ASSOCIATION OF RADICAL ANION WITH ALKALI CATIONS. IV. ESR STUDY OF THE 4-NITROBENZOPHENONE RADICAL ANION

Stanislav MIERTUŠ and Ondrej KYSEL
Polymer Institute,
Slovak Academy of Sciences, 809 34 Bratislava

Received March 2nd, 1979

The 4-nitrobenzophenone radical anion prepared by electrolysis was studied by ESR spectroscopy. On the basis of the interpretation of ESR spectra, the conformation of this system was estimated. The effect of the concentration of supporting electrolyte and of the presence of a proton-donor agent (C_2H_5OH) was examined. It is assumed that changes in hyperfine splitting constants are caused by association.

Recently, much attention has been devoted to the study of the formation of ion pairs from radical anions and alkali metal cations (or other cations)[1-3]. One of the most convenient methods for this study is ESR spectroscopy. The nitrobenzene radical anion was recently studied in detail[4]. It was found that formation of ion pairs as well as variation of the contra-ion concentration is accompanied by a considerable change in hyperfine splitting constants. In the present paper we concentrated on the study of a system of similar structure, *viz.* the 4-nitrobenzophenone radical anion. This system is interesting from several points of view: Knowledge of hyperfine splitting constants would help in estimating the conformation of this substance (twisting of individual rings). Another problem appears to lie in the association of this system with cations, as here there are two electron-acceptor centres. The present paper considers these problems.

EXPERIMENTAL

Methods and Calculations

4-Nitrobenzophenone radical anion was generated by electrolytic reduction at an Hg cathode in dimethylformamide in the presence of supporting electrolyte $(n\text{-}C_4H_9)_4NClO_4$ and $NaClO_4$. A Radelkis OH 404 potentiostat was employed to maintain the reduction potential constant (—1·0 V) *vs* S.C.E. A solution of the radical anion was transfered by nitrogen into a cell for ESR spectrum measurements. The ESR spectra were recorded using a Varian E-4 spectrophotometer. All details concerning the preparation of radical anions and experimental equipment were given in the preceding paper[5].

The total energy and spin densities were calculated by the restricted LHP-π (PPP-like) method[6] with limited configuration interaction[7], where all monoexcited $\psi_{C\beta}$ configurations were considered.

Standard parametrization was employed[8]. The total energy of the system was calculated so that the interaction energy of atoms not participating in the π system, expressed by empirical nonbonded potentials[14], was added to the total π energy. The geometry considered for 4-nitrobenzophenone radical anion is shown in Fig. 1. Twisting of the benzene rings was also included in the value of the resonance integral of the bond between carbon atoms joining the carbonyl group with aromatic ring as follows[9]:

$$\beta_{\mathrm{C-C'}} = \beta_0 \cos \alpha \,, \quad \alpha = \theta, \varphi \,, \tag{1}$$

where Θ and φ are the twist angles of unsubstituted and substituted rings (Fig. 1).

RESULTS AND DISCUSSION

ESR *Spectrum of Free* 4-*Nitrobenzophenone Radical Anion*

Since 4-nitrobenzophenone radical anion contains 1 nitrogen and 9 hydrogens, one could theoretically expect a complicated spectrum of 3 . 29 = 1536 lines. The spectrum measured in dimethylformamide in the presence of 10^{-1}M tetrabutylammonium perchlorate is remarkably simpler; it consists of 21 lines (Fig. 2*a*). Analysis of the spectrum indicates that it results from a splitting of nitrogen a_N (which is largest), of two equivalent protons with splitting constant $a_{H_1} \approx 1/2 a_N$ and of two other equivalent protons with a protons with a considerably lower constant a_{H_2}. The following values were obtained by simulating the spectrum on a computer (Fig. 2*b*): $a_N = 0{\cdot}532$ mT, $a_{H_1} = 0{\cdot}262$ mT and $a_{H_2} = 0{\cdot}038$ mT with a line width 0·025 mT and a line shape of the Gaussian type (60%) and Lorentzian type (40%). Assignment of the splitting constants to the respective protons was based on calculations of spin densities by the LHP–π method. Table I contains the results for the four conformations considered. Although agreement between the calculated and experimental hfc values is apparently best for the conformation with $\theta = 0°$ and $\varphi = 90°$, the experimental results do not support this interpretation. On comparing the splitting

