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Decomposition of Dithiocarbamates. VII.[1] The Decomposition of N-Monosubstituted Dithiocarbamic Acid in Alkaline Solutions

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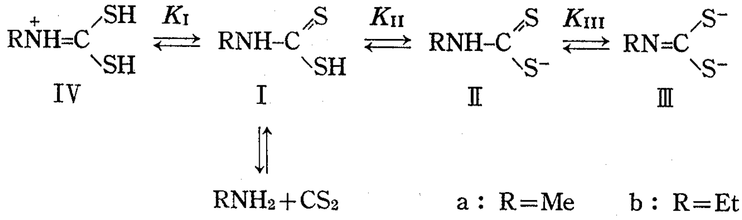
The decompositions of five N-monosubstituted dithiocarbamic acids (I) to isothiocyanate (V) and bisulfide ion were kinetically investigated over a wide range of alkali concentrations from pH to acidity function regions. The experimental first-order rate constants are proportional to the mole fraction of the anion form of I (II). The pH-rate profiles fit with an equation $k_{obs}=k[H^+]/(K_{III}+[H^+])$ (eq. 4). The decomposition proceeds directly *via* II but not *via* III, conjugate base of II. The reaction was retarded by the reverse reaction of V with bisulfide ion. The effects of the initial concentration of I and bisulfide ion on the rate are also discussed.

The formation and decomposition reactions of dithiocarbamic acid show complicated pH-dependence because of the existence of various dissociation forms of the acid, but have not been subjected to systematic studies.[3–5] We have previously established the entire dissociation scheme over as wide a range of acid and alkali concentrations as possible[6] and then the decomposition mechanism of N-monosubstituted dithiocarbamic acid (I) in acidic solutions[1a] (See eq. 1). The decomposition of dithiocarbamic acid is common to I and



$$\mathrm{R\overset{+}{N}H{=}C(SH)_2} \overset{K_{I}}{\rightleftarrows} \mathrm{RNH{-}C(=S)SH} \overset{K_{II}}{\rightleftarrows} \mathrm{RNH{-}C(=S)S^-} \overset{K_{III}}{\rightleftarrows} \mathrm{RN{=}C(S^-)_2} \qquad \text{(eq. 1)}$$

$$\mathrm{I} \rightleftarrows \mathrm{RNH_2 + CS_2}$$

a : R=Me b : R=Et
c : R=Pr d : R=Bz
e : R=C_6H_5

N,N-disubstituted dithiocarbamic acid in acidic solutions, but not in alkaline solutions[4]; though N,N-disubstituted dithiocarbamic acid is very stable, I decomposes into isothiocyanate (V).[7] The latter reaction is very important. It is used for the detection of a primary amine (Hofmann isothiocyanate test)[8] and for the preparation of V.[5] From the mechanistic viewpoint, this reaction also plays important roles in the preparation of many compounds including thiourea moiety.[5]

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[1] *a*) Part VI: See F. Takami, K. Tokuyama, S. Wakahara and T. Maeda, *Chem. Pharm. Bull.* (Tokyo), **21**, 594 (1973). A part of this paper was reported in a preliminary form: F. Takami, S. Wakahara and T. Maeda, *Chem. Letters*, **1972**, 409; *b*) Pyrimidines. Part XV, for Part XIV see Ref. 1*a*.

[2] Location: *Fukushima-ku, Osaka, 553, Japan.*

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[4] D.J. Halls, *Mikrochim. Acta*, **1962**, 62.

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[6] F. Takami, K. Tokuyama, S. Wakahara and T. Maeda, *Chem. Pharm. Bull.* (Tokyo), **21**, 329 (1973).

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Little was known about the kinetics of the decomposition reaction of I in alkaline solution. Wrónski has investigated the effect of alkali concentration on the rate in 0.01—3 N NaOH solutions and suggested the mechanism in eq. 2.⁹⁾ However, the reinvestigation of the mechanism seemed to be required judging from the following reasons. The pK'_{III} values to be *ca.* 13 determined kinetically are greatly differed from the values obtained spectrophotometrically, *e.g.* 17.6 for ethyldithiocarbamic acid (Ib) and 14.6 for phenyldithiocarbamic acid (Ie)⁶⁾ (See Table III). The fact that the stability of the sodium salt of methyldithiocarbamic acid (Ia) in solutions increased with increasing its concentration¹⁰⁾ also could not be explained by the mechanism. Recently, Chakrabarti and co-workers claimed the contribution of reaction, IIIa→Va, in acidic solutions at pH above 3.8¹¹⁾ but this is in conflict with our previous conclusion that the reaction, IIIa→Va, does not exist in such media.¹ᵃ⁾

$$\mathrm{II} \overset{K_{\mathrm{III}}}{\rightleftharpoons} \mathrm{III} \not\rightarrow \underset{\mathrm{V}}{\mathrm{RNCS}} + \mathrm{S}^{2-} \qquad \text{(eq. 2)}$$

It is therefore of interest to investigate the decomposition kinetically for the establishment of probable mechanism.

