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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, NEW YORK 27, N. Y.]

## Electron Spin Resonance Studies of Aromatic Polynitro Compounds<sup>1</sup>

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The three nitromesitylenes and two nitrodurenes have been reduced electrolytically in *N,N*-dimethylformamide solutions and their electron spin resonance spectra studied. Some spectra were also observed in dimethyl sulfoxide solutions. The e.s.r. spectra were obtained in conjunction with conventional and alternating current polarographic investigations. Different spectra were obtained at the successively higher polarographic waves. The first polarographic wave for each compound was found to be reversible and, except for trinitromesitylene, the expected number of nitrogen splittings were observed. At successively higher waves for all the compounds, a nitrogen splitting disappeared from the spectrum and the polarographic wave was irreversible. No interpretable e.s.r. spectra were obtained at polarographic waves above those for which only one nitrogen splitting remained in the spectrum. The radicals produced at the higher waves were not identical with the radicals of the parent compound with the same number of nitrogen splittings; e.g., the radical at the second wave of dinitromesitylene, which shows the splittings from only one nitrogen nucleus, is different from the radical generated at the first polarographic wave of mononitromesitylene. The two radicals with spectra containing two nitrogen splittings exhibited the alternating line width phenomenon to a marked extent.

### I. Introduction

In recent electron spin resonance studies of a number of aromatic polynitro compounds, Ward<sup>3,4</sup> observed that the radicals produced by alkali metal reduction exhibit hyperfine splittings from only one nitrogen nucleus. In the *m*-dinitrobenzene anion, he found two nitrogen splittings, but one was thirty times larger than the other.<sup>5</sup> These results were explained in terms of a tightly bound ion-pair complex between the alkali metal cation and the nitro group of the anion radical. Effects such as this are not observed, however, when the dinitrobenzene anions are generated by electrolytic reduction with bulky tetraalkylammonium ions as supporting electrolytes.<sup>6</sup>

During the course of an investigation into the alternating line width phenomenon in nitro compounds,<sup>7</sup> we were led to an examination, using electrolytic techniques, of the nitromesitylenes. These were also found by Ward to lead to only one nitrogen splitting. Our results indicated that several nitrogen splittings could be observed, but that different spectra were obtained at different polarographic waves. A detailed study has therefore been made of the three nitromesitylenes and two nitrodurenes. Electron spin resonance spectra were examined at successive polarographic waves, and conventional and alternating current polarographic studies were used in conjunction with the e.s.r. investigation.

### II. Experimental

Electron spin resonance measurements were performed at X-band frequencies using a spectrometer previously described.<sup>8</sup> Radicals were produced by electrolytic reduction in a cell out-

side the cavity of the spectrometer under conditions which allowed control of the potential and essentially complete reduction.<sup>9</sup> The techniques as well as the factors that determine the sharpness of the lines in the spectrum have been discussed in detail elsewhere.<sup>9</sup>

*N,N*-Dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) were used as solvents. Tetra-*n*-propylammonium perchlorate (TNPAP) and, in some instances, tetra-*n*-butylammonium perchlorate (TNBAP) were used as the supporting electrolyte. The concentrations of the reducible material ranged from 5 to 0.5 mM, and the solutions were 0.1 M in supporting electrolyte. In some experiments, but not all, lowering of the concentration below 1 to 2 mM improved the sharpness of the lines of the spectrum. Radicals which were quite stable at concentrations of a few millimolar became unstable at the lower concentrations. This instability was presumably caused by impurities in the solutions and/or on the walls of the electrolytic cell, e.s.r. sample tube, and interconnecting tubing. Reduction potentials were measured with respect to a silver-silver perchlorate electrode.<sup>9</sup> It should be noted that the potentials of this electrode tend to drift with time, and therefore we have taken care, whenever comparative determinations of potential were important, to perform them on the same day. No attempt has been made, however, to relate the potentials to an absolute scale.

Conventional oscillographic studies were undertaken using equipment described elsewhere.<sup>10</sup> Solutions for polarographic investigations were approximately 1 mM in reducible material, and nitrogen was bubbled through them to remove oxygen. The measurements were made at room temperature without temperature control.

