# *Electron Spin Resonance Study of Substituted Nitrobenzene Negative Ions Produced by Electroreduction*

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A number of organic anion radicals, obtained by chemical reduction with metals, have been studied by means of electron spin resonance (ESR). Since the formation of free radicals can be expected in the course of electrochemical reductions, it seemed to us that the radical formation could be conveniently detected by ESR measurements.

Austen et al.[1] electrolyzed certain organic compounds, such as anthracene anthraquinone and benzophenone, and observed the ESR spectra of the free radicals in a frozen state in a dimethylformamide (DMF) solution. This was the first time that the electrolytic formation of organic free radicals was proved directly. However, since the ESR measurements were performed in the frozen solid state, the hyperfine structure (hfs) was lost in the broadened absorption-line width, and no detailed information about the electronic structure could be obtained. A similar method was used by Geske and Maki,[2] who carried out the electrolysis in the cavity and recorded the ESR spectrum of the nitrobenzene anion radical in an acetonitrile solution at room temperature. These authors[3,4] also used this " in situ " method for their study of the ESR of many para-substituted nitrobenzene anion radicals, with interesting results.

Ever since, the electrolytic technique has been employed by many authors[5-8] as a convenient method for the preparation of free radicals for ESR measurements.

Recently some investigators have used ESR measurements for the elucidation of electrode processes by studying the radicals formed during electrolysis;[9,10] Rieger et al.,[11] for instance, elucidated the reduction mechanism of many aliphatic and aromatic nitrile compounds by studying the ESR spectra obtained at different electrode potentials.

The present communication will deal with the investigation of the hfs in the ESR spectra of a series of substituted nitrobenzene anion radicals, obtained by electrochemical reduction. The mechanism of the electrolytic reduction of some halonitrobenzenes will also be studied.

## Experimental

Nitrobenzene, a series of ortho-, para- and meta-substituted nitrobenzene derivatives, in the form of their chloro, bromo, iodo, methyl, methoxyl, amino, hydroxyl, cyano and aldehyde compound, as well as anthraquinone and naphthoquinone, were used. Most of the reagents were of an extra pure grade and were supplied by the Maruwaka Chemicals Co., Osaka; an they were used without further purification. Acetonitrile of an extra pure grade was used as a solvent in all ESR measurements unless otherwise mentioned. It was first dried with phosphorous pentoxide and then with anhydrous carbonate.

All solutions were approximately 1 mM and contained 0.1 M tetra-*n*-propylammonium perchlorate as the supporting electrolyte. The electrolytic cell was similar to that used by Geske and Maki.[2] Purified nitrogen gas was used for the de-oxygenation of the solutions; the electrolysis was carried out at a constant potential, the value of which was chosen in accordance with the results of polarographic measurements.

The ESR spectra of chloro, bromo and iodonitrobenzene were observed in both acetonitrile and a DMF solution. The DMF was dried with anhydrous potassium carbonate, and the fraction distilling at 152~153°C was used. The ESR spectrometer was an X-band instrument, manufactured by the Japan Electron Optics Co., Model JES-3B-type; it employs a rectangular reflection cavity, 100 kc./sec. field modulation, and a JES electromagnet with 300 mm.$\phi$ pole pieces. For all field measurements, the spectrum of the peroxylamine disulfonate anion radical, which shows three lines with a 13.0 gauss separation, due to nitrogen splitting, was referred to as the standard.

## Results and Discussion

**ESR Spectra.**—*Nitrobenzene.*—The spectrum of the nitrobenzene anion is shown in Fig. 1;

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[1] D. E. G. Austen, P. H. Given, D. J. E. Ingram and M. E. Peover, *Nature*, **182**, 1784 (1958).

[2] D. H. Geske and A. H. Maki, *J. Am. Chem. Soc.*, **82**, 2671 (1960).

