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The Electron-acceptor Strength of 2,5-Diazido-3,6-dichloro-*p*-benzoquinone

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It has been proposed by Hammond that unsaturated, uncharged compounds contained within the formula $C_wN_xO_yF_z$ comprise a class of organic π-electron acceptors.[1] Here fluorine may be considered as representative of other halogens.[2] He also showed that a high degree of unsaturation is a requisite for large electron affinities. From such a point of view, the evaluation of the effect of the azido group N_3 on the properties of a typical electron acceptor seemed to be of considerable interest. The acceptor strength of 2,5-diazido-3,6-dichloro-*p*-benzoquinone, $C_6N_6O_2Cl_2$, in terms of its complexing properties will be compared with that of *p*-chloranil, $C_6O_2Cl_4$.

The diazidoquinone was prepared by the reaction of sodium azide on chloranil dissolved in methanol and was then recrystallized from benzene.[3] The complexes of the diazidoquinone and *p*-chloranil with the following twenty-nine donors were examined in dichloroethane solutions for the charge-transfer absorptions: (1) phenothiazine, (2) *o*-tolidine, (3) phenoxazine, (4) perylene, (5) 1,5-diaminonaphthalene, (6) dimethyl-*p*-toluidine, (7) dichloro-*o*-tolidine, (8) benzidine, (9) dibromo-*o*-tolidine, (10) *N*-methylphenothiazine, (11) dimethylaniline, (12) phenyl-1-naphthylamine, (13) diphenylamine, (14) anthracene, (15) pyrene, (16) phenoxathiin, (17) *o*-anisidine, (18) 1,2-benzanthracene, (19) 4,4′-dimethoxybiphenyl, (20) *m*-toluidine, (21) *o*-toluidine, (22) *p*-dimethoxybenzene, (23) *p*-chloroaniline, (24) 1-naphthol, (25) aniline, (26) thianthrene, (27) 2-naphthol, (28) *m*-chloroaniline, and (29) triphenylene.

It is well known that one may write, as a good approximation:[4]

$$h\nu_{CT} = I_D - E_A - C, \qquad (1)$$

where $h\nu_{CT}$ is the energy of charge-transfer absorption, where I_D is the ionization potential of the donor molecule, where E_A is the electron affinity of the acceptor molecule, and where C represents the electrostatic energy in the dative bond structure and some other minor terms. The difference in $h\nu_{CT}$ for the complexes of a given donor with two acceptors, 1 and 2, is, then:

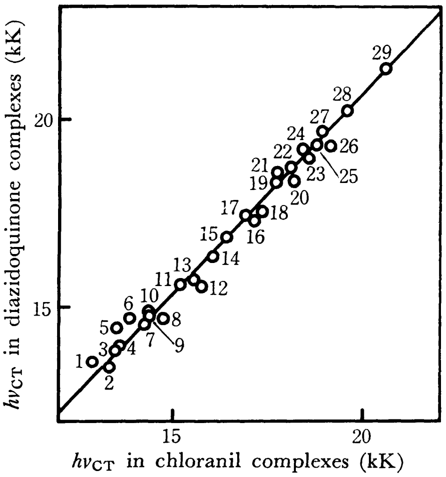

Fig. 1. Plots of wave numbers of maxima of the charge-transfer absorptions in the diazidoquinone complexes against those in the corresponding *p*-chloranil complexes. Point designation corresponds to the numbering of the donors given in the text.

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[1] P. R. Hammond, *Nature*, **206**, 891 (1965).

[2] P. R. Hammond, *J. Chem. Soc.*, *A*, **1968**, 145.

[3] K. Fries and P. Ochwat, *Ber.*, **56**, 1291 (1923).

[4] J. S. Ham, J. R. Platt and H. M. McConnell, *J. Chem. Phys.*, **21**, 66 (1953).

$$h\nu_{CT2} = h\nu_{CT1} + (E_{A1} - E_{A2}) + (C_1 - C_2). \qquad (2)$$

The term (C_1-C_2) need not be zero, but it may be as large as a few kK if the sizes and shapes of the acceptor molecules are very different.[5] In Fig. 1 the wave numbers of the absorption maxima in the diazidoquinone complexes with each of the above-mentioned donors are plotted against those in the corresponding *p*-chloranil complexes. The line was fitted by the method of least squares. The slope was found to be 1.018, the value is in excellent agreement with that required by Eq. (2). Although the (C_1-C_2) in the complexes of the present quinones is probably small, the intercept, 0.1 kK, is certainly within the limits of uncertainty in this term. Therefore, we may conclude that the electron affinity of 2,5-diazido-3,6-dichloro-*p*-benzoquinone is essentially the same as that of *p*-chloranil, which has been found to be 2.46 eV (19.8 kK) by the magnetron technique.[6] In other words, the azido group appears to be as effective as chlorine in improving the acceptor strength of *p*-benzoquinone.

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[5] Y. Matsunaga, This Bulletin, **42**, 2490 (1969).

[6] A. L. Farragher and F. M. Page, *Trans. Faraday Soc.*, **62**, 3072 (1966).