A macroelectrolysis was carried out for one compound, trinitromesitylene. A thermostated electrolytic cell equipped with a stirrer was employed that had a flat, square, platinum anode 1 cm.<sup>2</sup> in area. The cathode was a mercury pool which was also approximately 1 cm.<sup>2</sup> in area. A constant potential electrolysis was carried out using the Ag-AgClO<sub>4</sub> electrode to establish the reference potential.

Trinitromesitylene was obtained from K and K Laboratories, Inc. (m.p. 235–236°, lit.<sup>11</sup> 236°). Dinitromesitylene (m.p. 85–86°, lit.<sup>11</sup> 86°) and nitromesitylene (m.p. 45–46°, lit.<sup>11</sup> 45.5°) were obtained from Eastman Organic Chemicals. Dinitrodurene was prepared according to the procedure of Smith and Dobrovolny<sup>12</sup> (m.p. 211–212° uncor., lit.<sup>12</sup> 207–208°). Nitrodurene was made by the method of Smith and Taylor<sup>13</sup> (m.p. 113–114°, lit.<sup>13</sup>

(1) Supported in part by the U. S. Air Force through the Office of Scientific Research.

(2) Socony-Mobil Predoctoral Fellow, 1961–1962.

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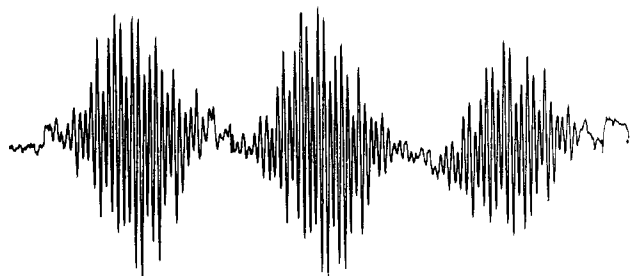


Fig. 1.—Derivative of the e.s.r. spectrum of the radical obtained from trinitromesitylene in DMF by reduction at the second polarographic wave using low amplitude field modulation. The magnetic field increases to the right.

100–105°). The solvents were distilled under nitrogen. DMF was distilled from anhydrous potassium carbonate and DMSO from calcium hydride. The purification of the supporting electrolyte is described elsewhere.<sup>14</sup>

### III. Results

In this section we shall describe the detailed results for each compound investigated. A summary of the polarographic and e.s.r. data is given in Tables I and II, respectively. E.s.r. spectra were recorded at different polarographic waves, and the reversibility of the waves was determined by oscillography. A number of the spectra exhibited an alternation of the line widths from one hyperfine component to another,<sup>7,15–18</sup> and others showed the splitting from fewer N<sup>14</sup> nuclei than the number contained in the starting material. Since the signal amplitude of the derivative of the e.s.r. spectrum is proportional<sup>19</sup> to  $(H_m/\Delta H)^2$ , where  $H_m$  is the amplitude of the field modulation used to obtain the derivative spectrum and  $\Delta H$  is the half-width of the e.s.r. line at half-maximum absorption, the relative amplitudes of the signals from different hyperfine components in a spectrum vary inversely as the squares of their line widths. Very broad lines may thus not be observed in a derivative spectrum with a field-modulation amplitude adjusted to give proper<sup>19</sup> recording of the narrow lines. When fewer nitrogen splittings were observed than the number expected from the starting material, we therefore also ran spectra at much higher field modulation amplitudes than normal. In most of the compounds studied, the hyperfine splittings from protons are very small, and the number of expected lines very large. For example, the number of proton lines for a particular value of the nitrogen nuclear spin quantum numbers in the dinitromesitylene anion is 56. As a result, no attempt was made to determine the proton hyperfine splitting constants from most of the spectra, although a few qualitative conclusions about these splittings were obtained.

**Trinitromesitylene (2,4,6-Trinitro-1,3,5-trimethylbenzene).**—Reduction of this material at the first polarographic wave initially produces a violet solution which becomes brownish red as electrolysis progresses. The solution gives a weak, unsymmetrical e.s.r. spectrum. It is interesting to note that because of its

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TABLE I  
POLAROGRAPHIC DATA<sup>a</sup>

