perimental error of the diffusion controlled rate in benzene.[40,44]

## Conclusion

No one mechanism appears to be capable of explaining the quenching of biacetyl luminescence by the quenchers studied in this work, which appears to be one of the few detailed studies of direct bimolecular quenching of the singlet and triplet states of the same molecule.[45] It appears that quenching may involve either electron or hydrogen abstraction by $B_1$ or $B_3$ and that either of these processes may be reversible. The results of our study are summarized in Table X. Some of the significant points revealed by this work are (a) the n,π* triplet of biacetyl shows considerably less reactivity toward hydrogen abstraction than the n,π* triplet states of monoketones; (b) reversible electron and reversible hydrogen abstraction can operate as mechanisms for quenching $B_1$ and $B_3$; (c) a generally greater enhancement of $k_q^f$ over $k_q^p$ is found for quenching involving polar electron or charge-transfer transition states; (d) $k_q^f$ values approach the magnitude expected for diffusion-controlled quenching for phenols, aromatic amines and tertiary amines; and (e) the rate of quenching by hydrogen abstraction can be suppressed (phenols) or enhanced (alcohols) by increasing solvent polarity. Finally, it should be stated that although it was not possible to devise a single mechanism consistent with all of our data, the mechanism of the primary photochemical act which quenches the n,π* states of biacetyl may be similar for all of the quenchers studied in Tables I–III, V; *i.e.*, the transition state for quenching may at one extreme be considered as an electron abstraction and the other extreme as a hydrogen atom abstract. Transition states in which the movement of the electron and a proton (to various degrees) toward the n,π* states would then be conceptually intermediate to these two extremes.

**Table X.** Summary of $k_q^p$, $k_q^f$ and Probable Quenching Mechanisms

| Quencher | $k_q^p$ | $k_q^f$ | Probable quenching mechanism |
|---|---|---|---|
| Alcohols | $10^3$–$10^7$ | $<10^6$ | Irreversible H abstraction |
| Phenols | $10^8$–$10^9$ | $10^9$–$10^{10}$ | Reversible H abstraction |
| Aromatic amines | $10^7$–$10^9$ | $10^9$–$10^{10}$ | Reversible e abstraction |
| Trialkyl-amines | $10^7$–$10^8$ | $10^9$–$10^{10}$ | Irreversible H or e abstraction |
| Dialkyl-amines | $10^7$–$10^8$ | $10^9$ | Irreversible H or e abstraction |
| Monoalkyl-amines | $10^7$–$10^8$ | $10^7$ | Irreversible H or e abstraction |

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(45) Comparisons of intramolecular photoreactions are known[12–14] but only recently has a comparison between the reactivity of an excited singlet and triplet of the same molecule toward a bimolecular reaction been studied; ref 11, ref 42, and L. A. Singer, G. A. Davis, and V. P Muralidharan, *J. Am. Chem. Soc.*, **91**, 897 (1969).

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# The Electrochemical Reduction of Nitrobenzyl Halides in Acetonitrile

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*Contribution from the Department of Chemistry, Kansas State University, Manhattan, Kansas 66502.* *Received May 28, 1969*

**Abstract:** The electrochemical reduction of nitrobenzyl chlorides and bromides has been studied in acetonitrile solution. Electrochemical and spectroscopic methods show that the reduction of a nitrobenzyl halide is initially a one-electron process which gives the corresponding anion radical. In the case of an anion radical of either *o*- or *p*-nitrobenzyl halide, halide ion is rapidly lost to give the neutral nitrobenzyl radical. Although the principal pathway for the reaction of the nitrobenzyl radical is dimerization, a small amount of the product of hydrogen atom abstraction is also observed. The subsequent reduction of the corresponding dinitrobibenzyl and nitrotoluene to the dianion and the anion radical, respectively, completes the over-all two-electron process. Decomposition of an anion radical of either *m*-nitrobenzyl chloride or *m*-nitrobenzyl bromide occurs more slowly than in the case of the *ortho* and *para* isomers. Although the short-term chronoamperometric and cyclic voltammetric results are consistent with a reaction pathway involving hydrogen atom abstraction and *m*-nitrotoluene formation, controlled-potential coulometry indicates that less than 40% of the theoretical amount of *m*-nitrotoluene is actually present. No other products, including a dimer, could be found electrochemically or by gas chromatography.

Numerous reports have appeared recently concerning the chemical,[1–5] photochemical,[6] and electrochemical[7–12] reduction of halogenated nitroaromatics to anion radicals in nonaqueous solvent systems. While several of the anion radicals are sufficiently stable so as to permit the recording of their electron spin resonance

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(1) N. Kornblum, R. E. Michel, and R. C. Kerber, *J. Amer. Chem. Soc.*, **88**, 5660 (1966).

