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Correlation between the Chemical Reactivity and the Unpaired Electron Distribution of Anion Radicals

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Anion radicals of mono-, di-nitrobenzophenones, dinitrobenzil, and nitrophenanthraquinone generated by reduction with alkali metal were studied by means of electron-spin resonance. The hyperfine coupling constant and the effect of the metal species on it were investigated. The correlation between the localization of the unpaired electron and the chemically reducible position was also discussed.

A large number of studies of anion radicals generated by the reduction of aromatic carbonyl compounds and aromatic nitro compounds, as made by means of ESR, have been reported.[1] The facility with which those compounds accept an electron and the rather great stability of the resultant anion radicals have attracted the attention of many investigators. Anion radicals can be generated by electrolytic reduction,[2] by reduction with alkali metal in a suitable solvent,[1,3] or by reduction with alkaline sodium dithionite in an aqueous solution.[4]

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[1] a) N. M. Atherton and S. I. Weissman, *J. Am. Chem. Soc.*, **88**, 1330 (1961); b) R. L. Ward, *J. Chem. Phys.*, **32**, 410 (1960); *J. Am. Chem. Soc.*, **83**, 1296 (1961); c) K. Maruyama, R. Tanikaga and R. Goto, This Bulletin, **35**, 1746 (1962); d) D. H. Geske, J. A. Ragle, M. A. Bambenek and A. L. Balch, *J. Am. Chem. Soc.*, **86**, 987 (1964); *etc.*

[2] A. H. Maki and D. H. Geske, *J. Am. Chem. Soc.*, **83**, 1852 (1961).

[3] R. L. Ward, *J. Chem. Phys.*, **30**, 852 (1959).

[4] P. L. Kolker and W. A. Waters, *J. Chem. Soc.*, **1964**, 1136.

The investigation of anion radicals resulting from the compounds with both nitro and carbonyl groups in a molecule is of much interest from the viewpoint of their free-spin localization and their chemical reactivity. In this study, all the anion radicals were generated by reduction with alkali metal in order to get information about the ion-pair between the anion radical and the metal cation.

Experimental

All the compounds used were synthesized in our laboratory. Their physical constants and the methods of synthesis are shown in Table 1. For the ESR measurement, the compound to be reduced was dissolved in *ca.* 10 m*l* of dry dimethoxyethane to give about a 10^{-3} M solution *in vacuo*, and then the anion radical was generated by bringing the solution in contact with the fresh surface of an alkali metal. A 3BX-type ESR spectrometer with a 100 kc modulation manufactured by the Japan Electron Optics Lab. was used in these measurements. The spectra obtained were calibrated by reference to the hyperfine coupling constant of peroxylamine disulfonate.

Results and Discussion

Unpaired Electron Delocalization of Anion Radicals. Mono- and Di-nitrobenzophenone Anion Radicals. The results shown in Table 2 indicate that the unpaired electron of anion radicals generated from nitrobenzophenones is localized only on a nitro-substituted phenyl group, although the compounds have two reducible functional groups.[5] This was definitely confirmed by the observation of the ESR spectrum of the anion radical of d_5-phenyl *p*-nitrophenyl ketone. The spectrum observed was just the same as that of the anion radical generated from *p*-nitrobenzophenone. This conclusion can also be substantiated by other observations. The anion radicals generated from 4-methyl-4′-nitrobenzophenone and from 4-methoxy-4′-nitrobenzophenone showed spectra similar to that of the *p*-nitrobenzophenone anion radical. Furthermore, each of the observed hyperfine structures of nitrobenzophenone anion radicals was very similar to each of those of the corresponding monohalogeno nitrobenzene anion radicals.[6,7] The anion radicals of nitrobenzophenones, therefore, can be considered to be anion radicals of benzoyl-substituted nitrobenzenes.

