Solvent Effect in Electron Spin Resonance Spectra and Electrochemical Reaction of Substituted Nitrobenzene Anion Radicals

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In order to examine the effect of solvents on the hyperfine splittings of anion radical the electron spin resonance spectra of substituted nitrobenzene anion radicals were studied. The effect of hydroxylic solvent is enhanced when the nitro group is forced out of the plane of the benzene ring due to the steric influence of the bulky functional group at the *ortho* position. The effect is reduced when the nitro group forms intramolecular hydrogen bond with the hydroxyl group at the *ortho* position. A model for the solvent effect considering the hindered rotation of the nitro group in the radical molecule caused by the formation of intermolecular hydrogen bond with solvent is found to be reasonable from a molecular orbital calculation, taking account of changes in molecular orbital parameters resulting from hydroxylic solvation. The shifts in polarographic half wave potentials with the solvent system as well as the dehalogenation reaction in the course of electrochemical reduction of halonitrobenzenes is interpreted by means of the model.

Several investigators have studied the solvent effect in electron spin resonance (ESR) spectra of organic anion radicals.[1–12] It is well-known that the hyperfine splittings in ESR spectra are influenced by the solvent characteristics as well as the species which interact with the radical in solution. The nitrogen coupling constant of di-*para*-anisyl nitric oxide increases with the increase of the dielectric constant of the solvent, the effect being remarkably enhanced in hydroxylic solvents such as water and alcohols.[2] The solvent effects of substituted nitrobenzene anion radicals were studied extensively by Adams and his co-workers[3–5] and summarized by Kitagawa;[6] the nitrogen coupling constant a^N of nitrobenzene anion radical produced electrochemically in aprotic solvents increases rapidly with the addition of a small amount of water. The effect is remarkable when the nitro group is sterically hindered. The presence of alkali metal cations also increases the a^N of *p*-chloronitrobenzene anion radical.[7] Theoretical studies of the dependency of the hyperfine splittings in ESR spectra on the solvent characteristics were undertaken by Reiger and Fraenkel[8] and Gendell *et al.*[9] on the assumption that the charge in the functional group is affected by the presence of localized complexes between the solvent and the functional group of the radical. Since then MO calculations have been recognized to be useful for the interpretation of the complicated phenomena observed in ESR spectra.[10–12] We have examined the solvent effect in ESR spectra as well as the electrochemical reduction of substituted nitrobenzene by MO calculation in order to clarify the nature of the solvent effect.

Experimental

All the nitro compounds, such as nitrobenzene, nitrophenol, 2-nitroresorcinol, nitrotoluene, nitroanisole, and halonitrobenzenes, were of G. R. grade and purified by recrystallization from benzene when necessary. Tetra-*n*-propyl ammonium perchlorate was prepared by adding perchloric acid to tetra-*n*-propyl ammonium hydroxide and purified by recrystallization from hot acetonitrile–water mixture. *N,N'*-Dimethylformamide (DMF) was dried over anhydrous potassium carbonate for a few days and then distilled twice taking the fraction boiling at 151—153 °C. Acetonitrile (ACN) was dried over anhydrous phosphorus pentoxide and the fraction distilled at 80—81 °C was used. The anion radicals were prepared by electrolytic reduction in DMF–water or ACN–water mixture containing 2×10^{-3} M nitro compound and 0.1 M tetra-*n*-propyl ammonium perchlorate. The cell and technique are described in detail elsewhere.[13–15] The coupling constants were calibrated with the splittings of nitrosodisulphonate anion.

Results and Discussion

Solvent Effect in ESR Spectra. The coupling constants of fluoronitrobenzene anion radicals in DMF–water mixture are given in Table 1. Assignments of the coupling constants to specific nuclei were made in accordance with Hückel MO calculation and INDO

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[1] Y. Deguchi, This Bulletin, **35**, 260 (1962).

[2] K. Umemoto, Y. Deguchi, and H. Takaki, *ibid.*, **36**, 560 (1963).

[3] L.H. Piette, P. Ludwig, and R.N. Adams, *J. Amer. Chem. Soc.*, **83**, 3909 (1961); **84**, 4212 (1962).

[4] P. Ludwig, T. Layloff, and R. N. Adams, *ibid.*, **86**, 4568 (1964).

