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Decomposition of Dithiocarbamates. IX.[1] The Effect of Carbon Disulfide on the Decomposition of N-Monosubstituted Dithiocarbamic Acids

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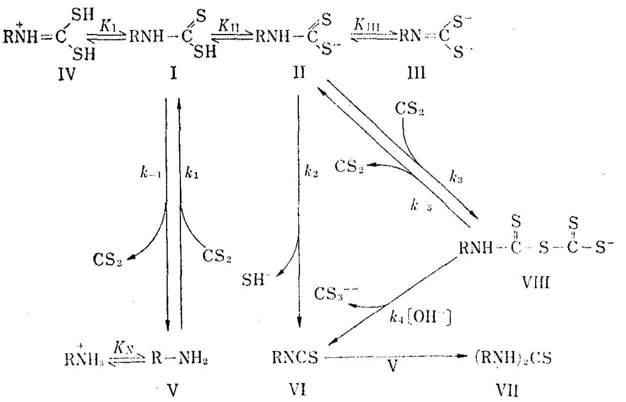
The effect of carbon disulfide on the decomposition of N-monosubstituted dithiocarbamic acids was kinetically investigated. In the preparation of I, the presence of excess of carbon disulfide was elucidated to accelerate the decomposition of I. The rate is proportional to $[CS_2]$, $[OH^-]$ and [I], respectively. This is explained by the pathway, $I \rightleftharpoons II \overset{CS_2}{\rightleftharpoons} VIII \xrightarrow{OH^-} VI$; carbon disulfide reacts with I to afford an adduct VIII, which plays an important role. The requirement of pH-control for preparation of I was interpreted by the results.

The establishment of preparative method of N-monosubstituted dithiocarbamic acid (I) is still an important problem, since its versatility and usefulness are increasing in the field of agrochemicals and synthetic intermediates for heterocyclic compounds.[3] The most conventional method for the preparation is the use of the reaction of a primary amine with carbon disulfide, where 1,3-disubstituted thiourea (VII) is isolated as a by-product.[3a] It is well-known that the yields of I are greatly influenced by the pH of the reaction media; for instance, the optimal value is 8—10 for the preparation of disodium ethylenebisdithiocarbamate.[4]



a : $R=C_6H_5$, b : $R=CH_3$

Chart 1

Previously, we have studied on the behavior of I over a wide range of acid and alkali concentrations and succeeded in the establishment of the dissociation[5] and decomposition schemes.[1,6,7] From the mechanical points of view, the reactions of I are summarized as shown in Chart 1 including its formation.[8]

The rate of formation of I is expressed as eq. 1. It is inversely proportional to hydrogen ion concentration at pH below the pK_a of amine (V) (pK_N) and independent at pH above

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[1] Part VIII: F. Takami, K. Tokuyama, S. Wakahara, Y. Fukui, and T. Maeda, *Chem. Pharm. Bull.* (Tokyo), 22, 267 (1974).

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

[3] *a*) G.D. Thorn and R.A. Ludwig, "The Dithiocarbamates and Related Compounds," Elsevier, New York, 1962, Chapter 4; *b*) N. N. Melnikov, "Chemistry of Pesticides," Springer-Verlag, New York, 1971, Chapter XVII.

[4] R.J. Gobeil, U.S. Patent 2,693,485 (1954) [*C.A.*, 12533*d* (1955)].

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

[6] F. Takami, K. Tokuyama, S. Wakahara, and T. Maeda, *Chem. Pharm. Bull.* (Tokyo), **21**, 594 (1973).

[7] F. Takami, K. Tokuyama, S. Wakahara, and T. Maeda, *Chem. Pharm. Bull.* (Tokyo), **21**, 1311 (1973).

[8] *a*) R. Zahradnik, *Collection Czech. Chem. Commun.*, **21**, 447 (1956); **23**, 1435 (1958); *b*) B. Philip and H. Dauzenberg, *Farserforschung u. Textiltechnik*, **19**, 23 (1968).

pK_N. The control in pH near or above pK_N is desirable for the preparation of I because of rapid formation in such a region. Equation 2 represents the decompositions of I. The first term which is dominant at acidic range becomes smaller with the increase of pH.$^{5)}$ The second term which is a main one at basic range is independent on pH because pK_{III} values are at far above pH region.$^{5)}$

$$\text{rate of formation} = \frac{k_1 K_N [CS_2][V^{total}]}{K_N + [H^+]} \qquad \text{(eq. 1)}$$

$$\text{rate of decomposition} = \left(\frac{[H^+]}{\frac{[H^+]^2}{K_I} + [H^+] + K_{II}} \cdot k_{-1} + \frac{[H^+]}{K_{III} + [H^+]} \cdot k_2 \right) [I^{total}] \qquad \text{(eq. 2)}$$

The above equations 1 and 2 indicate that the fast completion of the formation and the low yield of the by-product are expected at high pH-region, but fail to explain the presence of the upper limit of pH in the preparation of I.