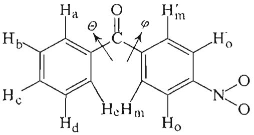

FIG. 1
Structure of 4-Nitrobenzophenone

constants of radical anions of 4-nitrobenzophenone and nitrobenzene[4] ($a_N = 0·848$ mT, $a_p = 0·421$ mT, $a_0 = 0·33$ mT, $a_m = 0·109$ mT) and of the *p*-nitrobenzaldehyde radical anion[10] ($a_N = 0·583$ mT, $a_0 = 0·295$ mT, a_0, $= 0·123$ mT, $a_m = 0·044$ mT), it can be seen that the magnitudes of individual 4-nitrobenzophenone radical anion constants are closer to the values for the *p*-nitrobenzaldehyde radical anion. This fact leads to the assumption that, in the most stable conformation, the carbonyl group is close to coplanar with the nitrophenyl ring, whereas the second ring is twisted. On the other hand, the *ortho* positions in *p*-nitrobenzaldehyde radical anion appear to be nonequivalent. This fact can be explained similarly as for the benzaldehyde radical anion (where different experimental values are found for the *ortho* positions[10]), and benzophenone radical anion[11] (with equivalent values for the *ortho* and *meta* positions at room temperature), by rotation of the benzene ring around the bond joining the carbonyl group with the aromatic ring. By lowering the temperature, the authors[11] distinguished non-equivalency of the *ortho* and *meta* positions in the benzophenone radical anion. Simultaneously, they found the value of the rotational barrier to be equal to 19 kJ mol^{-1}. Detailed quantum-chemical analysis by the INDO method of the possible mechanism of the rotation of the phenyl group around the C—C bond in the benzophenone radical anion was described earlier[13].

In our opinion, the ESR results for 4-nitrobenzophenone radical anion indicate the existence of rotation of the nitrophenyl ring around the C—C bond. This assumption is supported by calculations of the total energy. Calculations show, that

TABLE I

Calculated Spin Densities (ϱ_i) 4-Nitrobenzophenone Radical Anion

Position[a]	ϱ_i	ϱ_i	ϱ_i	ϱ_i	$a_i{}^b$, 10^{-4} T
	$\Theta = \varphi = 0°$	$\Theta = 90°, \varphi = 0°$	$\Theta = 0°, \varphi = 90°$	$\Theta = \varphi = 25°$	$\Theta = 0°, \varphi = 90°$
N	0·1775	0·1874	0·2226	0·1823	(+) 6·25
H'_0	0·0585	0·0672	0·0763	0·0621	(—) 2·19)
H_0	0·0516	0·0614	0·0763	0·0556	(—) 2·19
H'_m	0·0066	—0·0035	—0·0144	0·0036	(+) 0·41
H_m	0·0056	—0·0051	—0·0144	0·0029	(+) 0·41
H_a	0·0125	0·0000	0·0000	0·0085	0·00
H_c	0·0152	0·0000	0·0000	0·0116	0·00
H_e	0·0118	0·0000	0·0000	0·0088	0·00

[a] Positions denoted as in Fig. 1; [b] Constants a_i were calculated from ϱ_i according to the McConnell relation, where the Q constant is —2·87 mT for hydrogens and +2·84 mT for nitrogens.

both rings are in the most stable conformation twisted by ~25° ($\Theta = 28°$, $\varphi = 24°$). Because of the nonequivalence of the rings, there are two possible rotations around bonds connecting the benzene rings with the C=O group. The height of the rotational barrier of the unsubstituted ring ($\Theta = 90°$, $\varphi = 0°$) is 0·19 eV (18·3 kJ mol^{-1}) and rotation of the substituted ring ($\Theta = 0°$, $\varphi = 90°$) requires 0·40 eV (38·63 kJ mol^{-1}). Of course, these computations do not consider the solvent effect on the 4-nitrobenzophenone radical anion conformation. If the solvation energy for individual configurations is calculated according to relation[15]

$$E_{\text{solv}} = -\,1/2 \sum_{\mu,\nu} Q_\mu Q_\nu \gamma_{\mu\nu}(1 - 1/\varepsilon)\,, \tag{2}$$

