BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48 (7), 2207—2208 (1975)

Charge Transfer Interactions between Oxygen and the Anion Radicals of Tetracyanoquinodimethane and Tetracyanoethylene

Tadayoshi SAKATA, Toshihiro OKAI,* and Hiroshi TSUBOMURA
Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560

(Received February 24, 1975)

Synopsis. The spectra of the anion radicals of tetracyanoquinodimethane and tetracyanoethylene formed on porous Vycor glass change by introducing O_2 at 77 K. The main features are broadening and slight energy shift of the bands and appearance of a new band. These changes are explained by assuming the charge transfer interactions between O_2 and the anion radicals.

Anion radicals are expected to act as strong electron donors, since their ionization potentials are very low. It is expected therefore that they interact or react easily with O_2, a weak electron acceptor. Tsubomura *et al.* studied extensively the charge transfer (CT) interactions between O_2 and a large number of organic molecules.[1–3] In this paper, the interactions between O_2 and anion radicals of tetracyanoquinomethane (TCNQ) and tetracyanoethylene (TCNE) formed on Vycor glass are reported.

TCNQ and TCNE were adsorbed on porous Vycor glass plates *in vacuo* and their anions were produced by introducing triethylamine. The electronic absorption spectra of the anions agreed well with those reported in the literature.[4,5] The sample was cooled down to 77K and oxygen was introduced into the sample cell, since these anion radicals react easily with O_2 at room temperature.

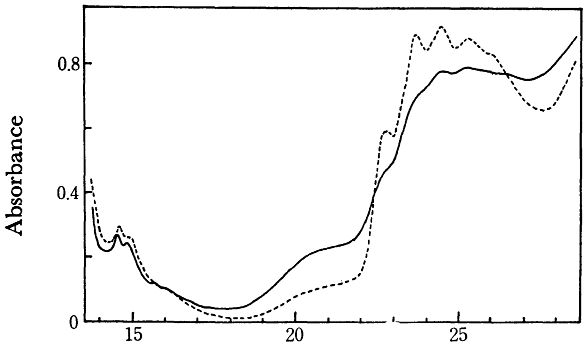

Fig. 1. Absorption spectra of $TCNQ^-$ at 77 K before (----) and after (——) the introduction of O_2.

Figure 1 shows the electronic absorption spectra of the anions before and after the introduction of O_2 at 77K. The band systems at ~15000 cm^{-1} showing some vibrational structures are attributable to the first excited state of $TCNQ^-$.[6] The strong band systems centered at around 25000 cm^{-1} is attributable to the second excited state of the anion. The weak absorption at 20500 cm^{-1} might be due to an impurity because it cannot be observed in the spectrum of $TCNQ^-$.[7]

The spectra show that the second band system of the anion becomes broad and the first one shifts slightly to red (~50 cm^{-1}), its intensity decreasing by the introduction of O_2. It is also shown that the absorption from 18000 to 22000 cm^{-1} swells, suggesting the appearance of a new absorption band. When O_2 is removed, the spectrum is mostly restored, showing that these spectral changes due to O_2 are reversible. Swelling of the absorption around 18000—22000 cm^{-1} with the introduction of O_2 and its reversibility with removal of O_2 were also observed in the case where *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine was used as a reducing agent instead of triethylamine.

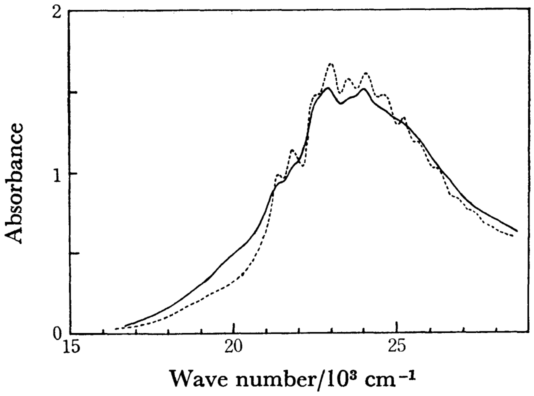

Fig. 2. Absorption spectra of $TCNQ^-$ at 77 K before (----) and after (——) the introduction of O_2.

Figure 2 shows similar results on $TCNE^-$. The vibrational structure characteristic of $TCNE^-$ almost disappears upon introduction of O_2, and the absorption around 20000 cm^{-1} swells, suggesting the appearance of a new band. The reversibility with O_2 removal was also observed.