Compound	$E_{1/2}$ , v.	Height of wave, arbitrary units	Reversibility
Trinitromesitylene	-1.00	17	Reversible <sup>b</sup>
	-1.15	..	Irreversible <sup>c</sup>
	-1.60	..	Irreversible <sup>c</sup>
Dinitromesitylene	-1.13	17	Reversible <sup>b</sup>
	-1.36	..	Irreversible <sup>c</sup>
	-1.60	..	Irreversible <sup>c</sup>
Mononitromesitylene	-1.32	18	Reversible <sup>b</sup>
	-1.62	..	Irreversible <sup>c</sup>
Dinitrodurene	-1.22	17	Reversible <sup>b</sup>
	-1.38	..	Irreversible <sup>c</sup>
Mononitrodurene	-1.39	19	Reversible <sup>b</sup>
	-1.72	..	Irreversible <sup>c</sup>

<sup>a</sup> All solutions were approximately 1 mM in reducible material and 0.1 M in the supporting electrolyte; in all cases the solvent was N,N-dimethylformamide. Potentials were measured with respect to a Ag-AgClO<sub>4</sub> reference electrode. <sup>b</sup> Reversible at frequencies above 10 c.p.s.; data taken with the apparatus described in ref. 10. <sup>c</sup> Irreversible up to frequencies of 500 c.p.s.

TABLE II  
ELECTRON SPIN RESONANCE DATA

Starting material	Solvent <sup>a</sup>	Polarographic wave	No. of N <sup>14</sup> nuclei obsd. in e.s.r. spectrum	N <sup>14</sup> splitting, $a^N$ , gauss	Approx. sepn. of small lines, gauss	Approx. envelope line width, gauss
Trinitromesitylene	DMF <sup>b</sup>	2nd	2	8.87	0.6	2.5
	DMF <sup>b</sup>	3rd	1	19.99	0.3	1.25
	DME <sup>c</sup>	.. <sup>a</sup>	1	12.6	..	..
Dinitromesitylene	DMF <sup>b</sup>	1st	2	7.21	0.6	2.5
	DMSO <sup>b</sup>	1st	2	7.46	..	..
	DMF <sup>b</sup>	2nd	1	18.17	0.6	2.0
	DMSO <sup>b</sup>	2nd	1	18.67	..	..
	DME <sup>c</sup>	.. <sup>a</sup>	1	14.6	..	..
Mononitromesitylene	DMF <sup>b</sup>	1st	1	15.93	1.0	4.0
	DME <sup>c</sup>	.. <sup>a</sup>	1	16.5	..	..
Dinitrodurene	DMF <sup>b</sup>	1st	2	7.01	0.25	0.9
	MeCN <sup>d</sup>	?	2	8.7	..	..
	DMF <sup>b</sup>	2nd	1	20.78	..	0.7
Mononitrodurene	DMF <sup>b</sup>	1st	1	19.73	0.2	1.5
	MeCN <sup>d</sup>	?	1	20.4	..	..

<sup>a</sup> DMF = N,N-dimethylformamide; DMSO = dimethyl sulfoxide; MeCN = acetonitrile; DME = 1,2-dimethoxyethane. The radicals obtained in DMF, DMSO, and MeCN were obtained electrolytically, while those in DME were generated by alkali metal reduction. <sup>b</sup> This work; errors in splittings are  $\pm 0.05$  gauss or less. <sup>c</sup> Work of R. L. Ward; see ref. 3 and 4. <sup>d</sup> Work of D. H. Geske and J. L. Ragle, see ref. 25.

threefold symmetry, the anion of trinitromesitylene is expected to be subject to a large Jahn-Teller distortion.<sup>20,21</sup> It is not clear whether or not the poor spectrum observed is related to this effect. A detailed study of the spectrum at the first wave was not made.

At the second polarographic wave in DMF a reddish brown solution is obtained from which the spectrum shown in Fig. 1 was recorded. This figure contains three equally spaced lines of approximately equal amplitude with small additional splittings on each line. The resolution of the high field line is the poorest, while that

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(21) H. C. Townsend and S. I. Weissman, *ibid.*, **32**, 309 (1960); J. R. Bolton and A. Carrington, *Mol. Phys.*, **4**, 271 (1961).