Experimental

Materials and Apparatus——The sodium salts of methyl (Ia), ethyl (Ib), propyl (Ic), benzyl (Id) and phenyldithiocarbamic acids (Ie) were synthesized by the methods appeared in literatures.¹²⁾ All reagents are commercial products of reagent grade. Absorbance changes were followed with a Hitachi two-wave length/double-beam spectrophotometer, model 356 and a Hitachi Perkin-Elmer UV-Vis spectrophotometer, model 139. The reactions were thermostated within 0.1° by a Haake FT thermostat circulater. The measurements of pH were made with a Towa-Dempa pH-meter, model HM-8.

Rate Measurements——i) In Alkaline Solutions: Rates were measured by following the change in absorbance at a wavelength between 284—291 nm of II.⁶⁾ Most of the reactions were run at the initial concentration of about 5×10^{-5}M of I in prescribed alkaline solutions, which were well-deairated with nitrogen gas before use; the solutions employed were 0.01—5M NaOH, 5—15M KOH and Sörensön buffer solutions.¹³⁾ The pH values of the buffer solutions at 80° were measured directly with the pH-meter. The reactions were carried out at 50—80° in ampules and then stopped on rapid cooling with ice-cold water to room temperature. At the initial concentration of I above 5×10^{-5}M, the measurements after rapid cooling were followed by diluting an aliquot to a value near 5×10^{-5}M of the initial concentration of I with 0.1N NaOH solution or water. First-order rate constants were calculated from plots of ln (A_t-A_∞) *vs.* time (minutes) by the least-squares method. Rates using the initial concentration of 5×10^{-5}M of I were calculated usually up to 50% decomposition and up to 20% decomposition when the deviation from the first-order law occurred in solutions of low pH values. In the reaction using the initial concentration above 5×10^{-5}M of I, where the deviation from the first-order law occurred, half-lives (minutes) were estimated graphically from the plots of absorbance *vs.* time (minutes). The results for Ia and Ie using this technique are given in Table I.

ii) In Acidic Solutions: The decomposition rates were measured by using the method previously reported¹ᵃ⁾ at pH 4.5—6.5 (See Teble II). The rates were too fast to estimate the parameters k and K_{II} separately. The parameter, k/K_{II}, was obtained to be $3.7_1\times10^4$ at 25° by the use of rate experession in Ref. 1*a*. Apparent activation energy E' and frequency factor log A' (min⁻¹) were calculated to be 13.8_2 kcal/mole and 9.3_8. Thus the rate equation 3 was obtained:

$$k_{\mathrm{obs}} = \frac{k}{K_{\mathrm{II}}}[\mathrm{H}^+] = 10^{9.3_8-13.8_2\times10^3/4.576T}\times[\mathrm{H}^+] \qquad \text{(eq. 3)}$$

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Table I. Kinetic Data for the Decomposition of Ia at 80° and Ie at 60° $[[\mathrm{I}_0]=5\times10^{-5}\mathrm{M}]^{a)}$

Ia		Ie	
pH or H₋	$k_{obs}\times10^3$ min⁻¹	pH or H₋	$k_{obs}\times10^2$ min⁻¹
7.4_6	$(1.4)^{b)}$	6.4_9	3.1×10
7.9_0	$(2.1)^{b)}$	7.1_5	9.9
9.1_0	4.6	7.9_8	(5.1)
10.0_8	5.2		$[1.0]^{b)}$
12.0_0	5.3	9.0_2	$(1.7\times10^{-1})^{b)}$
12.9_9	5.4	9.0_7	1.2
14.0_2	4.6	10.0_1	$(2.8\times10^{-1})^{b)}$
14.6_5	3.6	10.0_3	1.2
15.4_4	3.7	10.1_4	$[3.0\times10^{-2}]^{b)}$
	[3.5]	11.0_0	$(8.1\times10^{-1})^{b)}$
16.5_8	[2.7]	11.0_3	$[1.3\times10^{-1}]^{b)}$
16.9_0	[2.2]	11.1_0	1.7
17.1_4	[1.7]	12.0_0	1.6
17.3_9	[1.3]		$(7.8\times10^{-1})^{b)}$
18.2_3	$[3.9\times10^{-1}]$	12.9_9	1.5
			$(1.4)^{b)}$
			$[5.9\times10^{-1}]^{b)}$
		13.4_4	1.8
			(1.4)
		14.0_2	1.5
			(1.4)
			$[8.7\times10^{-1}]^{b)}$
		14.6_5	5.1×10^{-1}
		15.2_0	1.8×10^{-1}
			(2.0×10^{-1})

