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DECOMPOSITION OF DITHIOCARBAMATES. IV.(1) METHYLDITHIOCARBAMATE TO METHYLISOTHIOCYANATE IN ALKALINE SOLUTIONS(2)

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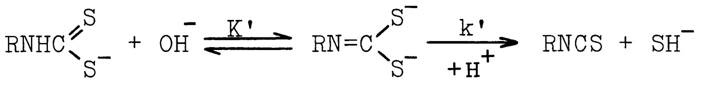
The title reaction was investigated over a range of pH 8 ~ H_- 18.2. The rate-pH profile fits with an equation $k_{obs} = k(H^+)/(K + (H^+))$. The decomposition proceeds directly via IV but not via its conjugate base V. The rate dependence on the initial concentration of IV is also discussed.

Although extensive studies have been reported,(3,4) the reaction of monoalkyldithiocarbamate (I) to alkylisothiocyanate (III) was not well understood. Wronski(3) claimed a reaction pathway shown in eq. (1) based on the finding of the kinetic expression $k_{obs} = k'K'[OH^-]/(1 + K'[OH^-])$; $K' = [II]/[I]\cdot[OH^-]$ (eq. 2).



$$\mathrm{RNHC}\genfrac{}{}{0pt}{}{S}{S^-} + OH^- \overset{K'}{\rightleftharpoons} \mathrm{RN{=}C}\genfrac{}{}{0pt}{}{S^-}{S^-} \xrightarrow[+H^+]{k'} \mathrm{RNCS} + SH^- \qquad (1)$$

I II III

The pK_a' values, however, were greatly differed from our values obtained spectrophotometrically (see Table). This large difference of the values, for instance, about 4 pK_a' units for ethyldithiocarbamate,(5) prompted us to carry out further studies on the reaction of methyldithiocarbamate (IV) (I, R = Me), kinetically.

Table. Dissociation constants pK_a' of dithiocarbamates $RNHCSS^-$

Compound	pK_a'	
R=	Wronski[a]	Present work
Ph	13.3(45°C) 13.6(55°C)	14.6-14.8(25°C)[b]
Et	13.2(70°C)	17.5(25°C) 17.6[b]
Me	------	17.6(25°C) 16.9(80°C)[c]

a Ref. 3. b Ref. 5. c Value obtained kinetically.

Kinetic experiments were carried out in well-deairated aqueous solutions of pH 8 ~ H_- 18.2 at 80°C. Initial concentrations of IV ($[IV]_0$) were 5×10^{-5} M unless otherwise stated. The rate of decrease of IV was followed by the decrease in optical density at 282 nm upto 50% decomposition. Contrary to Wronski's description, the values of pseudo first-order rate constants (k_{obs} min^{-1}) decreased with the increase of the alkaline concentrations in a form of dissociation curve as depicted in Fig. 1. The experimental points between pH 13 ~ H_- 18.2 best fit the solid line, derivable from equation $k_{obs} = k(H^+)/(K + (H^+))$ (eq. 3) which accords with kinetic scheme of eq. (4); k refers to the velocity constant of decomposition, and K to the dissociation constant. The constants are $k = 4.6 \times 10^{-3}$ min^{-1} and $K = 1.2 \times 10^{-17}$ M (pK_a = 16.9 at 80°C). Equation (4) led us to the

$$\mathrm{A} \underset{}{\overset{K}{\rightleftarrows}} \mathrm{AH} \xrightarrow{k} \mathrm{Products} \qquad (4)$$

conclusion that the decomposition reaction from IV to VI occurs directly via IV but not via V (eq. 5).

$$\mathrm{V(II,\ R = Me)} \overset{K}{\rightleftarrows} \mathrm{IV(I,\ R = Me)} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \underset{\mathrm{SH^-}}{\underset{+}{\mathrm{VI(III,\ R = Me)}}} \xrightarrow[+OH^-]{k_2} \begin{matrix}\text{Further}\\ \text{decomposition}\end{matrix} \qquad (5)$$

When the reaction was run at higher initial concentration of IV than 5×10^{-5} M, the rates gradually decreased and deviated from the first-order law as the reaction proceeded. The persistent curvature must be caused due to the reverse reaction (Fig. 2(a)). An approximately linear relationship existed between $\tau_{1/2}$ and $[IV]_o$. Further, the addition of SH^- into the reaction medium retarded the rate and a plot of $1/k_{obs}$ against (SH^-) gave a straight line (Fig. 2(b)).

