

THE REVIEW OF PHYSICAL CHEMISTRY OF JAPAN, VOL. 36, No. 2, 1966

THE EFFECT OF PRESSURE ON THE RATE OF  
THE BENZIDINE REARRANGEMENTII. *o, o'*-Hydrazotoluene

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The rates of the acid-catalysed rearrangement and of the oxidation of *o, o'*-hydrazotoluene in aqueous ethanol (96 vol. % EtOH) have been measured at pressures up to 3000 kg/cm<sup>2</sup>.

The rates of the rearrangements of one-proton and two-proton mechanisms were increased by pressure. In the two-proton mechanism, as a small negative volume of activation and a positive entropy of activation are observed, it seems likely that the second proton transfer is a pre-equilibrium.

The oxidation accompanied with the rearrangement in acidic solution includes two concurrent reactions: one is independent of [H<sup>+</sup>] and the other is inversely proportional to [H<sup>+</sup>], both being strongly accelerated by pressure. Because of the large negative volumes of activation, it is implied that each reaction goes through an ionic activated complex.

## Introduction

In 1922, Jacobson reviewed the benzidine rearrangement,<sup>1)</sup> but kinetic studies were scarcely carried out.

In 1950, Hammond and Shine<sup>2)</sup> found that the rearrangement of hydrazobenzene is of the second order in acid concentration, but since Carlin and Odioso discovered in 1953<sup>3)</sup> the abnormality that the rearrangement of *o, o'*-hydrazotoluene had an order in acid, not of 2 but of 1.6, kinetic studies have been carried out vigorously, and with the accumulation of new informations for the rearrangement, various reaction mechanisms have been suggested.

Because the plot of logarithm of *k*, where *k* represents apparent rate constant of hydrazobenzene rearrangement, against Hammett's acidity function ( $-H_0$ ), is linear with a slope of 2.1 and *k* was 4.8 times larger with D<sub>3</sub>O<sup>+</sup> than with H<sub>3</sub>O<sup>+</sup>, Ingold and his co-workers<sup>4)</sup> suggested that not only the first but the second proton transfer is a pre-equilibrium, and further, each reaction went through a polar-transition-state.

On the contrary, the rate measurement of the rearrangement in weak acid studied by Hammond,<sup>5)</sup>

(Received January 15, 1967)

1) P. Jacobson, *Ann.*, **428**, 76 (1922)

2) G. S. Hammond and H. J. Shine, *J. Am. Chem. Soc.*, **72**, 220 (1950)

3) R. B. Carlin and R. C. Odioso, *J. Am. Chem. Soc.*, **76**, 100 (1954)

4) C. A. Bunton, C. K. Ingold and M. M. Mhala, *J. Chem. Soc.*, 1906 (1957)

and the  $\pi$ -complex theory postulated by Dewar in 1945,<sup>6)</sup> although modified frequently, were opposed to Ingold's scheme in the point that the second proton transfer is a rate-determining step.

But evidently, the order in acid of the rearrangement of *o, o'*-hydrazotoluene increases with acidity in the wide range as proved by Ingold<sup>7)</sup> and present authors. Therefore, Dewar's theory is inconsistent with the kinetic results, with respect to *o, o'*-hydrazotoluene, at least.

Up to now, benzidine rearrangement has been entirely studied at atmospheric pressure, and the rate study under high pressure could not been found except the previous report<sup>8)</sup> showing that the rate of rearrangement of hydrazobenzene is slightly retarded by pressure. In the present experiment, the authors studied the effect of pressure on the rate of rearrangement of *o, o'*-hydrazotoluene and discussed the reaction scheme from the volumes of activation of the rearrangement.

Although there has already been a study<sup>9)</sup> at 1 atm for the oxidation of hydrazobenzene in alkaline solution in the presence of dissolved oxygen, there has not yet been any study of the oxidation of hydrazo-compounds in acidic solution. The authors also studied the pressure effect on the oxidation reaction.