a) The values in parentheses and square brackets are obtained at $[I_0]$ of 5×10^{-4}M and 5×10^{-3}M, respectively.
b) The values are ln $2/\tau_{1/2}$.

Table II. Kinetic Data for the Decomposition of Ie at Initial Concentration of 5×10^{-5}M

pH$^{a)}$	Reaction temp., (°C)	$k_{obs}\times10$ min⁻¹
4.5	25	8.37
	25	8.16
5.0$^{b)}$	15	2.18
	25	5.33
	35	1.04×10
5.5	25	1.06
5.8	25	6.54×10^{-1}
6.0	25	4.34×10^{-1}
6.3	25	2.08×10^{-1}
6.5	25	1.08×10^{-1}

a) The Briton-Robinson buffer solutions were used unless otherwise stated.
b) an acetate buffer

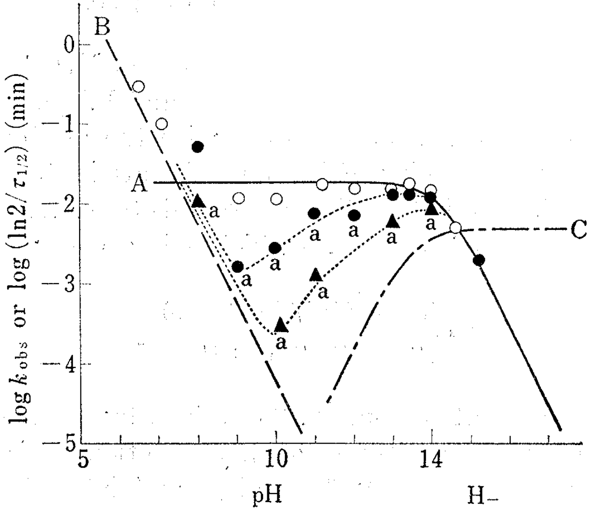

Fig. 1. Effects of pH and of Initial Concentration on the Rate of the Decomposition of Ie at 60°: $[I_0]$=○: 5×10^{-5}M; ●: 5×10^{-4}M; ▲: 5×10^{-3}M

a) The values are ln $2/\tau_{1/2}$.
line A: calculated from eq. 5 with $k=1.9\times10^{-2}$ min⁻¹ and $K_{III}=5.90\times10^{-15}$M
line B: calculated from eq. 3
line C: calculated from Wrŏnski's eq., $k_{obs}=k'K'[\mathrm{OH}^-]/(1+K'[\mathrm{OH}^-])$ with $k'=5.3\times10^{-3}$ min⁻¹ and $K'=2.7$M⁻¹ at 55°[9)]

Result and Discussion

Log *k*-pH Profiles in Dilute Solutions of I

The compounds chosen for study were methyl (Ia), ethyl (Ib), propyl (Ic), benzyl (Id) and phenyldithiocarbamic acids (Ie). The decomposition reaction may be conveniently followed by observing the decrease in absorbance due to II.[6] Two compounds, Ia and Ie, were investigated over an entire range of alkali as respective examples of aliphatic and aromatic compounds of I. The reactions were run at 50—80° with the initial concentration of 5×10^{-5} M of I. The concentrations of 5×10^{-3}—10^{-4} M of I were used at the strong alkali where no dependence of the initial concentration of I $[I_0]$ on the rate was observed. Reactions at high hydroxide ion concentration were followed to 50% completion, but those at lower pH were analyzed by initial rates up to 20% decomposition since the deviation from the first-order law was observed. The results are listed in Table I.