There have been a large number of experiments and calculations on the free-spin delocalization of the substituted nitrobenzene anion radicals.[2-7] For example, Geske and his co-workers[8] investigated the substituted nitrobenzene anion radicals by ESR. Their calculation on the nitrobenzene anion radical consisting with their experimental

TABLE 1. PREPARATION AND PHYSICAL CONSTANTS OF NITRO COMPOUNDS

Compound	Method of Synthesis	Mp, °C
Benzophenone		
p-Nitro-	Friedel-Crafts reaction[1]	138
m-Nitro-	Friedel-Crafts reaction[2]	95
o-Nitro-	Oxidation of *o*-nitrodiphenylmethane[3]	105
4-Methyl-4′-nitro-	Friedel-Crafts reaction[4]	122
4-Methoxy-4′-nitro-	Friedel-Crafts reaction[5]	121
4, 4′-Dinitro-	Oxidation of 4, 4′-dinitrodiphenylmethane[6]	189
3, 3′-Dinitro-	Nitration of benzophenone[7]	154.5—155.3
2, 2′-Dinitro-	Nitration of benzophenone[7]	194.8—195.0
Benzil		
4, 4′-Dinitro-	Nitration of dihydrobenzoin[8]	211.0—211.5
Phenanthraquinone		
2-Nitro-	Nitration of phenanthraquinone[9]	257
2, 7-Dinitro-	Nitration of phenanthraquinone[9]	302—303

1) G. Schroeter, *Ber.*, **42**, 3360 (1909).
2) R. Geigy and W. Koenigs, *ibid.*, **18**, 2401 (1885).
3) R. Geigy and W. Koenigs, *ibid.*, **18**, 2403 (1885).
4) H. Limpricht and E. Samietz, *Ann.*, **286**, 321 (1895).
5) K. Auwers, *Ber.*, **36**, 3898 (1903).
6) W. Staedel, *Ann.*, **194**, 347, 369 (1878).
7) W. Staedel, *ibid.*, **194**, 349 (1878), **283**, 164 (1894).
8) F. D. Chatterway and E. A. Coulson, *J. Chem. Soc.*, **1928**, 1363.
9) A. Werner, *Ann.*, **321**, 336 (1902).

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[5] For the analytic details of the ESR spectra, see K. Maruyama and R. Goto, *Rev. Phys. Chem. Japan*, **34**, 30 (1964).

[6] P. H. Lieger and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 609 (1963).

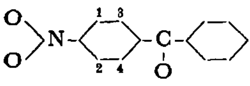
[7] T. Fujinaga, Y. Deguchi and K. Umemoto, This Bulletin, **37**, 822 (1964).

[8] D. H. Geske, J. A. Ragle, M. A. Bambenek and A. L. Balch, *J. Am. Chem. Soc.*, **86**, 987 (1964).

