Electron Transfer between Anion Radicals and Neutral Molecules as Revealed by Electron Spin Resonance Spectra

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Recently the anion radicals of various aromatic molecules have been prepared and their electron spin resonance and electronic absorption spectra extensively studied from both experimental and theoretical points of view. Anion radicals may be expected to possess low ionization potentials and, therefore, to be strong electron donors. This means that they may be able to form Mulliken type charge-transfer complexes with some electron acceptors.[1] Moreover, there may be a possibility that the complexes of this kind will exhibit interesting electric and magnetic properties. With these expectations, we have undertaken to study the interaction of some anion radicals with neutral aromatic molecules, mainly by measuring electron spin resonance spectra.

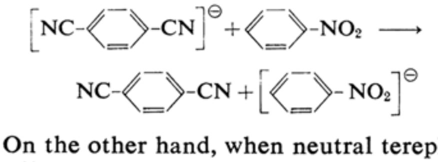
Experimental

Materials. — Commercial pyridine, benzonitrile and nitrobenzene of the G. R. grade were purified by distillation. Commercial *p*-dinitrobenzene, *p*-nitrotoluene, α-nitronaphthalene and 9-nitroanthracene of the G. R. grade were purified by repeated recrystallizations from ethanol. Their melting points are 173.5°C, 53.5°C, 61.5°C and 146°C respectively. Commercial terephthalonitrile was purified by repeated sublimations in vacuo; m. p. 222°C. Pyromellitonitrile was synthesized from pyromellitic acid through the following route. Pyromellitimide was obtained by heating ammonium pyromellitate[2] which had been prepared by neutralizing pyromellitic acid with aqueous ammonia. This pyromellitimide was then converted into pyromellitamide by aqueous ammonia. Pyromellitonitrile finally obtained by the dehydration of pyromellitamide was purified by repeated recrystallizations from ethanol. Nitrosobenzene was synthesized by the mild oxidation of phenylhydroxylamine with sodium chromate and purified by recrystallization from ethanol; m. p. 67.5°C. β-Nitronaphthalene was synthesized from the diazonium sulfate of β-naphthylamine by the addition of copper(I) oxide. Dimethoxyethane used as a solvent in the present experiment was carefully purified by the method described in a previous paper.[3]

The Preparation of Anion Radicals and the Measurement of ESR Spectra. — Anion radicals were prepared by the alkali metal reduction method in vacuo, as has been described in a previous paper.[3] Neutral molecules were added to the anion radical solutions in vacuo by the use of breakable joints. ESR spectra were measured at room temperature with a Hitachi ESR spectrometer model-18 (X band, 100 kc. modulation).

Results and Discussion

Let us take the nitrobenzene-terephthalonitrile system as an example and explain how the ESR spectrum of an anion radical changes upon the addition of a neutral molecule. First, the terephthalonitrile anion was prepared and the ESR spectrum was measured. The observed hyperfine structure was completely consistent with that obtained by Carrington and Todd[4] (see Fig. 1a). Thereafter, neutral nitrobenzene was added through the breakable joint in vacuo, and the ESR spectrum of the mixed solution was measured. The results are shown in Fig. 1b. The hyperfine structure of the terephthalonitrile anion disappeared and a new pattern, which could safely be assigned to that of the nitrobenzene anion,[5] was observed. At the same time, the color of the solution changed immediately from yellow (the color of the terephthalonitrile anion) to reddish purple (the color of the nitrobenzene anion). This clearly shows that the following electron transfer reaction occurs:


(1)

On the other hand, when neutral terephthalonitrile was added to the solution of the nitrobenzene anion, the hyperfine structure and the color of the solution remained unchanged. The above-mentioned experimental results lead to the conclusion that electron transfer does not occur from the nitrobenzene anion to the terephthalonitrile molecule but takes place only

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[1] R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952).

[2] H. Meyer and K. Steiner, *Monatsch. Chem.*, **35**, 391 (1914).

[3] A. Ishitani, K. Kuwata, H. Tsubomura and S. Nagakura, This Bulletin, **36**, 1357 (1963).

[4] A. Carrington and P. F. Todd, *Mol. Phys.*, **6**, 161 (1956).

[5] R. L. Ward, *J. Chem. Phys.*, **82**, 1296 (1961).