We assumed the presence of a decomposition reaction of I, which should occur at high pH region and make lower the yield of I. The anticipated reaction of I with both carbon disulfide and hydroxide ion was detected kinetically using phenyldithiocarbamic acid (Ia).$^{9)}$ Methyldithiocarbamic acid (Ib)$^{10)}$ was also subjected to the study.

Experimental$^{11)}$

Materials and Apparatus——The compound Ia was prepared by the method as described below, and Ib was synthesized as the sodium salt.$^{10)}$ All reagents were commercial products of reagent grade. A Yanagimoto Polarograph, model PA-2, was used. The reactions were thermostated within 0.1° by a Yanagimoto Constant-Temperature Bath For Polarograph, model PC-4, whose jacket was circulated by a Haake FT thermostat. The measurements of pH were made with a Towa-Dempa pH-meter, model HM-8.

Synthesis of Ia——a) A mixture of aniline (Va) (11.63 g) carbon disulfide (10 g) and 1 N NaOH (125 ml) was vigorously stirred at 26—28° for 4 hr and then filtered to give pale yellow crystals of 1,3-diphenylthiourea (VIIa) (4.64 g, 35%), mp 154° (decomp.).$^{12)}$ The filtrate was washed with ether (50 ml × 2) and then evaporated to dryness. The residue was extracted with acetone (100 ml × 3) and then the acetone solution was concentrated to about 20 ml. The addition of ether (50 ml) to the acetone solution gave pale yellow crystals of sodium salt of Ia$^{9)}$ as tri-hydrate (16.83 g, 55%).

b) A mixture of Va (11.63 g) and carbon disulfide (10 g) in water (100 ml) was stirred at 25—28° for 4 hr. During the reaction, the pH was measured by a pH-meter with an inserted electrode into the reaction mixture and kept to be 8—10 by adding 10% NaOH (about 55 g was used). The compound Ia (26.93 g, 88%) was obtained along with VIIa (0.27 g, 2%) in a procedure similar to the above.

Reaction of Ia with Va——A mixture of Ia (2.45 g) and Va (0.93 g) in 1 N NaOH (10 ml) was stirred at 25—28° for 4 hr. The pH of the mixture was adjusted to be 10—11 with 1 N acetic acid under cooling (5—6°) and then extracted with ether (10 ml × 3). The ether was evaporated under atomospheric pressure and then the residue was acidified with 5% hydrochloric acid to give VIIa (0.085 g, 4%).

Stability of Ia in 1 N NaOH Solution——A solution of Ia (2.45 g) in 1 N NaOH (10 ml) was stirred at 25—28° for 4 hr. The pH of the solution was adjusted to be 10—11 with 1 N acetic acid under cooling (5—6°) and then washed with ether (10 ml × 3). The solution was evaporated to dryness and then worked up in a manner similar to the synthesis of Ia. Ninety seven percent of Ia (2.38 g) was recovered.

Rate Measurements——a) Decomposition of I in the Presence of Carbon Disulfide: Air-free distilled water (0.4 ml) saturated with carbon disulfide was added to a well-deairated NaOH solution (8 ml) containing I (see Table I). The decreases of current with time at a constant value between −1.3 and −1.4 eV due to carbon disulfide was recorded at appropriate time interval. All the reactions were run up to 70%

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9) M. Delépine, *Compt. Rend.*, **144**, 1125 (1907).

10) H.L. Klöpping and G.J. Van Der Kerk, *Rec. Trav. Chim.*, **70**, 917 (1951); D.J. Halls, A. Townshend and P. Zuman, *Anal. Chim. Acta*, **40**, 459 (1968).

11) Melting points were measured on a hot stage apparatus and uncorrected. All solvents were removed under reduced pressure unless otherwise stated.

