

ESR AND ELECTRONIC ABSORPTION SPECTRA POSSIBLY ASSIGNABLE TO A RADICAL
ION IN THE SYSTEM OF DIAZOALKANE AND ELECTRON ACCEPTOR

Takumi Oshima and Toshikazu Nagai *

Institute of Chemistry, College of General Education, Osaka University,
Toyonaka, Osaka 560, Japan

(Received in Japan 7 July 1977; received in UK for publication 31 August 1977)

In our previous paper,¹ we reported that a number of electron acceptors cause the decompositions of a variety of diazoalkanes at ordinary temperature, presumably via radical cations of diazoalkanes. However the direct evidence for the presence of radical cations derived from diazoalkanes has not been given on the ESR and the electronic absorption measurements.

We report here the ESR and the electronic absorption spectra due to the radical ion pairs for approximately equimolar 9-diazo fluorene (9-DF) and 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ) or 2,3-dicyano-p-benzoquinone (DCNQ). As far as we know, this is the first observation of the radical ions due to diazoalkanes, though they were suggested as chemical intermediates by few authors.^{2,3}

As shown in Fig. 1a and 1b, the broad ESR signals observed immediately after mixing for the both systems in acetonitrile at 77 K changed to the hyper fine structures after warming up to 20 °C. At 77 K, although the above line broadening seems to be characteristic of the radicals in the frozen solvent, this phenomenon may arise through an interaction between the two component radical species involving a rapid electron exchange. At 20 °C, a signal due to a radical cation was not detected for DDQ system and the fine structure is apparently attributable to the radical anion of DDQ (Fig. 1a). However, for DCNQ, the spectrum (Fig. 1b) consists of a strong absorption accompanying a superimposed weak multiplet, which is not identical to that of an authentic DCNQ radical anion as seen in Fig. 1c.

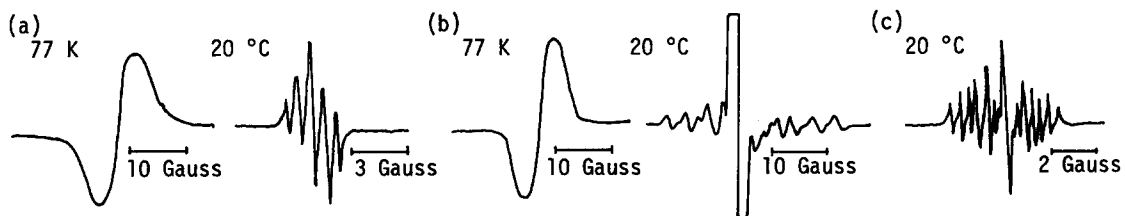


Fig.1. The ESR spectra of (a) 9-DF ($8.7 \times 10^{-2} \text{M}$)–DDQ ($8.8 \times 10^{-2} \text{M}$), (b) 9-DF ($1.0 \times 10^{-1} \text{M}$)–DCNQ ($1.0 \times 10^{-1} \text{M}$), and (c) the radical anion of DCNQ (Na salt) ($1.68 \times 10^{-4} \text{M}$) at 77 K and/or 20 °C in acetonitrile.

The strong absorption in Fig. 1b is regarded as resulting from the radical anion of DCNQ by considering that the line width is substantially equal to the total width of the authentic radical, the weak multiplet absorption, on the other hand, suggests the presence of another species, for which a counter radical cation derived from 9-DF is possibly responsible.

As to the electronic absorption measurements at 77 K employing EPA or 2-methyltetrahydrofuran as solvent, the colors of the dilute solutions of 9-DF–DDQ and 9-DF–DCNQ systems suddenly varied from nearly colorless to violet and purple respectively with the drop in temperature as seen in Fig. 2.