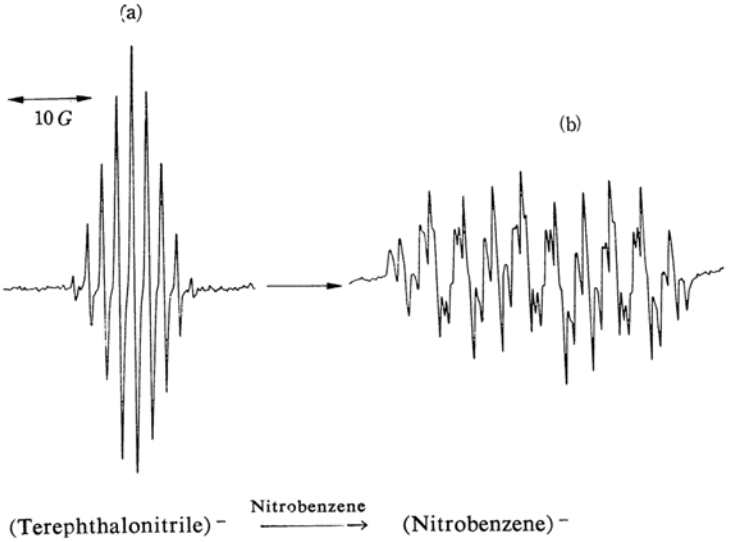
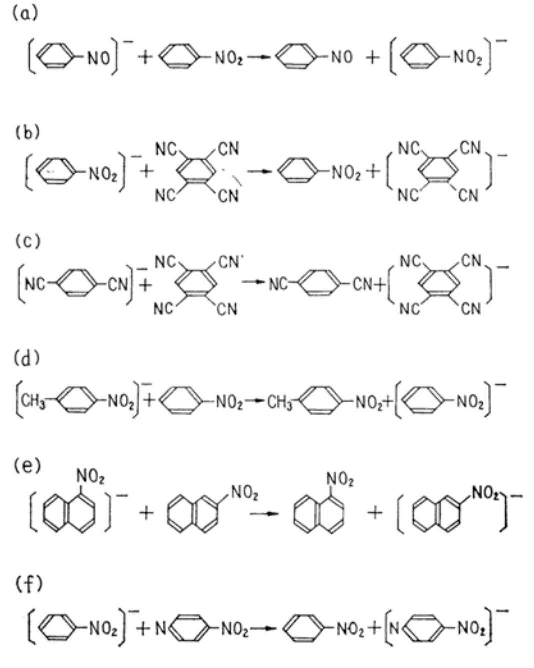


Fig. 1. The change in the ESR spectrum of the terephthalonitrile anion in dimethoxyethane by the addition of nitrobenzene.

in the direction shown in Eq. 1, and that, therefore, nitrobenzene is a stronger electron acceptor than terephthalonitrile is.

Similar experiments were carried out with more than ten systems. Typical examples are shown in Table I. All of them failed to show a tendency toward charge transfer complex formation, but, in all, the complete electron transfer occurred under the present experimental conditions. This may conceivably be due to the fact that the anion radicals are surrounded by polar solvent molecules and are stabilized largely by solvation energies. A similar electron transfer phenomenon from the naphthalene anion radical to anthracene has been reported by Wertz.[6]

TABLE I. ELECTRON TRANSFER BETWEEN SOME AROMATIC ANION RADICALS AND NEUTRAL MOLECULES



From the experimental results given in Table I, we could determine the order of the electron accepting abilities of various aromatic molecules. The results are shown below:

1) Pyridine < Benzonitrile < Terephthalonitrile < Nitrosobenzene < Nitrobenzene < Pyromellitonitrile < *m*-Dinitrobenzene
2) *p*-Nitrotoluene < Nitrobenzene
3) Nitrobenzene < 4-Nitropyridine
4) α-Nitronaphthalene < β-Nitronaphthalene
5) Nitrobenzene < α-Nitronaphthalene < 9-Nitroanthracene

Series 1 shows the effect of substituent groups upon the electron accepting ability. From this it may be inferred that the substituent groups increase the electron accepting ability of the benzene ring in the following order: $-CN < -NO < -NO_2$. In particular, it is noticeable that terephthalonitrile with two CN groups is a weaker electron acceptor than nitrobenzene or nitrosobenzene.

The order in series 2 can be understood by considering the electron releasing hyperconjugation effect of the methyl group. It is noticeable that the electron moves so completely between the two species, notwithstanding so small a difference in electron affinity,

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[6] J. Wertz, *Chem. Revs.*, 55, 922 (1955).

as in the system of nitrobenzene and *p*-nitrotoluene. Series 3 indicates that the pyridine nucleus is more electron attracting than is the benzene nucleus.

The results in series 4 can be explained by the fact that the nitro group at the β-position of the naphthalene nucleus is more sterically free and more strongly conjugated with the nucleus than is the nitro group at the α-position. This explanation may be said to be supported by the X-ray crystal analysis data showing that the nitro group of 1, 5-dinitronaphthalene is twisted by 67° from the aromatic ring plane,7) while the group of β-nitronaphthalene is coplanar with the naphthalene nucleus. Series 5 indicates that the electron affinity increases with an increase in the number of conjugated rings. This result seems to be consistent with the order of the magnitudes of the electron affinities evaluated theoretically with benzene, naphthalene and anthracene.8)

In this stage of the experiments, we can obtain only qualitative information about the electron affinities of aromatic molecules. However, by measuring the ESR spectra at various temperatures it may be possible to obtain some quantitative knowledge about the equilibrium of the $A^- + B \rightleftarrows A + B^-$ type, as was done by Hausser9) with the diphenylpicryl hydrazyl-tetramethyl-*p*-phenylenediamine system.

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7) J. Trotter, *Acta Cryst.*, **13**, 95 (1960).

8) N. S. Hush and J. A. Pople, *Trans. Faraday Soc.*, **51**, 600 (1955).

9) K. H. Hausser, *Naturwiss.*, **21**, 597 (1959).