[3] A. H. Maki and D. H. Geske, *J. Chem. Phys.*, **33**, 825 (1960).

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

[5] P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 2795 (1962); **39**, 609 (1963).

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

[7] P. H. Rieger and G. K. Fraenkel, ibid., **37**, 2811 (1962).

[8] I. Bernal, P. H. Rieger and G. K. Fraenkel, ibid., **37**, 1489 (1962).

[9] P. Ludwig and R. N. Adams, *Anal. Chem.*, **34**, 917 (1962).

[10] H. Lee and R. N. Adams, ibid., **34**, 1587 (1962).

[11] P. H. Rieger, I. Bernal, W. H. Reinmuth and G. K. Fraenkel, *J. Am. Chem. Soc.*, **85**, 683 (1963).

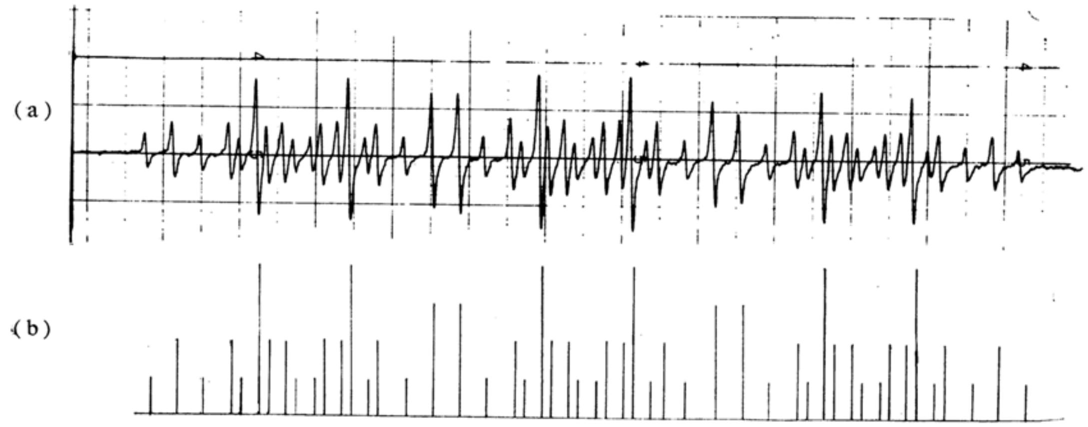


Fig. 1. (a) The ESR spectrum of nitrobenzene anion radical.
(b) Spectrum calculated based upon the coupling constants shown in the Table I.