The plots of logarithms of observed first-order rate constants, $\log k_{obs}$, *vs.* pH and/or H_-[14] are shown in Fig. 1 for Ie (open circle). The rate decreases as a function of pH both initially and finally, and becomes independent on pH in the middle region (pH 9—14). The initial decrease should occur due to the decrease of the rate of an acidic decomposition to give aniline and carbon disulfide, since the profile is accord with the theoretical line B calculated from eq. 3(T=333.2°K). The remaining profile is discernible as a dissociation curve which is assignable to alkaline decomposition to Ve. A very similar rate-pH profile was observed for Ia as shown in Table I; the rate is independent on pH in pH 8—H_- 17 and decreases in $H_->17$. These imply that the decomposition of I occurs directly from II, without aid of base as shown in eq. 4:

$$\mathrm{III} \overset{K_{\mathrm{III}}}{\rightleftharpoons} \mathrm{II} \xrightarrow{k} \mathrm{V} + \mathrm{SH}^- \qquad \text{(eq. 4)}$$

where k is the rate constant of decomposition. The above kinetic scheme discloses that of I in acidic solutions, $\mathrm{IV} \overset{K_\mathrm{I}}{\rightleftharpoons} \mathrm{I} \longrightarrow \mathrm{RNH_2} + \mathrm{CS_2}$[1a)]; the latter reaction proceeds *via* I in the parasitic equilibrium between I and IV (See eq. 1). The fact that the conjugate base III is unreactive is also consistent with the results found in the saponification of many amides.[15] The unreactivity of III must be attributed to the greater resonance stabilization than II.

The solid line (line A) from pH 9 to H_- 15, which best fits the experimental points in Fig. 1 was derived from eq. 5 which is in accord with the kinetic scheme of eq. 4. The parameters

$$k_{obs} = k[\mathrm{H}^+]/(K_{\mathrm{III}}+[\mathrm{H}^+]) \qquad \text{(eq. 5)}$$

$$1/k_{obs} = K_{\mathrm{III}}/k(\mathrm{h}_-)+1/k \qquad \text{(eq. 6)}$$

are calculated from eq. 6 obtained by the rearrangement of eq. 5 by replacing the term $[\mathrm{H}^+]$ with non-logarithmic acidity function (h_-)[14]: $k=4.6\times10^{-3}\,\mathrm{min}^{-1}$ and $K'_{\mathrm{III}}=1.2\times10^{-17}$ M for Ia and $k=1.9\times10^{-2}\,\mathrm{min}^{-1}$ and $K'_{\mathrm{III}}=5.9\times10^{-15}$ M for Ie (See Table III). The $\mathrm{p}K'_{\mathrm{III}}$ values thus obtained for Ia and Ie approximately agreed with those obtained spectrophotometrically at 25°.[6] Equation 5 is simplified to $k_{obs}=k$ at pH where II is not appreciably dissociated, since hydrogen ion concentration is much greater than K_{III}. Thus, the k values were safely determined in 0.1 N NaOH solution for Ib—d whose K_{III} values are calculated to be ca. 17 by the eq., $\mathrm{p}K_{\mathrm{III}}=0.48\ \mathrm{p}K_{\mathrm{N}}+12.43$.[6] The results are listed in Table III.

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TABLE III. Kinetic Parameters for the Decomposition of I in 0.1 N NaOH

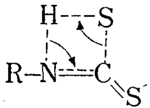
Compound (pK_a of parent amine, pK_N)[a]	Reaction temp., (°C)	$k_{obs}\times10^3$ (min^{-1})	E (kcal/mole)	log A (min^{-1})	$\Delta S^{\ddagger}$ 353.2°K, e.u.	pK'_{III}[b]
Ia(10.67)	60	$3.2_8\times10^{-1}$	30.9	16.8	+7.9	16.9(80°) (17.6)
	70	1.4_0				
	80	4.6_0				
Ib(10.70)	60	1.1_2	26.1	14.2	−4.0	(17.6) [13.2(70°)]
	70	3.1_3				
	80	$1.0_5\times10$				
Ic(10.75)	60	1.2_1	25.7	13.9	−5.4	(17.6)
	70	3.5_8				
	80	$1.0_9\times10$				
Id(9.35)	60	$9.2_1\times10^{-1}$	27.8	15.2	+0.6	(16.9)
	70	2.6_9				
	80	9.5_2				
Ie(4.60)	50	4.9_3	25.9	15.2	+0.6	14.2(60°) (14.6) [13.3(45°), 13.6(55°)]
	60	$1.5_1\times10$				
	70	$5.2_1\times10$				

a) D.D. Perrin, "Dissociation Constants of Organic Bases in Aqueous Solution," Butherworths, London, 1965

b) Values in parentheses and square brackets are those calculated from eq., $pK_{III}=0.48\ pK_N+12.43$[6] and reported by Wrónski, respectively.[9]