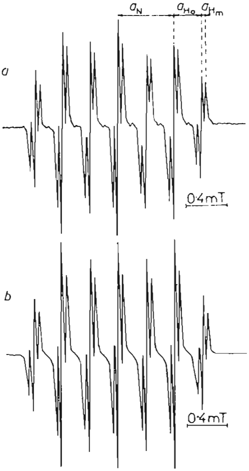

FIG. 2

a ESR Spectrum of $5\,.\,10^{-4}$M 4-Nitrobenzophenone Radical Anion in Dimethylformamide with 10^{-1} Tetrabutylammoniumperchlorate; *b* Theoretically Simulated ESR Spectrum of 4-Nitrobenzophenone Radical Anion

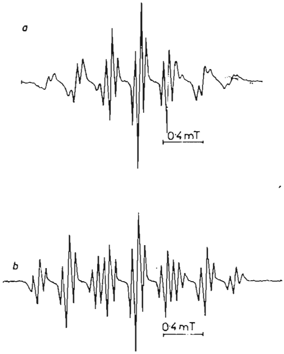

FIG. 3

ESR Spectrum of $5\,.\,10^{-4}$M 4-Nitrobenzophenone Radical Anion in Dimethylformamide

Supporting electrolyte: *a* 10^{-1}M-$NaClO_4$; *b* 10^{-1}M-$NaClO_4$ + $5\,.\,10^{-1}$M-C_2H_5OH.

where Q_μ, Q_ν are the net charges at atoms μ and ν, $\gamma_{\mu\nu}$, are electron repulsion integrals and ε the dielectric constant of medium (we consider dimethylformamide, $\varepsilon = 37{\cdot}5$), it will be found that the solvent effect tends to stabilize the conformations $\Theta = 90°$, $\varphi = 0°$ and $\Theta = 0°$, $\varphi = 90°$ more than the conformation $\Theta = 28°$, $\varphi = 24°$, so that the values of the rotational barriers will decrease to 0·14 eV (13·52 kJ) and 0·33 eV (31·86 kJ), respectively. As long as the real values are close to these values, rotation of the rings should exist at room temperature, which might explain the time average of the *ortho* and *meta* positions. For confirmation of this conclusion, ESR measurements at low temperatures are desirable.

The Effect of the Medium on the ESR *Spectrum of* 4-*Nitrobenzophenone*

We studied the effect of a change in the supporting electrolyte ($NaClO_4$) and in its concentration and of the addition of proton-donor agent C_2H_5OH on the ESR spectrum of 4-nitrobenzophenone radical anion tetrabutylammonium perchlorate. A change in the concentration exerts no marked effect on ESR spectrum (Table II). Replacement of supporting electrolyte by $NaClO_4$ as far as its concentration is equivalent that of 4-nitrobenzophenone ($5 \,.\, 10^{-4}$M) has practically no effect. An increase in the $NaClO_4$ concentration to $1 \,.\, 10^{-1}$M leads to an increase in all the constants, the most marked change being evident for a_N (Table II; Fig. 3*a*).

On adding the proton-donor ethanol, the spectrum changes still more (Fig. 3*b*). The hyperfine splitting constants increase at all three positions (Table II). As constant

TABLE II

Experimentally Found Hyperfine Splitting Constants for 4-Nitrobenzophenone Radical Anion in Dimethylformamide ($5 \,.\, 10^{-4}$M) with Various Supporting Electrolytes

