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The Photolysis of Sodium *N,N*-Dimethyldithiocarbamate and Hexamethyleneammonium Hexamethylenedithiocarbamate

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We have previously reported that sodium *N,N*-dimethyldithiocarbamate (SMTC) is photolyzed by light of the wavelength of 2537 Å. The absorption was attributed to the excitation of a sulphur-conjugated system. We also found carbon disulfide in the photo-decomposition products.[1] It was then considered desirable to make a more quantitative assessment of carbon disulfide for the purpose of elucidating the kinetics of the photolytic process.

Unless otherwise stated, the experiments were carried out with SMTC or hexamethyleneammonium hexamethylenedithiocarbamate (HMTC) solutions of $3—6\times10^{-5}$M. A deaerated solution was photolyzed in the same manner as before.[1] The produced carbon disulfide was transformed into potassium methylxanthate, which shows an optical absorption at 300 nm in methanol. The amount of the methylxanthate produced, and consequently the yield of carbon disulfide, increased as the

1) T. Yamase, H. Kokado and E. Inoue, *Kogyo Kagaku Zasshi*, **72**, 162 (1969).

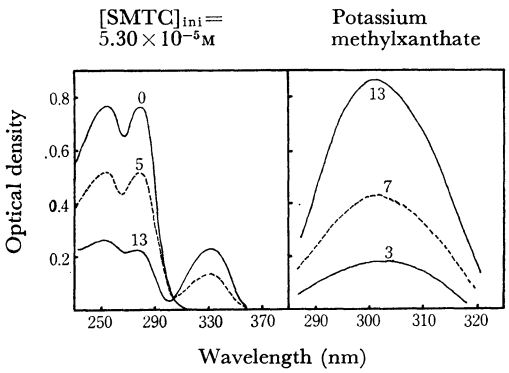

Fig. 1. Absorption spectra of SMTC solution and formed potassium methylxanthate.
Numbers indicate the illumination time (min) of SMTC solution

dithiocarbamate was photolyzed (Fig. 1). The experimental results can be represented as in the following equation, as was anticipated in the previous paper[1]:

$$-dC/dt=kC=dC'/dt=k(C'_\infty-C')$$

where C is the concentration of dithiocarbamate in mol/l and where C' and C'_∞ are the concentrations of carbon disulfide in mol/l at the illumination times of $t=t$ and $t=\infty$ respectively. Representing the concentration by the optical density of each absorption, some log plots derived from the rate formula are shown in Fig. 2. Juging from Fig. 1, the quantity of produced carbon disulfide

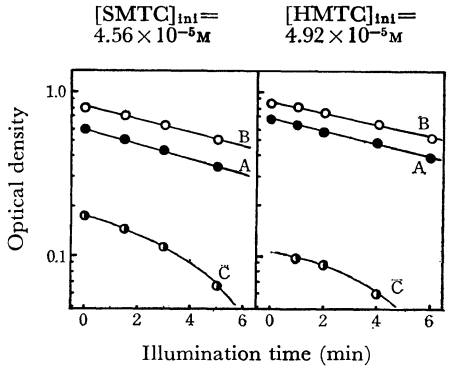

Fig. 2. Optical density as a function of illumination time:
A indicates optical density (O.D) of SMTC and HMTC at 280 nm and 282 nm, respectively.
B and C indicate $O.D_\infty$—O.D at 300 nm and 330 nm, respectively.

can be regarded as the same as the decrease in dithiocarbamate. When the initial concentrations of SMTC were 5.92×10^{-5}M and 4.56×10^{-5}M, the amounts of carbon disulfide produced by prolonged photolysis were 5.70×10^{-5}M and 4.49×10^{-5}M respectively. There remains scarcely any doubt that carbon disulfide is produced by a unimolecular reaction and that the photolysis proceeds by first-order kinetics.

After the photolysis of SMTC, the optical density at 330 nm was decreased and a new absorption appeared at 264 nm. It may be inferred that a stable species was produced *via* an unstable species with the absorption maximum at 330 nm. The change in the absorption of the solution after photolysis is shown in Fig. 3. Such a spectrum was

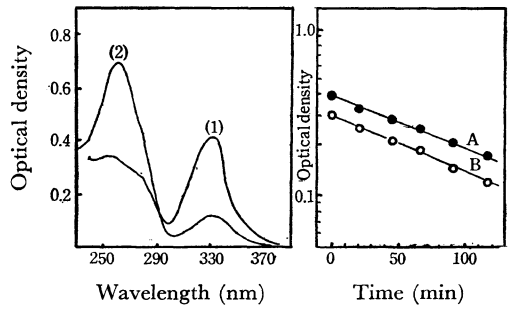

Fig. 3. Dark reaction after photolysis.
(1) and (2) indicate spectra of SMTC after 0 and 170 min, respectively;
A indicates optical density (O.D) at 330 nm.
B indicates $O.D_\infty$—O.D at 264 nm.
$[SMTC]_{ini}=1.06\times10^{-4}$M

not identified with that of dimethylamine, acetaldehyde, formaldehyde, or *N*-methylformaldehyde in an aqueous solution of pH 10, although all those substances had been anticipated as photoproducts. The quantum yield was unknown with regard to HMTC; however, we can easily infer that the quantum yield of HMTC is not far from the 0.11 which is observed in SMTC. This is evident from the fact that those two dithiocarbamates had almost the same slopes of photolytic rates and almost the same absorption coefficients[2]. The substance which has the absorption at 330 nm may be ascribed to an amine or imine derivative which reacts by the first-order process to show an absorption at 264 nm.

2) T. Yamase, H. Kokado and E. Inoue, *ibid.*, **71**, 1587 (1968).