Transition State

The calculated kinetic parameters are summarized in Table III. The small values of $\Delta S^{\ddagger}$ to be near zero are reasonably interpreted as an unimolecular decomposition.[16] In the transition state, the internal elimination as regarded one-stage cyclic process may occur in a possible cyclic structure (VI). The S-C σ-bond of II having an electron-attracting group should be more loose than that having an electron-donating one judging from the resonance stabilization.[1a] The looseness of the bond is favored to form VI. Thence, the rate of the former must be faster than that of the latter. As expected, the rate constant k decreases with the increase of pK_N as shown in Table III; the aliphatic compounds Ia—d are more stable than the aromatic one Ie.



VI

The Effects of Initial Concentration $[I_0]$

When the reaction was run at higher concentration of $[I_0]$ than 5×10^{-5} M at pH 10—14, the rates deviated from the first-order law as the reaction proceeded. As represented by closed circles and triangles in Fig. 1, the plots of ln 2/(half-lives, $\tau_{1/2}$) *vs.* pH indicate that the rate decreases with the increase of $[I_0]$; the profile differs from the line A as shown in the dotted lines. The persistent curvature and the dependence of $[I_0]$ on the rate must be caused due to the reverse reaction of V with bisulfide ion produced during the course of reaction.[17] The linear relationship exists between $\tau_{1/2}$ and $[I_0]$ as shown in Table IV and Fig. 2. The addition of bisulfide ion into the reaction medium retarded the rate and a plot of $1/k_{obs}$ against $[SH^-]$ gave also a straight line as described in Table V and Fig. 2.

Isothiocyanate (V) is easily hydrolyzed to an monothiocarbamate.[18] Consequently the combination of the decomposition of II and the reverse and hydrolysis reactions of V led us

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TABLE IV. Effect of $[I_0]$ on the Rates of the Decompositions of Ia at 80° and Ie at 60° in 0.1 N NaOH

Compound	$[I_0]\times10^3$ (M)	$\tau_{1/2}$min	k_1/k_2 a)	$k_1\times10^3$ a) (min^{-1})
Ia	$5.0_0\times10^{-2}$	129	6.2×10	5.1
	$5.5_2\times10^{-1}$	156		
	1.7_9	180		
	3.0_2	212		
	4.2_6	245		
	5.4_8	270		
Ie	$4.2_0\times10^{-2}$	46	1.4×10^2	1.7×10
	$2.8_2\times10^{-1}$	53		
	$4.1_7\times10^{-1}$	52		
	1.6_5	74		
	2.8_6	96		
	4.2_3	118		

a) calculated from eq. 11

TABLE V. Effect of $[SH^-]$ on the Rates of the Decompositions of Ia at 80° and Ie at 60° in 0.1 N NaOH ($[I_0]=5\times10^{-5}$M)

Compound	Added $[SH^-]\times10^3$ (M)	$k_{obs}\times10^3$ (min^{-1})	k_{-1}/k_2 a)	$k_1\times10^3$ a) (min^{-1})
Ia	0	5.3_9	3.2×10	5.2
	$4.3_4\times10^{-1}$	4.7_7		
	$8.5_1\times10^{-1}$	3.9_0		
	1.6_7	3.4_4		
	2.5_2	2.9_3		
	3.3_7	2.6_3		
	4.0_3	2.3_1		
Ie	$4.2_6\times10^{-1}$	$1.4_8\times10$	7.2×10	2.0×10
	$8.4_6\times10^{-1}$	$1.1_7\times10$		
	1.6_7	9.3_7		
	2.5_0	6.4_4		
	3.3_6	5.4_5		
	4.0_3	4.9_0		

a) calculated from eq. 12

to establish an overall decomposition pathway of I as shown in eq. 7. Applying a

$$\text{III} \overset{K_{\text{III}}}{\rightleftharpoons} \text{II} \xrightleftharpoons[k_{-1}[\text{SH}^-]]{k_1} \text{V} \xrightarrow{k_2[\text{OH}^-]} \text{RNHCSO}^- \qquad \text{(eq. 7)}$$

