Kinetics of the Selenium Dioxide-Catalyzed Hydrogen Peroxide Oxidation of Dimethylaniline in Aqueous Methanol

By Yoshiro OGATA and Iwao TABUSHI

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It has been reported that the oxidation of organic compounds with hydrogen peroxide was accelerated by selenium dioxide catalyst[1-3], but the mechanism of these reactions has not yet been clarified satisfactorily.

In general, there seem to be two main types of catalysts in organic oxidations with hydrogen peroxide; i. e., (i) the oxidation-reduction interaction between hydrogen peroxide and catalysts produces OH free radical, (e. g., in Haber-Weiss scheme[4] using Fenton's reagent) which can rapidly oxidize organic substances, and (ii) the combination of hydrogen peroxide with a catalyst gives peroxide as a relatively stable intermediate which is a more active oxidizing agent than hydrogen peroxide itself.

As the latter example, there are many organic and inorganic peroxides which oxidize organic substances without generating free radicals; for example, in the acid-catalyzed hydrogen peroxide oxidation of salicylaldehyde in acetic acid, intermediary peracetic acid reacted faster than hydrogen peroxide itself[5], and also Caro's acid, obtained from the reaction of hydrogen peroxide and sulfuric acid[6], was found to be a far more effective oxidant for tertiary amines than hydrogen peroxide itself[7,8].

As to the selenium dioxide-catalyzed reaction, there seems to be no direct evidence to decide which of these mechanistic types is operating. However, it has been reported that acrolein is oxidized to acrylic acid with neither hydroxylation nor polymerization, suggesting a non-radical mechanism for the reaction. But these peroxide intermediates may react by generating free radicals. For example, it has been considered that osmium, vanadium[9] and tungsten oxide[10] produced intermediary peroxides which could generate an OH radical during their reactions.

The present paper describes the rate data and a probable mechanism of the selenium dioxide-catalyzed hydrogen peroxide oxidation of dimethylaniline (DMA) in aqueous methanol in the presence of perchloric acid.

Experimental

Materials.—DMA and methanol were purified by duplicate fractional distillations.

Kinetic Procedures. — The reaction was carried out in brown flasks with ground-glass stoppers at 40, 50 and 60° (reflux condensers were used for runs at 60°). The solvent used was 50∼90 volume % aqueous methanol.

An aqueous methanol solution of DMA was mixed with an aqueous solution of hydrogen peroxide, selenium dioxide and perchloric acid after being thermostated at the reaction temperatures, thus the reaction was started. Aliquots were withdrawn at appropriate intervals of time to estimate the sum of the amount of selenium dioxide and hydrogen peroxide iodimetrically, using ammonium pyrophosphate as accelerator. Since no selenium was precipitated in the course of the reaction and the rate of selenic-acid formation was slow and also equilibrium amounts of intermediate complex were low as stated later, the amount of hydrogen peroxide was obtained as the difference of total oxidizing agents and the selenium dioxide initially present.

The hydrogen-peroxide content in a mixture of hydrogen peroxide and selenium dioxide was determined by introducing it into an aqueous solution of ceric sulfate and then titrating the excessive ceric ion potentiometrically with ferrous sulfate[11 12]. But this method could not be applied

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[1] C. W. Smith and R. T. Holm, *J. Org. Chem.*, **22**, 746 (1957).

[2] G. B. Payne and C. W. Smith, ibid., **22**, 1680 (1957).

[3] P. Seguin, *Compt. rend.*, **216**, 667 (1943).

[4] C. Walling, "Free Radicals in Solution", John Willey & Sons, Inc., New York, 1957, p. 566.

[5] Y. Ogata and I. Tabushi, *This Journal*.

[6] J. M. Monger and O. Redlich, *J. Phys. Chem.*, **60**, 797 (1956).

[7] E. Bamberger and L. Rudolf, *Ber.*, **35**, 1082 (1902).

[8] The rate constant in the neutral aqueous solution for Caro's acid oxidation of DMA is 10^7 times larger than that of hydrogen peroxide of triethylamine (S. D. Ross, *J. Am. Chem. Soc.*, **68**, 1484 (1946)).

[9] N. A. Milas, ibid., **59**, 2342 (1937).