## Experimentals

### Materials

G. R. grade reagent of 99.5 vol.-% EtOH, lithium chloride and hydrochloric acid were used for this work. *o, o'*-Hydrazotoluene (B) was synthesized by Cohen's method,<sup>10)</sup> recrystallized by 95 vol.-% EtOH and washed with petroleum ether, to get white crystal, m. p. 165°C. *o, o'*-Azotoluene (A) was synthesized by melting (B), and washed with hydrochloric acid, recrystallized from EtOH, to get red crystal, m. p. 54.6°C. *o, o'*-Tolidine (P) was recrystallized from alcohol, and its molecular extinction coefficients agreed with those obtained by Carlin.<sup>5)</sup>

### Procedure

HCl-LiCl aqueous solution of 0.42 ml/ was added to 10ml/ of 99.5 vol.-% EtOH. In the present experiment, the concentrations of the components in this aqueous solution were controlled so as to give the available concentrations after mixing, *i. e.* for EtOH, 96 vol.-%, and for hydrochloric acid and ionic strength, the fixed values considering the compressibility of EtOH. The concentration of dissolved oxygen was estimated to be about  $2 \times 10^{-3}$  mole/l.

Keeping this solution in the thermostat at constant temperature, a scanty amount of (B) was added. In the case of 1 atm runs, the solution was maintained in the thermostat throughout each run, and in the case of high pressure runs, an aliquot of this solution which was poured in a glass syringe was put into the cylindrical pressure vessel. The initial concentration of (B) was estimated to be about

5) M. D. Cohen and G. S. Hammond, *J. Am. Chem. Soc.*, **75**, 880 (1953)

6) M. J. S. Dewar, *Nature*, **156**, 784 (1945)

7) D. V. Banthorpe, C. Ingold and J. Roy, *J. Chem. Soc.*, 2436 (1962)

8) J. Osugi and T. Hitouji, *This Journal*, **34**, 88 (1964)

9) D. V. Blackadder and S. C. Hinshelwood, *J. Chem. Soc.*, 2898 (1957)

10) J. B. Cohen, "Practical Organic Chemistry", Macmillan, London (1949), p. 162

$5 \times 10^{-5} \sim 10^{-4}$  mole/l and the high pressure equipment employed was the same as that reported previously.<sup>6)</sup> As soon as the available pressure was fixed, 1~2 ml of the solution which had been maintained in the thermostat was neutralized by an ethanolic solution of sodium hydroxide, and the initial concentrations of (B), (A) and (P) were determined from the absorbances at 245, 285 and 320 m $\mu$ . After an appropriate time interval, pressure was withdrawn and the reaction was pursued by analysing each component in the reaction mixture by the same way.

The values of molecular extinction coefficients used for analysis are shown in Table 1.

Table 1 Molecular extinction coefficients ( $\epsilon \times 10^{-3}$ )

Compound	245 m $\mu$	285 m $\mu$	320 m $\mu$
<i>o, o'</i> -hydrazotoluene	20.1	4.03	0.123
<i>o, o'</i> -tolidine	3.94	21.8	5.60
<i>o, o'</i> -azotoluene	7.18	6.30	12.7

## Results

In this work, as the reaction was studied in the presence of dissolved oxygen, the rearrangement and oxidation proceeded concurrently. But the sum of each concentration of (B), (P) and (A) was