steady-state approximation for V, equations 8 and 9 were obtained;

$$\text{Rate} = k_2[\text{V}][\text{OH}^-] = \frac{[\text{H}^+]}{K_{\text{III}}+[\text{H}^+]}\,\frac{k_1k_2[\text{OH}^-]}{k_{-1}[\text{SH}^-]+k_2[\text{OH}^-]}\,[\text{I}^{\text{total}}] \qquad \text{(eq. 8)}$$

$$= \frac{[\text{H}^+]}{K_{\text{III}}+[\text{H}^+]}\,\frac{k_1}{k_{-1}[\text{SH}^-]/k_2[\text{OH}^-]+1}\,[\text{I}^{\text{total}}] \qquad \text{(eq. 9)}$$

where k_1, k_{-1} and k_2 represent the corresponding rate constants in eq. 7. At high concentration of hydroxide ion, the term $k_{-1}[\text{SH}^-]/k_2[\text{OH}^-]$ may become negligibly small, and then the rate is the first-order, whose constant can be expressed by eq. 5. At low concentration of hydroxide ion and/or at high $[I_0]$, the rate does not obey the first-order law, since $k_{-1}[\text{SH}^-]$-

$/k_2[OH^-]$ cannot be made negligible. When $[SH^-]$ equals $[I_0]$ minus $[I]$, eq. 8 is adequately approximated by eq. 10. On integrating eq. 10, eq. 11 is obtained. If sufficient amounts of $[SH^-]$ are added, eq. 8 is transformed to eq. 12. The experimental results are

$$\mathrm{Rate} = \frac{[H^+]}{K_{III} + [H^+]} \frac{k_1 k_2 [OH^-]}{k_{-1}([I_0]-[I]) + k_2[OH^-]} [I^{total}] \qquad \text{(eq. 10)}$$

$$\tau_{1/2} = \frac{K_{III} + [H^+]}{k_1[H^+]} (ln\, 2 - 1/2) \frac{k_{-1}}{k_2[OH^-]} [I_0] + ln\, 2 \qquad \text{(ep. 11)}$$

$$1/k_{obs} = \frac{K_{III} + [H^+]}{[H^+]} \frac{k_{-1}}{k_1 k_2 [OH^-]} [SH^-] + 1/k_1 \qquad \text{(eq. 12)}$$

consistent with equations 11 and 12 as already shown in Fig. 2.

From the two sets of data, the k_1 values were calculated as the intercepts and the k_{-1}/k_2 as the slopes of equations 11 and 12. Respective data are listed in Tables IV and V for Ia and Ie. Thus obtained constants, k_1, indicate that the values determined at $[I_0]=5 \times 10^{-5}$M in 0.1N NaOH solution are safely obtained without the obstruction of the reverse reaction. The values of the nucleophilicity ratio of SH^- to OH^-, k_{-1}/k_2, agree with the relative nucleophilicity ratio (*ca.* 100) of RS^- to RO^-,[19,20] though the dissociation of SH^- to S^{2-} was not taken into consideration for eq. 8.[21]

The experimental result of Wrónski[9] is represented by the line C in Fig. 1. He failed to measure the formation rate of V and observed only the apparent rate-dependence on the concentration of hydroxide ion, because the decomposition was carried out with the higher $[I_0]$. Another worker's result that the rates for Ib increased linearly with the decrease of the concentration of hydroxide ion at about pH 9 should also be the apparent rate-dependence on pH because of higher $[I_0]$ employed.[22]

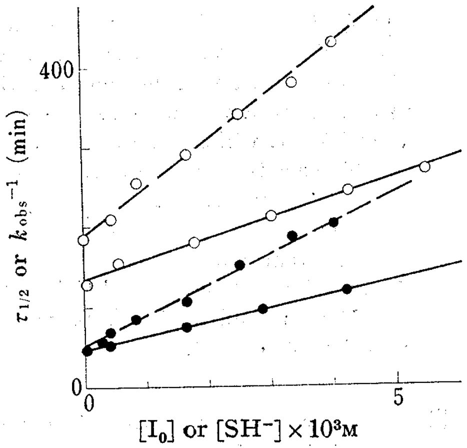

Fig. 2. The Dependences of $\tau_{1/2}$ on $[I_0]$ (Solid Lines) and of k_{obs}^{-1} on $[SH^-]$ (Dashed Lines) for the Decompositions of Ia at 80° (○) and Ie at 60° (●) in 0.1N NaOH

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