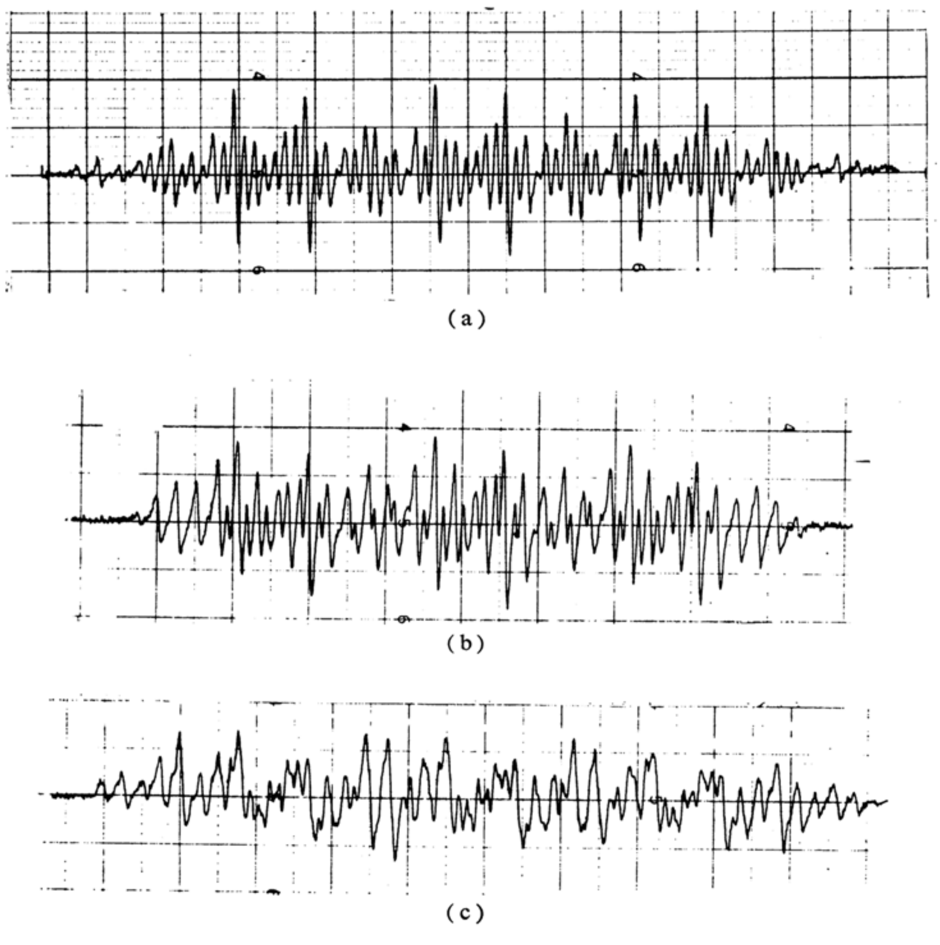
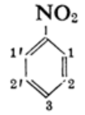
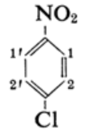
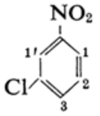
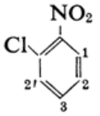
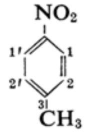
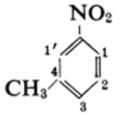
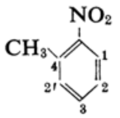
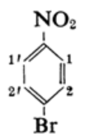
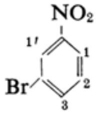
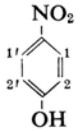
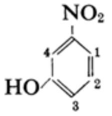
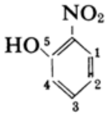
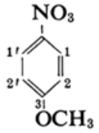
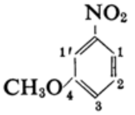
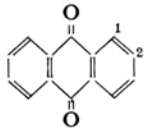
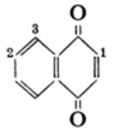


Fig. 2. ESR spectra of (a) *p*- (b) *m*- (c) *o*-nitrotoluene anion radicals.

TABLE I. ESR HYPERFINE COUPLING CONSTANTS

| | |
|---|---|
|  | $a_N=10.62$ $a_{H_1}=3.30$ $a_{H_2}=1.03$ $a_{H_3}=3.82$ |
|  | $a_N=9.70$ $a_{H_1}=3.42$ $a_{H_2}=1.12$ |
|  | $a_N=9.60$ $a_{H_1}=3.20$ $a_{H_2}=0.93$ $a_{H_3}=4.07$ |
|  | $a_N=9.95$ $a_{H_1}=3.30$ $a_{H_2}=1.13$ $a_{H_3}=3.92$ |
|  | $a_N=11.0$ $a_{H_1}=3.31$ $a_{H_2}=1.14$ $a_{H_3}=3.90$ |
|  | $a_N=10.7$ $a_{H_1}=3.39$ $a_{H_2}=1.09$ $a_{H_3}=3.84$ $a_{H_4}=1.09$ |
|  | $a_N=11.3$ $a_{H_1}=3.32$ $a_{H_2}=1.04$ $a_{H_3}=3.74$ $a_{H_4}=3.32$ |
|  | $a_N=9.80$ $a_{H_1}=3.36$ $a_{H_2}=1.13$ |
|  | $a_N=9.78$ $a_{H_1}=3.36$ $a_{H_2}=1.02$ $a_{H_3}=4.22$ |
|  | $a_N=13.8$ $a_{H_1}=3.14$ $a_{H_2}=0.72$ |
|  | $a_N=12.3$ $a_{H_1}=2.76$ $a_{H_2}=0.92$ $a_{H_3}=2.98$ $a_{H_4}=3.33$ |
|  | $a_N=12.5$ $a_{H_1}=3.59$ $a_{H_2}=0.61$ $a_{H_3}=3.59$ $a_{H_4}=1.01$ $a_{H_5}=0.46$ |
|  | $a_N=11.5$ $a_{H_1}=3.33$ $a_{H_2}=1.06$ $a_{H_3}=0.31$ |
|  | $a_N=10.3$ $a_{H_1}=3.30$ $a_{H_2}=1.04$ $a_{H_3}=3.80$ $a_{H_4} \ll 0.1$ |
|  | $a_{H_1}=0.95$ $a_{H_2}=0.31$ |
|  | $a_{H_1}=3.30$ $a_{H_2}=0.60$ $a_{H_3}=0.30$ |

