroxide contents were determined iodometrically.

The SM-catalyzed oxidation was carried out in aqueous media at pH 0.5~6.2 and in aqueous sulfuric acid. No appreciable change in the rates was observed when the oxidation was started by mixing TDG with a prepared mixture of SM and hydrogen peroxide, or when the reaction was carried out in a brown flask.

The kinetics of oxidation by YPM was studied by means of the iodometry of active oxygen in a buffered reaction mixture of YPM and TDG.

Ultraviolet Absorption Spectra.—Absorption spectra (210~500 mμ) were measured with a SM-H_2O_2 system in order to obtain some information on active species in the SM-catalyzed hydrogen peroxide oxidation. An absorption maximum was observed at the wavelength of 310 mμ with a solution at pH 4.7 or at 326 mμ with one at pH 0.8. No absorption maximum appeared in 210~500 mμ with an aqueous solution of hydrogen peroxide-TDG and with an aqueous solution of TDG-SM.

Reaction Products Criterion.—To examine the reaction products, a mixture of SM (0.002 mol.), hydrogen peroxide (0.12 mol.) and TDG (0.1 mol.) in 100 ml. of water was kept standing at 25° for two hours. After the evaporation of the water under reduced pressure, the residue was dissolved in alcohol, the SM being filtered off. On recrystallization from alcohol crystals (11.3 g.) of thiodiglycol sulfoxide (82%) were obtained; m. p. 110.5~111.5°C (lit.[4] m. p. 111°C).

Upon the treatment of thiodiglycol sulfoxide (15×10^{-3} M), the reaction product, with a mixture of SM (1×10^{-4} M) and H_2O_2 (8×10^{-3} M) at 25°C and pH 4.7 or 0.8 for 4 hr., no appreciable oxidation occurred.

Results and Discussion

The Examination of the Catalyst Activity.—Sulfides, in general, can be oxidized to sulfoxides by hydrogen peroxide at room temperature.[5] Ross[1] has reported that the second-order rate constant for the uncatalyzed hydrogen peroxide oxidation of thiodiglycol (TDG) in aqueous solutions of pH 4~6 was 2.17×10^{-3} l. mol^{-1} sec.$^{-1}$ at 25°C.

Our examinations of the catalytic activities of various inorganic compounds at 25°C and pH 4.7 gave the following data:

Compounds with some activity:

$Na_2MoO_4 > Na_2WO_4 \gg H_2SeO_3 \gg NH_4VO_3$, Na_2TeO_4, $UO_2(OAc)_2$, and $Cu(OAc)_2$

Compounds with no activity:

$AgNO_3$, $MgCl_2$, $BaCl_2$, $CaCl_2$, $Zn(OAc)_2$, $ZnSO_4$, $CdCl_2$, $HgCl_2$, $Hg(OAc)_2$, $Al_2\cdot(SO_4)_3$, $Na_2B_4O_7$, $NaBO_3$, $NaBO_2$, Tl_2SO_4, $Zr(OAc)_4$, $NaHCO_3$, Na_2CO_3, $Pb(OAc)_2$, $NaNO_3$, NaH_2PO_4, $Na_2P_2O_7$, Na_2HPO_3, $(NaPO_3)_n$, $Cr_2(SO_4)_3$, Cr_2O_3, K_2SO_4, $Na_2S_2O_3$, $KHSO_4$, $Mn(OAc)_2$, $KClO_3$, $KClO_4$, $NaClO_2$, $NaBrO_3$, KIO_3, KIO_4, $CoSO_4$, $Co(OAc)_2$, $Ni(OAc)_2$, and V_2O_5

