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The Photoconductivity in a CCl_4 Solution of *N,N*-Dimethylaniline

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We have examined the photoconductivity in the solution of *N,N*-dimethylaniline in carbon tetrachloride. The carbon tetrachloride used was of a spectrograde and was not purified further. The *N,N*-dimethylaniline was purified by repeated vacuum distillation. The solution showed a remarkable photoconductivity upon ultraviolet irradiation (320—400 nm).

Since carbon tetrachloride is transparent at the wavelength of the exciting light, the photocurrent must be associated with the excited *N,N*-dimethylaniline.

However, since the solution of *N,N*-dimethylaniline in inert solvents such as cyclohexane, *n*-hexane, or benzene was not photoconductive, the photocurrent seems to be caused by an interaction between *N,N*-dimethylaniline and carbon tetrachloride. There are two possibilities in the mechanism of the interaction: energy transfer from the amine to the halide, and charge transfer in the excited states.[*1] The latter was proposed by Latowsky in studying the photo-reactions in an ethanolic solution of aromatic amines and aromatic halides.[1]

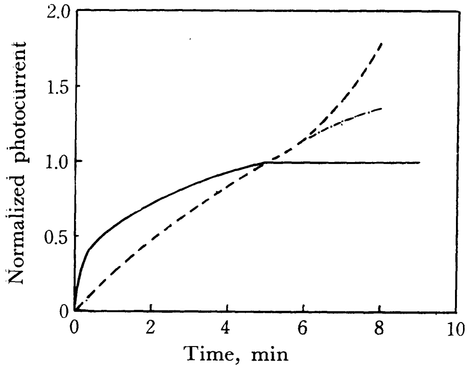


Fig. 1. Photocurrent profiles of solutions of three solutes in CCl_4.

(—·—·) *N,N*-dimethylaniline
(-----) MGCN
(———) MGH.

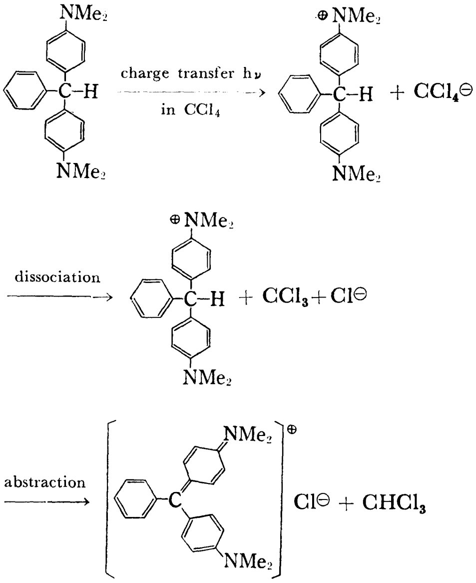
Exciting light, $\lambda = 320-400$ nm, from a 100 W high pressure Hg lamp. 3 V/cm.

In the charge-transfer mechanism the elementary processes are: (1) light absorption by *N,N*-dimethylaniline, (2) the electron transfer from the excited molecule to a carbon tetrachloride molecule, (3) the dissociation of the carbon tetrachloride anion to the chloride ion and the trichloromethyl radical,[2] and (4) various reactions which are initiated by the radicals.

To get some evidence for the charge-transfer mechanism, leuco malachite green (MGH) and malachite green leuconitrile (MGCN) were studied instead of *N,N*-dimethylaniline. The absorption spectra due to the dimethylanilino group in both materials are similar to those of *N,N*-dimethylaniline.[3]

Both materials, when dissolved in CCl_4, induced a photocurrent, the MGH solution became green, but the MGCN solution did not.

These results can be easily understood by assuming the charge-transfer mechanism for the initial photoinduced processes in these systems. A plausible mechanism for the dye formation is as follows:



[*1] In this system, there is a possibility of a weak charge-transfer interaction even in the ground state. See K. M. C. Davis and M. F. Farmer, *J. Chem. Soc., B*, **1967**, 28

1) T. Latowsky, *Z. Naturforschg.*, **23a**, 1127 (1968).

2) N. R. Daly and R. G. Ridley, *Nature*, **202**, 895 (1964).

3) A. H. Sporer, *Trans. Faraday Soc.*, **57**, 983 (1961).

The failure of color to develop in the MGCN solution indicates that the CN abstraction from the center carbon atom of MGCN is difficult.

By analogy with the results on these leucobases of malachite green, we may deduce that the photoconduction of the system is caused by the charge transfer from excited *N*,*N*-dimethylaniline molecules to CCl_4 molecules.