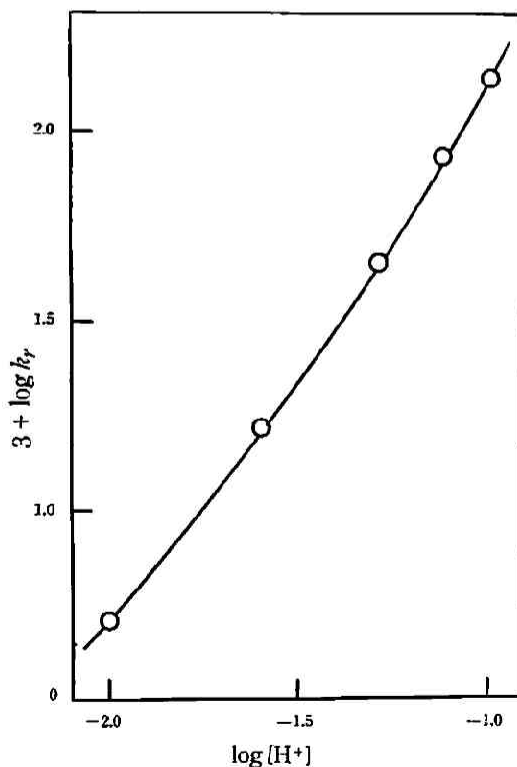


Fig. 1 Plot of logarithms of apparent first order rate constants against those of  $[H^+]$ , 20°C,  $\mu=0.1$  in 96 vol.% EtOH

maintained constant within the error of 1%. Therefore, the rearrangement and oxidation products are only (P) and (A), respectively. These results were consistent with Ingold's<sup>2)</sup> and Carlin's.<sup>3)</sup>

As the overall rate of disappearance of (B) was proportional to [B], the apparent rate constant of the rearrangement,  $k_r$ , and that of the oxidation,  $k_{ox}$ , were obtained by dividing the overall rate constant of the decrease of (B), into the ratio of [P] to [A].

$$-\frac{d}{dt}[B]_{obs} = (k_r + k_{ox})[B]_{obs}. \quad (1)$$

### Rearrangement

In the case of ionic strength,  $\mu=0.1$ , the curve of Fig. 1 was obtained by plotting  $\log k_r$  against  $\log [H^+]$ , the slope of which increased with acidity. And the plots of  $k_r/[H^+]$  against  $[H^+]$  give straight lines as shown in Fig. 2. The result is indicated by the following relation.

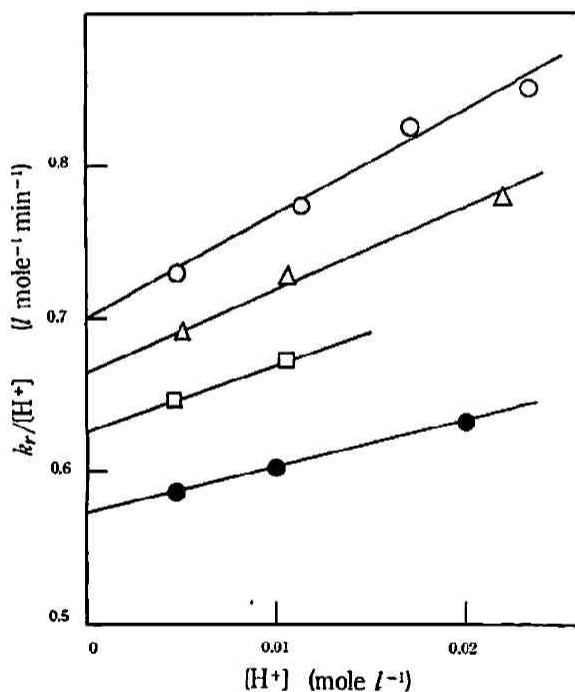


Fig. 2 Relationship between the apparent first order rate constants of rearrangement and  $[H^+]$  (24.7°C)  
Pressure (kg/cm<sup>2</sup>): ● 1, □ 1000, △ 2000, ○ 3000

$$\frac{k_r}{[H^+]} = k_1 + k_2[H^+] \quad (2)$$

Therefore, it is evident that two reactions occur concurrently; one is of the first order in  $[H^+]$  (one-proton mechanism), and the other is of the second order in  $[H^+]$  (two-proton mechanism). This event is consistent with the results observed by Ingold. From Fig. 2, the rate constant  $k_1$  of one-proton mechanism and the rate constant  $k_2$  of two-proton mechanism can be obtained (Table 2).