TABLE I. CATALYZED HYDROGEN PEROXIDE OXIDATION OF TDG IN AQUEOUS SOLUTIONS AT 25°C AND pH 4.7

Initial concn.: H_2O_2, 0.02570 M; TDG, 0.03960 M

Catalyst	Concn. of catalyst M×10^{-4}	Rate constant[a]		Catalyst coeff.[a]	
		$k_2\times10^3$ l. mol^{-1} sec^{-1}	$k_1\times10^3$ sec^{-1}	k_2^c l^2 mol^{-2} sec^{-1}	k_1^c l. mol^{-1} sec^{-1}
Na_2MoO_4	1	—	6.56	—	6.54
Na_2WO_4	1	69.2	—	670	—
H_2SeO_3	10	4.12	—	1.93	—
NH_4VO_3	10	2.54	—	0.35	—
Na_2TeO_4	10	2.42	—	0.23	—
$UO_2(OAc)_2$	10	2.39	—	0.20	—
$Cu(OAc)_2$	10	2.37	—	0.18	—
None	0	2.17	—	—	—

a) $v=k_2[H_2O_2][TDG]=(k_0+k_2^c[\text{Catalyst}])[H_2O_2][TDG]$ or $v=k_1[TDG]=k_1^c[\text{Catalyst}][TDG]$.

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[3] N. J. Kobosev and N. N. Sokolov, *Z. anorg. u. allgem. Chem.*, **214**, 321 (1933).

[4] J. Bougault and P. Robin, *Compt. rend.*, **171**, 355 (1920).

[5] M. Gazdar and S. Smiles, *J. Chem. Soc.*, 93, 1833 (1908).

Compounds with side reactions:

$CuCl_2$, $CuSO_4$, $Ce_2(SO_4)_3$, $ZrOCl_2$, $NaNO_2$, $NaHSO_3$, KSCN, $K_2Cr_2(SO_4)_4$, $Fe_2(SO_4)_3$, $K_3Fe(CN)_6$, $K_4Fe(CN)_6$, $NaBiO_3$, and Na_2TeO_3

It is evident in Table I that molybdate and tungstate are both active catalysts, while selenous acid is less active. However, the other four, NH_4VO_3, Na_2TeO_4, $UO_2(OAc)_2$ and $Cu(OAc)_2$, show only a small activity. It is of interest to note that the rate of SM-catalyzed oxidation is independent of the concentration of hydrogen peroxide, following the first-order kinetics with TDG, while the oxidations with other catalysts satisfy the second-order kinetics. The comparison of the catalytic activities of sodium molybdate (SM) and tungstate seems less significant, since their kinetics are different. It is obvious, however, that the completion of oxidation with molybdate is faster than that with tungstate. The SM-catalyzed oxidation will be discussed in detail later.

