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ELECTRON SPIN RESONANCE STUDIES OF RADICAL-ANIONS OF NITROBENZOPHENONES

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Anion-radicals of nitrobenzophenones were studied by using an electron spin resonance spectromer. Anion-radicals were generated by the reduction of the corresponding nitrobenzophenones with alkali metals. Lithium, sodium and potassium were used in this investigation. Hyperfine splittings due to nitrogen and protons were determined. The hyperfine splitting constant due to nitrogen atom varies with the species of alkali metals systematically.

Introduction

A large number of such studies of radical-anions generated by the reduction of aromatic carbonyl compounds and aromatic nitro compounds as made by means of ESR have been reported[1]. The addition of an electron to an aromatic nitro compound or carbonyl compound yields a radical-anion. The facility with which those compounds accept an electron and rather large stability of the resulting radical-anion have attracted the attention of investigators.

Thus radical-anions can be generated by electrolytic reduction[2][3], by reduction with an alkali metal[1][4] in a suitable solvent or by reduction with alkaline sodium dithionite[5] in aqueous solution.

Recently an appreciable change of the hyperfine splitting constant of an anion-radical in different solvents or by different reducing methods, has been noticed. Kolker and Waters[5] recognized that the hyperfine splitting constant (a_N) due to nitrogen atom of nitrobenzene derivatives formed in water was all much larger than those for radicals formed in dry methyl cyanide. It was found by one of the authors that the splitting constant due to hydrogen atom (a_H) for radical-anion of phenanthraquinone also varies with the species of metal[1-c]. The present investigation is concerned with anion-radical of nitrobenzophenones generated by reduction with alkali metal in non-aqueous media.

Experimental

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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, *Bull. Chem. Soc. Japan*, 35, 1746 (1962), *ibid.*, **37**, 553 (1964) etc.

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

[3] L. H. Piette, P. Ludwig and R. N. Adams, *ibid.*, **84**, 4212 (1962)

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

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

The nitrobenzophenone derivatives were prepared as described in Table 1 and recrystallized before use. They were dissolved in 10 m*l*. of dimethoxyethane to give about 10^{-3} mol/*l* solution *in vacuo*. Radical-anions were generated by the contact of the solution with the fresh surface of an alkali metal. The spectra were all calibrated by reference to the hyperfine splitting constant of peroxylamine disulphonate (13 gauss). The ESR spectrometer with 100 KC modulation was used in this investigation.

Table 1 Preparation of nitrobenzophenone derivatives and their physical constants

Benzophenone	Method of preparation	Melting point (°C)
p-nitro-	Friedel-Crafts reaction6)	138
m-nitro-	〃 7)	95
o-nitro-	Oxidation of *o*-nitro-diphenylmethane8)	105
p-nitro, *p*′-methyl-	Friedel-Crafts reaction9)	122
p-nitro, *p*′-methoxy-	〃 10)	121
p, *p*′-dinitro-	Oxidation of *p*, *p*′-dinitro-diphenylmethane11)	189

Results and Discussion

Similar to the anion-radical of benzophenone12) and of phenanthraquinone, the variation of hyperfine splitting constant with different alkali metals as a reducing agent was also found in this case. Table

Table 2 Splitting constants (in gauss) for radical-anions of mono-nitrobenzophenones
Solvent: Dimethoxyethane

Substance	Alkali metal	a_N	a_{H_1}	a_{H_2}	a_{H_3}	a_{H_4}	a_M
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
〃	Electrolytic in CH_3CN	6.35	2.98	2.98	0.55	0.55	—
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*1)	—	—	—	—	—	—
〃	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

*1) Radical-anion could not be produced.

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6) G. Schroeter, *Ber*., **42**, 3360 (1909)
7) R. Geigy and W. Koenigs, *ibid*., **18**, 2401 (1885)
8) R. Geigy and W. Koenigs, *ibid*., **18**, 2403 (1885)
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10) K. Auwers, *Ber*., **36**, 3898 (1903)
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12) N. Hirota, Thesis, Washington University, St. Louis 30, Mo., U. S. A.