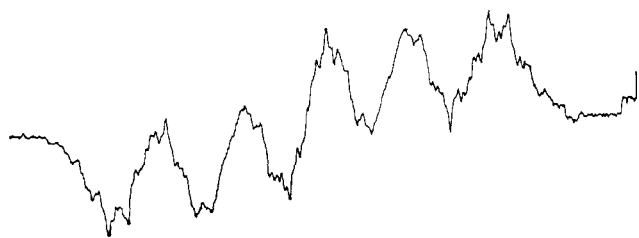


Fig. 2.—Derivative of the e.s.r. spectrum of the radical obtained from trinitromesitylene in DMF by reduction at the second polarographic wave using high amplitude field modulation (compare with Fig. 1).

of the central line is the best, and since the resolution is an indication of the width, it is evident that the integrated intensity of each line is at least approximately the same. The spectrum in Fig. 1 can thus be readily interpreted as arising from a large splitting ( $a^N = 17.7$  gauss) from a single  $N^{14}$  nucleus together with small, incompletely resolved, proton splittings. But when the amplitude of the field modulation is increased from the value of about 0.07 gauss used to obtain the spectrum in Fig. 1 to a value of about 5 gauss, the spectrum found for the same radical is that shown in Fig. 2. Two additional lines are now observed, spaced at positions intermediate to those of the lines in Fig. 1. The radical generated at the second polarographic wave of trinitromesitylene thus contains the splittings from two equivalent  $N^{14}$  nuclei. The intermediate lines, corresponding to  $M_N = \pm 1$ , where  $M_N$  is the total  $z$  component of the nitrogen nuclear spin angular momentum,<sup>22</sup> are broader than those for  $M_N = 0$  or  $\pm 2$ , and thus are not observed in a spectrum recorded at a low amplitude of the field modulation as in Fig. 1. These spectra thus illustrate the alternating line width phenomenon.<sup>7,15-18</sup> More significant for our present purposes is the appearance of splittings attributable to only two nitrogen nuclei from a starting material which contained three nitrogen atoms.

Reduction of trinitromesitylene in DMF at the third polarographic wave produces an orange-red solution and gives a spectrum with three equally spaced main envelopes of approximately equal intensity. Each envelope contains small unresolved splittings. The qualitative appearance of the spectrum was similar to that in Fig. 4 (see below). Spectra obtained at high amplitude of the field modulation do not show the presence of any intermediate lines, and we therefore conclude that a radical with splittings attributable to only one nitrogen nucleus is obtained at the third polarographic wave of trinitromesitylene.

**Dinitromesitylene (2,4-Dinitro-1,3,5-trimethylbenzene).**—The spectrum of the violet radical produced from dinitromesitylene in DMF at its first polarographic wave is shown in Fig. 3. Three main envelopes of equal spacing and approximately equal intensity, each possessing considerable structure, are observed, together with small irregular lines interspersed between the main envelopes. Recordings of this spectrum taken at larger amplitude of the field modulation show that again the spectrum arises from two equivalent nuclei of spin  $I = 1$  but that the  $M_N = \pm 1$  lines are much broader than the  $M_N = 0$  and  $\pm 2$  lines.<sup>22</sup> The high-field line ( $M_N$

(22) Since the signs of the hyperfine splittings were not determined, the sign of the magnetic quantum number has been arbitrarily assigned to be positive on the high-field side of the spectrum.

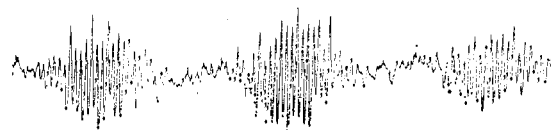


Fig. 3.—Derivative of the e.s.r. spectrum of the radical obtained from dinitromesitylene in DMF by reduction at the first polarographic wave. Magnetic field increases to the right.

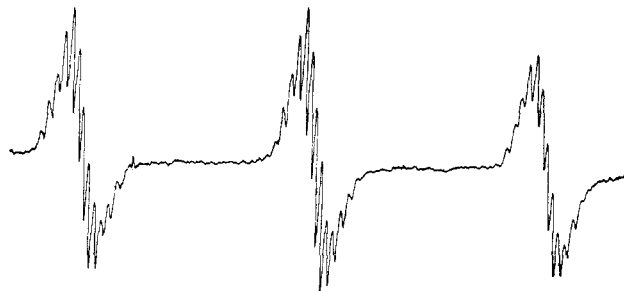


Fig. 4.—Derivative of the e.s.r. spectrum of the radical obtained from dinitromesitylene in DMF by reduction at the second polarographic wave. Magnetic field increases to the right.