[10] G. A. Bogdonov and T. I. Berkengeim, *Chem. Abstr.*, **49**, 2842 (1955); Zhur. Fiz. Khim., **26**, 1659 (1952).

[11] F. J. Hughes and D. S. Martin Jr., *J. Phys. Chem.*, **59**, 410 (1955).

[12] H. H. Willard and P. Young, *J. Am. Chem. Soc.*, **52**, 553 (1930).

in the presence of DMA, because a rapid oxidation of DMA took place.

Selenate and selenic acid were determined gravimetrically by precipitating lead selenate by the addition of aqueous lead nitrate[13a)] or acetate[13b)] in aqueous ethanol solution.

Reaction Products.—To examine the reaction products, nearly equimolar amounts of hydrogen peroxide and DMA were used. A mixture of 50 cc. of 1 M methanol solution of DMA, 10 cc. of 0.2 M aqueous solution of selenium dioxide, 6 cc. of 30% aqueous hydrogen peroxide and 2 cc. of concentrated perchloric acid (ca. 10 N) were introduced into a flask with a reflux condenser and heated to 50° for 20 hr. and then at 60° for 5 hr.

After methanol was distilled on a water bath, the residual aqueous solution was treated with potassium hydroxide until it became weakly basic. The solution was cooled and, after filtration of potassium perchlorate, freed from remaining DMA (ca. 1 g.) by extraction with ether.

The residual aqueous layer was neutralized and condensed under a reduced pressure, then poured into a boiling aqueous solution of picric acid (10 g. of picric acid in 200 cc. of water) to precipitate the picrate of DMA oxide[14)]. The precipitate consisted of yellow crystals (10.7 g.) and brown amorphous material (2.5 g.); the former, after several recrystalization from ethanol showed no depression of m. p. on admixture with the authentic sample[14)]. The brown material was also found to yield the same crystals but with difficulty. The total yield of the oxide amounted to 73% on the basis of the hydrochloride, obtained on the addition of hydrochloric acid into the picrate of DMA oxide.

Vinyl Polymerization. — DMA and peroxide (hydrogen peroxide or benzoyl peroxide) and/or selenium dioxide were added in acrylonitrile, thermostated at 50° in flasks with ground-glass stoppers, to start the reaction. After appropriate time, cold methanol was poured into the reaction mixture to stop the reaction and to precipitate the polymer produced. The precipitates obtained were filtered, dried and weighed. The results are summarized in Table VII.

TABLE I

THE EFFECT OF CONCENTRATION OF SELENIUM DIOXIDE ON k_0: $[DMA]=5/30$ M, $[HClO_4]=2/30$ M and $[H_2O_2]=$ca. 0.017 M

$[SeO_2]$, M	k_0, min^{-1}	$k_0/[SeO_2]$ l. mole min^{-1}
1/250	2.68×10^{-3}	0.670
2/750	1.76×10^{-3}	0.660
1/750	9.02×10^{-4}	0.676
1/1500	$4,37\times10^{-4}$	0.651

TABLE II

THE EFFECT OF CONCENTRATION OF DMA ON k_0 AT 40, 50 AND 60°

[DMA] M	$[HClO_4]$ M	$[SeO_2]$ M	k_0, min^{-1} $\times10^4$	$\frac{k_0}{[SeO_2]}$ l. mole min^{-1}
Temp. 40°				
5/30	2/30	1/750	4.74	0.356
7.5/45	2/45	1/1125	3.39	0.382
6/45	2.4/45	1/1125	2.74	0.308
5/45	2.0/45	1/1125	2.10	0.236
4/45	1.6/45	1/1125	1.97	0.222
4/45	1.6/45	2/1125	4.25	0.238
2/45	0.8/45	2/1125	2.59	0.143
Temp. 50°				
5/30	2/30	1/750	9.02	0.676
7/45	2.8/45	1/1125	5.40	0.607
6/45	2.4/45	1/1125	5.04	0.567
5/45	2.0/45	1/1125	4.30	0.484
4/45	1.6/45	1/1125	3.40	0.382
3/45	1.2/45	1/1125	3.06	0.344
2/45	0.8/45	1/1125	2.16	0.243
1/45	0.4/45	1/1125	1.60	0.180
Temp. 60°				
8/45	3.2/45	1/1125	12.4	1.396
6/45	2.4/45	1/1125	10.8	1.220
5/45	2.0/45	1/1125	9.82	1.105
4/45	1.6/45	1/1125	8.92	1.002
3/45	1.2/45	1/1125	7.55	0.850
2/45	0.8/45	1/1125	6.30	0.709
1/45	0.4/45	1/1125	5.11	0.576