(2) N. Kornblum, R. E. Michel, and R. C. Kerber, *ibid.*, **88**, 5662 (1966).

(3) N. Kornblum, T. M. Davies, G. W. Earl, N. L. Holy, J. M. Manthey, M. T. Musser, and R. T. Swiger, *ibid.*, **90**, 6219 (1968).

(4) N. Kornblum, T. M. Davies, G. W. Earl, N. L. Holy, R. L. Kerber, M. T. Musser, and D. H. Snow, *ibid.*, **89**, 725 (1967).

(5) G. A. Russell and W. C. Danen, *ibid.*, **88**, 5663 (1966).

(6) G. A. Russell and W. C. Danen, *ibid.*, **90**, 347 (1968).

(7) G. Klopmann, *Helv. Chim. Acta*, **44**, 1908 (1961).

(8) A. Streitwieser, Jr., and C. Perrin, *J. Amer. Chem. Soc.*, **86**, 4938 (1964).

(9) J. Grimshaw and J. S. Ramsey, *J. Chem. Soc.*, *B*, 60 (1968).

(10) T. Kitagawa, T. P. Layloff, and R. N. Adams, *Anal. Chem.*, **35**, 1086 (1963).

(11) T. Fujinaga, Y. Deguchi, and K. Umemoto, *Bull. Chem. Soc. Jap.*, 37, 822 (1964).

(12) J. G. Lawless and M. D. Hawley, *J. Electroanal. Chem.*, **21**, 365 (1969).

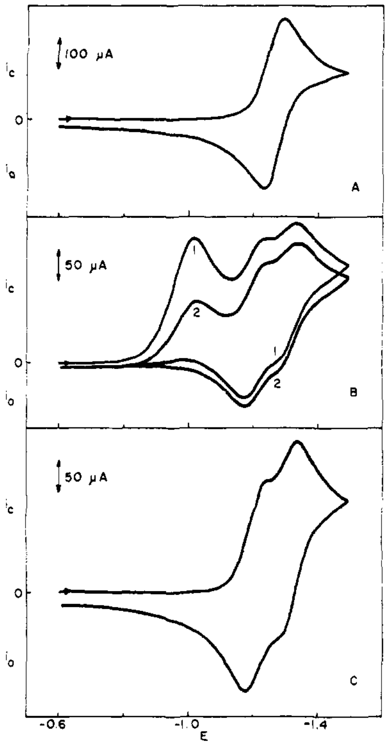

Figure 1. Cyclic voltammograms in 0.1 *M* TEAP–acetonitrile at a scan rate of 80.6 mV/sec; (A) 3.58 × $10^{-3}$ *M o*-nitrotoluene; (B) 2.58 × $10^{-3}$ *M o*-nitrobenzyl chloride: (C) 2.44 × $10^{-3}$ *M* 2,2′-dinitrobibenzyl.

spectra,$^{10,11}$ another group of halogenated nitrobenzenes$^{10-12}$ and nitrobenzyl halides$^{1-7,9}$ lose halide ion to give the corresponding neutral radicals. Dimerization,$^{7,9}$ reaction with anions to form anion radicals,$^{1-6}$ and hydrogen atom abstraction$^{12}$ have been among those reaction pathways reported for these radicals.

The electrochemical reduction of aromatic halides has been shown to involve both radical$^{7,9}$ and carbanion intermediates.$^{13}$ Although carbanion formation has been suggested in the electrochemical reduction of halogenated nitrobenzenes,$^{10,11}$ recent evidence has shown that the nitrobenzene formation is the result of hydrogen atom abstraction by nitrophenyl radical.$^{12,14}$ No dimerization of nitrophenyl radicals has yet been reported from electrochemical studies, although dimerization has been observed electrochemically with other phenyl radicals.$^{15}$ The coulometric reduction of *p*-nitrobenzyl bromide has been shown to give a dimer,$^{7-9}$ but an explanation of the polarographic results for this and other nitrobenzyl halides has not yet been offered.

We report herein the electrochemical reduction of the *o*-, *p*-, and *m*-nitrobenzyl bromides and chlorides in acetonitrile. The electrochemical reduction of these compounds will be shown to be initially a one-electron reduction which gives the corresponding anion radical as the electrode product. Dimerization or hydrogen abstraction is shown to follow the loss of halide ion from the anion radical. Distribution of products will be determined from an analysis of the exhaustively electrolyzed solutions, spectral studies at optically transparent electrodes, and an analysis of cyclic voltammetric and chronoamperometric data. Rate constants for the loss of halide ion from the anion radical will be estimated.