[5] J. Q. Chambers, T. Layloff, and R. N. Adams, *J. Phys. Chem.*, **68**, 661 (1964).

[6] T. Kitagawa, *Rev. Polarog.* (Kyoto), **12**, 11 (1964).

[7] T. Kitagawa, T. Layloff, and R. N. Adams, *Anal. Chem.*, **36**, 925 (1964).

[8] P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 2811 (1962).

[9] J. Gendell, J. H. Freed, and G. K. Fraenkel, *ibid.*, **37**, 2832 (1962).

[10] W. M. Gulick, Jr., and D. H. Geske, *J. Amer. Chem. Soc.*, **87**, 4049 (1965).

[11] W. M. Gulick, Jr., W. E. Geiger, Jr., and D. H. Geske, *ibid.*, **90**, 4218 (1968).

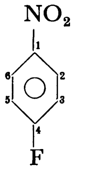
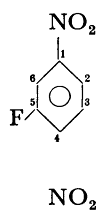
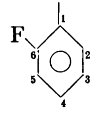
[12] D. H. Geske, J. L. Ragle, M. A. Bambenek, and A. L. Balch, *ibid.*, **86**, 987 (1964).

[13] K. Umemoto, Y. Deguchi, and T. Fujinaga, This Bulletin, **36**, 1539 (1963).

[14] T. Fujinaga, Y. Deguchi, and K. Umemoto, *ibid.*, **37**, 822 (1964).

[15] K. Umemoto, *ibid.*, **40**., 1058 (1967).

Table 1. Coupling constants of fluoronitrobenzene anion radicals in DMF–water mixture (in gauss)

		Water content (%)					
		0[a)]	5	10	20	50	90
	a^N	9.95	11.37	12.01	12.53	13.59	14.34
	$a_2^H=a_6^H$	3.56	3.49	3.49	3.46	3.44	3.48
	$a_3^H=a_5^H$	1.12	1.11	1.12	1.12	1.12	1.12
	a^F	8.55	8.16	8.05	8.05	8.05	8.06
	a^N	8.86	10.04	10.67	11.30	12.36	13.27
	a_2^H	2.99	2.89	2.92	2.92	2.92	2.92
	a_3^H	0.97	1.02	1.02	1.05	1.08	1.12
	a_4^H	3.43	3.31	3.30	3.32	3.30	3.32
	a_6^H	3.22	3.32	3.30	3.32	3.30	3.32
	a^F	4.02	3.89	3.82	3.74	3.62	3.62
	a^N	9.29	10.72	11.23	12.14	13.46	14.59
	a_2^H	3.64	3.60	3.52	3.49	3.37	3.45
	$a_3^H=a_5^H$	1.05	1.08	1.09	1.09	1.09	1.12
	a_4^H	4.34	4.04	3.88	3.76	3.47	3.45
	a^F	6.67	6.75	6.62	6.66	6.52	6.45

a) Assignments of the coupling constants to specific nuclei were made in accord with our Hückel MO calculation for *o*, *p*-isomers and with the INDO MO calculation[16)] of Pople *et al.* for *m*-isomer.

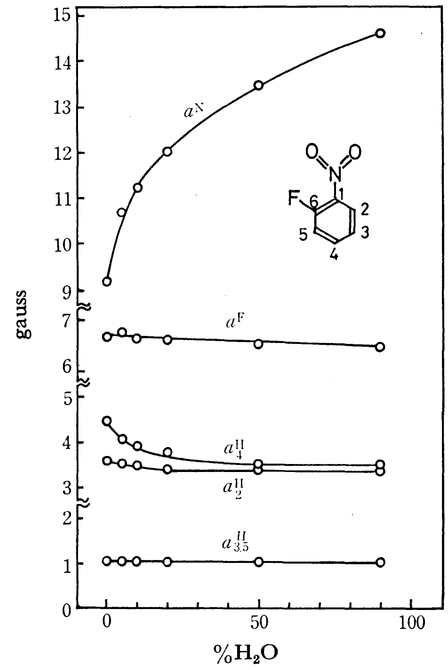


Fig. 1. Hyperfine coupling constants of *o*-fluoronitrobenzene anion radical shown as a function of water content in DMF–water mixture.