TABLE II. RATE DATA ON THE OXIDATION OF TDG WITH SM-H_2O_2 IN THE RANGE OF $[H_2O_2]>2[SM]$

Initial concn., $M\times10^3$			pH (Added compound)	Temp., °C	$k_1\times10^4$ sec^{-1}
[SM]	$[H_2O_2]$	[TDG]			
A) Effect of initial concentrations of hydrogen peroxide and TDG					
0.050	5.070	2.670	4.7 (AcOH-AcONa)	25	2.57
0.050	5.098	5.340	4.7 (AcOH-AcONa)	25	2.76
0.050	5.012	8.010	4.7 (AcOH-AcONa)	25	2.75
0.050	12.50	8.010	4.7 (AcOH-AcONa)	25	2.67
0.050	25.02	10.68	4.7 (AcOH-AcONa)	25	2.82
2.0	5.63	9.03	4.7 (AcOH-AcONa)	0	18.3
2.0	8.53	9.03	4.7 (AcOH-AcONa)	0	18.8
2.0	8.47	4.51	4.7 (AcOH-AcONa)	0	18.2
0.025	9.705	9.027	0.8 (H_2SO_4)	25	12.2
0.025	9.705	13.54	0.8 (H_2SO_4)	25	12.2
0.025	6.470	13.54	0.8 (H_2SO_4)	25	12.2
B) Effect of the acidity of the solutions					
0.025	11.12	12.17	−0.60[a] (H_2SO_4)	25	11.9
0.025	11.12	12.17	−0.31[a] (H_2SO_4)	25	11.8
0.025	11.12	12.17	+0.02[a] (H_2SO_4)	25	12.2
0.025	11.12	12.17	+0.15[a] (H_2SO_4)	25	12.5
None	52.99	42.43	−0.60[a] (H_2SO_4)	25	75.8[b]
None	52.99	42.43	−0.31[a] (H_2SO_4)	25	133[b]
None	52.99	42.43	−0.04[a] (H_2SO_4)	25	236[b]
None	52.99	42.43	+0.15[a] (H_2SO_4)	25	355[b]
C) Effect of temperature					
0.025	8.52	9.03	4.7 (AcOH-AcONa)	0	0.275
0.025	8.46	9.03	4.7 (AcOH-AcONa)	5	0.401
0.025	9.85	9.03	4.7 (AcOH-AcONa)	10	0.599
0.025	10.80	12.17	4.7 (AcOH-AcONa)	20	1.15
0.025	13.53	16.22	4.7 (AcOH-AcONa)	25	1.62
0.025	10.80	12.17	4.7 (AcOH-AcONa)	30	2.09
0.025	8.52	9.03	0.8 (H_2SO_4)	0	2.97
0.025	8.46	9.03	0.8 (H_2SO_4)	5	4.01
0.025	9.85	9.03	0.8 (H_2SO_4)	10	5.66
0.025	10.80	12.17	0.8 (H_2SO_4)	20	9.54
0.025	13.53	16.22	0.8 (H_2SO_4)	25	11.9
0.025	10.80	12.17	0.8 (H_2SO_4)	30	15.9
None	52.99	42.43	4.7 (AcOH-AcONa)	20	14.0[b]
None	52.99	42.43	4.7 (AcOH-AcONa)	25	21.1[b]
None	52.99	42.43	4.7 (AcOH-AcONa)	30	31.5[b]
None	52.99	42.43	4.7 (AcOH-AcONa)	35	45.9[b]

a) Acidity function, $-H_0$.

b) Second-order rate constant (l. mol^{-1} sec^{-1}); $v=k_2\,[H_2O_2]\,[TDG]$.

Peroxytungstates have been suggested as active oxidation species in the tungstate-catalyzed epoxidation of olefins,[6] and peroxyselenious acid, in the selenium dioxide-catalyzed oxidation of dimethyl aniline[7] and ketones.[8]

No catalytic action of vanadic acid, a well-known catalyst,[9] was observed under these conditions, although a faint activity was appreciable with ammonium vanadate. Faint catalytic activities were also observed with sodium tellurate, cuprous acetate and uranyl acetate. The uranyl acetate is known to catalyze the hydrogen peroxide oxidation of primary amines.[10] Ferric and ferrous salts showed no appreciable activity.

The Mechanism of SM-catalyzed Oxidation. —*Rate Equations.*—The rate of SM-catalyzed oxidation is independent of the concentration of hydrogen peroxide and is first-order with respect to TDG if the concentration ratio of hydrogen peroxide vs. SM exceeds 2, as Table II-A and Fig. 1 show. These pseudo-first order rates are proportional to the concentration of SM (Fig. 2). Thus, if $[H_2O_2] > 2\,[SM]$, the rate equation is expressed as:

$$v = k_1\,[TDG] = k_1^c\,[SM]\,[TDG] \qquad (2)$$

($[SM]$ is the initial concentration of Na_2MoO_4.) However, if $[H_2O_2]/[SM]$ is less than 2, the rate is second-order (Table III and Fig. 1):

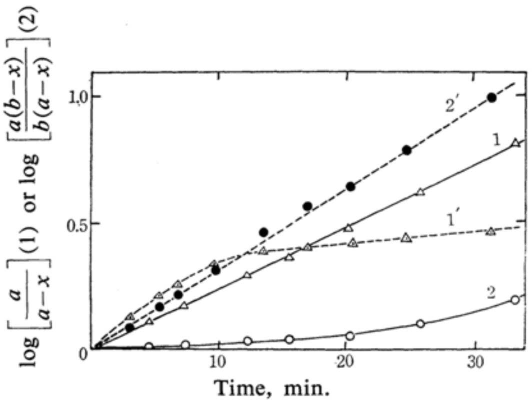

Fig. 1. Comparison of first-order (1) and second-order (2) rate equations at 0°C and pH 4.7.