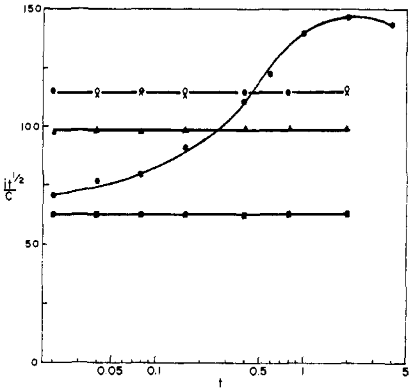

Figure 2. $it^{1/2}/C$ *vs. t* in 0.1 *M* TEAP–acetonitrile at an applied potential of −1.5 V: (●) *m*-nitrobenzyl chloride; (○) *o*-nitrobenzyl chloride; (×) *p*-nitrobenzyl chloride; (▲) 2,2′-dinitrobibenzyl; (■) *m*-nitrotoluene.

## Results and Discussion

***o*-Nitrobenzyl Chloride.** The cyclic voltammetric behavior of *o*-nitrobenzyl chloride in acetonitrile with tetraethylammonium perchlorate as the supporting electrolyte is shown in Figure 1B. Three reduction waves are seen near −1.00, −1.26, and −1.36 V on the first cathodic sweep. After reversal of the potential scan at −1.49 V, only two oxidative waves corresponding to the reoxidation of the product from the two more cathodic processes are seen on the anodic sweep. Subsequent cathodic sweeps show that the magnitude of the first cathodic peak decreases markedly, while the second and third cathodic waves grow in intensity relative to the first wave.

In order to estimate the number of electrons involved in the several cathodic processes, chronoamperometric $it^{1/2}/C$ values were compared under diffusion-controlled conditions for *o*-nitrobenzyl chloride, 2,2′-dinitrobibenzyl, and *m*-nitrotoluene. The reduction of *m*-nitrotoluene at −1.5 V, which is known to be a diffusion-controlled, reversible one-electron process,$^{16}$ gave a value of 62.5 A sec$^{1/2}$ mole$^{-1}$ cm$^3$ from $t$ = 20 msec to $t$ = 2 sec (Figure 2). With the same applied potential, a constant value of 98 A sec$^{1/2}$ mole$^{-1}$ cm$^3$ was obtained for 2,2′-dinitrobibenzyl. Since the diffusion coefficient of 2,2′-dinitrobibenzyl should be somewhat less than that for *m*-nitrotoluene, this result indicates that 2,2′-dinitrobibenzyl is reduced at the potential of −1.5 V in an over-all two-electron process. The second and third cathodic peaks in the cyclic voltammogram *o*-nitrobenzyl chloride must then arise from successive one-electron reduction of 2,2′-dinitrobibenzyl (eq 1). The value of 115 A sec$^{1/2}$ mole$^{-1}$ cm$^3$ for the reduction of *o*-nitrobenzyl chloride is consistent with an over-all two-electron reduction which gives the dianion of 2,2′-dinitrobenzyl as the final electrode product.

The data presented above show that *o*-nitrobenzyl chloride is reduced initially to its anion radical in a one-electron step

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(13) S. Wawzonek, R. C. Duty, and J. H. Wagenkneckt, *J. Electrochem. Soc.*, **111**, 74 (1964).

(14) E. T. Seo and R. F. Nelson, *ibid.*, in press.

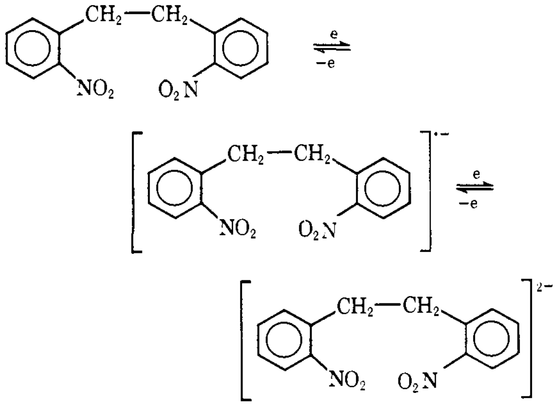
(15) P. H. Rieger, I. Bernal, W. H. Reinmuth, and G. K. Fraenkel, *J. Amer. Chem. Soc.*, **85**, 683 (1963).

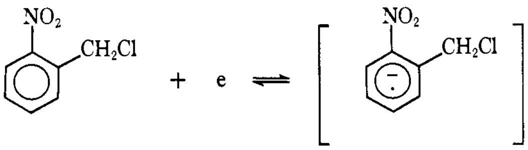
(16) D. H. Geske, J. L. Ragle, M. A. Bambanek, and A. L. Balch, *ibid.*, **86**, 987 (1964).

