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THE UV SPECTRA AND DISSOCIATION CONSTANTS OF SOME DITHIOCARBAMATES (1)

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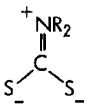
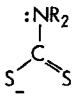
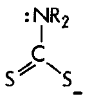
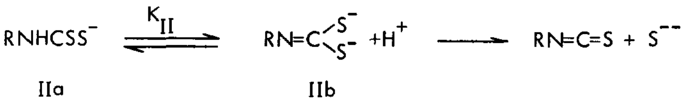
It is well known that the water soluble salts of dithiocarbamates show two UV absorption bands of fairly high intensity, one in the neighbourhood of 250 nm, and the other at about 290 nm (2). Koch assigned the band of shorter wavelength to the extreme structure I to be associated with polarization of the nitrogen conjugation, and that of the longer wavelength to the canonical structures Ia and Ib due to sulfur conjugation (3). Janssen has reversed Koch's assignment on the basis of the spectral data on 70 thion compounds (4), though no reliable support to his idea was obtained from his quantum-mechanical calculations (5). In this paper we wish to report the unambiguous assignment for the above two bands and the dissociation constants of some dithiocarbamates.


I


Ia


Ib

Wronski has studied the decomposition of N-monosubstituted dithiocarbamates in alkaline solutions and reported that the kinetic data were in agreement with decomposition via a fast pre-equilibration between monothiolate IIa and dithiolate IIb followed by the decomposition of IIb to give the isothiocyanate and S^{--} ion (6). From the rate-pH profile the ionization constant for the equilibrium was determined. The values of pK_{II}' lie between 13 and 14; 13.3_9 (20°C), 13.7_2 (30°C) and 13.9_6 (40°C) for dithiocarbamate, 13.3_1 (45°C) and 13.5_7 (55°C) for phenyldithiocarbamate and 13.2_2 (70°C) for ethyldithiocarbamate (7).



$$RNHCSS^- \overset{K_{II}}{\rightleftharpoons} RN{=}C\begin{matrix}S^-\\S^-\end{matrix} + H^+ \longrightarrow RN{=}C{=}S + S^{--} \qquad \text{eq. 1}$$

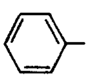
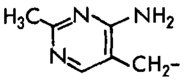
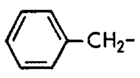
IIa IIb

If the equilibrium between IIa and IIb exists in the pH region, the intensity due to IIa should reasonably decrease as the equilibrium shifts to the right and that due to IIb should increase. This idea was experimentally proved as shown in Fig. 1. The UV spectra of phenyldithiocarbamate change greatly in concentration between 1 and 5 mole/l of caustic alkaline solution, but scarecely in pH region. The intensity of the band at the longer wavelength 291 nm, decreased as alkaline concentration increased; on the other hand, that of the band at shorter wavelength, 257 nm, increased. These spectral changes should be due to reversible process IIa $\rightleftharpoons$ IIb, in equation 1, since the spectra showed an isosbestic point at 275 nm and the peak at 291 nm disappeared in strong alkaline medium reappeared by dilution with water.

Similar behaviors were observed in the UV spectra of [(4-amino-2-methyl-5-pyrimidyl)methyl]-dithiocarbamate and benzyldithiocarbamate; the spectra of the former compound changed to a great extent in a range of 5-10 mole/l and the latter in a range of 10-15 mole/l of KOH solution, respectively. These results agree with the Koch's assignment but not with Janssen's.

The above findings enabled us to calculate the values of ionization constant K_{II}' which are listed in Table I.

Table I. UV Spectra and pK_{II}' of dithiocarbamates $RNHCSS^-$ at 25°C

Compound	λmax (nm)		pK_{II}' *
R =	IIa	IIb	
	291	257	14.6 (0.937), 14.6 (0.979), 14.8 (0.912)
	284	253	16.2 (0.971), 16.4 (0.997), 16.5 (0.882)
	284	251	16.9 (0.992), 17.1 (0.991)

* For the calculation of K_{II}', the following equation was used; $E_{obs} = (E_{IIa} - E_{obs})h_-/K_{II}' + E_{IIb}$, where h_- refers to non-logarithmic acidity function and E to the absorbances of the substance of the subscript. The values in the parentheses are correlation coefficients.