TABLE 2. HYPERFINE COUPLING CONSTANTS OF ANION RADICALS*4

Substance	Alkali metal	a_N	a_{H_1}*5	a_{H_2}*5	a_{H_3}*5	a_{H_4}*5	a_M*6
p-Nitrobenzophenone	Li	8.41	3.10	3.10	0.68	0.68	0.00
	Na	8.14	3.10	3.10	0.62	0.62	0.30
	K	7.41	2.91	2.91	0.68	0.68	0.20
m-Nitrobenzophenone	Li	8.14	2.81	2.62	2.45	0.90	0.00
	Na	8.07	3.02	2.72	2.44	0.81	0.30
	K	7.37	3.28	2.88	2.49	0.87	0.20
o-Nitrobenzophenone	Li*2	—	—	—	—	—	—
	Na	7.80	3.03	2.60	0.82	0.82	0.10
	K	7.29	2.96	2.57	0.79	0.79	0.00
4, 4′-Dinitrobenzophenone	Li	7.96	3.05	3.05	0.77	0.77	0.00
	Na	7.14	2.83	2.83	0.63	0.63	0.27
	K	6.37	2.79	2.79	0.65	0.65	0.17
4-Methoxy-4′-nitrobenzophenone	Li	8.45	3.02	3.02	1.00	1.00	0.00
	Na	7.90	3.11	3.11	0.76	0.76	0.30
	K	7.24	3.02	3.02	0.75	0.75	0.15
4-Methyl-4′-nitrobenzophenone	Li	8.50	3.02	3.02	0.94	0.94	0.00
	Na	8.03	3.02	3.02	0.72	0.72	0.25
	K	7.10	2.92	2.92	0.66	0.66	0.10
3, 3′-Dinitrobenzophenone	Li	10.60	4.17	3.78	3.47	1.11	0.00
	Na	10.45	4.27	3.80	3.30	1.07	0.37
	K	9.28	4.33	3.79	3.22	1.16	0.17
2, 2′-Dinitrobenzophenone	Li*1	—	—	—	—	—	—
	Na	9.40	4.36	3.25	1.20	1.20	0.00
	K	9.33	4.28	3.25	1.20	1.20	0.00
4, 4′-Dinitrobenzil*2	Li*1	—	—				
	Na	0.00	0.85				
	K	0.00	0.84				
	Rb	0.00	0.84				
4, 4′-Dinitrobenzil*3	Li	5.17	—	2.58			
	Na	4.90	—	2.10			
	K	4.82	—	2.18			
	Rb	4.00	—	2.10			
2-Nitrophenanthraquinone	K	0.00	1.94	0.97	0.44		
2, 7-Dinitrophenanthraquinone	K	0.00	1.94	0.97	0.44		

*1 Anion radical could not be obtained.
*2 Anion radical which shows the smaller overall splitting.
*3 Anion radical which shows the larger overall splitting.
*4 Measurements are all conducted at 18—20°C, Solvent: Dimethoxyethane.
*5 Positions of protons are listed below.
*6 Coupling constant due to alkali metal.



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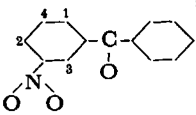

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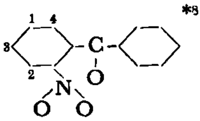

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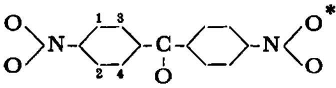

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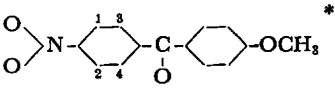

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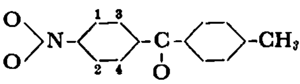

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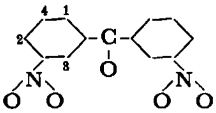

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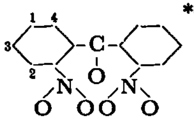

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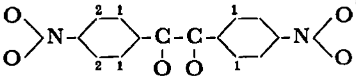

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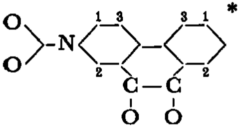

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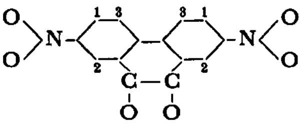

*7)

*7) Assignment of splittings to positions was done on the basis of the experiments.
*8) Assignment of splittings to positions was done tentatively from a comparison with a result of SHMO calculation.

result showed that $\sim$65% of the free spin was localized on the nitro group. Since such a substituent as a halogen atom or a carbonyl group can not induce an drastic change in the free-spin delocalization—— as can be deduced from a comparison with the coupling constant due to the nitrogen atom of the nitro group, the position of the highest free-spin density is on the nitro group.

Anion radicals of dinitrobenzophenone generated from $2,2'$-, $3,3'$- and $4,4'$-dinitrobenzophenone showed spectra indicating that the unpaired electron was delocalized only on one phenyl group; their ESR spectra quite resemble that of the anion radical generated from the corresponding mononitrobenzophenone.[5] Therefore, the position of the highest free-spin density is on one of two nitro groups for the same reason as has been given above.