**Table I.** Controlled-Potential Coulometry Results[a]

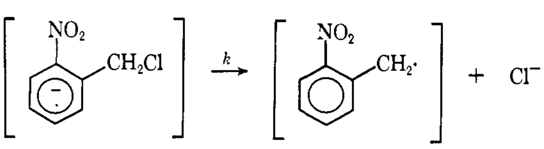
| Compound | Concentration, m$M$ | $-E_{\text{applied}}$ | $n_{\text{appl}}$, $F$/mole | Products, % yield[b] Dimer | Nitrotoluene |
|---|---|---|---|---|---|
| $o$-Nitrobenzyl chloride | 2.01 | 1.04 | 1.05 | 92.3 | 14.9 |
| $o$-Nitrobenzyl bromide | 2.10 | 1.02 | 0.95 | 90.3 | 13.1 |
| $p$-Nitrobenzyl chloride | 1.89 | 1.02 | 0.97 | 96.3 | 4.5 |
| $p$-Nitrobenzyl bromide | 2.17 | 1.02 | 0.91 | 96.5 | 3.7 |
| $m$-Nitrobenzyl chloride | 1.92 | 1.10 | 1.01[c] | | 29.0 |
| | 2.26 | 1.10 | 0.55[d] | | 39.3 |
| $m$-Nitrobenzyl bromide | 0.74 | 1.25 | 0.58[e] | | 10.6 |

[a] The acetonitrile solutions contained 0.10 $M$ tetraethylammonium perchlorate. The products were analyzed independently of one another by flame-ionization gas chromatography. Unless other otherwise specified, less than 1% of the starting material remained unelectrolyzed. With the exceptions of the $m$-nitrobenzyl halides, electrolysis times were less than 15 min. [b] Yields are calculated upon the percentage of the nitrobenzyl electrolyzed. [c] Since $m$-nitrotoluene is reduced concurrently with the starting material, the electrolysis was stopped at this point. Approximately 8.8% of the starting material remained to be electrolyzed. No evidence for dimer formation could be found. [d] Approximately 43% of the starting material remained to be electrolyzed. [e] Electrode fouling accompanied the reduction of $m$-nitrobenzyl bromide. The electrolysis was stopped when the faradaic current reached background levels; 36.0% of the starting material remained to be electrolyzed.


(1)

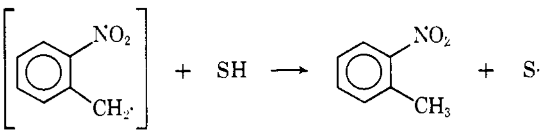

(2)

The anion radical then loses chloride ion to yield $o$-nitrobenzyl radical


(3)

The fact that the loss of chloride ion from the anion radical is rapid is demonstrated by the absence of an anodic wave corresponding to the reoxidation of the anion radical. The $o$-nitrobenzyl radicals then dimerize to form 2,2′-dinitrobibenzyl which is rapidly reduced at this potential to its dianion, completing the over-all two-electron process. The dimerization step must also be rapid as evidenced by the fact that $it^{1/2}/C$ corresponds to a two-electron process for all values of $t$ in the time range studied (Figure 2).

Although cyclic voltammetry leaves little doubt that 2,2′-dinitrobibenzyl is the principle product of decomposition of $o$-nitrobenzyl chloride anion radical, exhaustive electrolysis of a solution of $o$-nitrobenzyl chloride at −1.04 V gives a second product, $o$-nitrotoluene, in small yield (Table I). The latter is the anticipated product if $o$-nitrobenzyl radical abstracts a hydrogen atom from the solvent. Since $o$-nitrotoluene is electroactive at the potential used in the chronoamperometric work, it would be immediately reduced in a one-electron step to its anion radical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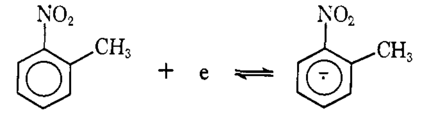
(5)

The over-all process, reduction of $o$-nitrobenzyl chloride to $o$-nitrotoluene anion radical and chloride ion, is also two electrons and compatible with both the cyclic voltammetric (Figures 1A and 1B) and chronoamperometric results.

**$p$-Nitrobenzyl Chloride.** The cyclic voltammogram of $p$-nitrobenzyl chloride (Figure 3A) is seen to differ significantly from that of $o$-nitrobenzyl chloride (Figure 1B). On the first cathodic sweep, two cathodic processes are observed near −0.97 and −1.22 V. Upon reversal of the potential scan at −1.39 V, a single oxidation wave corresponding to the reoxidation of the product of the second cathodic process is seen at −1.15 V. The first cathodic process is again identified as the one-electron reduction (Table I) of $p$-nitrobenzyl chloride to its anion radical. The anion radical rapidly loses chloride ion, as evidenced by the absence of anodic wave for the reoxidation of the anion radical to $p$-nitrobenzyl chloride, to give an electroactive species which is reduced at the more negative of the two cathodic processes. Although the electrochemical behavior of this new system does match that of 4,4′-dinitrobibenzyl[17] (Figure 3B), as nearly as good fit can also be obtained with $p$-nitrotoluene (Figure 3C). Exhaustive electrolysis of $p$-nitrobenzyl chloride at the potential of the first wave (−1.02 V) gave 4,4′-dinitrobibenzyl and $p$-nitrotoluene in 96.3 and 4.5% yield, respectively. The $n$ value of 0.97 confirms the interpretation that the first reduction is a one-electron process.