it is very similar to that obserbed by Geske and Maki²⁾ though there is a slight difference in the hyperfine coupling constants. This difference might be due to the presence of traces of water in the solvent used, in accordance with the results we reported previously when dealing with the solvent effect on the width of the line due to nitrogen coupling in the cases of diphenyl nitric oxide¹²⁾ and di-*p*-anisyl nitric oxide.¹³⁾ It was shown there that the nitrogen-coupling constant obtained in an aqueous solution was larger than that obtained in acetonitrile. Piette et al.¹⁴⁾ also examined the dependence of the nitrogen coupling constant of nitro compounds on the water content of the solvent and showed that the presence of small quantities of water considerably increases the magnitudes of the constant.

*Nitrotoluene*.—The ESR spectra of electrolytically reduced *o*-, *m*- and *p*-nitrotoluenes are shown in Figs. 2a, 2b and 2c. The coupling constants given in Table I are in good agreement with the observed spectra. The coupling constants were assigned to each proton by referring to the results of Hückel's molecular orbital (MO) method of calculation. It was found that all three methyl protons had the same coupling constant; this shows that there is a hyperconjugative interaction between the methyl group rotating at high speed and the ring $\pi$ system. In the case of *o*-nitrotoluene, one would expect that the molecule will have an unequal spin distribution in the ring system because of the molecular asymmetry; however, the two protons in the meta position to the nitro group showed the same coupling constant.

