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DECOMPOSITION OF DITHIOCARBAMATES. III.[1) ETHYLDITHIOCARBAMIC ACID IN CONCENTRATED SULFURIC ACID SOLUTIONS[2)

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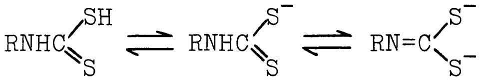
The UV spectral changes and decomposition rates of ethyldithiocarbamic acid (I) were investigated in sulfuric acid solutions. The presence of the S-protonated form (IV) was established. The observed first-order rate constants fit with the rate expression, $k_{obs} = kK/(h_0 + K)$, derivable from the proposed mechanism, $IV \overset{K}{\rightleftharpoons} I \xrightarrow{k} EtNH_2 + CS_2$.

No comprehensive interpretation has been provided to account for the protonation of dithiocarbamic acids. Various complicating protonated forms were presented.3,4) It is very important problem to determine the protonated forms correctly for the establishment of the decomposition pathways.

As a part of research in wide concentration ranges of acid and alkali, we have confirmed the presence of equilibria shown in equation 1; acid form (I) $\rightleftharpoons$ anion form (II) in weak acid solutions5) and II $\rightleftharpoons$ conjugate base (III) in caustic alkali solutions.6) The present paper extends the work to the investigation of protonation and decomposition of ethyldithiocarbamic acid (Etdtc) in aqueous sulfuric acid solutions from 10 to 70 w/w% concentrations photometrically and kinetically.

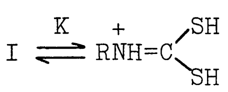


(eq. 1)

I II III

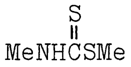
UV-spectra. The UV spectrum of the acid form (I) of Etdtc in 10 w/w% sulfuric acid solution displayed two absorption maxima at 236 and 267 nm. No appreciable changes of the spectra were observed in the solutions containing between 10 and 40 w/w% sulfuric acid. In more concentrated solutions, however, the intensity of the band at longer wavelength decreased and that of shorter wavelength increased with the increase of acid concentrations. A selection of the absorption curves is shown in Fig. 1. The spectra showed an isosbestic point at about 255 nm and the peak at 267 nm, once disappeared in a 68.7 w/w% sulfuric acid solution, reappeared by dilution with water.

The spectral changes should appear due to the shift of the equilibrium between I and it's conjugate acid (IH^+) from I to IH^+. The ionization constant K for $IH^+ \rightleftharpoons I + H^+$ was estimated to be 6×10^3 M (pKa = -3.8) using equation $E = (E_{IH^+} - E)h_0/K + E_I$, where E's are absorbances at 267 nm, and h_0 is Hammett's non-logarithmic acidity function. The value of pKa was not so precisely determined since the decomposition of I existed to small extent. The similar hypsochromic changes in UV spectra between II (255, 285 nm) and III (255 nm),[6] and between V (243, 268 nm)[7] and VI (243 nm) indicated the presence of the chromophore $N{=}C{<}^{S}_{S}$ in III and VI and, consequently, in IH^+ (242 nm).



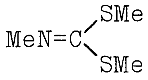
$$I \overset{K}{\rightleftharpoons} RNH{=}\overset{+}{C}(SH)_2$$

IV (= IH^+)



$$MeNH\overset{\overset{S}{\|}}{C}SMe$$

V



$$MeN{=}C(SMe)_2$$

VI

In addition, O-protonation on amides[8] and carbamic acids[9] suggests the protonation on the sulfur of thiocarbonyl group of I in the case of I to IH^+. Thence the structure of IH^+ is assumed to refer to the S-protonated conjugate acid (IV).

Decomposition Reactions. Decomposition rates were measured at initial concentrations of about 10^{-2} M of Etdtc in carefully deairated sulfuric acid solutions, by following the decrease of absorbance at 250-267 nm at 25°C.

The values of pseudo-first-order rate constants (k_{obs} min^{-1}) decreased in a form of dissociation curve with the increase of acid concentrations as depicted in Fig. 2. The solid line, which best fits the experimental points, was derived from equation $k_{obs} = kK/(h_0 + K)$ which is in accord with kinetic scheme of equation 2. The constants which provide the best fit of the curve are $k = 2.5 \times 10^{-2}$ min^{-1} and $K = 6.5 \times 10^3$ M (pKa = -3.8).

$$\begin{tikzcd} I \arrow[r, "k"] \arrow[d, shift left, "+H^+"] & EtNH_2 + CS_2 \\ IV \arrow[u, shift left, "-H^+"] & \end{tikzcd} \qquad \text{(eq. 2)}$$

Complete deairation of the reaction media and initial concentrations (10^{-2} M or more) of Etdtc were both required to measure the rates accurately. A lack of one of the both requirements caused the side reaction to form N,N'-diethylthiuram disulfide.[10] A similar oxidation was observed previously but the structure of the product was not determined.[7]