Although the separation of anodic and cathodic peak potentials ($E_{\text{p,a}} - E_{\text{p,c}} \cong 70$ mV) for 4,4′-dinitrobibenzyl indicates a one-electron reduction process, thin layer chronoamperometry with current integration[18] shows unequivocally that $n = 2$ (experimental $n$ =

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[17] J. E. Harriman and A. H. Maki, *J. Chem. Phys.*, **39**, 778 (1963).

[18] A. T. Hubbard, R. A. Osteryoung, and F. C. Anson, *Anal. Chem.*, **38**, 692 (1966).

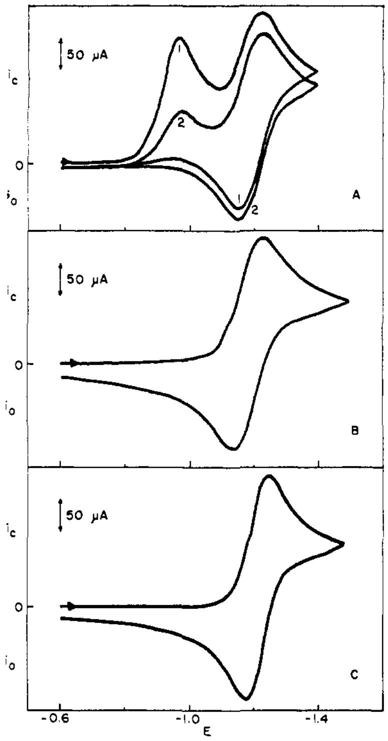


Figure 3. Cyclic voltammograms in 0.1 *M* TEAP–acetonitrile at a scan rate of 80.6 mV/sec: (A) 2.31 × $10^{-3}$ *M* *p*-nitrobenzyl chloride; (B) 1.78 × $10^{-3}$ *M* 4,4′-dinitrobibenzyl; (C) 2.68 × $10^{-3}$ *M* *p*-nitrotoluene.

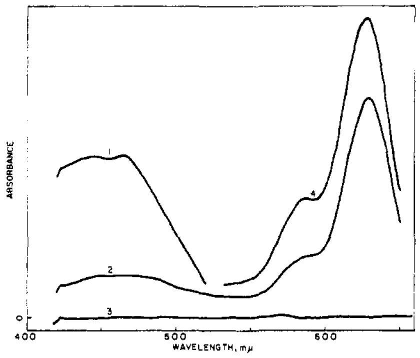


Figure 4. Visible spectra of species produced during reduction at an optically transparent gold minigrid electrode. All solutions are 0.1 *M* TEAP–acetonitrile: (1) *p*-nitrotoluene at −1.6 V; (2) *p*-nitrobenzyl chloride at −1.6 V; (3) *p*-nitrobenzyl chloride with an open circuit; (4) 4,4′-dinitrobibenzyl at −1.6 V.

2.07). Chronoamperometric values of $it^{1/2}/C$ (Figure 2) confirm the interpretation that 4,4′-dinitrobibenzyl is reduced in a two-electron step to its dianion at −1.5 V.

Supporting evidence for the two-electron reduction of *p*-nitrobenzyl chloride to the dianion of 4,4′-dinitrobibenzyl and *p*-nitrotoluene anion radical is obtained from a spectral examination of the reduction products at an optically transparent, gold minigrid electrode.[19] Figure 4 shows the visible absorption spectra of the reduction products of *p*-nitrotoluene, 4,4′-dinitrobibenzyl, and *p*-nitrobenzyl chloride. Although no quantitative results should be attached to these spectra, it can be seen qualitatively that the reduction product of 4,4′-dinitrobibenzyl predominates. In addition, a small amount of *p*-nitrotoluene anion radical can also be seen at 470 mμ. Recording of the absorption spectrum of the reduction product of 4,4′-dinitrobibenzyl below 530 mμ cannot be given because of absorption of the unreduced material in this region.