2 shows the splitting constants for the nitrobenzophenone radical-anions, formed by the reduction with alkali metals, vary for alkali metal species. Dimethoxyethane was used as a solvent because of the favorable solvating power for the radical-anions. The representative spectra observed were shown in Fig. 1. Radical-anion generated by the reduction with alkali metal, in general, forms ion-pair in an usual

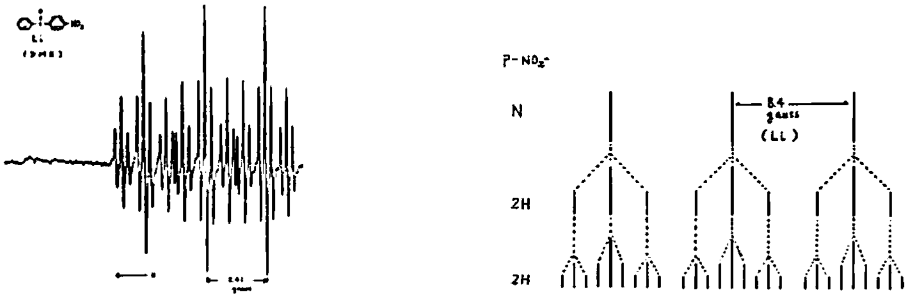

Fig. 1-a Anion-radical of *p*-nitrobenzophenone (Li^+)

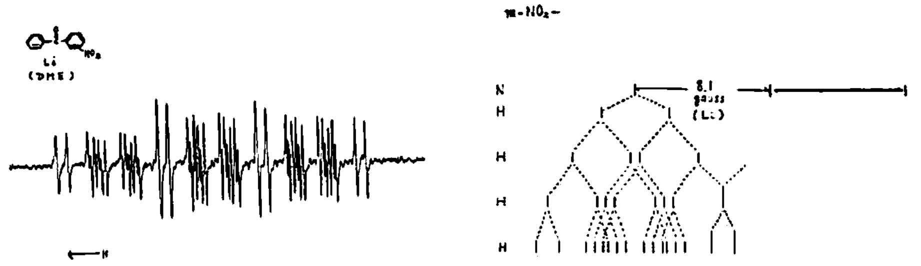

Fig. 1-b Anion-radical of *m*-nitrobenzophenone (Li^+)

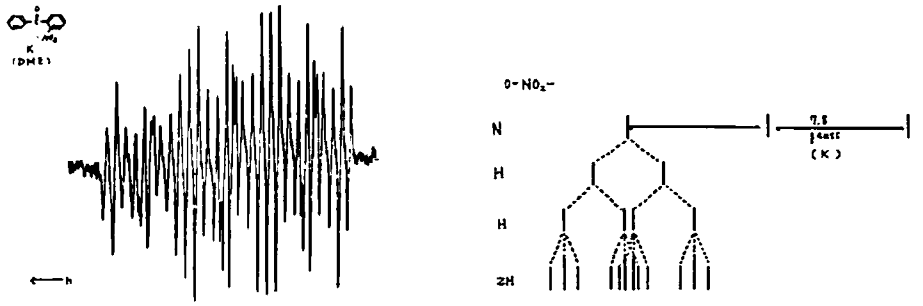

Fig. 1-c Anion-radical of *o*-nitrobenzophenone (K^+)

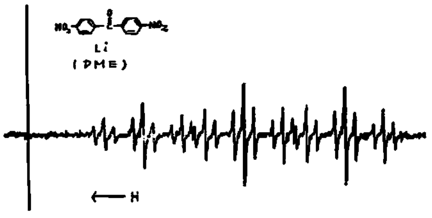

Fig. 1-d Anion-radical of *p*, *p′*-dinitro-benzophenone (Li^+)

Fig. 1 Electron spin resonance spectra and theoretical reconstruction for radical-anions organic solvent. In the metal ketyl of benzophenone and its alkyl derivatives metal cation is attached to the neighbor of carbonyl group. So the position of the largest free spin density is a carbonyl carbon in this case[12].