	$[TDG]_{init}$ (a), M×10^3	$[H_2O_2]_{init}$ (b), M×10^3	[SM] M×10^3
1 (△), 2 (○) ——	9.03	8.53	1
1′(▲), 2′(●) ------	5.42	3.70	2

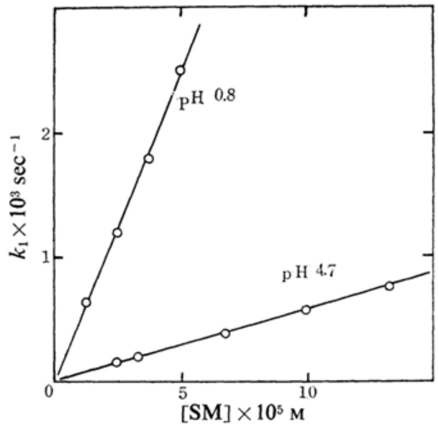

Fig. 2. Effect of concentration of SM on the rate in the range of $[H_2O_2] > 2[SM]$ at 25°C.

TABLE III. RATE DATA ON THE OXIDATION OF TDG WITH $SM\text{-}H_2O_2$ IN THE RANGE OF $[H_2O_2] < 2[SM]$; pH=4.7 (AcOH-AcONa) at 0°C

Initial concn. M×10^3			k_2' a)
[SM]	$[H_2O_2]$	[TDG]	l. mol^{-1}. sec^{-1}
2.0	0.924	1.806	0.856
2.0	1.924	1.806	0.862
2.0	2.879	1.806	0.749
2.0	2.879	2.709	0.706
2.0	2.879	4.514	0.786
2.0	3.611	1.924	0.860
2.0	3.695	5.417	0.711
4.0	2.879	4.514	0.856
6.0	2.879	4.514	0.783

a) $v = k_2'$ [Active oxygen] [TDG]

$$v = k_2'\,[\text{Active oxygen}]\,[TDG] \qquad (3)$$

Here, [Active oxygen] expresses the concentration of active oxygen determined iodometrically. The value of k_2' holds constant while [SM] is vavied, in so far as $[H_2O_2] < 2[SM]$.

The pseudo-second order rate constant of the uncatalyzed oxidation is calculated from Table II-C and Table VI to be acout 2.0×10^{-3} l. mol^{-1} sec^{-1}, which is about 1/400 of the value of k_2', 0.797 l. mol.$^{-1}$ sec^{-1}. Hence, k_2' is not the rate for hydrogen peroxide itself, but that for other active oxidizing species.

It is quite probable that one mole of SM is transformed quantitatively to a reactive intermediate by two moles of hydrogen peroxide:

$$SM + 2H_2O_2 \overset{\text{fast}}{\rightleftharpoons} \text{intermediate}$$

$$\frac{1}{2}\ (\text{intermediate}) + (HOCH_2CH_2)_2S$$

$$\xrightarrow{\text{slow}} (HOCH_2CH_2)_2SO$$

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[6] a) M. Mugdan and D. P. Young, ibid., **1949**, 2988; b) K. A. Saegebarth, *J. Org. Chem.*, **24**, 1212 (1959); c) Z. Raciszewski, *J. Am. Chem. Soc.*, **82**, 1267 (1960).

[7] Y. Ogata and I. Tabushi, This Bulletin, **32**, 215 (1959).

[8] N. Sonoda and S. Tsutsumi, ibid., **32**, 505 (1959); **33**, 1440 (1960); **34**, 1006 (1961).

[9] W. Treibs, *Chem. Ber.*, **72**, 1194 (1934).