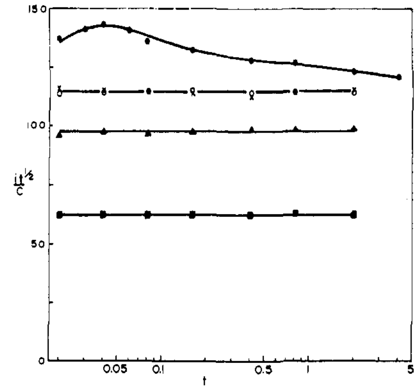


Figure 5. $it^{1/2}/C$ *vs.* *t* in 0.1 *M* TEAP–acetonitrile at an applied potential of −1.5 V: (●) *m*-nitrobenzyl bromide; (○) *o*-nitrobenzyl bromide; (×) *p*-nitrobenzyl bromide; (▲) 2,2′-dinitrobibenzyl; (■) *m*-nitrotoluene.

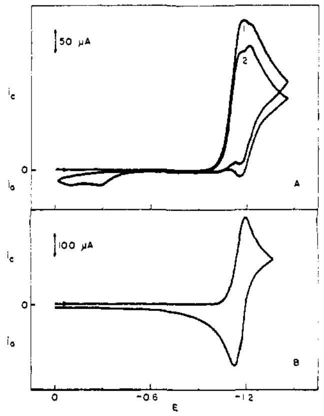


Figure 6. Cyclic voltammograms in 0.1 *M* TEAP–acetonitrile at a scan rate of 80.6 mV/sec: (A) 2.34 × $10^{-3}$ *M* *m*-nitrobenzyl chloride; (B) 4.60 × $10^{-3}$ *M* *m*-nitrotoluene.

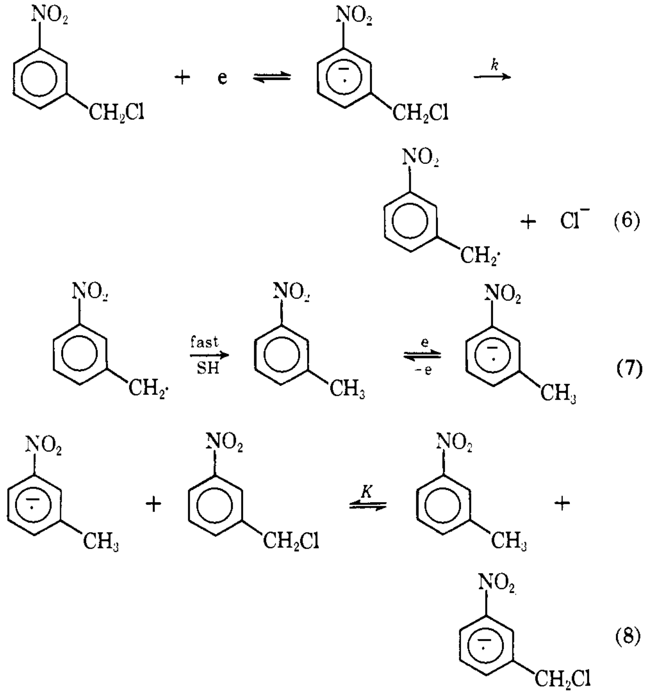
***o*- and *p*-Nitrobenzyl Bromides.** The electrochemical behavior of the *o*- and *p*-nitrobenzyl bromides differ little from the corresponding nitrobenzyl chlorides. Following the initial one-electron reduction of a nitrobenzyl bromide, the anion radical rapidly loses bromide ion to give the nitrobenzyl radical. 2,2′-Dinitrobibenzyl and 4,4′-dinitrobibenzyl, the dimerization products of the *o*- and *p*-nitrobenzyl radicals, respectively, are subsequently reduced in a two-electron step to the corresponding dianions at slightly more negative potentials (Figure 5). As in the controlled-potential coulometry of the chlorides, small amounts of nitrotoluene are also formed (Table I).

***m*-Nitrobenzyl Chloride and Bromide.** On a cathodic sweep of the cyclic voltammogram of *m*-nitrobenzyl chloride (Figure 6), the reduction of the parent species at −1.12 V is followed closely by a peak for the reduction of one or more products arising from the decomposition of the *m*-nitrobenzyl anion radical. Only a small peak corresponding to the reoxidation of the second reduction product is apparent on the reverse, anodic sweep. The absence of appreciable anodic current, even after

[19] R. W. Murray, W. R. Heineman, and G. W. O'Dom, *Anal. Chem.*, **39**, 1666 (1967).

several cycles, is indicative of a fast solution redox reaction involving *m*-nitrobenzyl chloride and a reduction product from the second cathodic process.[12]

Chronoamperometric and cyclic voltammetric results indicate that the loss of chloride ion from *m*-nitrobenzyl chloride is considerably less rapid than in its *ortho* and *para* isomers. Chronoamperometric $it^{1/2}/C$ values (Figure 2) are seen to vary smoothly from a value corresponding to $n = 1$ at short times, pass through a maximum of $n = 2.2$ at 2 sec, and then decrease slowly. This behavior is predicted by the digital simulation of the processes described by eq 6–8 when $K \geq 10$ and the diffusion coefficients are equal.[20–22] The best fit of the chronoamperometric data and the theoretical working curve is obtained when the value of the rate constant for



the *m*-nitrobenzyl chloride anion radical is 2.5 $sec^{-1}$.