It is well known that isothiocyanates[6)] decompose in the presence of OH^-. Consequently, the combination of the reverse and decomposition reactions of VI led us to establish an overall decomposition pathway of IV in alkaline solutions as shown in eq. (5). Applying a steady-state approximation for VI, eq. (6) was obtained, though the dissociation[7)] of SH^- to S^{2-} was not taken into consideration. At high concentration of OH^-, the term $k_{-1}(SH^-)/k_2(OH^-)$ may become negligibly small, and then the rate is the first-order, whose constant can be expressed as eq. (3). At low concentration of OH^- and/or at high concentration of $[IV]_o$, the rates do not obey the first-order law, since $k_{-1}(SH^-)/k_2(OH^-)$ can not be made negligibly small. The convenient eq. (7) can be derived from eq. (6). If sufficient amounts of SH^- existed, the reaction obeys the first-order kinetics, whose constant is given by eq. (8). The experimental results are consistent with eqs. (7) and (8) as shown in Fig. 2.

$$\text{Rate} = \frac{(H^+)}{K + (H^+)} \cdot \frac{k_1}{k_{-1}(SH^-)/k_2(OH^-) + 1} [IV^{total}] \qquad (6)$$

$$\tau_{1/2} = \frac{K + (H^+)}{k_1(H^+)} \left[(\ln 2 - 1/2) \frac{k_{-1}}{k_2(OH^-)} [IV]_o + \ln 2 \right] \qquad (7)$$

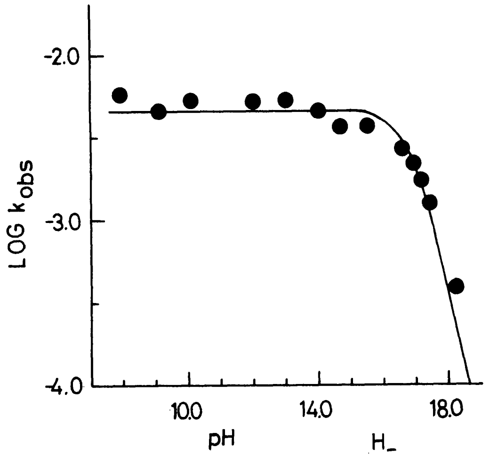


Fig. 1

Rate profile for the decomposition of methyldithiocarbamate at 80 °C.

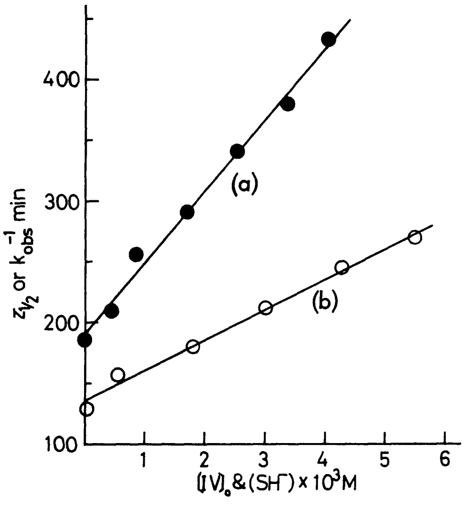


Fig. 2

The dependence of $\tau_{1/2}$ on $[\mathrm{IV}]_0$(●) and of k_{obs}^{-1} on (SH^-) (○) in 0.1N-NaOH solutions at 80 °C

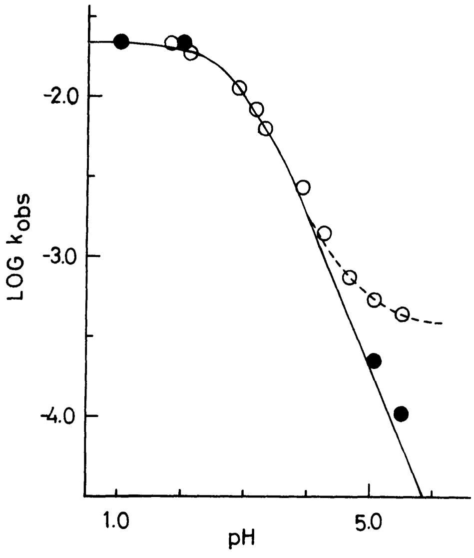


Fig. 3

Rate profiles for the decomposition of methyldithiocarbamic acid at 25 °C

● present work

○ work by Joris et al.

$$k_{obs} = \frac{(H^+)}{K + (H^+)} \cdot \frac{k_1 k_2 (OH^-)}{k_{-1}(SH^-) + k_2(OH^-)} \qquad (8)$$

Under alkaline conditions at pH 13, the reverse reaction with SH^- greatly contributes to decrease the rate, since k_{-1} $(SH^-)/k_2(OH^-)$ increased with the decrease of the concentration of OH^-. Equation (6) indicates that in solutions of lower OH^- concentration the deviation from the first-order law will be observed at earlier stages of the reaction. In solutions of pH 8 ~ 10 the deviation was, as expected, observed at above 20% decomposition even at initial concentration of IV of 5×10^{-5} M. The rate constants were obtained there from the initial rates upto 20% decomposition (Fig. 1).

Recently, Joris et al.$^{8)}$ reported another result that the decomposition reaction of IV into VI was involved in weakly acidic solutions. The rate-pH profile deviated at pH >4 from the theoretical curve for the decomposition leading to carbon disulfide and methylamine. They attributed the deviation to the presence of the decomposition reaction IV → VI. Our reinvestigation at pH 5.0 and 5.5 under strictly non-oxidative conditions resulted in no deviation from the theoretical curve$^{8)}$ as shown in Fig. 3. Their erroneous results must be obtained because of the ignorance of the oxidation.$^{9)}$

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