[10] K. Kar and C. Berther, ibid., **93**, 132 (1960).

TABLE IV. RELATION OF ABSORBANCE WITH THE RATIO $[H_2O_2]/(2[SM])$
$[SM]=0.5\times10^{-3}$ M, pH=4.7

$[H_2O_2]\times10^3$ M	$\frac{[H_2O_2]}{2[SM]}$ (A)	$E_{1cm.}$ (310 mμ)	$\frac{E_{1cm.}\ (310\ m\mu)}{0.492}$ (B)	B/A
0.1635	0.164	0.072	0.147	0.900
0.3270	0.327	0.152	0.310	0.950
0.4905	0.491	0.226	0.460	0.938
0.6792	0.679	0.327	0.665	0.983
1.358	1.36	0.496	—	—
2.038	2.04	0.486	—	—
3.232	3.23	0.490	—	—
40	40	0.495	—	—

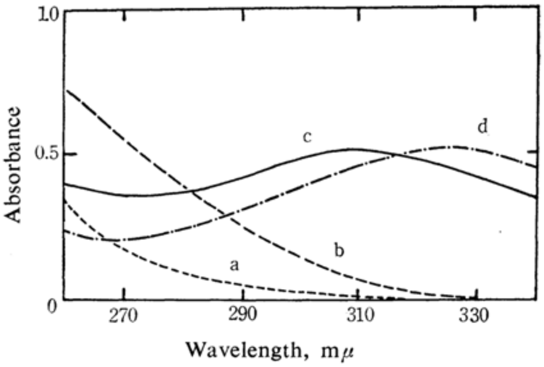

Fig. 3. Absorption spectra of SM-H_2O_2 in aqueous solutions (a) SM at pH 4.7 (AcOH-AcONa) (b) SM at pH 0.8 (H_2SO_4) (c) SM-H_2O_2 at pH 4.7 (AcOH-AcONa) (d) SM-H_2O_2 at pH 0.8 (H_2SO_4).

Assuming that the formation of the intermediate is rapid and complete and that excess hydrogen peroxide has no effect on the rate, the rate sould be independent of the concentration of hydrogen peroxide when $[H_2O_2]>2[SM]$.

Reactive Species in Solutions.—The formation of the complex, YPM, was expected from the previous equations; this expectation was confirmed by the identification of YPM by means of ultraviolet spectrophotometry, together with the comparison of the data on oxidation by SM-H_2O_2 with those on oxidation by YPM.

TABLE V. OXIDATION OF TDG WITH YPM AT 0°C AND pH 4.7 (AcOH-AcONa)

Initial concn., M×10³		k''_2 [a]
[Active oxygen]	[TDG]	l. mol⁻¹ sec⁻¹
0.831	1.806	0.824
1.661	1.806	0.694
1.661	3.612	0.792

a) $v=k''_2$ [Active oxygen] [TDG]

As shown in Fig. 3, an absoption maximum appeared at 310 mμ (pH 4.7) or at 326 mμ (pH 0.8) in the aqueous hydrogen peroxide-SM system, each maximum being identical with that of synthetic YPM at the corresponding pH. The absorbance of the aqueous hydrogen peroxide-SM system was determined at pH 4.7 with various concentrations of hydrogen peroxide while [SM] was kept constant (Table IV). The absorbance at 310 mμ did not increase with an increasing amount of hydrogen peroxide in the range of $[H_2O_2]>2[SM]$. Therefore, two moles of hydrogen peroxide and one mole of SM react almost quantitatively to yield YPM. The shift of the absorption maximum up to 326 mμ (pH 0.8) suggests that YPM may exist in another form in the realm of higher acidity.