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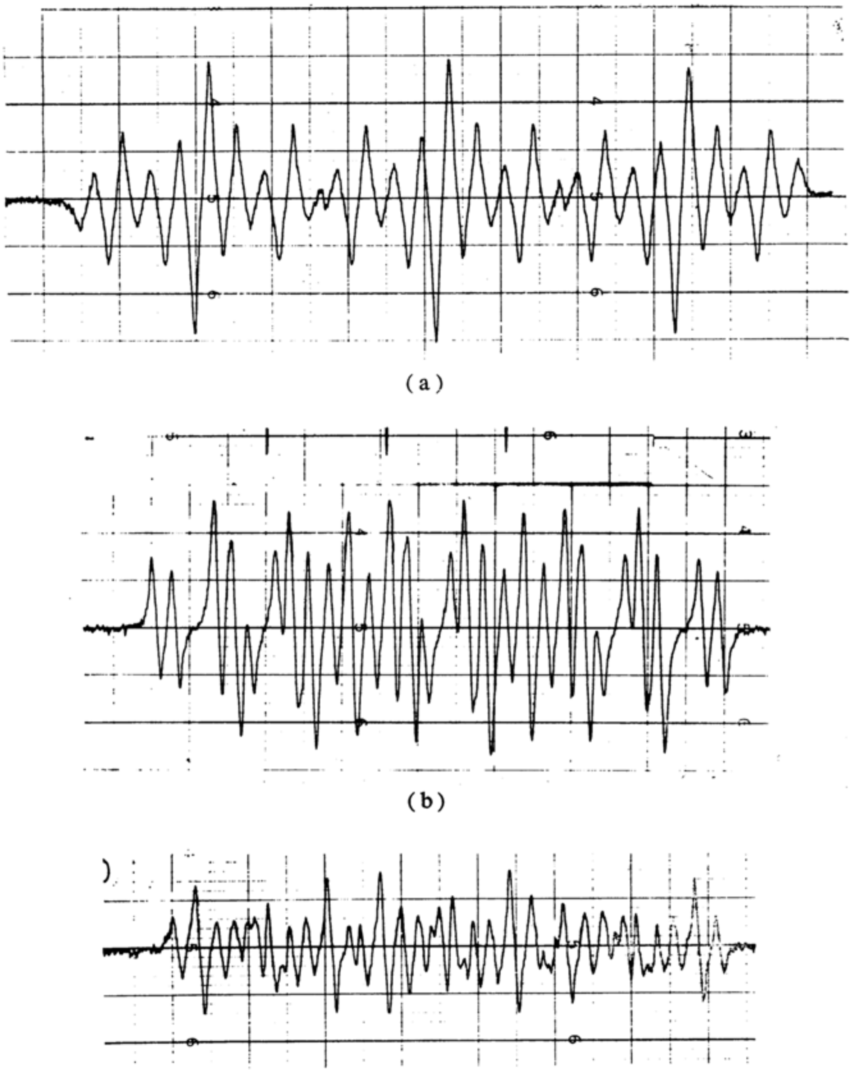
12) Y. Deguchi, This Bulletin, **35**, 260 (1962).

13) K. Umemoto, Y. Deguchi and H. Takagi, ibid., **36**, 560 (1963).

14) L. H. Piette, P. Ludwig and R. N. Adams, *J. Am. Chem. Soc.*, **84**, 4212 (1962).



(a)

(b)

(c)

Fig. 3. ESR spectra of (a) *p*- (b) *m*- (c) *o*-nitrochlorobenzene anion radicals.

In the case of *m*-nitrotoluene, the two ortho protons were found to be equivalent. Hence, the spin distribution in the molecule seems to be little affected by the substitution of a ring proton with a methyl group. The nitrogen-coupling constats are a little larger than that of the nitrobenzene anion, showing that the methyl group has an electron-repelling effect. The fact that the ortho and para isomers have a larger nitrogen-splitting constant than the meta compound explains why the electron-repelling effect of the methyl group is directed towards the ortho and para positions.

*Chloronitrobenzene.*—The ESR spectra of the reduced ortho, meta and para isomers are shown in Figs. 3a, 3b and 3c. Once again the coupling constants shown in Table I agree well with the observed spectra. It was not possible to obtain an hfs spectrum of chlorine. Wertz and Vivo,[15] who studied the ESR spectra of chloro compounds in an aqueous solution, were also unable to observe the hfs of the chlorine because of the small nuclear magnetic moment of this atom. As in the case of nitrotoluene, the two meta protons of the ortho isomer and two ortho protons of the meta isomer have the same coupling constant. Hence, the chloro-substitution seems to affect the spin distribution of the molecule very little. The nitrogen-coupling constants were somewhat smaller than that of the nitrobenzene anion because of the electron-attracting effect of the chlorine

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[15] J. E. Wertz and J. L. Vivo, *J. Chem. Phys.*, **23**, 2441 (1955).