Fig. 3 illustrates the plots of  $\log(k^p/k^1)$  against  $P$  for  $k_1$  and  $k_2$ , where  $k^1$  and  $k^p$  are rate constants at 1 atm and  $P$  kg/cm<sup>2</sup>, respectively. The slopes of these curves were extrapolated to  $P=0$ , and by

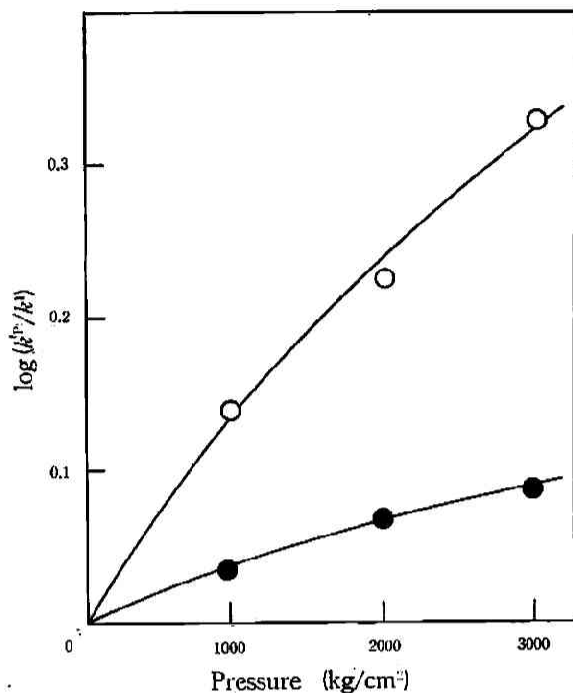


Fig. 3 Dependence of the rates of the rearrangement on pressure (24.7°C)

●  $k_1$   
○  $k_2$

Table 2 Rate constants for rearrangement ( $\mu=0.02$ )

Temp. (°C)	Pressure (kg/cm <sup>2</sup> )	$k_1$ (l mole <sup>-1</sup> min <sup>-1</sup> )	$k_2$ (l <sup>2</sup> mole <sup>-2</sup> min <sup>-1</sup> )
20.0	1	0.37	1.8
20.0	3000	0.396	4.2
24.7	1	0.573	3.0
24.7	1000	0.626	4.4
24.7	2000	0.669	5.0
24.7	3000	0.703	6.4
28.5	1	0.943	5.4
28.5	3000	1.17	12.5
33.0	1	1.62	8.0

using equation (3) the volumes of activation of one-proton,  $\Delta V_1^\ddagger$ , and of two-proton,  $\Delta V_2^\ddagger$ , were calculated. Further, the energies of activation  $E_1^\ddagger$ ,  $E_2^\ddagger$  and the entropies of activation  $\Delta S_1^\ddagger$ ,  $\Delta S_2^\ddagger$  were obtained at each pressure (Table 3).

Table 3 Kinetic data for rearrangement (24.7°C,  $\mu=0.02$ )

	Volume of activation (cc mole <sup>-1</sup> )	Pressure (kg/cm <sup>2</sup> )	Energy of activation $E^\ddagger$ (kcal mole <sup>-1</sup> )	Entropy of activation $\Delta S^\ddagger$ (cal mole <sup>-1</sup> deg <sup>-1</sup> )
$k_1$ (one-proton)	$\Delta V_1^\ddagger$ , -2.5	1	20.9	+0.6
		3000	21.6	+3.3
$k_2$ (two-proton)	$\Delta V_2^\ddagger$ , -7.2	1	21.0	+4.1
		3000	21.9	+8.9

$$\frac{\partial}{\partial P} \ln k = -\frac{\Delta V^\ddagger}{RT} \quad (3)$$

### Oxidation

The results shown in Fig. 4 can be interpreted by the next relations, (4) or (4'), and the numerical values of  $k_{01}$  and  $k_0$  were given (Table 4).