Another outstanding phenomenon of these mono- and dinitrobenzophenone anion radicals was that the hyperfine coupling constant due to the nitrogen atom varied systematically with the species of alkali metal. This may be unambigously attributable to the ion-pair formation between the anion radical and the cation. It was found that the ^{13}C hyperfine coupling constant of benzophenone carbonyl carbon also varied with the species of alkali metal[9]; it was ascribed to the existence of the ion-pair.

Dinitrobenzil Anion Radicals. The anion radicals of dinitrobenzil obtained by reduction with alkali metals showed some unusual phenomena. Typical observed ESR spectra are shown in Fig. 1. By the usual procedure an unsymmetrical spectrum with a larger overall splitting was observed, regardless of the species of alkali metals. However, a symmetrical spectrum with a smaller overall splitting could be observed if it was very much diluted. This change from the unsymmetrical to the symmetrical was dependent on the temperature and on the ionic size of the cation with which anion radical was forming the ion-pair. In general, we could observe the unsymmetrical spectrum at lower temperatures, even if it was diluted. Moreover, if metallic lithium was used for the reduction, only the unsymmetrical spectrum could be observed, while if metallic rubidium was used, then the symmetrical spectrum with the smaller overall splitting was easily observed. From the results described above, it may

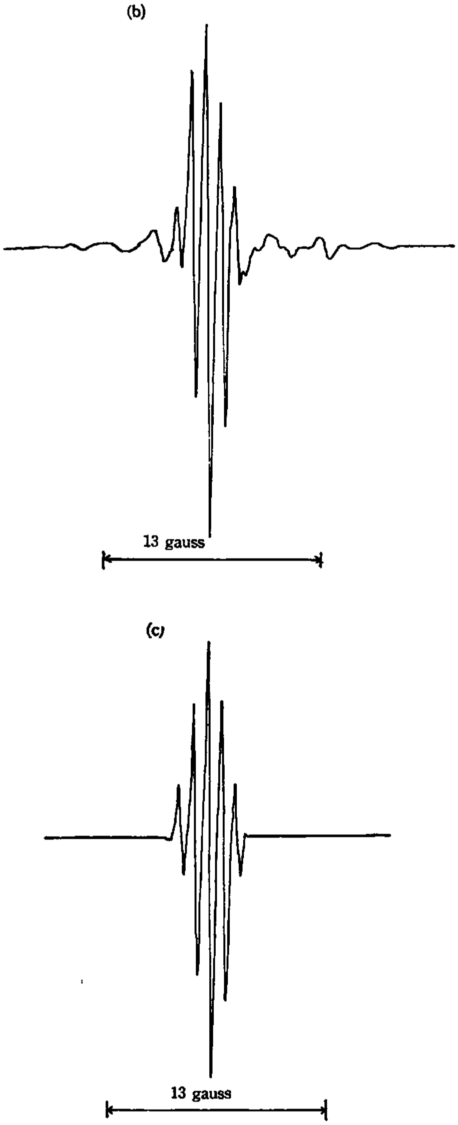

Fig. 1. ESR spectra of sodium dinitrobenzil anion radical.
(a) in a higher concentration
(b) in a medium concentration
(c) in a extremely diluted concentration

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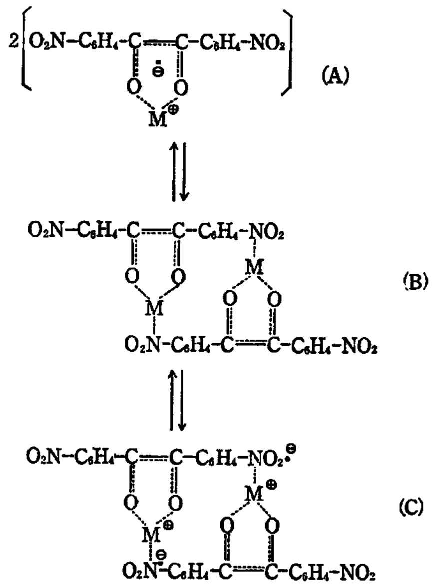
[9] N. Hirota, *ibid.*, **89**, 32 (1967).

be concluded that there is an equilibrium between the ion-pair monomer, which shows a symmetrical spectrum, and the ion-pair dimer, which shows a spectrum with a larger overall splitting. Therefore, the spectrum actually observed in usual concentrations is a superposition of the two.