Results and Discussion

Rate Equations. — The rate of the selenium dioxide-catalyzed hydrogen peroxide

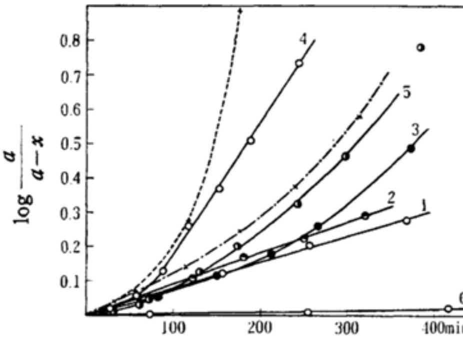

Fig. 1. The effects of acidity and substituent on the rate; solid lines correspond to DMA, where $[DMA]=5/30$ M, $[SeO_2]=1/750$ M and $[HClO_4]$: 1. 1/30 M, 2. 2/30 M, 3. 4/30 M, 4. 5/30 M, 6. 4/3 M; dotted line corresponds to *p*-methoxydimethylaniline where [amine]=2.25/30 M, $[SeO_2]=1/750$ M, $[HClO_4]=1.6/30$ M; broken line corresponds to *p*-methyldimethylaniline where [amine]=5/30 M, $[SeO_2]=1/750$ M, $[HClO_4]=2/30$ M.

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13) a) R. Ripan-Tilici, *Z. Anal. Chem.*, **102**, 28 (1935).
b) P. Spaw, *Bull. Soc. Chim. France*, [5], **3**, 159 (1936).

14) E. Bamberger and F. Tschirner, *Ber.*, **32**, 342 (1899).

oxidation of DMA was much faster than the uncatalyzed reaction with selenium dioxide or hydrogen peroxide alone. The rate of consumption of hydrogen peroxide was of first-order with hydrogen peroxide (equation 1) as shown in Fig. 1.

$$-\frac{\mathrm{d}[H_2O_2]}{\mathrm{d}t}=k_0[H_2O_2] \qquad (1)$$

The pseudo first-order rate constant k_0 was found to be proportional to the concentration of selenium dioxide, when the concentrations of DMA and perchloric acid were both kept constant (Fig. 2), while it was linearly related to the concentration of DMA in the range of 5/30∼1/45 M, when the concentration of selenium dioxide was constant and the apparent acidity of the solution estimated by pH meter was kept constant by changing the concentration of perchloric acid, where the ionic strength was controlled by the addition of neutral salt (sodium perchlorate) (see Fig. 3).

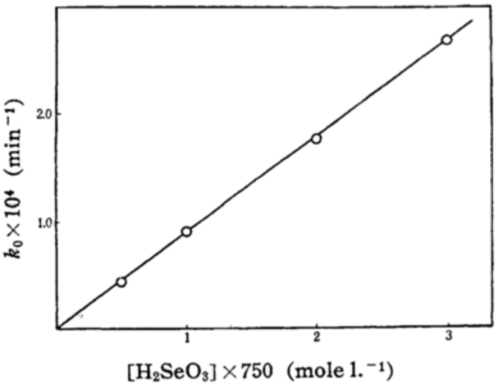


Fig. 2. The effect of concentration of selenium dioxide on the rate; where [DMA] = 5/30 M and $[HClO_4]$ = 2/30 M at 50°.

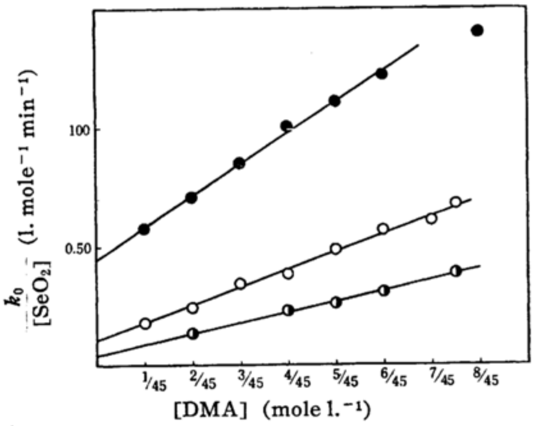


Fig. 3. The effect of concentration of DMA on the rate at various temperature.