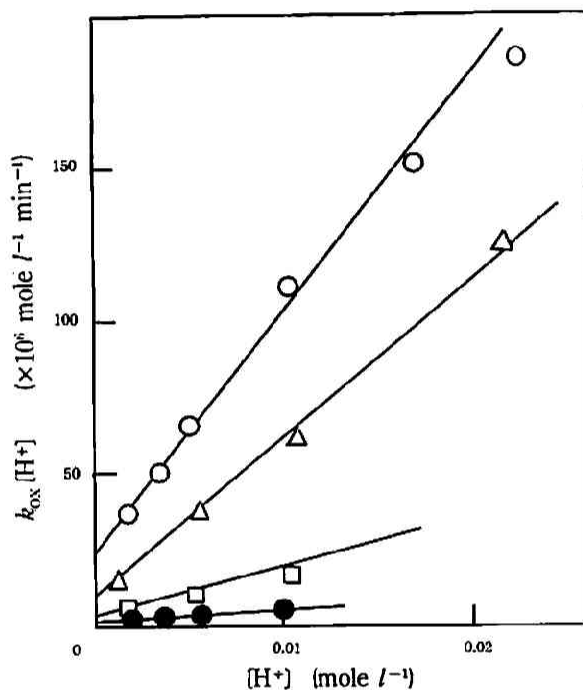


Fig. 4 Relationship between the apparent first order rate constants of oxidation and  $[H^+]$  (24.7°C)

Pressure (kg/cm<sup>2</sup>): ● 1, □ 1000, △ 2000, ○ 3000

$$k_{ox}[H^+] = k_0[H^+] + k_{01} \quad (4)$$

$$k_{ox} = k_0 + \frac{k_{01}}{[H^+]} \quad (4')$$

Table 4 Rate constants for oxidation ( $\mu = 0.02$ )

Temp. (°C)	Pressure (kg/cm <sup>2</sup> )	$k_{01} \times 10^6$ (mole l <sup>-1</sup> min <sup>-1</sup> )	$k_0 \times 10^4$ (min <sup>-1</sup> )
20.0	1	0.25	2.3
20.0	2000	5.0	26
20.0	3000	10	63
24.7	1	0.5	3.0
24.7	1000	3.0	12
24.7	2000	10	50
24.7	3000	23	80
28.5	1	1.0	5.0
28.5	3000	50	120
33.0	1	4.0	8.5

Fig. 5 shows the dependence of  $k_0$  and  $k_{01}$  on pressure, and  $\Delta V_0^\ddagger$  and  $\Delta V_{01}^\ddagger$  can be obtained by the way mentioned above, and the energies of activation  $E_0^\ddagger$ ,  $E_{01}^\ddagger$  were also obtained. These results are shown in Table 5.

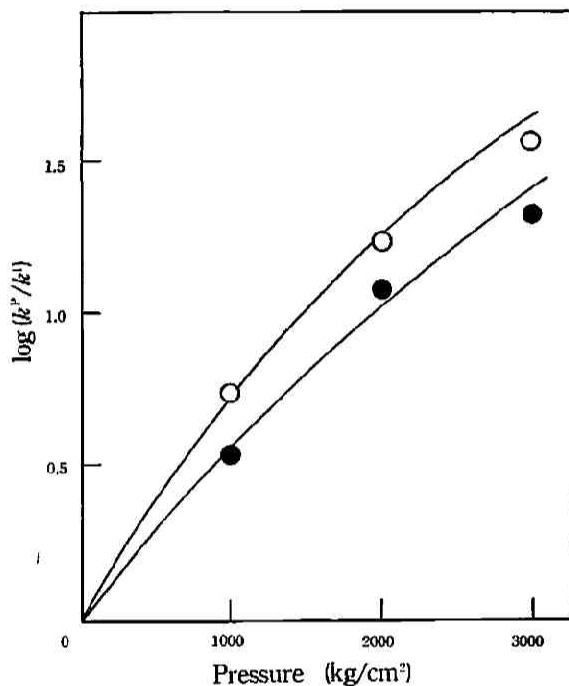


Fig. 5 Dependence of the rates of the oxidation on pressure (24.7°C)