Because the peak potentials for the reduction of *m*-nitrobenzyl chloride and *m*-nitrotoluene are separated by less than 80 mV, it is impossible to reduce exhaustively *m*-nitrobenzyl chloride without concurrent reduction of *m*-nitrotoluene. Reduction of the latter should not change the current efficiency, however, as long as the anion radical is stable and the solution redox reaction (eq 8) occurs. Controlled-potential electrolysis of a solution of *m*-nitrobenzyl chloride to the point $n = 1.00$ removed 91% of the starting material but gave only *ca.* 29% of the theoretical yield of *m*-nitrotoluene. The deeply colored solution gave no other components in appreciable amounts which could be detected by flame-ionization gas chromatography. Spectral examination of the products formed at the electrode surface of an optically transparent electrode showed not only absorption at the wavelength for *m*-nitrotoluene anion radical, but absorption throughout the entire visible region.

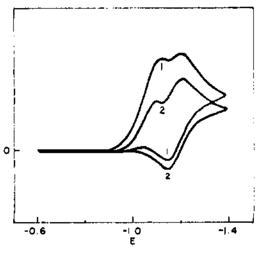


Figure 7. Cyclic voltammogram of *m*-nitrobenzyl bromide in 0.1 *M* TEAP–acetonitrile at a scan rate of 80.6 mV/sec.

Inspection of the cyclic voltammogram of *m*-nitrobenzyl chloride (Figure 6) shows that small amounts of additional electroactive species appear near −0.1 V as a result of the first cathodic–anodic sweep. Since *m*-nitrotoluene exhibits only a reversible one-electron reduction near −1.2 V, the additional processes must result from other, undetermined pathways of decomposition. A cyclic voltammetric examination of the *m*-nitrobenzyl chloride solution reduced to the point where $n = 1.0$ revealed only the presence of *m*-nitrotoluene in the yield indicated above.

A comparison of $it^{1/2}/C$ data for *m*-nitrobenzyl bromide (Figure 5) and chloride (Figure 2) shows that the anion radical of *m*-nitrobenzyl bromide decomposes more rapidly. The chronoamperometric and cyclic voltammetric behavior (Figure 7) of *m*-nitrobenzyl bromide are consistent with the following processes: one-electron reduction of *m*-nitrobenzyl bromide to its anion radical, loss of bromide ion from the anion radical, formation of *m*-nitrotoluene by hydrogen atom abstraction of the *m*-nitrobenzyl radical, and reduction of *m*-nitrotoluene to its anion radical. The absence of appreciable oxidation current on the anodic sweeps is again indicative of a solution redox reaction involving the product of the second cathodic process, *m*-nitrotoluene anion radical, and the starting material, *m*-nitrobenzyl bromide.

While *m*-nitrotoluene is the only reduction product identifiable by gas chromatography in the controlled-potential coulometry of *m*-nitrobenzyl bromide, the yield (Table I) is but 11% of the theoretical. Severe electrode fouling accompanied the reduction, causing the cessation of current before 1 F/mole could be added. Analysis of this partially electrolyzed solution by cyclic voltammetry showed only the presence of a small amount of *m*-nitrotoluene and the remaining, unelectrolyzed starting material. The absence of other products discernible by gas chromatography and cyclic voltammetry, general absorption of the electrolyzed solution throughout the visible region, and severe fouling of the electrode surface during electrolysis suggest the formation of polymeric species.

Although fouling was more serious for *m*-nitrobenzyl bromide, a moderate amount of fouling was also present during the controlled-potential reduction of the chloride. The increase in electrode fouling upon substitution of the chloride by bromide is paralleled by an increase in the rate of halide loss from the anion radical and, presumably, a higher concentration of *m*-nitrobenzyl radicals. If dimerization were competitive with hydrogen atom abstraction, 3,3′-dinitrobibenzyl would

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(20) M. D. Hawley and S. W. Feldberg, *J. Phys. Chem.*, **70**, 3459 (1966).

(21) R. N. Adams, M. D. Hawley, and S. W. Feldberg, *ibid.*, **71**, 851 (1967).

(22) Although fouling of the electrode surface is noted in the long-term, exhaustive reduction of *m*-nitrobenzyl bromide and chloride, chronoamperometric *i–t* data show no evidence of electrode fouling. Replicate runs on the same electrode surface gave superimposable curves for *t* as large as 20 sec.