MO methods.[16)] The graphical shifts in coupling constants of nitrogen, proton, and fluorine nuclei of *o*-fluoronitrobenzene anion radical are shown in Fig. 1 as a function of water content. Similar shifts in a^N of some other substituted nitrobenzene anion radicals are summarized in Figs. 2a and 2b. We see that a^N increases with the increase of water content, the splittings of nuclei at *meta* and *ortho* positions showing little change. The figures present an excellent comparison. In the case of fluoronitrobenzene, nitroanisole, and nitrotoluene (Fig. 2a), the shifts in a^N of *ortho* isomers are greater than those of *meta* or *para* isomers, and the shift in a^N of a radical with a bulkier substituent at the *ortho* position is remarkably enhanced with the increase of the water content. In the case of *o*-nitrophenol anion radical which forms an intramolecular hydrogen bond[13)] (Fig. 2b), the shift in a^N is smaller than in the case of *para* and *meta* isomers. The shift in a^N of 2-nitroresorsinol anion radical which forms two intramolecular hydrogen bonds[4)] is much smaller. These observations are in good accord with the following general aspects of the solvent effect of substituted nitrobenzene anion radicals:[4)] i) When the nitro group forms intramolecular hydrogen bonds the solvent effect is impeded as the nitro group is rendered to be a weaker proton acceptor. ii) When the nitro group forms a localized complex with solvent molecules and is sterically hindered by the substituent at the *ortho* position in such a way as to be twisted out of plane of the benzene ring, the solvent effect is much more effective than in the unhindered cases. The second model is based on the fact that a substituted nitrobenzene anion radical having a sterically hindered nitro group has a larger nitrogen splitting and smaller ring proton splittings than unhindered substituted nitrobenzene anion radicals.[17)] In general, the nitro group of *ortho* substituted nitrobenzene is known to be sensitive to the steric influence of the substituent at the *ortho* position and the twisting effect is operative in some cases, *e.g.*, in the case of *o*-nitrotoluene the twisted angle of the nitro group has been

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16) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill Book Co., New York (1970) Chap. 4; J.A. Pople, D.L. Beveridge, and P.A. Dobosh, *J. Amer. Chem. Soc.*, **90**, 4201 (1968).

17) D. H. Geske and J. L. Ragle, *J. Amer. Chem. Soc.*, **83**, 3532 (1961).

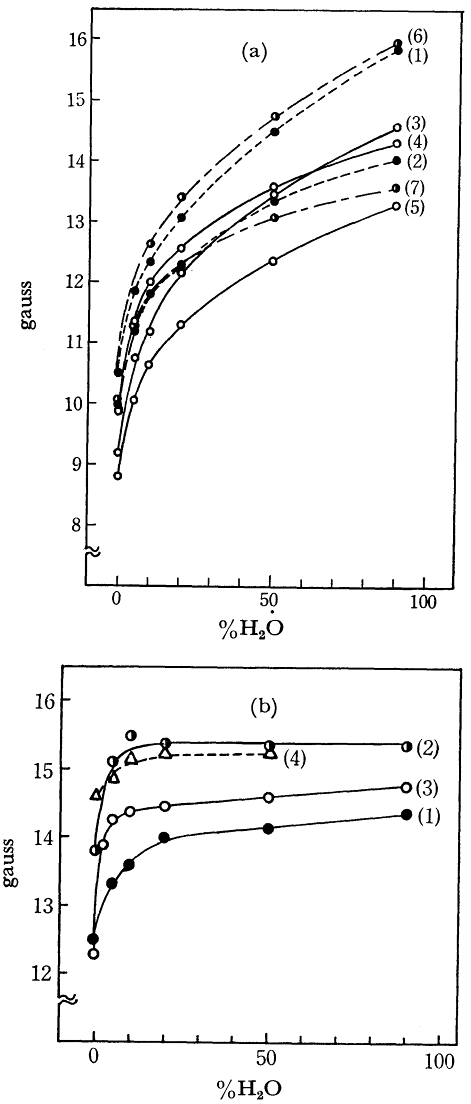

Fig. 2. Nitrogen coupling constants of substituted nitrobenzene anion radicals shown as the function of water content.