The main conclusion to be drawn from these results is that the decomposition solely takes place via I to ethylamine and carbon disulfide as shown in equation 2. The direct decomposition via IV would not contribute to overall decomposition rates of any detectable amounts if it were existed.[4]

Combination of equations 1 and 2 leads us to further conclusion that an

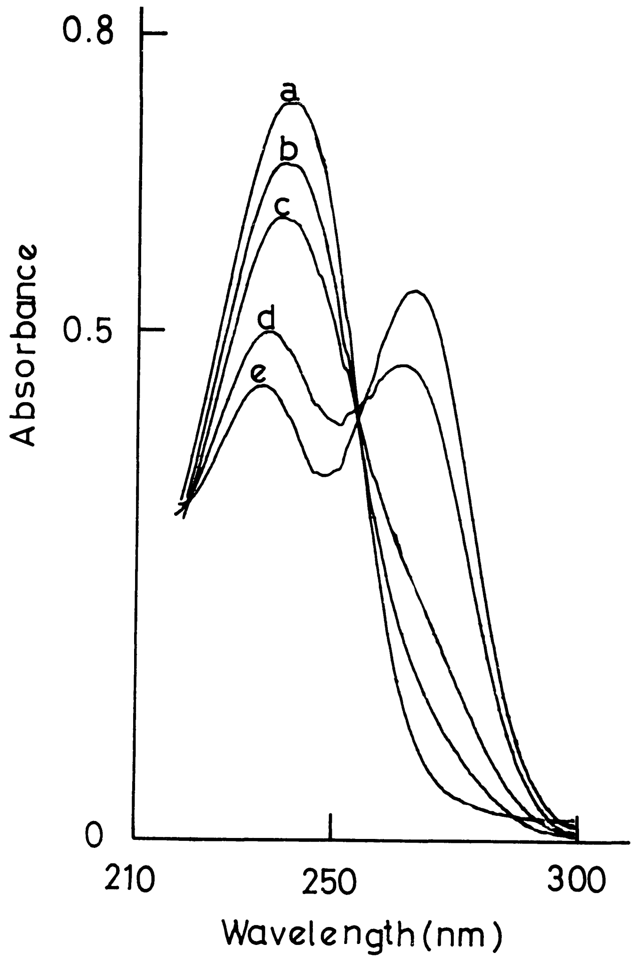


Fig. 1. Absorption spectra of Etdtc (I) in various sulfuric acid solutions at 25°C.
a: 68.7 w/w%, b: 58.7 w/w%,
c: 57.3 w/w%, d: 49.2 w/w%,
e: 40.1 w/w%.

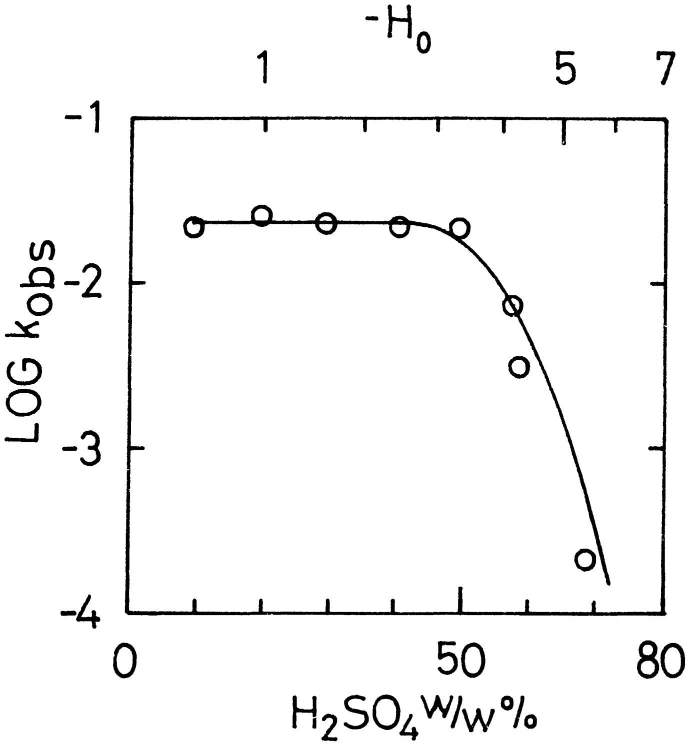


Fig. 2. Rate profile for the decomposition of Etdtc (I) at 25°C.

N-monosubstituted dithiocarbamic acid in wide concentration ranges of acid and alkali can be represented as the followings:

$$\mathrm{IV} \rightleftharpoons \mathrm{I} \rightleftharpoons \mathrm{II} \rightleftharpoons \mathrm{III}.$$

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