$= +2$ ) in Fig. 3, as in the other spectra, is of lower amplitude than the  $M_N = 0$  and  $-2$  lines. The spectrum of this radical at the first polarographic wave in DMSO shows similar, but not identical, fine structure within the  $M_N = \pm 1$  lines. The radicals generated at the first polarographic wave of dinitromesitylene and at the second polarographic wave of trinitromesitylene both give e.s.r. spectra which show the splitting from two nitrogen nuclei, but the nitrogen splitting constants are significantly different (see Table II), and the qualitative appearance of the spectra shows that the proton splittings are also different.

Reduction of dinitromesitylene in DMF at the second polarographic wave produces a reddish brown solution with the e.s.r. spectrum shown in Fig. 4. The splitting from only one nitrogen nucleus is observed, and spectra recorded at high amplitudes of the field modulation do not show any lines interspersed between the lines of the main triplet. The data in Table II indicate that the radical generated at the third polarographic wave from trinitromesitylene is different from the radical produced at the second wave from dinitromesitylene, even though both spectra show a splitting from only one  $N^{14}$  nucleus.

**Nitromesitylene (2-Nitro-1,3,5-trimethylbenzene).**—The radical generated on reduction in DMF at the first polarographic wave is red. The e.s.r. spectrum obtained, shown in Fig. 5, indicates the presence of a single  $N^{14}$  nucleus and small splittings from protons. Reduction at higher potentials produces a mixture of radical species that could not be identified, a result which is typical of the electrolysis of nitrobenzenes at high potentials.<sup>23</sup>

**Dinitrodurene (1,4-Dinitro-2,3,5,6-tetramethylbenzene).**—Reduction at the first polarographic wave of a DMF solution of dinitrodurene gives a golden brown solution with an e.s.r. spectrum containing five principal lines which exhibit additional fine structure. The spectrum, which has been reproduced elsewhere,<sup>7</sup> shows marked alternation of the line widths, the  $M_N = \pm 1$  lines being considerably broader than the  $M_N = 0$  and  $\pm 2$  lines.

(23) B. Barton and N. Steinberger, unpublished results obtained in these laboratories.

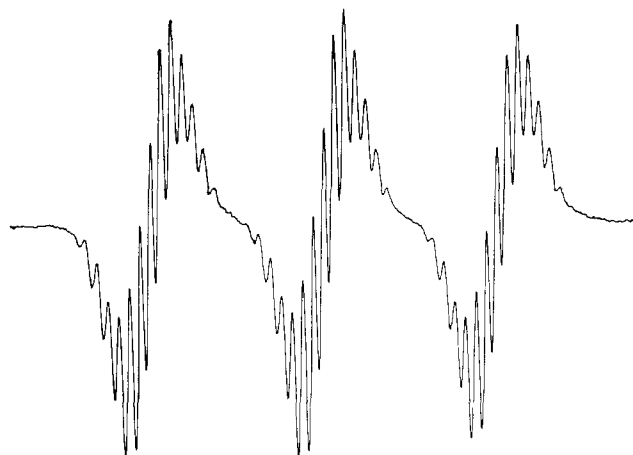


Fig. 5.—Derivative of the e.s.r. spectrum of nitromesitylene obtained at the first polarographic wave in DMF. Magnetic field increases to the right.

Reduction at the second polarographic wave gives rise to a red-brown solution. The e.s.r. spectrum now possesses three equally spaced lines of approximately the same intensity and about 0.7 gauss wide. Barely observable fine structure was present on the main envelopes at low amplitudes of field modulation. Additional lines were not observed at higher values of the field modulation amplitude.

**Nitrodurene (1-Nitro-2,3,5,6-tetramethylbenzene).**—Reduction of this compound at the potential of the first polarographic wave yields a dark red solution which displays a three-line e.s.r. spectrum. The lines are of approximately equal intensity and show a small amount of fine structure. The nitrogen splitting constants (see Table II) are significantly different from those obtained from dinitrodurene at its second polarographic wave.

**Macroreduction of Trinitromesitylene.**—For all the polynitro compounds studied, the e.s.r. spectra of the radicals generated at polarographic waves above the first exhibit splittings from fewer nitro groups than contained in the starting material. A macroscale electrolysis of trinitromesitylene was therefore performed at the second polarographic wave in order to determine if the nitrogen content would be reduced.

