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Charge-transfer Complex of Sydnones

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Synopsis. The complex formation of 3-methylsydnone, 3-phenylsydnone, and 3,4-diphenylsydnone with TCNE was described. From the electronic absorption spectra of the complexes, ionization potentials of sydnones are estimated.

Due to their unique mesoionic character, sydnones have been the subject of continued study since their discovery in 1935.[1] It was reported[2] that sydnones formed complexes with Friedel-Crafts catalysts, and in all cases the bonding occurred through the exocyclic oxygen atom, which was deduced from the shift of carbonyl absorption in IR spectra. The mole ratio of sydnone to metal chloride was reported to be 1 : 1. It was also reported[3] that 3-phenylsydnone formed a loose complex with iodine in acetonitrile but the complex was not isolated. In this report we describe the complex formation study of sydnone with π-acid.

The electronic-absorption spectrum of a solution of 3-methylsydnone and tetracyanoethylene (TCNE) in dichloromethane showed absorption muximum at 405 nm, which cannot be attributed to the starting materials but to a new molecular species. We assume that the absorption band in this region is due to the presence of 3-methylsydnone–TCNE charge-transfer complex. 3-Phenylsydnone and 3,4-diphenylsydnone also formed charge-transfer complex with TCNE, showing characteristic absorption bands as shown in Table. The concentration dependence of the electronic absorption spectra of these complexes was analyzed by method of Benesi-Hildebrand.[4] From the result, the molar ratio in the complex is assumed to be 1 : 1 as in the case of 3-phenylsydnone–iodine complex.[3] Ionization potentials (I_p) of sydnones are estimated from the empirical relationship:[5]

$$\tilde{\nu}_{\max} = 0.487 I_p - 1.30 \text{ (eV)}$$

as shown in Table 1.

Table 1. Complexes formed between sydnones and TCNE (solvent, CH_2Cl_2; temperature, about 20 °C)

π-Base	$\lambda_{\max}$ (nm)	I_p (eV)
3-Methylsydnone	405	9.0
3-Phenylsydnone	405	9.0
3,4-Diphenylsydnone	495	7.8

The IR spectra of sydnone–TCNE complexes in dichloromethane did not show appreciable differences in comparison with that of each component. These complexes were not isolated as a crystal but dissociated to each component when the solvent was evaporated in a vacuum.

References

1) J. C. Earl and A. W. Mackney, *J. Chem. Soc.*, **1935**, 899.

2) a) T. S. L. Mao, *Dissertation Abstr.*, **25**, 1602 (1964). b) P. S. Gentile and T. S. L. Mao, *J. Inorg. Nucl. Chem.*, **27**, 867 (1965). c) T. S. L. Mao, U. S. At. Energy Comm. TID 20068 (1963); *Chem. Abstr.* **62**, 2488 (1965).

3) H. Yamada and K. Kozima, *J. Amer. Chem. Soc.*, **82**, 1543 (1960).

4) H. A. Benesi and J. H. Hildebrand, *ibid.*, **71**, 2703 (1949).

5) R. E. Merrifield and W. D. Phillips, *ibid.*, **80**, 2778 (1958).