(a): In DMF–water mixture
1: *o*-nitrotoluene
2: *p*-nitrotoluene
3: *o*-fluoronitrobenzene
4: *p*-fluoronitrobenzene
5: *m*-fluoronitrobenzene
6: *o*-nitroanisole
7: *m*-nitroanisole

(b): In ACN–water mixture
1: *o*-nitrophenol
2: *p*-nitrophenol
3: *m*-nitrophenol
4: 2-nitroresorcinol

estimated to be 34°.[18] The chlorine atom is suggested to be about as effective as a methyl group with regard to its steric influence on an adjacent nitro group.[4] The fluorine atom is certainly less effective than chlorine atom. Nonetheless, if hydrogen bond complex is formed the nitro group should be dislocated to accommodate the added bulky group. This situation should be reflected in the observed extra sensitivity of the splittings (Table 1).[19]

In order to verify the applicability of the model of solvent effect, the Hückel MO calculation was performed for *o*-fluoronitrobenzene anion radical by taking account of the following two factors[8,12,20] i) The oxygen Coulomb integral α_0 of the nitro group increases as a result of hydroxylic solvation since the oxygen atom in the nitro group becomes more electronegative by forming intermolecular hydrogen bonds with solvents, ii) the resonance integral β_{CN} between the nitro group and the benzene ring decreases when the conjugation between the nitro group and the benzene ring is reduced by twisting of the nitro group. The calculated distribution of the unpaired electron spin densities of *o*-fluoronitrobenzene anion radical is summarized in Table 2. By using these densities the calculated hyperfine coupling constants were obtained from the relations

$$a^{N} = A\rho^{N} - B\rho^{O} \tag{1}$$

$$a_i^{H} = Q\rho_i^{C} \tag{2}$$

where ρ^{N} and ρ^{O} denote the electron spin densities on nitrogen and oxygen atoms, respectively, and ρ_i^{C} denotes the spin density on the *i*-th carbon atom to which the *i*-th hydrogen atom is bonded. A, B, and Q are constants. Equation (1) was given by Rieger and Fraenkel. They gave $A=99$ and $B=71$ gausses as values which fit their experimental nitrogen splittings.[8] Equation (2) was given by McConnel,[21] Q being estimated to be -30 gauss for hydrocarbon anion radicals.[22] The values of a^{N} and a_i^{H} obtained from Eqs. (1) and (2) by using our spin densities did not agree with the experimental results. However, the calculated results may still be used for studying the relative magnitude of the observed shift in splittings. The calculated shifts in a^{N}, a_2^{H}, and a_4^{H} with the increase of the Coulomb integral of the oxygen atom α_0 are graphically shown in Fig. 3a and those with the decrease of the resonance integral β_{CN} in Fig. 3b. The origin of the curves were so chosen that the calculated results might coincide with the experimental results. The calculated shifts in a^{N} and a_4^{H} with the increase of α_0 qualitatively correlates with the experimental results, namely a^{N} increases and a_4^{H} decreases (Figs. 1 and 3a). However, the change in the observed a_4^{H} was not reproduced by calculation, a more evident contradiction being shown for a_2^{H} which was found to show a slight increase by calculation and a slight decrease by experiment. On the other hand, the calculated shift in a^{N}, a_2^{H}, and a_4^{H} with the decrease of β_{CN} is qualitatively correlated with the experimental results; a^{N} increases and both a_2^{H} and a_4^{H} decrease. However, the relative magnitudes of the changes in a_2^{H} and a_4^{H} were calculated to be comparable. The experiment indicated that the magnitude of the change in a_4^{H} is greater than that in a_2^{H}. Hence, neither the increase of α_0 nor the decrease of β_{CN} reflects precisely the nature of the solvent effect by itself. However, the

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[18] B. M. Wepster, "Progress in Stereochemistry," Vol. 2, ed. by W. Klyne and P. B. D. de la Mare, Butterworths, London (1958) p. 110.

[19] The out-of-plane bending of the nitro group, the other possibility of steric effect, seems to be less probable, since the ring nuclei splittings were observed to be affected by the solvent system (*cf.* Refs. 4 and 17).

[20] T. Yonezawa, C. Nagata, H. Kato, A. Imamura, and K. Morokuma, "Ryoshi Kagaku Nyumon," (Introduction to Quantum Chemistry) Kagakudojin, Kyoto (1963) Chap. 2; see also Chap. 4 in Ref. 23.

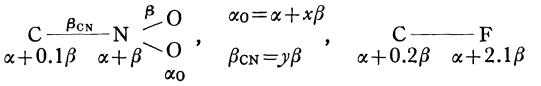
[21] H. M. McConnel, *J. Chem. Phys.*, **24**, 633, 764 (1956).