These results can be explained by assuming weak charge transfer (CT) interactions between O_2 and the anion radicals (A^-). The vertical CT energy (E^{V}_{CT}) from A^- as an electron donor to O_2 can be expressed by[10]

$$E^{V}_{CT} = I^{V}_{P}(A^-) - E^{V}_{A}(O_2) + P(A\cdots O_2^-) - P(A^-\cdots O_2) \qquad (1)$$

where I^{V}_{P} and E^{V}_{A} are the vertical ionization potential and the vertical electron affinity, respectively, and $\Delta P = P(A\cdots O_2^-) - P(A^-\cdots O_2)$ represents the change in the polarization energy during the optical transition. Taking $I^{V}_{P}(A^-)$ to be roughly equal to $E_A(A)$, $I^{V}_{P}(TCNQ^-)$ and $I^{V}_{P}(TCNE^-)$ are estimated to be 1.7 eV[11] and 2.0 eV,[12] respectively. The adiabatic electron affinity of O_2 was determined to be 0.43 eV.[13] The vertical one, $E^{V}_{A}(O_2)$, is probably a littly negative.[1] As a counter balance to the adoption of $E_A(A)$ values for $I^{V}_{P}(A^-)$ which must cause some underestimation, it seems most

---

* Present address: Nippon Paint Co., Ltd., Osaka.

appropriate here to take $E_A^V(O_2)$ to be roughly zero. Inspite of the difficulty in evaluating the polarization energies rigorously, it seems reasonable to assume 1.0 eV for the value of ΔP.[14] Under these evaluations, the transition energies E_{CT}^V for $TCNQ^- \cdots O_2$ and $TCNE^- \cdots O_2$ are obtained as 2.7 eV (22000 cm^{-1}) and 3.0 eV (24000 cm^{-1}), respectively, in fair agreement with the spectral position where swelling occurs.

The reversible change of the absorption spectra around 20000 cm^{-1} for both anions is thus reasonably attributable to the CT interactions between O_2 and the radical anions. The small red shift and intensity change for the first band of $TCNQ^-$ and the broadening of the band shape in both cases are then explained by the CT interaction between O_2 and the anion radicals.

References

1) H. Tsubomura and R. S. Mulliken, *J. Amer. Chem. Soc.*, **82**, 5966 (1960).

2) H. Ishida, H. Takahashi, H. Sato, and H. Tsubomura, *ibid.*, **92**, 275 (1970).

3) H. Ishida, and H. Tsubomura, *J. Photochem.*, **2**, 285 (1974).

4) L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson, and W. E. Mochel, *J. Amer. Chem. Soc.*, **84**, 3374 (1962).

5) M. Sofue and S. Nagakura, This Bulletin, **38**, 1048 (1965).

6) D. A. Lowitz, *J. Chem. Phys.*, **46**, 4698 (1967).

7) A very small amount of α,α-dicyano-*p*-toluoylcyanide might be formed, since this compound has a strong absorption at 480 nm.[8,9]

8) W. R. Hertler, H. D. Hartzler, D. S. Acker, and R. E. Benson, *J. Amer. Chem. Soc.*, **84**, 3387 (1962).

9) K. Nakatani, T. Sakata, and H. Tsubomura, This Bulletin, to be published.

10) T. Sakata, T. Okai, H. Sugimoto, and H. Tsubomura, This Bulletin, **46**, 2698 (1973).

11) G. Briegleb, *Angew. Chem.*, **76**, 326 (1964).

12) L. E. Lyons and L. D. Palmer, *Chem. Phys. Lett.*, **21**, 442 (1973).

13) J. L. Pack and A. V. Phelps, *J. Chem. Phys.*, **44**, 1870 (1966).

14) For the CT complex between O_2 and I^- in ethanol, E_{CT}^V is about 4.4 eV.[15] Using $I_P^V(I^-)=3.1$ eV and $E_A^V(O_2)=0.15$ eV, ΔP is obtained as 1.45 eV. Therefore $\Delta P=1.0$ eV in our case seems to be a reasonable value, taking the difference of the environments and the ionic radii into consideration.

15) H. Levanon and G. Navon, *J. Phys. Chem.*, **73**, 1861 (1969).