The results shown in Table 2 indicate the free spin is localized only on the nitro-substituted phenyl group of mono-nitrobenzophenone skeleton and there is no appreciable free spin on non-substituted aromatic ring. This was definitely confirmed by the observation of ESR spectrum of radical-anion of d_6-phenyl *p*-nitrophenyl ketone. The spectrum obtained was quite the same to that of radical-anion generated from *p*-nitrobenzophenone. This conclusion can be also supported by the observation of ESR spectra of radical-anions generated from *p*'-methyl, *p*-nitrobenzophenone and of *p*'-methoxy, *p*-nitrobenzophenone (see Table 3). The spectra have essentially the same construction to that of radical-anion generated from *p*-nitrobenzophenone. Moreover, a_N varies with species of metal cation making an ion-pair. The more electronegative is the alkali metal, the larger is a_N. These phenomena are attributable to the strong electronegativity of nitro group and the electrostatic attraction of an metal cation attached to the neighbor of a nitrogroup in the radical-anion ion-pair.

Table 3 Splitting constants (in gauss) for radical-anions of *p*-substituted *p*-nitrobenzophenones
Solvent: Dimethoxyethane

Substance	Alkali metal	a_N	a_{H_1}	a_{H_2}	a_{H_3}	a_{H_4}	a_M
p, *p*'-dinitrobenzophenone	Li	7.90	3.00	3.00	1.00	1.00	0.00
〃	Na*2)	7.10	—	—	—	—	—
〃	K*2)	6.10	—	—	—	—	—
p-nitro, *p*'-methoxybenzophenone	Li	8.45	3.02	3.02	1.00	1.00	0.00
〃	Na	7.90	3.11	3.11	0.76	0.75	0.30
〃	K	7.24	3.02	3.02	0.75	0.75	0.15
p-nitro, *p*'-methylbezophenone	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

*2) These radical-anions did not give an well resolved spectrum.

Splitting constants for radical-anions of *p*'-substituted *p*-nitrobenzophenones are tabulated in Table 3. These radical-anions also show the systematic variation of a_N according to the electronegativity of metal cation. Although the observed spectra indicate that the free spin is localized only on the phenyl group substituted by a nitro group in *p*'-substituted *p*-nitrobenzophenone radical-anion, it can be found that *p*'-substituent has a definite effect on a_N by a comparision with the obtained a_N of these radical-anions. The nature of this effect, however, is not yet clear. It appears to be of somewhat inductive nature.

It is interesting to mention that the radical-anion of *p*, *p*'-dinitrobenzophenone shows again a spectrum indicating that free spin is localized only on one nitrophenyl group. This may be attributable to an ion-pair formation at one of two nitro groups. The similar phenomenon was found on the radical-anion of *m*-dinitrobenzene[13] generated by reduction with alkali metal. Namely, a nitrogen atom of

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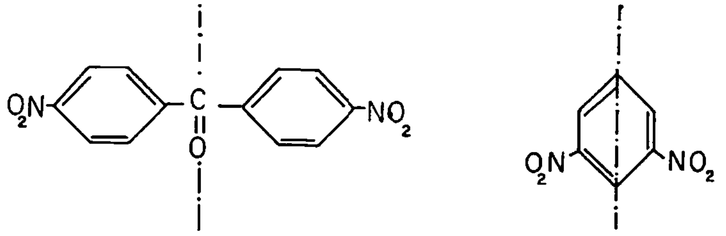
[13] R. L. Ward, *J. Am. Chem. Soc.*, **83**, 1296 (1960), *J. Chem. Phys.*, **32**, 410 (1960)

two nitro groups has a larger hyperfine interaction with free electron in its radical-anion and this is ascribed to the ion-pair formation. Thus the existence of a nodal plane, such as described in Fig. 2, will be supposed in the lowest vacant molecular orbital of *p*, *p*′-dinitrobenzophenone.



(a) *p*, *p*′-dinitrobenzophenone *m*-dinitrobenzene

Fig. 2 A nodal plane in the lowest vacant molecular orbital

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