[22] A. Carrington, *Quart. Rev.*, **17**, 67 (1963).

TABLE 2. CALCULATED ENERGY LEVEL OF THE LOWEST VACANT ORBITAL m AND π ELECTRON DENSITY $(c_r^{l.v})^2$ OF o-FLUORONITROBENZENE

	$y=1.0$			$x=1.0$			
	$x=1.0$	$x=1.2$	$x=1.4$	$y=0.8$	$y=0.6$	$y=0.4$	$y=0.2$
m[a]	−0.3153	−0.2458	−0.1825	−0.3415	−0.3678	−0.3912	−0.4080
O	0.1815	0.1661	0.1501	0.1982	0.2155	0.2321	0.2450
N	0.3140	0.3472	0.3760	0.3567	0.4032	0.4492	0.4857
1	0.0132	0.0066	0.0025	0.0124	0.0100	0.0060	0.0019
2	0.0993	0.1008	0.1027	0.0747	0.0496	0.0256	0.0071
3	0.0002	0.0000	0.0001	0.0003	0.0003	0.0002	0.0001
4	0.1024	0.1013	0.1017	0.0783	0.0526	0.0275	0.0077
5	0.0073	0.0057	0.0045	0.0061	0.0044	0.0025	0.0007
6	0.0859	0.0899	0.0941	0.0641	0.0420	0.0214	0.0059
F	0.0147	0.0163	0.0181	0.0108	0.0069	0.0034	0.0009

a) $\alpha+m\beta$ is the energy level of the lowest vacant orbital in units of the standard α and β in the Hückel MO calculation. MO parameters are as follows (see also Refs. 14 and 20).



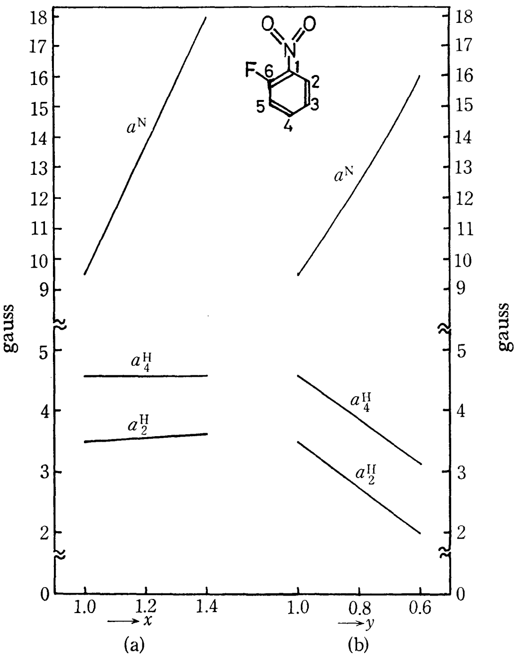


Fig. 3. (a) Calculated hyperfine coupling constants shown as a function of oxygen Coulomb integral parameter x: $\alpha_O=\alpha+x\beta$, $\beta_{CN}=\beta$.
(b) Calculated hyperfine coupling constants shown as a function of resonance integral parameter y between the nitro group and the benzene ring: $\alpha_O=\alpha+\beta$, $\beta_{CN}=y\beta$.

experimental results can be reproduced by combining both effects: A larger shift in a_4^H than a_2^H is expected by combining the two results (Figs. 3a and 3b). The expectation agrees very well with the experimental results. Thus, for the solvent effect the following model seems to be reasonable; the nitro group of the o-fluoronitrobenzene anion radical is strongly solvated with water, the solvated nitro group being simultaneously twisted out of the plane of the benzene ring. The model of solvent effect was first suggested by Ludwig *et al.*[4] as the most likely for *ortho* substituted nitrobenzene anion radicals based on the results of MO calculation for nitrobenzene anion radical given by Rieger and Fraenkel. The reason why the model of the solvent effect given by Ludwig *et al.* is acceptable, although their model was not derived from a precise MO calculation for *ortho* substituted nitrobenzene anion radical itself but for the unsubstituted nitrobenzene anion radical, can be understood as follows. For the shift in splittings, the MO calculation made by Rieger and Fraenkel and by us for both nitrobenzene and o-fluoronitrobenzene give similar results. Both a^N and a_2^H increase with the increase of α_0, while a^N increases and a_2^H as well as a_4^H decrease with the decrease of β_{CN}, indicating that the tendency of the shift in splittings with the variation of α_0 and β_{CN} is insensitive to the species of the substituent as well as the position of the substitution. It is also expected that the results (Figs. 3a and 3b) can be applied to *meta* or *para* mono substituted nitrobenzene anion radicals. Thus, the experimental results where the relative magnitudes of the shift in splittings of mono substituted nitrobenzene anion radicals are in the order *ortho*>*meta*>*para* isomers, can be attributed to the steric influence of the substituent on the nitro group.