The electrolysis was carried out on 50 ml. of a solution which was 0.0076 *M* in trinitromesitylene and 0.1 *M* in TNPAP at a potential of  $-1.3$  v. using the apparatus described in section II. The maximum current was 30–40 ma., and the current dropped in an approximately exponential manner with time. No attempt was made to determine the number of coulombs passed in the electrolysis. The electrolysis was run for 18 hr. The resulting solution was poured into 200 ml. of absolute ethanol to destroy the radical and then evaporated under vacuum to remove the alcohol. After adding 100 ml. of water, the DMF solution was extracted with small portions of benzene until the extracted portions were colorless. The extracts were combined and dried with anhydrous magnesium sulfate, the benzene removed by vacuum distillation, and a small residue of DMF removed under high vacuum. The brownish red residue was extracted with absolute ethanol, the solution concentrated by evaporation, and the hot solution treated with cold, anhydrous ether, which caused the material to precipitate as brownish red crystals.

The elemental analysis of the brownish red crystals is: C, 57.73; H, 7.31; N, 13.34; O (by difference), 21.64. The calculated percentage composition of trinitromesitylene is: C, 42.36; H, 3.55; N, 16.47; O, 37.62; while that of dinitromesitylene is: C, 51.42; H, 4.79; N, 13.32; O, 30.44. Although the product of macroreduction has a lower relative nitrogen content than the starting material, the relative amount of carbon and hydrogen has increased, and the relative oxygen content has dropped considerably. It is thus not possible to determine the nature of the reduction product by elemental analysis, and further investigation of its structure was not attempted.

#### IV. Discussion

Our results show that in the series studied, a nitrodurene or nitromesitylene containing  $n$  nitro groups gives an e.s.r. spectrum on reduction at the  $m$ th polarographic wave which has  $N^{14}$  hyperfine splittings from  $(n - m + 1)$  nitrogen nuclei. This rule does not apply when  $m > n$  (for example, a mixture of radicals is obtained when nitromesitylene is reduced at the second polarographic wave), and only a weak, uninterpretable spectrum is obtained when trinitromesitylene is reduced at the first polarographic wave. The spectra of radicals having splittings from two nitrogen nuclei show a strong alternating line width effect, while those having splittings from only one nitrogen nucleus do not exhibit an alternation in line width. Each compound has a reversible one-electron wave followed by higher waves that are irreversible, and the reduction potential of the  $m$ th wave ( $m > 1$ ) of the compound with  $n$  nitro groups is the same (within the experimental error of  $\pm 0.05$  v.) as the potential of the  $(m - 1)$  wave of the analogous compound with  $(n - 1)$  nitro groups.

In the nitromesitylene series, radicals exhibiting the splittings from only one nitrogen nucleus have nitrogen splittings in the order: trinitromesitylene (third wave)  $>$  dinitromesitylene (second wave)  $>$  nitromesitylene (first wave). The radicals showing splittings from two nitrogen nuclei have splittings in the order: trinitromesitylene (second wave)  $>$  dinitromesitylene (first wave). Similarly, the radical generated from the dinitrodurene anion which shows only one nitrogen splitting has a larger splitting constant than found in the mononitrodurene anion. These data, as well as the differences in the appearance of the incompletely resolved proton hyperfine structure, show that the radicals produced at higher polarographic waves are not simply the result of nitro group elimination followed by replacement with a proton. The ambiguous result obtained from the macroreduction also indicates that the irreversible reaction at the higher waves is a complex one. Nitro group elimination on reduction has been observed in the aliphatic series, however, by Stock,<sup>24</sup> who found that a nitrite ion is eliminated from 2,2-dinitropropane on the addition of two electrons.