Supporting electrolyte	Concentration mol l^{-1}	a_N	a_{Ho}	a_{Hm}
			10^{-4} T	
Tetrabutylammoniumperchlorate	$5 \,.\, 10^{-4}$	5·32	2·62	0·38
Tetrabutylammoniumperchlorate	10^{-1}	5·32	2·62	0·38
$NaClO_4$	$5 \,.\, 10^{-4}$	5·30	2·62	0·38
$NaClO_4$	10^{-1}	5·80	2·68	0·40
$NaClO_4$ + C_2H_5OH	10^{-1} $5 \,.\, 10^{-1}$	6·55	2·85	0·55
$NaClO_4$ + C_2H_5OH	10^{-1} 1·0	6·80	2·90	0·60

a_N increases most and is no longer $2 . a_{H_O}$, the experimental spectrum changes markedly. This will also be manifested in a change in the spectrum over the range of triplets adjacent to the medium triplet, so that the original triplets become quartets and quintets respectively, well identifiable in the presence of 1M-C_2H_5OH (Fig. 3*b*).

All the hyperfine splitting constants are summarized in Table II. The variations in constants observed are probably connected with the formation of associates taking place in the presence of $NaClO_4$ at higher concentrations and especially in the presence of C_2H_5OH, where a hydrogen bond is probably formed between ethanol and the nitro group. A marked increase in the hyperfine splitting constant for nitrogen indicates that Na cations and ethanol associate with the radical anion in the vicinity of the NO_2 group (where they form associates with oxygen atoms similarly as with nitrobenzene[4]) rather than near the C=O group. However, the alkali metal hyperfine splitting was not measured. Hirota[16] observed the same for fluorenone radical anion and Na^+ in dimethylformamide, where no alkali metal hyperfine splitting was measured but formation of associates was observed on the basis of ^{13}C splitting. This indicates that the strongly polar solvent dimethylformamide solvates individual ions, so that solvent-separated associates are probably formed. As the equivalency of hydrogens H_0, H'_0 and H_m, H_m is also maintained in the formation of the associates mentioned, it can be assumed that they will not significantly affect the rate of rotation of the substituted ring around the C—C′ bond.

Thus the effects investigated also occurred in the electronic spectra of the 4-nitrobenzophenone radical anion[12], where, analogous to nitrobenzene, a hypsochromic shift of the absorption band by $500 - 1\,500\ cm^{-1}$ in the presence of $NaClO_4$ or ethanol was found.

REFERENCES

1. Hirota N. in the book: *Radical Ions* (E. T. Keiser, L. Kevan, Eds). Wiley-Interscience, New York 1968.
2. Szwarc M.: *Carbanions, Living Polymers and Electron Transfer Processes.* Wiley-Interscience, New York 1970.
3. Szwarc M. (Ed.): *Ions and Ion Pairs in Organic Reactions.* Wiley-Interscience, New York 1972.
4. Stevenson G. R., Echegoyen L., Lizardi L. R.: J. Phys. Chem. *76*, 1439, 2058 (1972); J. Phys. Chem. *77*, 1027 (1973).
5. Miertuš S., Kyseľ O., Danciger J.: This Journal *45*, 360 (1980).
6. Longuet-Higgins H. C., Pople J. A.: Proc. Roy. Soc. *68A*, 591 (1955).
7. Hinchliffe A., Ali A. M.: Theor. Chim. Acta *5*, 271 (1966).
8. Hinze I., Jaffé H. H.: J. Amer. Chem. Soc. *84*, 540 (1962).
9. Hochman P., Zahradník R., Kvasnička V.: This Journal *33*, 3478 (1968).
10. Steinberger N., Fraenkel G. K.: J. Chem. Phys. *40*, 723 (1964).
11. Takeshita T., Hirota N.: J. Chem. Phys. *51*, 2146 (1969).

12. Miertuš S.: Unpublished results.
13. Bernardi F., Guera M., Pedulli G. F.: J. Phys. Chem. *78*, 2144 (1974).
14. DeCoen J. L., Lefante G., Liguori M. A., Damiani A.: Nature (London) *216*, 1910 (1967).
15. Jano I.: C. R. Acad. Sci. *261*, 103 (1965).
16. Hirota N.: J. Amer. Chem. Soc. *89*, 32 (1967).