Table V shows the rate data on the oxidation of TDG by YPM, data which satisfy the second-order kinetics:

$$v=k_2''\ [\text{Active oxygen}]\ [\text{TDG}] \qquad (4)$$

Here, [Active oxygen] means the concentration of the active oxygen determined iodometrically. This pseudo-second order rate constant, k_2'', is identical with k_2' in Eq. 3 within the range of experimental error. These facts suggest the following mechanism at pH 3∼6:

$$Na_2MoO_4 \overset{\text{fast}}{\rightleftarrows} 2Na^+ + MoO_4^{2-} \qquad (5)$$

$$MoO_4^{2-} + 2H_2O_2 \overset{\text{fast}}{\rightleftarrows} HMoO_6^- + H_2O + OH^- \qquad (6)$$

$$HMoO_6^- + (HOCH_2CH_2)_2S \xrightarrow{\text{slow}} HMoO_5^- + (HOCH_2CH_2)_2SO \qquad (7)$$

$$HMoO_5^- + (HOCH_2CH_2)_2S \xrightarrow{\text{fast}} H^+ + MoO_4^{2-} + (HOCH_2CH_2)_2SO \qquad (8)$$

Assuming that all the SM is converted to $HMoO_6^-$ in this pH range and that a and b are the initial concentrations of $HMoO_6^-$ and TDG respectively, and x, the decrease of TDG at time t, the rate is expressed as:

$$v=k_2''\ [HMoO_6^-]\ [\text{TDG}]$$
$$=k_2''\left(a-\frac{x}{2}\right)(b-x)$$

or

$$k_2''t=\frac{2}{b-2a}\ \ln\ \frac{2a(b-x)}{b(2a-x)} \qquad (9)$$

Equation 9 is equal to Eqs. 3 and 4, and satisfies Eq. 2, if $[HMoO_6^-]$ is constant and equal to the initial concentration of SM.

SM reacts with two moles of hydrogen peroxide to form Na_2MoO_6 (YPM) and with four moles of hydrogen peroxide to form red sodium peroxymolybdate Na_2MoO_8, an unstable peroxide decomposing to YPM at room temperature.[3,11] It has been found that YPM exists in a neutral aqueous solution in the form of monoanion II.[12]

$$\underset{\text{(I)}}{MoO_2(OOH)(OOH)} \rightleftarrows \underset{\text{(II)}}{MoO_2(OO^-)(OOH)+H^+}$$

Here the first ionization constant of I, K_1, is 3×10^{-3} and the second ionization constant, K_2, is 7×10^{-10}; hence the dissociation of II is almost negligible in a neutral solution.[12] When [SM] exceeds 2×10^{-3} M, SM exists in the form of polymolybdate,[13] which reacts also with hydrogen peroxide to give II.[14] These facts strongly suggest that the active species at pH 3~6 is $HMoO_6^-$.

The Effect of Acidity.—The effect of the acidity of the solution on the SM-catalyzed oxidation rate is shown in Table II-B and Fig. 4. The rate increases with the increasing acidity of the solution; the plot of log k vs. pH in the pH range of 2~3 fits a line of the unit slope (Fig. 4).

The rate constant at pH below 2 becomes independent of the acidity, as is obvious from the data obtained in dilute aqueous sulfuric acid (Table II-B). However, the uncatalyzed oxidation is accelerated by acid at pH below 2, and this is probably the well-known acid catalysis in the hydrogen peroxide oxidation. The plot of log k_2 vs. $-H_0$ gave a straight line with a slope of 0.90. The activation energies were calculated to be 11.2 kcal. mol^{-1} at a pH above 3 and 9.21 kcal. mol^{-1} at a pH below 2 (Table VI).

These facts imply two distinct active species, those at pH values below 2 and those above 3. Furthermore, the ultraviolet absorption spectrophotometry described above also endorses the presence of two active species at different pH's. It is most probable that YPM at pH above 3 exist as $HMoO_6^-$ (II), while at pH below 2 they exist as H_2MoO_6 (I), which should be more active than $HMoO_6^-$. The ratio of $[H_2MoO_6]$ to $[HMoO_6^-]$ was calculated to be 100 : 3 at pH 1 and 1 : 30 at pH 4 by means of the first ionization constant of H_2MoO_6 as determined by Csányi.[12] The shift of the absorption maximum from 310 to 326 mμ with a decreasing pH value is explicable by the transformation of $HMoO_6^-$ to H_2MoO_6. Considering the ionization constants of H_2MoO_6, H_2MoO_6 should be about nine times as active as $HMoO_6^-$ at 25°C.