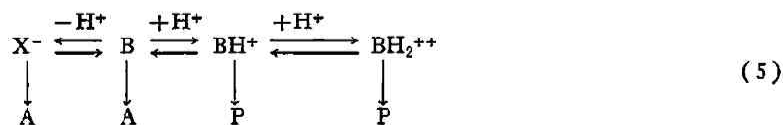
●  $k_0$   
○  $k_{01}$

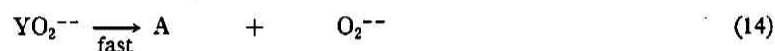
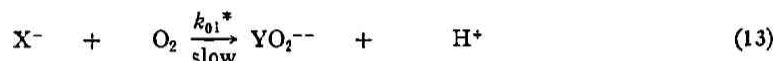
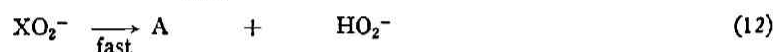
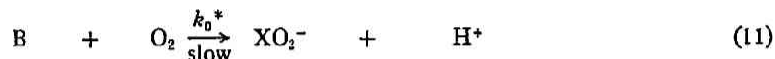
Table 5 Kinetic data for oxidation (24.7°C,  $\mu=0.02$ )

	Volume of activation (cc mole <sup>-1</sup> )	Pressure (kg/cm <sup>2</sup> )	Energy of activation $E^\ddagger$ (kcal mole <sup>-1</sup> )
$k_0$ (non-proton)	$\Delta V_0^\ddagger$ , -40	1	19
		3000	14.6
$k_{01}$	$\Delta V_{01}^\ddagger$ , -50	1	37
		3000	33

### Discussion

From the events of Figs. 2 and 4, it can be easily understood that not only the rearrangement reaction, but also the oxidation reaction proceeds through two concurrent processes respectively. As the general reaction scheme, the following can be proposed.





where  $X^-$  and  $Y^{--}$  are the substances which are produced by the loss of one and two protons from B.

### Rearrangement

When the reaction (6) is a pre-equilibrium, assuming the stationary state with respect to  $[BH_2^{++}]$ , the rate of rearrangement is given by equation (15),

$$\frac{d}{dt}[P] = k_1^* K_1 [H^+] [B]_{\text{obs}} + \frac{k_2^* k' K_1 [H^+]^2}{k'_{-1} + k_2^*} [B]_{\text{obs}}, \quad (15)$$

where  $[B]_{\text{obs}}$  is the concentration of  $[B]$  observed after the neutralization of reacting solution with sodium hydroxide, that is,

$$[B]_{\text{obs}} = [B] + K_1 [H^+] [B] + \frac{k' K_1 [H^+]^2}{k'_{-1} + k_2^*} [B]. \quad (16)$$

As it is assumed that the second and third terms of the right hand side of equation (16) are both negligible,  $[B]_{\text{obs}}$  is nearly equal to  $[B]$ .

From equation (15),

i) if  $k'_{-1} \gg k_2^*$ , i.e., equation (9) is a rate-determining step,

$$\frac{d}{dt}[P] = k_1^* K_1 [H^+] [B]_{\text{obs}} + k_2^* K' K_1 [H^+]^2 [B]_{\text{obs}} \quad (17)$$

where  $K' = k' / k'_{-1}$ ,

ii) if  $k' < k'_{-1} \ll k_2^*$  i.e., (7) is a rate-determining step,

$$\frac{d}{dt}[P] = k_1^* K_1 [H^+] [B]_{\text{obs}} + k' K_1 [H^+]^2 [B]_{\text{obs}}. \quad (18)$$

Each of equations (17) and (18) can explain the kinetic order observed, but neither can demon-



strate which the rate-determining step is.

