

FORMATIONS AND REACTIONS OF RADICAL IONS IN THE SYSTEMS OF
DIAZOCOMPOUNDS AND ELECTRON ACCEPTORS

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We wish to report here that a number of diazocompounds undergo decomposition through the corresponding radical ion intermediates under the influence of a variety of electron acceptors such as chloranil(la), tetracyanoquinodimethane(lb), 2,3-dichloro-5,6-dicyano-p-benzoquinone(lc), and tetracyanoethylene(ld).

When phenyldiazomethane(2a) was mixed with an equimolecular la in dry acetonitrile under ordinary conditions, nitrogen gas evolved vigorously. Spectrophotometric measurements of this reaction showed a rapid decay of the diazoabsorption accompanying an increasing absorption in the shorter wavelength with a new peak at 450 nm, as shown in Fig. 1. This new peak is identical to the radical anion of la¹. The radical ion formation in this system was also confirmed by the ESR spectrum due to chloranil semiquinone², though no signal of a counter radical cation derived from 2a was observed in this condition, probably due to the instability of the radical cation.

Furthermore, la caused the decompositions of diazocompounds such as p-nitrophenyl-, 3,3'-dinitrodiphenyl-, diphenyldiazomethane(2b), and 9-diazofluorene, exhibiting the chloranil semiquinone in the ESR measurements in acetonitrile. In general, these stable diazocompounds required several hours or days for the complete decompositions in contrast with 2a.

As to lb, lc, and ld, they also revealed the respective radical anions^{3,4,5}, as seen in Fig. 2.

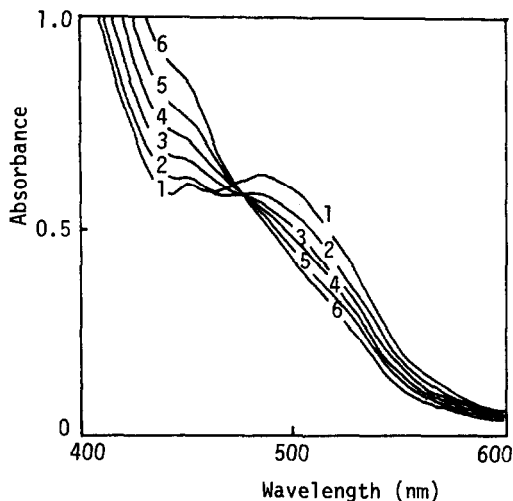


Fig. 1. Electron absorption spectra in the reaction of $\underline{2a}$ ($3.05 \times 10^{-2} M$) with $\underline{1a}$ ($3.05 \times 10^{-2} M$) in CH_3CN at $13^\circ C$; 3 minutes intervals, optical length 1 cm.

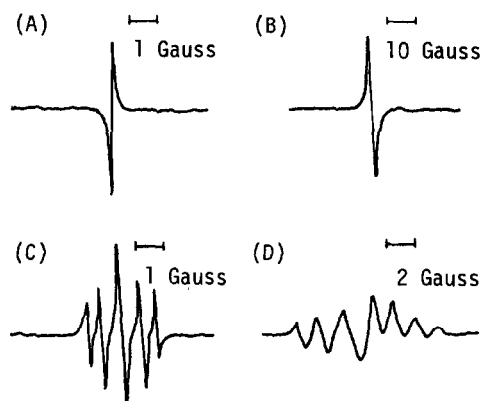
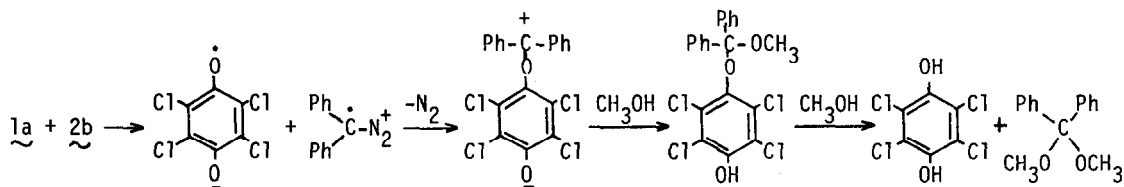


Fig. 2. ESR spectra of the radical anions derived from $\underline{1a}$, $\underline{1b}$, $\underline{1c}$, and $\underline{1d}$ in the presence of almost equimolecular $\underline{2b}$: (A) $\underline{1a}$, in CH_3CN ; (B) $\underline{1b}$, in CH_3CN ; (C) $\underline{1c}$, in CH_3CN ; (D) $\underline{1d}$, in THF.

The generations of radical ions in the present system are also supported from the fact of the chemical follow-up reactions: when $\underline{2b}$ was treated with $\underline{1a}$ in the presence of excess methanol, benzophenonedimethylketal (in 72% yield) and tetrachlorohydroquinone (69%) were isolated. The following mechanism involving a radical ion will be recommended to account for the products.



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