(1)

M⊕: metal cation
M: atomic metal

There must be a rapid equilibrium among the ion-pair monomer (A) and ion-pair dimers (B and C), for the observed spectrum is unusually broad. The symmetrical five line spectrum (intensity ratio; 1 : 4 : 6 : 4 : 1) with the smaller overall splitting (4.1 gauss) will correspond to the A structure, while the spectrum with the larger overall splitting (19.9 gauss) will correspond to the C structure. The B structure seems to be a transient stage for the electron-transfer reaction. This may be explained by the fact that the overall splitting of the spectrum of α-diketone ketyls is, in general, about 5 gauss, while that of anion radicals of nitro compounds is larger than 10 gauss, consisting of three equivalent lines due to the nitrogen atom accompanying with the other hyperfine structure.[1-8,10] For example, the overall splitting of potassium benzil ketyl is 4.5 gauss and the hyperfine coupling constant due to the four hydrogen atoms occupying the position α to α-dicarbonyl group is 0.96 gauss. Estimating from the hyperfine coupling constant (0.85 gauss), ~75% of the free-spin is localized on the α-dicarbonyl group in A.

Mono- and Di-nitrophenanthraquinone. The anion radicals of 2-nitro- and 2, 7-dinitrophenanthraquinone, both generated by reduction with alkali metal, showed quite similar symmetrical ESR spectra, with an overall splitting of about 7 gauss. The solution of anion radicals was pink, but it turned into a green diamagnetic solution if it was present in a high concentration. Analogous phenomena have been found in the case of phenanthraquinone ketyls.[11] The hyperfine structure of 2, 7-dinitrophenanthraquinone can be analysed as a spectrum consisting of three sets of two equivalent hydrogen atoms (the coupling constants are 1.94 gauss, 0.97 gauss, and 0.44 gauss respectively). Estimating from the coupling constants obtained, more than 70% of the free spin is localized on the α-dicarbonyl group in the anion radical of 2-nitro- or 2, 7-dinitrophenanthraquinone. Thus, the unpaired electron delocalizes only on the aromatic ring, is highly concentrated on the α-dicarbonyl group, and does not delocalize on the nitro group.

The hyperfine coupling constants obtained are summarized in Table 2.

Correlation between Chemical Reactivity and Unpaired-electron Distribution. In the compounds which have two or three functional groups in a molecule, the problem of which group is the most reactive for a reagent is of great interest to the organic chemist. Nitrobenzophenones, nitrobenzil, and nitrophenanthraquinone have two or three functional groups for the reduction. From the results of the ESR study we can determine the position which has the highest free-spin density in a molecule. The positions to be reduced and the positions of the highest free-spin density in the compounds which have two or more functional groups are tabulated in Table 3. As can be seen in Table 3, there is a definite correlation between the most reactive position of a compound for the chemical reduction and the highest free-spin density of the anion radical generated from the corresponding compound. In nitrobenzophenone anion radicals, the position of the highest free-spin density is on the nitro group, and nitrobenzophenone can be reduced at the nitro group to the corresponding reduced compound, regardless of the species of the reducing reagent.

By the reduction of dinitrobenzil, both α-dicarbonyl and nitro groups can be reduced at the same time; the results obtained by ESR study show the existence of an equilibrium between the anion radical monomer and the anion radical dimer in the system because the concentration of the substrate is high enough to form the dimer. As has been described above, the unpaired electron delocalizes mainly on the α-dicarbonyl group in the monomer anion radical, whereas the unpaired electron delocalizes mainly on the nitro group in the anion radical dimer. The experimental results, therefore, completely support the idea that

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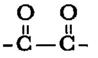
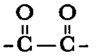
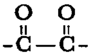
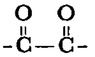
10) R. Dehl and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 1793 (1963).