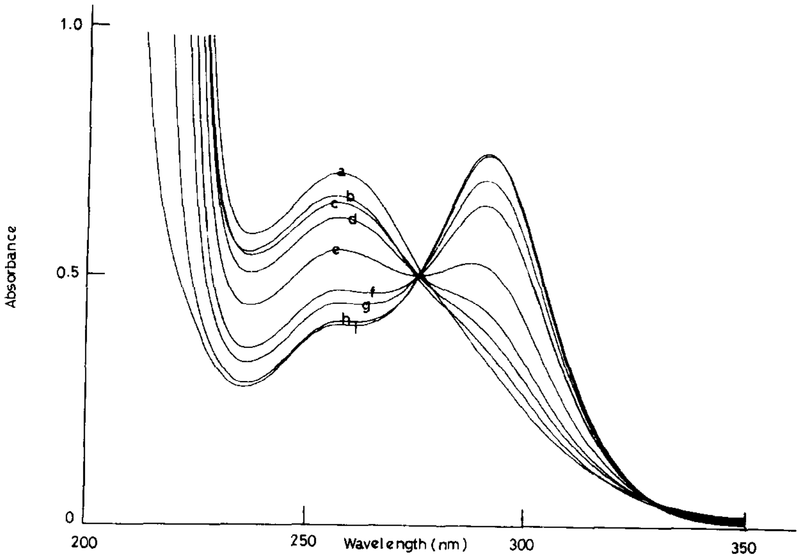


Fig. 1. Absorption spectra of phenyldithiocarbamate (10.1 γ/ml) in various caustic alkaline solutions at 25°C. a: 5 mole/l, b: 4 mole/l, c: 3.5 mole/l, d: 3 mole/l, e: 2 mole/l, f: 1 mole/l, g: 0.5 mole/l, h: 0.1 mole/l, i: 0.001 mole/l.

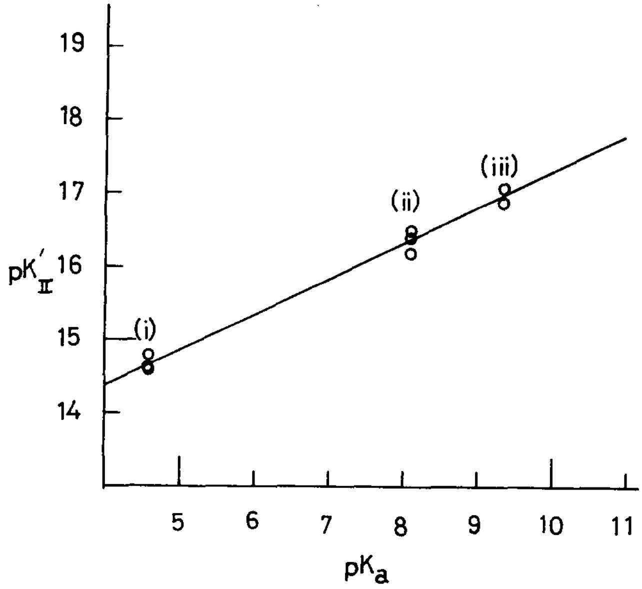


Fig. 2. Brønsted plot of pK_{II}' vis pKa of starting amine. (i) phenyldithiocarbamate, (ii) [(4-amino-2-methyl-5-pyrimidyl)methyl] dithiocarbamate, (iii) benzyldithiocarbamate.

The Brønsted plot of pK_{II}' vis pKa of the corresponding starting amine showed a linear relationship with a correlation coefficient $\gamma = 0.994$ as shown in Fig. 2. Equation 2 predicts the pK_{II}' of ethyl-

$$pK_{II}' = 0.49 \text{ pKa of amine} + 12.41 \qquad \text{eq. 2}$$

dithiocarbamate to be ca 17.6 ($EtNH_2$: pKa 10.63), which differs too greatly from the value of the Polland author (6); the results show a failure of the Wronski's assignment of the dissociation of IIa to IIb based on the analysis of rate-pH profile. Accordingly, it seems to be required for his mechanistic expression to introduce a role of at least one of species such as IIa and SH^- and/or S^{--} liberated during the course of reaction.

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6. M. Wronski, Chem. Abst. 55, 4113 (1961).
7. These values were obtained by the following equation, where K is the equilibrium constant reported by Wronski (6).

$$pK_{II}' = 14 - \log K$$