TABLE II. $^{14}N$ COUPLING CONSTANTS OF SUBSTITUTED NITROBENZENE

| | -OH | $-NH_2$ | $-OCH_3$ | $-CH_3$ | -Br | -Cl | -CN | -CHO | $-NO_2$* |
|---|---|---|---|---|---|---|---|---|---|
| para | 13.8 | 12.2 | 11.5 | 11.0 | 9.80 | 9.70 | 7.05 | 5.91 | 1.74 |
| meta | 12.3 | — | 10.3 | 10.7 | 9.78 | 9.60 | 9.09 | 6.60 | 4.68 |
| ortho | 12.7 | 12.3 | 11.4 | 11.3 | — | 9.95 | 7.70 | 7.55 | 3.22 |

* Data from Ref. 3.

atom. The nitrogen-coupling constants of the ortho isomers of nitrotoluene and nitrochlorobenzene are little larger than those of the corresponding meta and para isomers, indicating a small steric effect. It has been pointed out by Geske and Ragel[16] that the $a_N$ value in an aromatic anion radical approaches that of the aliphatic counterpart when the nitrogroup is twisted out of the plane of the benzene ring by steric effects of bulky substituents.

*Bromonitrobenzene.*—The ESR spectra of the reduced para and meta isomers were very similar to those of the corresponding chloronitrobenzene compounds. However, the ortho isomer showed the same ESR spectrum as the nitrobenzene anion radical, indicating that the elimination of the bromine atom occurs prior to the formation of the free radical.

*Iodonitrobenzene.*—The electrolytic reduction products of ortho, meta and para isomers all showed the same ESR spectrum as the nitrobenzene anion radical. This once again indicates that the iodine is eliminated prior to the reduction of the nitro group.

*Other Substituted Nitrobenzenes.*—The coupling constants of other substituted nitrobenzene anion radicals are also listed in Table I. The different nitrogen-coupling constants are given in Table II; the substituents are arranged according to their increasing electron-attracting effect. Electron-attracting substituents generally reduce the nitrogen-coupling constant, whereas the electron-repelling substituents increase it. In both cases, the electron effect is more pronounced in the case of ortho and para than in the case of meta substitution. *o*-Nitrobenzaldehyde gave an abnormally large nitrogen-splitting constant, and the usual order observed with electron-attracting groups, viz. para<ortho<meta, does not hold; this seems to indicate a strong ortho effect of the aldehyde group.

As regards nitrophenol, the authors have discussed the effect of hydrogen bonding in a previous publication.[17]

**Hückel's Molecular Orbital Calculations.**—Using the coupling constants shown in Table I, the spin density distribution could be calculated from the following relation: $a_i^H = Q_{CH}^H \rho_i^\pi$, where $Q_{CH}^H = 28$ gauss[18] and, for the methyl group, $a_{CH_3}^H = Q_{CCH_3}^H \rho^\pi$, where $Q_{CCH_3}^H = 30$ gauss.[19] By Hückel's MO method, the spin density in the molecules could also be calculated. The results are listed in Table III, where the parameters employed in this calculation are also listed. The calculated spin density in the ortho and para positions relative to the nitro group is in fairly good agreement with the experimental values; by contrast the calculated meta position is not in agreement with the experimental results. Rieger and Fraenkel[5] calculated the spin density distribution for some nitrile and nitro compounds by both Hückel's MO method and McLachlan's procedure, which employs the concept of approximate configuration interaction; these authors also found that Hückel's MO method generally gave good results for ortho- and para- but not for meta-substitution, while McLachlan's approximation method generally gave very good agreement with the experimental results.