Solvent Effect in Polarographic Half-Wave Potentials. It is known that a correlation exists between polarographic half-wave potential $E_{1/2}$ and the energy of the lowest vacant orbital m such as[23])

$$-E_{1/2} = -bm + c \tag{3}$$

where m is the energy in unit of β, b and c are both constants. The values $b=3.0$ and $c=1.0$ were obtained as values which fit our experimental results. Half-wave potentials calculated from Eq. (3) as well as the experimental results are given in Table 3. Comparison of the calculated values with the experimental values indicates that there are three characteristic cases. Firstly, for fluoronitrobenzene, in which little steric effect is expected, the calculated values correlate very

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23) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York, London (1961) Chap. 7; see also Chap. 3 in Ref. 20.

TABLE 3. HALF-WAVE POTENTIALS $E_{1/2}$ AND ENERGIES OF THE LOWEST VACANT ORBITALS m OF SUBSTITUTED NITROBENZENES

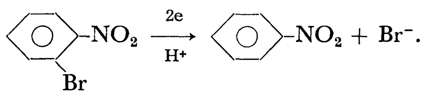
	$-m$[a]	$-E_{1/2}$ V *vs.* SCE	
		calcd	obsd
o-fluoronitrobenzene	0.315	1.05	1.05
m-fluoronitrobenzene	0.2964	0.99	0.97
p-fluoronitrobenzene	0.3174	1.06	1.07
o-chloronitrobenzene	0.3074	1.02	1.06
m-chloronitrobenzene	0.2962	0.99	0.93
p-chloronitrobenzene	0.3085	1.03	0.99
o-nitrotoluene	0.2974	0.998	1.26[c]
m-nitrotoluene	0.2959	0.992	1.18[c]
p-nitrotoluene	0.2975	1.00	1.20[c]
o-nitrophenol	0.3403	1.12	0.83
m-nitrophenol	0.2970	0.99	1.08
p-nitrophenol	0.3461	1.14	1.12

a) MO parameters are the same as those used in previous works (Refs. 13 and 14).
b) Data in DMF cited in Ref. 24.
c) Data in ACN cited in Ref. 12.

well with the experimental results *viz.*, the order of the half-wave potential is *meta*>*ortho*>*para* isomers. Secondly, for chloronitrobenzene and nitrotoluene, in which steric hindrance of the nitro group is expected for *ortho* isomers, experimental results show that the order of the half-wave potential is *meta*>*para*>*ortho* isomers, while calculation shows it to be *meta*>*ortho*>*para* isomers. Thirdly, for nitrophenol, in which intramolecular hydrogen bond is expected for *ortho* isomers, experimental results show the order to be *ortho*>*meta*>*para* isomers, and calculation *meta*>*ortho*>*para* isomers. As is evident from the calculated values of m (Table 2), the energy level of the lowest vacant orbital falls with the increase of α_0 while it is enhanced with the decrease of β_{CN}. Thus, when hindered rotation of the nitro group is expected to be operative the half-wave potential will shift to more negative, resulting in a potential series of *meta*>*para*>*ortho* isomers. On the other hand, when intramolecular hydrogen bond is expected the half-wave potential will shift to less negative, resulting in a potential series of *ortho*>*meta*>*para* isomers. The expectation agrees very well with the experimental results of nitrotoluene, chloronitrobenzene and nitrophenol.