Considering equations (17) and (18), it is evident that these apparent volumes of activation of one-proton mechanism,  $\Delta V_1^\ddagger$ , and of two-proton mechanism,  $\Delta V_2^\ddagger$  are represented as follows,

$$\Delta V_1^\ddagger = \Delta V_{K_1} + \Delta^*V_1^\ddagger \quad (19)$$

$$\Delta V_2^\ddagger = \Delta V_{K_1} + \Delta V_{K'} + \Delta^*V_2^\ddagger \quad (20)$$

or 
$$\Delta V_2^\ddagger = \Delta V_{K_1} + \Delta V_{K'} \quad (21)$$

where  $\Delta V_{K_1}$  and  $\Delta V_{K'}$  are the changes of the volumes in equilibria (6) and (7), respectively, and  $\Delta^*V_1^\ddagger$ , for example, represents the volume of activation accompanying the step (8).

Assuming that  $\Delta V_{K_1}$  is small negative,<sup>11)</sup> it seems likely that  $\Delta^*V_1^\ddagger$  scarcely contributes to the apparent volume of activation  $\Delta V_1^\ddagger$ , because the observed value is small negative,  $-2.5$  cc/mole.

In the two-proton mechanism, it may be assumed that in equation (20) the contribution of  $\Delta^*V_2^\ddagger$  to  $\Delta V_2^\ddagger$  is as small as that of  $\Delta^*V_1^\ddagger$  to  $\Delta V_1^\ddagger$ , and so, from equations (19), (20) and (21),

$$\Delta V_2^\ddagger - \Delta V_1^\ddagger = \Delta V_{K'} \quad \text{or} \quad \Delta V_{K'}$$

As this difference can be obtained from the experimental results,

$$\Delta V_2^\ddagger - \Delta V_1^\ddagger = (-7.2) - (-2.5) = -4.7 \text{ cc/mole,}$$

it is not unreasonable to regard the value,  $-4.7$  cc/mole, as the same as the value of the volume change of protonation of aniline in aqueous acidic solution, as observed by Hamann.<sup>11)</sup>

Then, it seems likely that the second proton transfer is a pre-equilibrium. The fact that the observed entropies of activation are not negative shows that perhaps there might not be included a slow proton transfer step, because if  $\text{H}_3\text{O}^+$  and substrate were bound together in the transition state, the entropies of activation would probably be negative.<sup>12)</sup>

### Oxidation

Considering the scheme mentioned above, the following rate equation can be derived for the oxidation reaction,

$$\frac{d}{dt}[A] = k_0^*[O_2][B]_{\text{obs}} + \frac{k_{01}^*K_2[O_2]}{[H^+]^2}[B]_{\text{obs}} \quad (22)$$

and it can explain the observed kinetic order.

Applying Hinshelwood's postulate<sup>9)</sup> for the oxidation reaction of hydrazobenzene in the presence of dissolved oxygen in alkaline solution to the case of hydrazotoluene, the elementary steps could be described as follows,



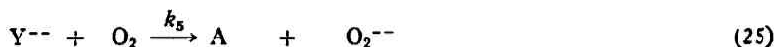
11) S. D. Hamann and W. Strauss, *Trans. Faraday Soc.*, **51**, 1684 (1956)

E. Whalley, *Trans. Faraday Soc.*, **55**, 798 (1959)

12) E. Whalley, "Advances in Physical Organic Chemistry vol (2)", Academic Press, London and New York (1964), p. 129

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hence,

$$-\frac{d}{dt}[B] = \frac{k_4 k_5 K_3 [O_2] [B]}{[H^+] \{k_{-4} [H^+] + k_5 [O_2]\}} \quad (26)$$