12) B. Pawlewski, *Chem. Ber.*, **37**, 158 (1904).

decomposition at 25°. Pseudo first-order rate constants were calculated from plots of ln (i_t-i_∞) *vs.* time (min) by the least-squares method. The results for Ia and Ib are given in Table I.

TABLE I. Observed First Order Rate Constant (k_{obs}) for the Decomposition of I in the Presence of Carbon Disulfide[a)]

Compound	$[OH^-]$, N	$[I]_0$, M	k_{obs}, min^{-1}
Ia	$3.0_5\times10^{-1}$	$9.5_2\times10^{-3}$	$3.6_5\times10^{-2}$
	$2.5_7\times10^{-1}$	$9.5_2\times10^{-3}$	$3.0_7\times10^{-2}$
	$2.0_0\times10^{-1}$	$9.5_2\times10^{-3}$	$2.2_7\times10^{-2}$
	$1.0_5\times10^{-1}$	$9.5^2\times10^{-3}$	$1.3_2\times10^{-2}$
	$1.0_5\times10^{-1}$	$9.5_2\times10^{-3}$	$1.2_2\times10^{-2}$
	$4.7_6\times10^{-2}$	$9.5_2\times10^{-3}$	$6.9_0\times10^{-3}$
	$1.0_5\times10^{-1}$	$4.7_9\times10^{-3}$	$1.0_0\times10^{-2}$
	$1.0_5\times10^{-1}$	$9.5_2\times10^{-3}$	$1.2_2\times10^{-2}$
	$1.0_5\times10^{-1}$	$1.4_4\times10^{-2}$	$1.4_9\times10^{-2}$
	$1.0_5\times10^{-1}$	$1.9_0\times10^{-2}$	$1.6_9\times10^{-2}$
	$1.0_5\times10^{-1}$	$2.8_5\times10^{-2}$	$1.9_5\times10^{-2}$
	$1.0_5\times10^{-1}$	$3.8_1\times10^{-2}$	$2.5_9\times10^{-2}$
Ib	$4.9_4\times10^{-1}$	$9.8_8\times10^{-2}$	$6.0_7\times10^{-2}$
	$2.4_7\times10^{-1}$	$9.8_8\times10^{-2}$	$3.0_1\times10^{-2}$
	$1.9_8\times10^{-1}$	$9.8_8\times10^{-2}$	$2.5_1\times10^{-2}$
	$1.4_8\times10^{-1}$	$9.8_8\times10^{-2}$	$2.4_1\times10^{-2}$
	$9.8_8\times10^{-2}$	$9.8_8\times10^{-2}$	$1.4_5\times10^{-2}$
	$4.9_4\times10^{-2}$	$9.8_8\times10^{-2}$	$8.3_0\times10^{-3}$
	$9.8_8\times10^{-2}$	$9.8_8\times10^{-2}$	$1.3_4\times10^{-2}$
	$9.8_8\times10^{-2}$	$4.3_4\times10^{-2}$	$6.1_7\times10^{-3}$
	$9.8_8\times10^{-2}$	$1.9_9\times10^{-1}$	$2.4_4\times10^{-2}$

a) at 25°

b) The rates of formation of Ia were obtained at 25° by Philip's method in the presence of excess of Va (2.71×10^{-2}M).[8b)] The rate constant of eq. 1 was simplified to $k_{obs}=k_1[RNH_2]$ at the pH measured. The second-order rate constant k_1 was calculated from the above equation. $k_{obs}\times10^3$ (min^{-1}): 3.8_1 at pH 8.1; 3.9_5 at pH 9.1. $k_1\times10$ (l·mole^{-1}·min^{-1}): 1.4_1 at pH 8.1; 1.4_6 at pH 9.1.

c) The rate of decomposition of carbon disulfide was measured by the usual way[13)] and obtained to be 7.2×10^{-2} min^{-1} at 25° in 1 N NaOH.

Result and Discussion

The compound Ia is prepared as the sodium salt by the reaction of aniline (Va) with carbon disulfide in the presence of equivalent of sodium hydroxide.[9)] We examined the yields of Ia to ascertain the existence of an optimal pH which was found for the synthesis of disodium ethylenebisdithiocarbamate.[4)] The compound Ia was obtained in 88% yield when the pH of the reaction solution was maintained between 8 and 10 by the gradual addition of sodium hydroxide solution. Until the uptake of the alkali was almost ceased, 4 hr were required. Without pH-control, the yield decreased greatly to 55% after the same reaction period, where 1,3-diphenylthiourea (VIIa) was yielded as a main by-product (35%). The yield of VIIa indicated that at least 17.5% of Ia decomposed to the isothiocyanate (VIa).