Hence, rate equation 1 can be modified to

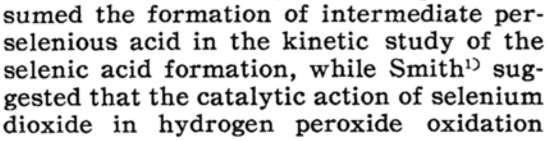
$$-\frac{\mathrm{d}[H_2O_2]}{\mathrm{d}t}=k[H_2O_2][SeO_2][DMA] + k'[H_2O_2][SeO_2] \qquad (2)$$

The first term of equation 2 may correspond to the rate-determining attack of an intermediate comples between selenium dioxide and hydrogen peroxide on DMA molecule[15].

The reaction is different from the peracetic acid oxidation[4] in that the main route of complex formation can not be a slow step, since no induction period was observed and the difference between the rates with variation of the time of allowing the mixture of hydrogen peroxide and selenium dioxide to stand before a solution of DMA was added.

The rate of the peroxide consumption in aqueous methanol in the absence of DMA was found to be considerably less than the second term of equation 2 (see Table VIII), thus the second term of equation 2 should mainly express a reaction involving the participation of DMA and only partly a reaction independent of DMA. The former reaction may be a slow reaction between hydrogen peroxide and selenium dioxide to produce an intermediate complex II, which reacts with DMA rapidly.

Hence two complexes I and II may be possible, which respectively react with DMA slowly and rapidly.



where $k_4 \gg k_2 \gg k_1$, so that the formation of the complex II is the rate determining step in the lower reaction.

Active Oxidizing Species.—Hughes[11] assumed the formation of intermediate perselenious acid in the kinetic study of the selenic acid formation, while Smith[1] suggested that the catalytic action of selenium dioxide in hydrogen peroxide oxidation

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[15] Although the possibilities of the complex formation between H_2O_2 and DMA, or SeO_2 and DMA, followed by the oxidation by the other oxidizing agent may be conceivable, these mechanisms are less probable, since the accelerating effect of selenium dioxide on the H_2O_2 oxidation is not limited to amines but was observed also in aldehydes[1], ketones[2] and olefins[3].

might be due to the formation of selenic acid or its higher peroxides.

To clarify this point, we examined the participation of selenate in the reaction. The reaction with sodium selenate instead of hydrogen peroxide and selenium dioxide or that using sodium selenate and hydrogen peroxide instead of hydrogen peroxide and selenium dioxide was fairly slow (Table III, V), hence selenic acid or a complex of selenic acid and peroxide can not be an active species, I or II. This conclusion is in accord with our observation that the rate of selenic-acid formation estimated cerimetrically was slower than the main reaction, and also with Hughes' data[11].

TABLE III

THE RATE OF DISAPPEARANCE OF SELENATE IN THE OXIDATION OF DMA WITH SELENATE ALONE, ESTIMATED BY GRAVIMETRY OF LEAD SELENATE: [DMA] = 1/5 M, [Na_2SeO_4] = 735 mg. in 50 cc. and [$HClO_4$] = 4/50 M at 50°

Time, min.	0	88	262	394
$PbSeO_4$, mg.	117.0	116.2	117.3	115.8

TABLE IV

THE RATE OF DISAPPEARANCE OF HYDROGEN PEROXIDE IN A MIXTURE OF HYDROGEN PEROXIDE AND SELENIUM DIOXIDE BY MEANS OF BACK TITRATION OF EXCESS CERIC ION WITH AN AQUEOUS FERROUS SULFATE SOLUTION: 1 m. mole of H_2O_2, 5 m. mole of SeO_2 and 4 m. mole of $HClO_4$ were mixed with 15 cc. of water and 28 cc. of methanol

Time, min.	0	110	191	∞
$FeSO_4$ required	1.37	1.91	2.53	27.90[a]

a) The theoretical vol. of $FeSO_4$ necessary for the complete disappearance of hydrogen peroxide.

