

## Communications to the Editor

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Decomposition of Dithiocarbamates in weakly Acidic Solutions<sup>1)</sup>

Many workers have studied kinetically the decomposition of dithiocarbamates (I) in weakly acidic solutions of pH range.<sup>2)</sup> The decomposition occurs in all cases *via* a fast proton pre-equilibration step followed by a subsequent rate-determining decomposition of the protonated species to corresponding amine (IV) and carbon disulfide.<sup>3)</sup> Miller and Latimer have proposed an S-protonated form (II) or its intramolecularly hydrogen-bonded form (III) as a protonated species.<sup>4)</sup>

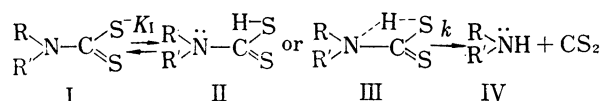
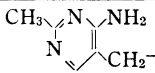


Chart 1

There are no established concepts for the rate-determining step though the proton-transfer II→IV<sup>4)</sup> or the N-C bond cleavage III→IV<sup>5)</sup> was taken from stereochemical point of view. However, the electronic feature to affect the rate is not so clear. A linearity was found between logarithms of rate constants (log *k*) and p*K*<sub>a</sub> of dithiocarbamic acids (p*K*<sub>1</sub>′); log *k* increased with the increase of p*K*<sub>1</sub>.<sup>6)</sup> The used compounds seemed to be not suitable for the detection of the electronic effect because the steric crowding of the substituents on the nitrogen atom causes the acceleration of the rate.<sup>4)</sup>

Considerable importance of the reaction<sup>2)</sup> prompted us to study the mechanistic pathway. Our strategy was to examine the inductive effects of substituents of the nitrogen atom by using three N-monosubstituted dithiocarbamates derived from primary amines of different p*K*<sub>a</sub>, where the steric factors should be removed. Kinetic measurements were performed spectrophotometrically at 25°. Rate constants and p*K*<sub>1</sub>′ were calculated from apparent first-order rate constants. The data are summarized in Table and Fig. 1.

TABLE I. Rate and Dissociation Constants at 25° and UV Spectra of I (R′=H)<sup>a)</sup>

R	<i>k</i> min <sup>-1</sup>	p <i>K</i> <sub>1</sub> ′	p <i>K</i> <sub>a</sub> (R-NH <sub>2</sub> )	λ <sub>max</sub> (mμ)	
				I (0.1N NaOH)	II (1N HCl)
	1.80 × 10 <sup>-1</sup>	1.6 <sub>3</sub>	8.25	253, 284	243, 267
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> -	6.12 × 10 <sup>-2</sup> (7.59 × 10 <sup>-2</sup> )	2.5 <sub>4</sub>	9.35	251, 284	240, 272
C <sub>2</sub> H <sub>5</sub> -	3.32 × 10 <sup>-2</sup> (1.70 × 10 <sup>-2</sup> )	3.2 <sub>0</sub>	10.63	253, 284	238, 269

a) The values in parentheses are reported in the literature 3.

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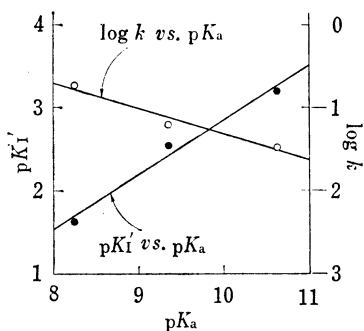
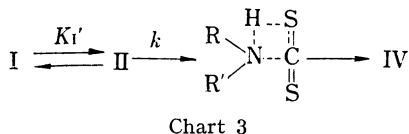
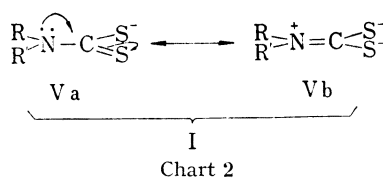


Fig. 1. Brønsted Plots of  $\log k$  and  $pK_I'$  against  $pK_a$  of Corresponding Amine



Respective Brønsted plots of  $\log k$  and  $pK_I'$  against  $pK_a$  of corresponding amine give a good linearity. Figure manifests that an electron-donating group on the nitrogen atom increases the stability of I. If the proton-transferring in the step II→IV were the rate-determining step, the rate should increase with increasing the basicity of the nitrogen atom, as Miller, *et al.* noted,<sup>4)</sup> contrary to the above finding.

An alternant explanation can be given by taking into consideration of the conjugation of II. It is well known that I is stabilized with resonance between canonical forms (Va) and (Vb).<sup>1,2)</sup> Ultraviolet (UV) absorptions of I in 250 and 280  $\mu$  regions appear due to this resonance.<sup>1)</sup> The spectra of II also display the corresponding two bands at about 240 and 270  $\mu$ , as shown in Table, though the absorption maxima of II are displaced to lower wavelength. It is a clear indication that II is still stabilized with the resonance. An electron-donating group on the nitrogen atom increases the resonance stabilization. Thus, the rate-determining step must be the N-C bond cleavage. The resonance naturally demands that the lone-pair electrons of nitrogen atom and the  $\pi$ -electrons of thiocarbonyl group lie on the same plane. The steric requirement rules out the possibility of the intramolecularly hydrogen bonded form II<sup>4,5)</sup> in the ground state.

The final problem was that the internal proton-transferring occurs whether before or after the N-C bond cleavage. The formation of I or II must be initiated by the attack of lone-pair electrons on nitrogen atom of IV to the carbon atom of carbon disulfide acting as a Lewis acid. The rule of microscopic reversibility suggests that the proton-transferring occurs before the N-C bond cleavage or at least synchronously. However, the proton-transferring before the N-C bond cleavage will hardly occur, since the net charge (Q) of nitrogen atom was calculated to be positive due to the resonance.<sup>7)</sup> Therefore, the increase of basicity of the nitrogen atom on the losing of N-C bond into the critical distance will assist the proton-transferring.

In conclusion, we propose a mechanism as shown in Chart 3.

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