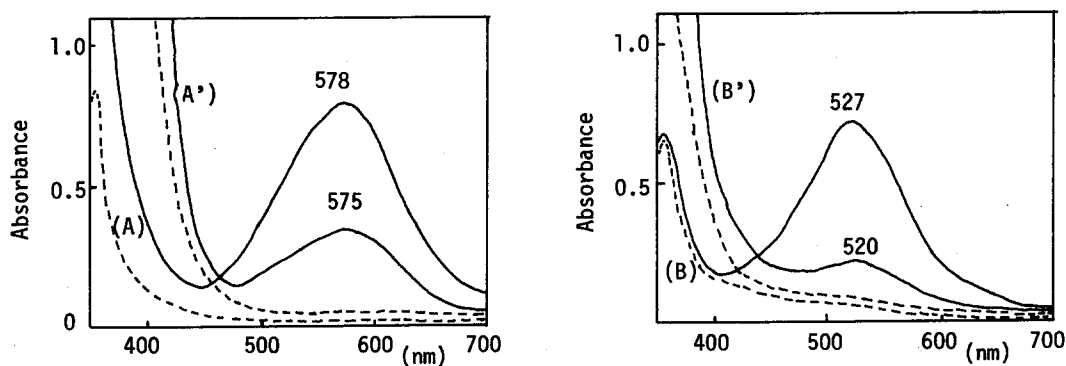


Fig.2. The electronic absorption spectra of 9-DF–DDQ and 9-DF–DCNQ at 77 K (—) and 20 °C (---); (A) in EPA, 9-DF ($3.5 \times 10^{-3} \text{M}$), DDQ ($3.5 \times 10^{-3} \text{M}$); (A') in 2-methyltetrahydrofuran, 9-DF ($1.1 \times 10^{-2} \text{M}$), DDQ ($1.1 \times 10^{-2} \text{M}$); (B) in EPA, 9-DF ($3.5 \times 10^{-3} \text{M}$), DCNQ ($3.5 \times 10^{-3} \text{M}$); (B') in 2-methyltetrahydrofuran, 9-DF ($1.2 \times 10^{-2} \text{M}$), DCNQ ($1.1 \times 10^{-2} \text{M}$): optical length 1 mm.

These new absorptions were stable at 77 K, but rapidly disappeared with the increase of temperature. The fact that the polar EPA brought about the increase in the absorptions compared with 2-methyltetrahydrofuran implies the absorptions attributable to the considerably polarized species. Here, the possibility of the free radical cation can be excluded by the finding of the different absorption maxima between DDQ and DCNQ. In addition, the free radical anions have quite different absorption curves.⁴ Furthermore, the same absorption as at 77 K could be found at 20 °C for DDQ system when the concentration was raised up, though it was rapidly decaying (Fig. 3a). The rapid decay and the appearance in relatively high concentration suggest that the species attributable to this absorption is considerably unstable and slightly present at 20 °C compared with at 77 K. Hence, these absorptions should be resulted from some transient complex species for which the electron acceptors would be markedly responsible.

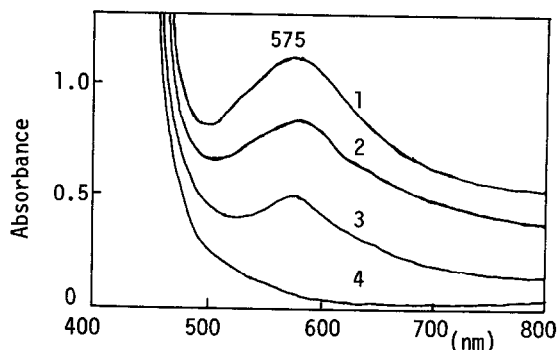
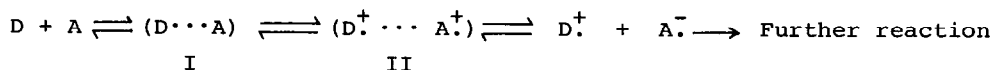


Fig. 3a. Time dependence of the electronic absorption spectra in the system of 9-DF ($9.3 \times 10^{-2} \text{M}$) and DDQ ($9.25 \times 10^{-2} \text{M}$) in 2-methyltetrahydrofuran at 20 °C; (1) immediately after mixing, (2) 5 min. (3) 30 min, (4) 2 hr: optical length 1 mm.

In general, it is considered that a chemical reaction proceeding by way of a charge-transfer complex involves the several transient intermediates as follows.



Taking into account this consideration, it is natural to believe that the present systems involve the charge-transfer complexes (I) and the radical ion pairs (II) prior to the free radical ions. So, in order to know whether the above

absorptions resulted from I or II, the electronic absorption spectrum as a Nujol mull for DDQ system(Fig.3b) was compared with those in the polar mediums mentioned above. This attempt brought about a new broad band with a peak at 672 nm which seems to be the result of the formation of the charge-transfer complex(I) because the IR spectrum measured after the preparation was essentially similar to a superposition of the spectra of the components.⁵

Accordingly, the most reasonable conclusion may be that the electronic absorptions at low temperature or at high concentration are attributed to the formations of radical ion pairs(II) as also supported from the observations of the ESR spectra.

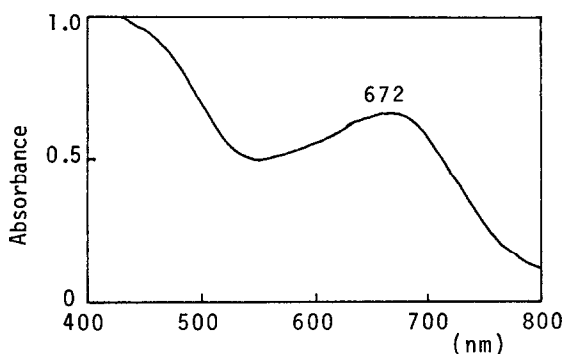


Fig.3b. The electronic absorption spectrum of equimolar 9-DF and DDQ as a Nujol mull.

REFERENCES

1. T. Oshima, A. Yoshioka, and T. Nagai, Tetrahedron Letters, 1789(1977).
2. H. Lind and E. Fahr, Tetrahedron Letters, 4505(1966).
3. W. Jugelt and F. Pragst, Angew. Chem., Int. Ed. Engl., 7, 290(1968).
4. Y. Iida, Bull. Chem. Soc. Jpn., 44, 1777(1971).
5. Y. Matsunaga, J. Chem. Phys., 41, 1609(1964).