11) K. Maruyama, This Bulletin, **37**, 553 (1964).

TABLE 3. THE REDUCED GROUP AND GROUP HAVING THE HIGHEST FREE SPIN DENSITY

Substance	Group having highest free spin density	Reducing reagent	Product
Benzophenone			
p-Nitro-	$-NO_2$	Sn+HCl	*p*-Aminobenzophenone[1]
		Zn+NaOH	4, 4'-Dibenzoylazo- and 4, 4'-dibenzoylazoxybenzene[2]
m-Nitro-	$-NO_2$	Sn+HCl	*m*-Aminobenzophenone[3]
		Zn+NaOH	3, 3'-Dibenzoylazo- and 3, 3'-dibenzoylazoxybenzene[2]
		Electroly. (alkaline)	3, 3'-Dibenzoylazo- and 3, 3'-dibenzoylazoxybenzene[4]
		Electroly. (acidic)	*m*-Aminobenzophenone[4]
o-Nitro-	$-NO_2$	Sn+HCl	*o*-Aminobenzophenone[3]
		Zn+NaOH	*o*-Aminobenzophenone[5]
4, 4'-Dinitro-	$-NO_2$	Sn+HCl	4, 4'-Diaminobenzophenone[6]
3, 3'-Dinitro-	$-NO_2$	$SnCl_2$	3, 3'-Diaminobenzophenone[7]
		Na-Hg	3, 3'-Diaminobenzhydrol[8]
2, 2'-Dinitro-	$-NO_2$	Sn+HCl	2, 2'-Diaminobenzophenone[9]
Benzil			
Non-substituted	 $-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-$	$SnCl_2$	Benzoin[10]
4, 4'-Dinitro-	 $-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-$	Sn+HCl	4, 4'-Diaminodesoxybenzoin[11]
p-Nitrobenzaldehyde	$-NO_2$[14]	$SnCl_2$	*p*-Aminobenzaldehyde[12]
		$Zn+NH_4Cl$	*p*-Hydroxyaminobenzaldehyde[13]
p-Nitroacetophenone	$-NO_2$[14]	Zn+HCl	*p*-Aminoacetophenone[15]
m-Nitroacetophenone	$-NO_2$[14]	Zn+HCl	*m*-Aminoacetophenone[16]
		Electroly. (acidic)	*m*-Aminoacetophenone[4]
Phenanthraquinone			
2-Nitro-	 $-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-$	$C_6H_5NHNH_2$ CH_3COOH	2-Nitro-9, 10-dihydroxyphenanthrene[17]
		$H_2S+C_2H_5OH$	2-Nitro-9, 10-dihydroxyphenanthrene[17]
		Sn+HCl	2-Amino-9, 10-dihydroxyphenanthrene[18]
2, 7-Dinitro-	 $-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-$	$C_6H_5NHNH_2$ $+CH_3COOH$	2, 7-Dinitro-9, 10-dihydroxyphenanthrene[17]
		$H_2S+C_2H_5OH$	2, 7-Dinitro-9, 10-dihydroxyphenanthrene[17]
		Sn+HCl	2, 7-Diamino-9, 10-dihydroxyphenanthrene[18]
m-Dinitrobenzene		Na_2S_2	*m*-Nitroaniline[19]
		Sn+HCl	*m*-Nitroaniline[19]
		Electroly.	*m*-Nitroaniline[17]
Naphthalene[20]		$Na+C_2H_5OH$	1, 4-Dihydronaphthalene[21] 1, 4, 5, 8-Tetrahydronaphthalene

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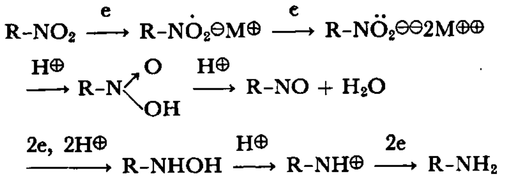
the more reactive position is the position of the highest free-spin density. Thus, if the chemical reduction is performed under extremely diluted conditions, it can be supposed that dinitrobenzoin will be the reduction product.