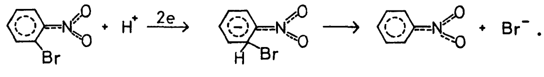
The half-wave potentials of halonitrobenzenes were reported to shift to less negative with increasing the concentration of water in DMF.[24] The shift in half-wave potentials of *ortho, meta*, and *para* isomers, at 20 per cent water content, were found to be 0.17 V, 0.17 V, 0.18 V, respectively, for fluoronitrobenzene and 0.17 V, 0.17 V, 0.19 V, respectively, for chloronitrobenzene and 0.14 V, 0.16 V, 0.18 V, respectively, for bromonitrobenzene and 0.14 V, 0.14 V, 0.17 V, respectively, for iodonitrobenzene, indicating that the relative magnitude of the shift in half-wave potential is generally in the order *ortho*<*meta*<*para* isomers. It is now evident that the hindered rotation of the nitro group resulting from the hydroxylic solvation will make the half-wave potential shift to more negative, while the hydroxylic solvation alone will make it shift to less negative. Thus, the slightest shift in half-wave potentials of *ortho* isomers and the most pronounced shift for *para* isomers with the increase of water concentration would be understood.

Solvent Effect in Electrochemical Reduction of Halonitrobenzene. The electrochemical reduction of mono substituted halonitrobenzene has been studied by ESR spectroscopy as well as by voltammetry, attention being paid to the elimination of the halogen atom. The chlorine atom of *o*-chloronitrobenzene and the bromine atom of *o*-bromonitrobenzene were eliminated by electrolytic reduction at mercury pool cathode and the ESR spectrum of nitrobenzene anion radical was observed.[14,24–26] When phenol or water was added as proton donors the elimination of the halogen atom was impeded. A survey of the proposed reaction mechanism for the elimination of the halogen atom of halonitrobenzene indicates that two electrons should be involved in this reaction.[24] Thus, the dehalogenation reaction at the electrode is shown schematically as follows by taking *o*-bromonitrobenzene as an example



(4)

The process is considered to be a kind of electrophilic aromatic substitution reaction. The following transition state is acceptable in view of the fact that the aromatic substitution reaction under consideration proceeds following the electrochemical reduction



(5)

(I) (II) (III)

The reactivity of the aromatic substitution reaction was studied by Fukui and his co-workers, and an index called the frontier electron density or superdelocalizability correlated with the stability of the transition state similar to the state (II) has been proved to be useful for elucidating the reactivity of the aromatic substitution.[27] The frontier electron density of the reaction under consideration is the electron density of the lowest vacant orbital of halonitrobenzene. It is formulated as $f_r^N=2(C_r^{lv})^2$. This index is reduced in magnitude (Table 2) with the reduction of the conjugation between the nitro group and the benzene ring. Thus, the dehalogenation reaction should be expected to be impeded as increasing the strong hydro-

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[24] T. Fujinaga, T. Arai, and C. Kitazawa, *Nippon Kagaku Zasshi*, **85**, 811 (1964); T. Fujinaga, K. Izutsu, K. Umemoto, T. Arai, and K. Takaoka, *ibid.*, **89**, 105 (1968); T. Fujinaga, K. Umemoto, and T. Arai, *Denki Kagaku*, **34**, 135 (1966).

[25] T. Kitagawa and R. Nakashima, *Rev. Polarog.* (Kyoto), **13**, 115 (1966).

[26] T. Kitagawa, T. Layloff, and R. N. Adams, *Anal. Chem.*, **35**, 1086 (1963).

[27] Chap. 5 in Ref. 19 and Chap. 11 in Ref. 23.

xylic solvation.[28] The expectation is well correlated with experimental observation. A similar decrease of reactivity of the halogen atom of halonitrobenzene due to the hindered rotation of the nitro group has been summarized by Hammond and Hawthone;[29] the reactivity against piperidine decreases when the nitro group is sterically hindered. In conclusion, this model will constitute a major physical picture of solvent effect although it may not be conclusive, in so far as rigorous synthetic investigations by various experimental methods are still insufficient.

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28) The frontier electron density as well as the superdelocalizability indicate that the most reactive position of *ortho* substituted nitrovenzene anion radical is not *ortho* but *para* position. No sample reactions are known to verify this. Our present interest is to know how the reactivity of the ring substitution reaction changes with the value of β_{CN}, irrespective of the reaction position.

29) G. K. S. Hammond and M. F. Hawthone, "Steric Effect in Organic Chemistry," ed. by M. S. Newman, John Wiley & Sons, Inc., New York, London (1956) Chap. 3.