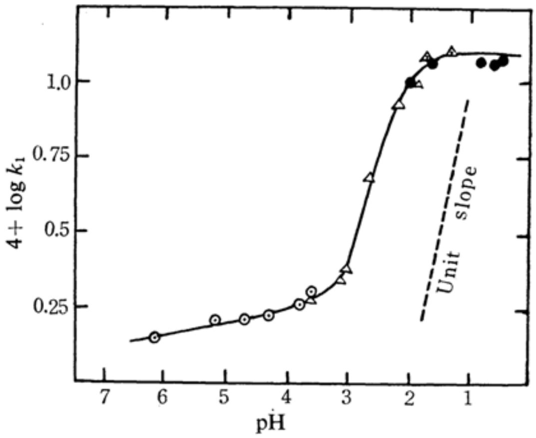

Fig. 4. Effect of pH of reaction mixture on the first-order rate constant k_1 at 25°C.
⊙ AcOH-AcONa
△ HCl-KCl
◬ HCl
● H_2SO_4

TABLE VI. ENERGY OF ACTIVATION AND ENTROPY OF ACTIVATION (calcd. from Table II-C)

[SM] M×10^{-5}	pH	ΔE kcal. mol^{-1}	ΔS (25°C) cal. deg^{-1}· mol^{-1}
None	4.7	14.25	−32.3
2.5	4.7	11.17	−38.4
2.5	0.8	9.21	−41.0

Summary

The catalytic activities of some inorganic compounds for the hydrogen peroxide oxidation of thiodiglycol (TDG) have been examined in aqueous media at 25°C and at pH 4.7. It has been found that the order of catalytic activities was: Na_2MoO_4, $Na_2WO_4 \gg H_2SeO_3 >$ NH_4VO_3, Na_2TeO_4, $UO_2(OAc)_2$, $Cu(OAc)_2$. The rates of oxidation using all these catalysts, except sodium molybdate, may be expressed as $v=k_2[H_2O_2][TDG]$.

The kinetics of this reaction has been

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[11] L. J. Csányi, *Acta. Chim. Acad. Sci. Hung.*, **14**, 269 (1958); *Chem. Abstr.*, **52**, 19647 (1958).

[12] J. J. Csányi, *Maggar Kém. Folyóirat*, **61**, 1 (1955); *Chem. Abstr.*, **49**, 15412 (1955).

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studied in detail, especially with the sodium molybdate (SM) catalyst, by means of iodometry. The oxidation in the range $[H_2O_2] > 2[SM]$ follows the pseudo-first-order kinetics: $v = k_1{}^c[SM][TDG]$. The rate at pH below 2 is several times faster than that at pH 3∼6, the energies of the activation at pH's below 2 and at 3∼6 being 9.21 and 11.2 kcal. mol^{-1} respectively. The oxidation in the range of $[H_2O_2] < 2[SM]$ follows the second-order kinetics: $v = k_2{}'$ [Active oxygen] [TDG]. The values of $k_2{}'$ were identical with the second-order rate constants obtained in the oxidation of thiodiglycol by yellow sodium peroxymolybdate. It is probable that dihydroperoxymolybdate, $HMoO_6{}^-$, produced rapidly from Na_2MoO_4 and hydrogen peroxide, oxidizes thiodiglycol. The increase in the rate with a decreasing pH may be due to the transformation of $HMoO_6{}^-$ to more active H_2MoO_6, since the Na_2MO_4-hydrogen peroxide system gave two different ultraviolet absorption maxima corresponding to $HMoO_6{}^-$ and H_2MoO_6 at pH 4.7 and 0.8 respectively.

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