Much as in the case of dinitrobenzil, the reduction products of mono- and dinitrophenanthraquinone are mono- and dinitro-9, 10-dihydrophenanthrene if reduction is performed under mild conditions using such reducing reagents as hydrogen disulfide and phenylhydrazine.[12] However, both nitro and α-dicarbonyl group can be reduced if one uses such a strong reducing reagent as tin and hydrochloric acid. The free-spin density of nitrobenzaldehyde anion radicals has been investigated by Rieger and Fraenkel[13]; the position of the highest free-spin density is on the nitro groups for all isomers. By the chemical reduction they are all reduced at the nitro group to give amino- or azobenzaldehydes according to the species of reducing reagent. Such a general rule can be applied even to the aromatic hydrocarbon. For example, the position of the highest free-spin density is the α-position in the naphthalene anion radical, and 1, 4-dihydro- or 1, 4, 5, 8-tetrahydronaphthalene is the first reduction product of naphthalene with metallic sodium and ethanol. Although it is generally accepted that the first stage of the reduction is the formation of the anion radical, the successive steps remain ambiguous. From the above discussion, however, it seems plausible that the successive reduction step is the formation of the dinegative ion which is in a state of contact ion-pair with the counter cation. The counter cation might be a cation from heavy metal, a cation from alkali metal, an ammonium cation, and or even a proton. In support of this discussion, it is instructive to consider the reduction of m-dinitrobenzene. The anion radical of the compound has been studied in detail by several investigators. If one reduces m-dinitrobenzene with alkali metal,[1b,3]: one of the two nitro groups has a higher free-spin density as a result of ion-pair formation, whereas if one reduces it electrolytically,[14] then the two nitro groups have an equivalent free-spin density. By the chemical reduction of m-dinitrobenzene with the usual mild reducing reagents, one of the two nitro groups can be reduced to amino, hydroxyamino, or azo groups, *etc.*[15] Even if the compound is reduced electrolytically, one of the two nitro groups can be reduced predominantly.[16] These experimental results suggest that there is a contribution of the ion-pair even in the course of the electrolytic reduction. Although the stable anion radical of m-dinitrobenzene has two equivalent nitro groups in such a aprotic solvent as acetonitrile, a proton might be a counter cation of the ion-pair in an electrolysis conducted in a protic solvent which is a usual solvent in electrolytic reduction, and the accession of a proton to the anion radical may cause the localization of an electron on one of the two nitro groups. Thus, for example, the reduction of nitro group may proceed as in Eq. (2);



$$\begin{aligned}
&\mathrm{R\text{-}NO_2} \xrightarrow{e} \mathrm{R\text{-}N\dot{O}_2{\ominus}M{\oplus}} \xrightarrow{e} \mathrm{R\text{-}N\ddot{O}_2{\ominus\ominus}2M{\oplus\oplus}}\\
&\xrightarrow{H\oplus} \mathrm{R\text{-}N(\rightarrow O)OH} \xrightarrow{H\oplus} \mathrm{R\text{-}NO + H_2O}\\
&\xrightarrow{2e,\ 2H\oplus} \mathrm{R\text{-}NHOH} \xrightarrow{H\oplus} \mathrm{R\text{-}NH{\oplus}} \xrightarrow{2e} \mathrm{R\text{-}NH_2}
\end{aligned}$$

M⊕: metal cation (2)

Therefore, it may be concluded that the chemical reduction proceeds with an ion-pair formation in every case.

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