If  $k_{-4} [H^+] \gg k_5 [O_2]$ ,

$$-\frac{d}{dt}[B] = \frac{k_4 k_5 K_3 [O_2]}{k_{-4} [H^+]^2} [B] \quad (27)$$

on the other hand, if  $k_{-4} [H^+] \ll k_5 [O_2]$ .

$$-\frac{d}{dt}[B] = \frac{k_4 K_3}{[H^+]} [B] \quad (28)$$

But the second term of equation (4') is inversely proportional to  $[H^+]$  and the rate of decrease of *o*, *o*'-hydrazotoluene was sensitive to the concentration of dissolved oxygen; so, neither (27) nor (28) can interpret the experimental results.

From the comparison of equation (4') with (22),  $k_0$  and  $k_{01}$  are represented by the relation (29).

$$k_0 = k_0^* [O_2], \quad k_{01} = k_{01}^* K_2 [O_2] \quad (29)$$

Considering the change of the concentration of dissolved oxygen due to compression, the apparent volumes of activation shown in Table 5 will be described by the following relationships,

$$\Delta V_{01}^\ddagger = \Delta^* V_{01}^\ddagger + \Delta V_{K_2} - RT \frac{\partial}{\partial P} \ln \alpha \quad (30)$$

$$\Delta V_0^\ddagger = \Delta^* V_0^\ddagger - RT \frac{\partial}{\partial P} \ln \alpha \quad (31)$$

where  $\alpha$  is the ratio of volume of the solution at 1 atm to that at  $P$  kg/cm<sup>2</sup>, i.e.,  $\alpha = v^1/v^p$ .

It being estimated that  $RT \frac{\partial}{\partial P} \ln \alpha \approx 2$  cc/mole,<sup>13)</sup> these reduce to,

$$\Delta^* V_{01}^\ddagger + \Delta V_{K_2} = -48 \text{ cc/mole}$$

$$\Delta^* V_0^\ddagger = -38 \text{ cc/mole.}$$

In the present case, as it is known that  $\Delta V_{K_2} \approx -10 \sim -15$  cc/mole,<sup>14)</sup>  $\Delta^* V_{01}^\ddagger$  and  $\Delta^* V_0^\ddagger$  come to have large negative values.

$$\Delta^* V_{01}^\ddagger \approx \Delta^* V_0^\ddagger \approx -30 \sim -40 \text{ cc/mole.}$$

Thus it seems likely that the oxidation reaction goes through two paths, the transition states of which are both very polar.

The apparent energies of activation for  $k_0$  and  $k_{01}$  are described respectively, as follows,

13) P. W. Bridgman, *Proc. Am. Acad. Arts Sci.* **49**, 42 (1913)

14) S. D. Hamann, "Physico-Chemical Effects of Pressure", Butterworths Scientific Publications, London (1958), Chapter 9, p. 160

$$\Delta H_0^\ddagger = \Delta^* H_0^\ddagger, \quad \Delta H_{01}^\ddagger = \Delta^* H_{01}^\ddagger + \Delta H_{K_2}$$

where  $\Delta H_{K_2}$  is an enthalpy change of the dissociation equilibrium (10).

Assuming that the enthalpies of activation of the steps (11) and (13) are the same order, and that the enthalpy change of the equilibrium (10) is larger than that of the dissociation of *o*-toluidinium ion in aqueous solution which was estimated to be 8 kcal/mole,<sup>15)</sup> the difference between the apparent energy of activation for  $k_0$  and that for  $k_{01}$  may be attributed to the enthalpy change of the step (10).

Anyway, the results obtained through this work seems not to be inconsistent with Ingold's "polar-transition-state theory", although the present authors could not give any conclusive evidence. And further studies are in progress.

#### Acknowledgement

The authors express their deep sense of gratitude to Mr. K. Hamanoue for his helpful advice through this work.

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15) T. W. Zawidzki, H. M. Papée, W. J. Canady and K. J. Laidler, *Trans. Faraday Soc.*, **55**, 1738 (1959)