TABLE V

THE EFFECTS OF ADDED MATERIALS ON THE RATE: [SeO_2] = 1/750 M, [DMA] = 5/30 M and [$HClO_4$] = 2/30 M at 50°

Added material		$k_0 \times 10^3$, min^{-1}
Na_2SeO_4	100 mg. in 30 cc. of solution	1.13
Na_2SeO_4	46 mg. in 30 cc. of solution	1.02
Na_2SeO_4	25 mg. in 30 cc. of solution	0.951
Na_2SeO_4	0 mg.	0.902[b]
$NaClO_4$	1/30 M	0.895
Hydroquinone	2.5 mg. in 30 cc. of solution	0.896
None	time of standing was 0 min.[a]	0.893
None	time of standing was 60 min.	0.898

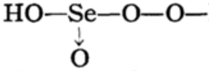
a) In the other runs, time of standing was 15~30 min.

b) In the absence of selenium dioxide, the rate was considerably low.

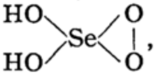
When besides hydrogen peroxide and selenium dioxide a large amount of sodium selenate was added, a small increase in the rate was observed and the increment was proportional to the concentration of sodium selenate added (Table V). But no salt effect was observed with the addition of sodium perchlorate (Table V). This fact suggests that the increment may be due to the selenium dioxide existing in a selenate solution.

The rate of hydrogen peroxide consumption in the absence of DMA was followed cerimetrically as well as iodimetrically, but no remarkable change in concentration of hydrogen peroxide was observed. This fact suggests that concentrations of I and II are both very small in their equilibrium states.

It may well be assumed that I and II are a kind of peroxide such as



$HO{-}\underset{\underset{O}{\downarrow}}{Se}{-}O{-}O{-}H$ (perselenious acid) or



, but no information of I and II could be obtained by us by means of ultraviolet absorption spectroscopy.

Effects of Acidity and Substituents.—Rates of the reaction satisfied equation 2 only at a relatively low concentration of perchloric acid (less than 0.1 M where DMA 5/30 M). In this range, the k_0 values was found to increase with increasing concentration of the acid. But at higher a concentration of the acid (more than 4/30 M where DMA 5/30 M), a tendency of induced reaction was observed in the early stage (before reaching the pseudo-first order kinetics), and it became remarkable as the acidity increased. Typical examples are shown in Fig. 1. This behavior made the quantitative investigation of the effect of acidity difficult, but qualitatively, the rate began to decrease markedly through maximum ([$HClO_4$] ≒ 5/30 M = [DMA]) as the acidity increased. This decrease of rate may be ascribed to a decrease in the concentration of DMA by the protonation. The first small increase of the rate, inexplicable by the change of the concentration of DMA, may be due to the suppression of the dissociation of acids I and/or II (equation 4) just as discussed in the case of Caro's acid[16] if I and II have

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[16] Y. Ogata and I. Tabushi, This Bulletin, 31, 969 (1958).

their pK_a values near the acidity of maximum rate.

$$\mathrm{DMA}+\mathrm{H}^+ \overset{\text{mobile}}{\rightleftarrows} \mathrm{DMAH}^+ \qquad (3)$$

$$\mathrm{HO_2SeOOH} \overset{\text{mobile}}{\rightleftarrows} \mathrm{HSeO_4}^- + \mathrm{H}^+ \qquad (4)$$

$$\mathrm{DMA}+\mathrm{HO_2SeO_2H} \xrightarrow{\text{slow}} \text{prod.} \qquad (5)$$

The rate of the oxidation of *p*-methyl- and *p*-methoxydimethyl-anilines showed a tendency toward induced reaction even at the low acidity, so that their kinetics could not be followed, but, qualitatively these substituents increased the rate, which supports the above electrophilic substitution mechanism.

Other Factors Influenceing the Rate.—Rate measurements carried out at 40, 50 and 60° gave linear relations of k_0 vs. DMA (Fig. 3) and thus gave the values of k and k' at these temperatures. From these values activation energies and log PZ were calculated, but as to k', Arhenius plot did not give a straight line, probably because the second term of equation 2 contained more than one reaction (for example, selenic acid formation, spontaneous decomposition of hydrogen peroxide and oxidation of methanol). Activation energies and other data were summarized in Table VIII.