At first sight it might appear that the spectra generated at the higher polarographic waves result from elimination of an  $NO_2^-$  ion followed by coupling of two of the neutral aromatic radical fragments and subsequent reduction of the dimer. If a mechanism of this sort occurred at the second wave in the reduction of trinitromesitylene, dinitromesitylene, or dinitrodurene,

(24) J. T. Stock, *J. Chem. Soc.*, 4532 (1957).

the molecules produced would be derivatives of 2,2',-6,6'-tetramethylbiphenyl, and the two halves would probably be twisted out of planarity with each other because of steric repulsion between the methyl groups. The conjugation between the two rings would be reduced by this twisting, and the unpaired electron might be trapped in only one-half of the radical. This mechanism would consequently account for the number of observed nitrogen splittings in the spectra obtained at the second wave from trinitromesitylene, dinitromesitylene, and dinitrodurene. It is difficult to extend the mechanism, however, to explain the spectrum found at the third polarographic wave of trinitromesitylene. It would also be somewhat surprising if coupling occurred at the highly hindered positions between the two methyl groups of the radical fragments.

The nitrogen hyperfine splittings in the nitromesitylenes and nitrodurenes are all larger than those of the related unmethylated nitrobenzenes.<sup>6,14,25</sup> The nitrogen splitting in DMF solutions of the nitrobenzene anion is<sup>26,27</sup> 9.70 gauss, while the results range from 15.93 to 20.78 gauss (Table II) for the radicals of the nitromesitylene and nitrodurene series that show splitting from only one nitrogen nucleus. Similarly, the nitrogen splitting in the *m*-dinitrobenzene anion is<sup>27</sup> 3.97 gauss as compared to 7.21 gauss for the dinitromesitylene anion and 8.87 gauss for the radical from the trinitromesitylene that has two nitrogen splittings, while the splitting of 1.48 gauss for the *p*-dinitrobenzene anion in DMF<sup>26,27</sup> is to be compared with the 7.01-gauss splitting from the dinitrodurene anion in DMF. The nitrogen splitting from the mononitrodurene anion, 19.13 gauss, is also larger than the 15.93 splitting from the mononitromesitylene anion. These results are consistent with the work of Geske and Ragle,<sup>25</sup> who demonstrated that the nitrogen splitting in methyl-substituted nitrobenzene anions increases with the degree of steric hindrance in the neighborhood of the nitro group. A theoretical analysis<sup>27</sup> of the nitrogen hyperfine splittings in nitroaromatic anions shows that this increase in splitting with steric hindrance is consistent with Geske and Ragle's hypothesis that a nitro group rotated out of the plane of the aromatic ring traps a major portion of the spin density. To apply these results to the nitromesitylenes, consider the order of the nitrogen splittings in the radicals which have spectra with the same number of nitrogen splittings: The nitrogen splitting of the radical generated at the first polaro-

graphic wave (and therefore containing the normal number of nitrogen splittings) is smaller than the splittings produced from other starting materials at higher polarographic waves and thus the latter have more sterically-hindered nitro groups. Similar conclusions apply to the nitrodurene series.

Ward's spectra<sup>3,4</sup> of the nitromesitylene radicals generated by alkali metal reduction are all different from ours (see Table II). He finds only one nitrogen splitting and this splitting increases in the order: nitromesitylene > dinitromesitylene > trinitromesitylene. This is the reverse of the order we obtained for the spectra that show only one nitrogen splitting. On the basis of reduction potential alone, the alkali metal reductions correspond to higher potentials than the highest used in our investigation. This conclusion follows from the observation that naphthalene can be reduced by an alkali metal, and its reduction potential<sup>26</sup> in DMF vs. the Ag-AgClO<sub>4</sub> electrode is -3.2 v., a value larger (in absolute value) than any employed in the reductions of the nitromesitylenes (Table I). Other disparities in e.s.r. spectra are observed when radicals produced by alkali metal and electrolytic reduction are compared.<sup>3-6,27</sup> In the nitrobenzene and isomeric dinitrobenzene anions, most of the differences between the radicals generated electrolytically at the first polarographic wave and those obtained with alkali metals can be interpreted as arising from ion-pair formation. The electrolytic reduction of these unsubstituted nitrobenzenes at potentials above the first polarographic wave but below the effective potential of the alkali metals, however, yields complex radical mixtures, the spectra of which have not been interpretable.<sup>23</sup> Both the temperature and the specific alkali metal also appear to influence the course of the alkali metal reductions.

Although the present results on the hindered nitrobenzenes show that the reduction potential affects the radical produced, it is also evident that the potential alone does not determine the course of the reduction reaction. The details of this reaction are not understood, but it is influenced by the nature of the reducing agent (electrolytic or alkali metal), by the steric hindrance, and perhaps by the temperature and the solvent.

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