**Electrochemical Process.**—*Nitrobenzene.*—The nitrobenzene anion radical was generated by electrolysis at −1.3 V. vs. SCE (saturated calomel electrode), that is, at a potential slightly more negative than that of the first wave in the polarogram. The radical was stable for about 30 min. It is known that at the potential of the second wave the mono negative ion is further reduced to the dinegative radical, which is generally rapidly protonated by the reaction with the solvent. Therefore, no ESR spectrum would be cxpected a priori. However, an ESR spectrum was observed in the potential range of the second wave, although the intensity was reduced to some extent. This shows that the process corresponding to the second wave is slower than the radical formation. When phenol was added as a proton donor to the 1 mM nitrobenzene DMF solution, the radical formation at −1.3 V. vs. SCE was not affected until the concentration of the added phenol reached about 2 mM; at higher potentials, the stability of the radical decreased. Upon the further addition of phenol, the rate of the radical formation at the potential of the first wave

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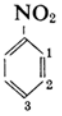
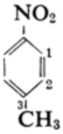
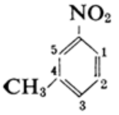
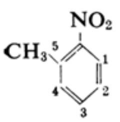
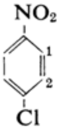
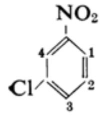
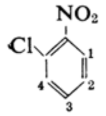
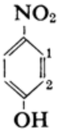
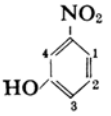
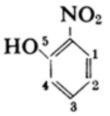
16) D. H. Geske and L. Ragle, *J. Am. Chem. Soc.*, **83**, 3532 (1961).

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

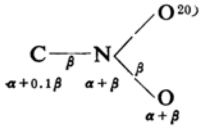
18) H. S. Jarrett, *J. Chem. Phys.*, **25**, 1289 (1956).

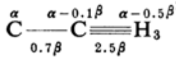
19) D. J. E. Ingram, "Free Radicals as Studied by Electron Spin Resonance," Butterworths Scientific Publications, London (1958), p. 116.

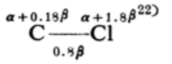
TABLE III. CALCULATED AND EXPERIMENTAL SPIN DENSITY

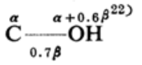
| Position | | Spin density | |
|---|---|---|---|
| | | experimental | calculated |
|  | 1 | 0.120 | 0.0942 |
| | 2 | 0.038 | 0.0023 |
| | 3 | 0.136 | 0.1030 |
|  | 1 | 0.118 | 0.09356 |
| | 2 | 0.041 | 0.00202 |
| | 3 | 0.130 | 0.10190 |
|  | 1 | 0.121 | 0.09397 |
| | 2 | 0.039 | 0.00226 |
| | 3 | 0.137 | 0.10280 |
| | 4 | 0.039 | 0.00224 |
| | 5 | 0.121 | 0.09447 |
|  | 1 | 0.1194 | 0.09401 |
| | 2 | 0.0372 | 0.00202 |
| | 3 | 0.1335 | 0.10238 |
| | 4 | 0.0372 | 0.00252 |
| | 5 | 0.1194 | 0.09305 |
|  | 1 | 0.1220 | 0.09351 |
| | 2 | 0.0400 | 0.00085 |
|  | 1 | 0.1145 | 0.09243 |
| | 2 | 0.0332 | 0.00231 |
| | 3 | 0.1450 | 0.10129 |
| | 4 | 0.1145 | 0.09633 |
|  | 1 | 0.1180 | 0.09674 |
| | 2 | 0.0404 | 0.00083 |
| | 3 | 0.1400 | 0.10232 |
| | 4 | 0.0404 | 0.00484 |
|  | 1 | 0.1122 | 0.09091 |
| | 2 | 0.0257 | 0.00063 |
|  | 1 | 0.0985 | 0.08719 |
| | 2 | 0.0329 | 0.00248 |
| | 3 | 0.1063 | 0.09614 |
| | 4 | 0.1189 | 0.10279 |
|  | 1 | 0.1282 | 0.10520 |
| | 2 | 0.0218 | 0.00067 |
| | 3 | 0.1282 | 0.09956 |
| | 4 | 0.0360 | 0.01777 |
| | 5 | 0.0164 | 0.04044 |

Parameters used in this calculation are as follows.