TABLE VI

THE EFFECT OF SOLVENT COMPOSITION ON THE RATE. TEMP. 50° $[\mathrm{SeO_2}]=1/750$ M

vol. % of methanol	[DMA], M	k_0, min^{-1} $\times 10^4$
50	3/30	4.13
66.7	3/30	6.40
66.7	5/30	9.02
80	5/30	14.8
90	5/30	24.2
95	5/30	28.4

TABLE VII

POLYMERIZATION OF ACRYLONITRILE ADDED WITH VARIOUS REAGENTS ACRYLONITRILE; 5 cc.

BPO mg.	DMA mg.	30% $\mathrm{H_2O_2}$	$\mathrm{SeO_2}$ mg.	Time min.	Polymer obtained mg.
20	60	0	0	2.2	0
20	60	0	0	4.0	24.9
20	60	0	0	11.0	598.5
20	60	0	2	300.0	0[c]
20	60	0	0	4.5	86.8
0	60	2 drops	0	2 days	0
0	60	2 drops	2	2 days	0
20	60	0[a]	0	4.0	46.0
0	60	2 drops[b]	0	2 days	0
0	0	2 drops	2	2 days	0
0	0	0	0	Several days	0

a) 0.1 cc. of water was added.
b) 2 drops of conc. $\mathrm{HClO_4}$ were added.
c) The solution was slightly turbid.

TABLE VIII

TEMPERATURE COEFFICIENTS, ACTIVATION ENERGY AND ACTIVATION ENTROPY OF k AND k'

$k_{60}/k_{50}=5.95(\mathrm{l.}^2\ \mathrm{mole}^{-2}\ \mathrm{min}^{-1})/3.36(\mathrm{l.}^2\ \mathrm{mole}^{-2}\ \mathrm{min}^{-1})=1.74$
$k_{50}/k_{40}=3.36/1.93=1.77$
$\Delta H^{\ddagger}(40 \text{ and } 50^\circ)=11.50$ kcal./mole
$\Delta H^{\ddagger}(50 \text{ and } 60^\circ)=11.86$ kcal./mole
av. $\Delta H^{\ddagger}=11.68$ kcal./mole
$\Delta S^{\ddagger}(50^\circ)=11.8$ E. U.
$k'_{60}/k'_{50}=4.02\ (0.446/0.110)$[a]
$k'_{50}/k'_{40}=2.45\ (0.110/0.045)$[a]

a) The unit of the constants is l. mole^{-1} min^{-1}.

The addition of water to methanol markedly decreases the rate (Table VI). This marked solvent effect may partly be attributed to the participation of water in the formation of the intermediate (perselenious acid), since it was reported[11] from the oxygen isotope exchange study that the formation of perselenious acid from selenious acid was attained through dehydration of selenious acid as shown in equations 6 and 7,

$$\mathrm{H_2SeO_3} \rightleftarrows \mathrm{H_2O}+\mathrm{SeO_2} \qquad (6)$$

$$\mathrm{SeO_2}+\mathrm{H_2O_2} \rightleftarrows \mathrm{HO_2SeOOH} \qquad (7)$$

and partly to the suppression of the dissociation of the attacking acids I and/or II.

Possibility of Free Radical Mechanism.—The observation that sulfur dioxide and hydroperoxide initiated vinyl polymerization[17]

$$\mathrm{ROOH}+\mathrm{SO_2} \rightarrow \mathrm{RO}\cdot + \cdot[\mathrm{SO_3H}] \qquad (8)$$

may suggest the possibility of a free radical mechanism of the reaction of selenium dioxide with hydrogen peroxide. But the addition of a small amount of hydroquinone has no appreciable effect on the rate at lower acidity of the solution where no induced reaction has been observed[18].

Furthermore, the tests of the polymerization of acrylonitrile was carried out, indicating that the free radical mechanism was not operating. The polymerization of acrylonitrile was tested in the presence

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[17] E. I. Thinyakova, B. A. Dolgoplosk and V. N. Reich, *Izvestia A. N. SSSR*, **1957**, 851.