On the contrary to the latter experiment, the kinetic results previously obtained[7)] show that the formation and the decomposition of Ia should proceed at constant rates under such conditions, and the amounts of decomposition should not be more than 4% for 4 hr at 25°. In fact, Ia was recovered almost quantitatively after the reaction of Ia in 1 N NaOH solution for 4 hr. The decomposition rate of Ia must be estimated by solving the following kinetic

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13) H. Dauzenberg and B. Philip, *Faserforschung u. Textiltechnik,* **20**, 213 (1969).

scheme precisely; Va $\xrightarrow{k_1,\, CS_2}$ Ia $\xrightarrow[-SH^-]{k_2}$ VIa $\xrightarrow{V_a}$ VIIa, but if the decomposition reaction, Ia$\longrightarrow$VIa+SH$^-$, were sole one, the yield of VIa or VIIa could not be above 4%. The increase of the yield of VIIa without the pH-control is understandable by assuming the reaction of the anion form of I (II) and carbon disulfide. A possible pathway should be written as follows; II $\underset{k_{-3},\, -CS_2}{\overset{k_3,\, CS_2}{\rightleftarrows}}$ VIII $\xrightarrow[-CS_3^{--}]{k_4,\, OH^-}$ VI $\xrightarrow{V}$ VII. This mechanism was unequivocally established by measuring the decomposition rates of I in the presence of carbon disulfide.

The rates were polarographically followed at 25° by observing the decrease of carbon disulfide in the presence of excess of I or hydroxide ion compared with the amount of carbon disulfide. The apparent first-order rate constants (k_{obs}) are proportional to [OH$^-$] and the initial concentration of I ([I]$_0$) (see Table I and Fig. 1). As carbon disulfide independently decomposes in an alkaline solution (Chart 2),[13] the rate of decrease of carbon disulfide is expressed by eq. 3, which was derived by applying the steady-state approximation for VIII. Under the assumption of

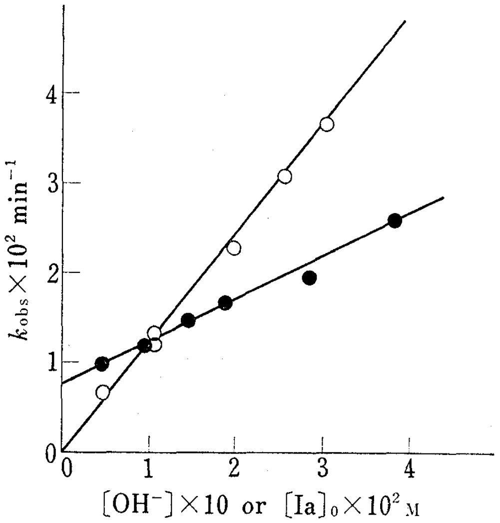
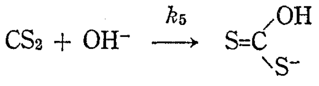


Fig. 1. The Effects of Hydroxide Ion and Concentration of Ia on the Rate at 25°

The plots of k_{obs} *vs.* [OH$^-$] (○) were measured at [Ia]$_0$=9.52×10^{-1} M and of k_{obs} *vs.* [Ia]$_0$ (●) at [OH$^-$]=1.05×10^{-1} M.



$$CS_2 + OH^- \xrightarrow{k_5} S{=}C(OH)S^-$$

Chart 2

$$\text{rate} = \left(\frac{k_3k_4[I]}{k_{-3}+k_4[OH^-]} + k_5\right)[OH^-][CS_2] \qquad \text{(eq. 3)}$$

$k_{-3}\gg k_4[OH^-]$, eq. 3 is simplified to eq. 4;

$$\text{rate} = \left(\frac{k_3k_4[I]}{k_{-3}} + k_5\right)[OH^-][CS_2] \qquad \text{(eq. 4)}$$

From the dependence of the rate on [OH$^-$] or [I]$_0$ in Table I, the parameter k_3k_4/k_{-3} for Ia was calculated using the obtained parameter k_5. The data are listed in Table II including those for Ib.