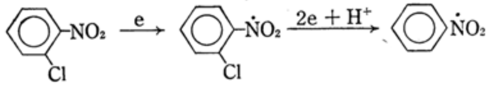






decreased as well, indicating rapid protonation and, hence, a decreased life time of the free radical.

*Chloronitrobenzene.*—The reducttion products of the three isomers of chloronitrobenzene, prepared by electrolysis at −1.3 V. vs. SCE in an acetonitrile solution, showed an ESR spectrum. In DMF the para and meta isomers gave their characteristic spectra. When the applied potential was changed from −1.2 V. to −2.0 V. vs. SCE the generated radical species showed little change, although the intensity of the spectrum decreased at potentials lower than −1.8 V. vs. SCE. When the ortho isomer was electrolyzed at −1.3 V. vs. SCE in a 1 mM DMF solution, its ESR spectrum could be observed soon after the electrolysis began, but after about fifteen minutes the spectrum showed the beginning formation of the nitrobenzene radical, which after 45 min. was the major component present. When the applied voltage was changed to −1.5 V. vs. SCE the ESR spectrum became identical with that of the nitrobenzene anion radical, indicating a dehalogenation reaction according to:



The ease of dehalogenation in the case of the ortho isomer might be due to steric reasons. When phenol was added in about an equimolar quantity, the dehalogenation was impeded, and when a quantity about three times greater was added, no dehalogenation was observed at potentials above −1.7 V. vs. SCE; no radical formation could be detected at lower potentials because of enhanced protonation.

*Bromonitrobenzene.*—The reduction products of the para and meta isomers gave their characteristic ESR spectra when prepared by electrolysis at −1.3 V. vs. SCE in an acetonitrile solution, whereas the ortho derivative, under the same conditions, showed the ESR spectrum of the nitrobenzene anion, indicating dehalogenation in the DMF solution.

In the DMF solution the meta isomer did not show any sign of dehalogenation in the potential range from −1.1 V. to −2.0 V. vs. SCE, whereas the ortho isomer was completely dehalogenated. The reduction product of the para isomer showed its own characteristic spectrum when prepared by electrolysis at −1.0 V. vs. SCE in a 1 mM solution; at −1.3 V. vs. SCE the beginning formation of the

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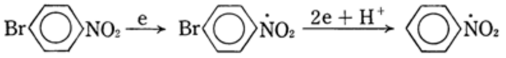
20) J. I. F. Alonso., *Compt. rend.*, **233**, 403 (1951).

21) C. A. Coulson and U. A. Crawford, *J. Chem. Soc.*, **1953**, 2052.

22) H. H. Jaffé, *J. Chem. Phys.*, **20**, 279 (1952).

nitrobenzene anion radical could be observed, while as the electrolysis proceeded, the formation of increasing quantities of nitrobenzene anion could be seen. At $-1.6$ V. vs. SCE a clear spectrum of the nitrobenzene anion alone could be observed. When the concentration of the para isomer was raised to 5 mM, the spectrum of the reduced para isomer alone was observed in the potential region from $-1.0$ V. to $-1.4$ V. vs. SCE, whereas at lower potentials dehalogenation became evident. These results suggets the following electrode process:



*Indonitrobenzene.*—All three isomers showed the formation of the nitrobenzene anion radical, even in a 5 mM solution at $-1.2$ V. vs. SCE both in acetonitrile and in the DMF solution. Hence, complete dehalogenation occurred in all cases. The reaction can be represented by:

The experiments show that the ease with which the halonitrobenzenes are dehalogenated during the electrolytic reduction follows the order:

$p, m$-Cl, $m$-Br $<$ $o$-Cl $<$ $p$-Br $<$ $o$-Br,
$p, m, o$-I

This series seems to indicate that the ease of dehalogenation depends on steric considerations.

Details of the polarographic studies of the halonitrobenzenes will be reported later.[23]

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[23] T. Fujinaga and T. Arai, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), in press.