[18] At higher acidities, hydroquinone markedly consumed hydrogen peroxide under these reaction conditions.

of BPO+DMA, (hydrogen peroxide+DMA), (hydrogen peroxide+selenium dioxide+DMA), (hydrogen peroxide+selenium dioxide), (hydrogen peroxide+selenium dioxide+DMA+perchloric acid) or (BPO+DMA+selenium dioxide), where BPO means benzoyl peroxide. In most of these experiments, no polymerization was observed. But two exception were observed; i. e., the reagent (BPO+DMA) could easily initiate the polymerization in accord with previous investigators[19], and the reagent (BPO+DMA+selenium dioxide) initiated it only with great difficulty.

These observations indicate that (i) the interaction of hydrogen peroxide and DMA can not produce any effective free radical; (ii) selenium dioxide has an effective inhibitory action for the radical polymerization; (iii) I or II can not participate in the radical chain.

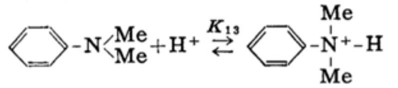
The Over-all Reaction Mechanism.—The results obtained above suggest a set of steps for the over-all reaction.

$$H_2SeO_3 \overset{K_9}{\rightleftarrows} SeO_2+H_2O \quad (9)$$

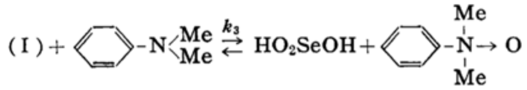
$$SeO_2+H_2O_2 \overset{K_{10}}{\rightleftarrows} HO_2SeOOH\ (I) \quad (10)$$

$$H_2SeO_3+H_2O_2 \underset{k_2}{\overset{k_1}{\rightleftarrows}} \text{complex (II)} \quad (11)$$

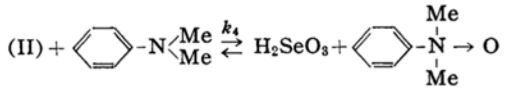
$$(I) \overset{K_{12}}{\rightleftarrows} HO_2SeO_2^-+H^+ \quad (12)$$



$$C_6H_5\text{-}N(Me)_2+H^+ \overset{K_{13}}{\rightleftarrows} C_6H_5\text{-}N^+(Me)_2\text{-}H \quad (13)$$



$$(I)+C_6H_5\text{-}N(Me)_2 \overset{k_3}{\rightleftarrows} HO_2SeOH+C_6H_5\text{-}N(Me)_2\rightarrow O \quad (14)$$



$$(II)+C_6H_5\text{-}N(Me)_2 \overset{k_4}{\rightleftarrows} H_2SeO_3+C_6H_5\text{-}N(Me)_2\rightarrow O \quad (15)$$

K's denote mobile equilibrium constants and k's denote rate constants, of which k_1 and k_3 correspond to those of rate-determining steps via complex II and I, respectively.

Summary

The selenium dioxide-catalyzed oxidation of dimethylaniline with hydrogen peroxide was investigated kinetically at 40∼60° in 50∼95 volume % aqueous methanol. The rate of the consumption of hydrogen peroxide at constant acidity of the reaction mixture was expressed as

$$v=k[H_2O_2][SeO_2][\text{Dimethylaniline}] + k'[H_2O_2][SeO_2]$$

The first term of this equation seems to correspond to the rate of a reaction between dimethylaniline and a complex (I) produced rapidly from selenium dioxide and hydrogen peroxide, while the second term corresponds mainly to a slow reaction between selenium dioxide and hydrogen peroxide to yield the complex (II) followed by a rapid reaction with dimethylaniline. The energy of activation was 11.7 kcal.

When perchloric acid was added to the reaction mixture, the pseudo-first-order rate constant with respect to hydrogen peroxide first increased and then decreased via a maximum, which was explicable by the assumptions of the dissociation of the intermediate and the protonation of dimethylaniline. Electron-releasing groups tended to increase the rate. An increase of the water content in the solvent methanol decreased the rate. There was no evidence for the radical mechanism under these experimental conditions.

Department of Industrial Chemistry
Faculty of Engineering
Kyoto University
Sakyo-ku, Kyoto

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[19] e. g., L. Horner and E. Schwenk, *Ann.*, **566**, 69 (1949); L. Horner, *Angew. Chem.*, **62**, 359 (1950), *J. Polymer Sci.*, **18**, 438 (1955); M. Imoto, T. Otsu and K. Kimura, ibid., **15**, 495 (1955).