Table II. Rate Constants for the Decomposition of I in the Presence of Carbon Disulfide[a)]

Compound	p*K*a of parent amine (pK_N)[b)]	k_3k_4/k_{-3} (l^2·mole^2·min^{-1})[c)] From [OH$^-$]-dependence	k_3k_4/k_{-3} (l^2·mole^2·min^{-1})[c)] From [I]$_0$-dependence
Ia	4.60	5.4	4.6
Ib	10.67	0.7$_0$	0.7$_6$

a) at 25°
b) D. D. Perrin, "Dissociation Constants of Organic Bases in Aqueous Solution," Butherworths, London, 1965, p. 58 for Va and p. 13 for Vb.
c) mean values

An electron-attractive substituent on nitrogen atom resulted in a faster decomposition of Ia than Ib. Since it should decrease the resonance stabilization of $\text{N-C}\langle^{\text{S}}_{\text{S}}$ moiety of VIII,[5] and also make easier the proton removal of N-H by the attack of hydroxide ion to be essencial for the initiation of the reaction, the base-catalyzed elimination of trithiocarbonate from the intermediate VIII is expected easily to occur for the compound having an electron-attractive group.

On the basis of the above-mentioned results, the formation and decomposition pathways are shown in Chart 1. The requirement of pH-control for the synthesis of Ia is well-interpreted by the theoretical pH-rate profiles of the reactions of Chart 1 which are shown in Fig. 2 under the assumption that the concentration of carbon disulfide is 2.22×10^{-2} M.[14] Fig. 2 clearly shows that the decompositions are minimum at pH 9—10. This value was close to our experimental data. The alkaline decomposition rate of eq. 2 should become negligibly small under the synthetic condition because of the increase of the reverse reaction between VI and bisulfide ion.[7] Thence, at the range near pH 9—10 the decomposition reactions which dominantly occur are those of Ia → Va and of Ia→ VIIIa→ VIa.

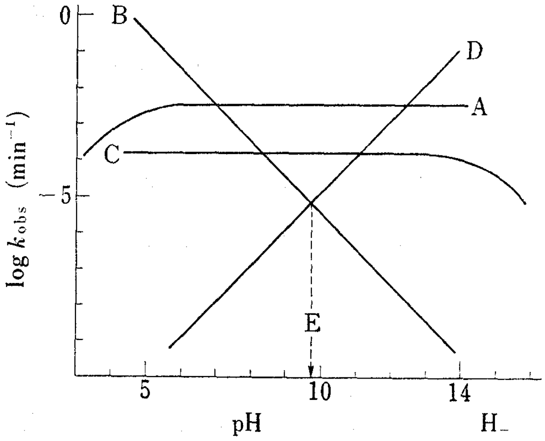


Fig. 2. Theoretical Rate-pH Profiles for the Formation and Decompositions of Ia at 25°

line A: derived from eq. 1 with $k_1 = 1.46 \times 10^{-1}$ l·mole^{-1}·min^{-1}, $K_N = 2.51 \times 10^{-5}$M and $[CS_2] = 2.22 \times 10^{-2}$ M,[14] line B: derived from $k_{obs} = k_{-1}[H^+]/K_{II}$ with $k_{-1}/K_{II} = 3.71 \times 10^4$ l·mole^{-1}·min^{-1},[7] line C: derived from the second term of eq. 2 with $k_2 = 10^{15.2 - 25.9 \times 10^3/4.576T}$ and $K_{III} = 2.51 \times 10^{-15}$ M,[7] line D: derived from $k_{obs} = k_3 k_4 [OH^-][CS_2]/k_{-3}$ with $k_3 k_4/k_{-3} = 5.4$ l^2·mole^{-2}·min^{-1} and $[CS_2] = 2.22 \times 10^{-2}$ M, point E: optimal pH for the preparation of Ia

Conclusively, the pH-control for the preparation of I is quite critical to exclude the undesirable decomposition of I *via* VIII which occurs to a considerable extent in the presence of carbon disulfide at a higher pH ranges.

Acknowledgement We are grateful to Professor Y. Inubushi, University of Kyoto, who has read and criticized the manuscript.

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14) H. Stephen and T. Stephen, "Solubilities of Inorganic and Organic Compounds," Vol. I, Pergamon, New York, 1963, p. 369.