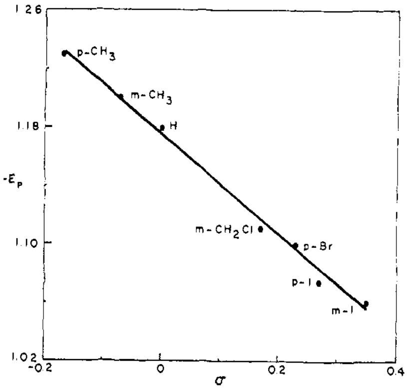

Figure 8. Relation of $\sigma$ substituent constants to reduction potentials of *m*- and *p*-nitrobenzenes in acetonitrile.

Table II. Cyclic Voltammetry Data for the Nitrobenzyl Halides and Their Reduction Products

| Compd | $E_p$ | $E_{1/2}$[a] | $k$, sec$^{-1}$ |
|---|---|---|---|
| *m*-Nitrobenzyl chloride | −1.13 | −1.09 | 2.5[b] |
| *m*-Nitrobenzyl bromide | −1.08 | −1.09 | 35[b] |
| *p*-Nitrobenzyl chloride | −0.97 | −1.09 | $2 \times 10^4$ [c] |
| *p*-Nitrobenzyl bromide | −0.86 | −1.09 | $6 \times 10^8$ [c] |
| *o*-Nitrobenzyl chloride | −1.01 | −1.15 | $6 \times 10^5$ [c] |
| *o*-Nitrobenzyl bromide | −0.91 | −1.15 | $2 \times 10^9$ [c] |
| *m*-Nitrotoluene | −1.20 | −1.17 | |
| *p*-Nitrotoluene | −1.23 | −1.20 | |
| *o*-Nitrotoluene | −1.29 | −1.26 | |
| 4,4′-Dinitrobibenzyl | −1.23 | −1.20 | |
| 2,2′-Dinitrobibenzyl | 1.23 | −1.20 | |
| | −1.33[d] | −1.30[d] | |

[a] Steric interactions of $CH_3$, $CH_2Br$, and $CH_2Cl$ substituents *ortho* to a nitro group are assumed to be equal and to cause a 60-mV cathodic shift in the half-wave potentials ($E_{p,o\text{-nitrotoluene}} - E_{p,p\text{-nitrotoluene}} = -60$ mV). The reaction constant, $\rho$, is 0.33 V and was determined from the data given in Figure 8. The following substituent constants were used: $\sigma_{o,CH_2Cl} = \sigma_{p,CH_2Cl} = \sigma_{p,CH_2Br} = \sigma_{o,CH_2Br} = 0.18$; $\sigma_{m,CH_2Cl} = \sigma_{m,CH_2Br} = \sigma_{p,CH_2Cl} = 0.17$. The values of $\sigma_{p,CH_2Cl}$ and $\sigma_{p,CH_2Cl}$ were obtained from P. Zuman, "Substituent Effects in Organic Chemistry," Plenum Press, New York, N. Y., 1967, Chapter 3. [b] Calculated from chronoamperometric data, Figures 2 and 5. [c] Calculated from the equation: $E_p = E_{1/2} = (-RT/nF[0.78 - \ln (k/a)^{1/2}]$, where $a = 3.25$ sec$^{-1}$. See ref 23 for details. [d] Corresponds to the reduction of 2,2′-dinitrobibenzyl anion radical to the dianion.

be the expected product. The absence of such a species may be due to its reduction at these potentials and subsequent decomposition to give higher molecular weight species.

Although the decompositions of the anion radicals of the *o*- and *p*-nitrobenzyl halides occur too rapidly to be studied here by chronoamperometric techniques, estimates of the rate constants for the loss of halide ion can be obtained from cyclic voltammetric reduction potentials. The effect of a followup chemical reaction on the location of the peak reduction potential is readily seen from the Nernst equation—removal of the reduction product causes an anodic shift in the reduction potential. Therefore, if the half-wave potential is known, the difference between the observed peak potentials ($E_p$) and half-wave potentials ($E_{1/2}$) can be related to the rate constant of the chemical reaction.[23] Substituents adjacent to the nitro group cause an additional problem. Steric interaction of *ortho* substituents in substituted nitrobenzenes is known to cause twisting of the nitro group from the plane of the benzene ring.[16] In the absence of a rapid followup chemical reaction, this renders the reduction more difficult to occur, causing a cathodic shift in the peak reduction potential.[16,24] It has been assumed in these calculations that a $CH_2X$ substituent adjacent to a nitro group will be oriented in such a way as to minimize its size; hence, we have assumed that the steric interactions of the $CH_3$, $CH_2Cl$, and $CH_2Br$ substituents do not differ significantly. The steric interaction was determined experimentally by measuring the difference in the peak reduction potentials for *o*- and *p*-nitrotoluene (Table II). The value found here, −60 mV, is in excellent agreement with previous reports for the steric interaction in *o*-nitrotoluene in acetonitrile[16] and dimethylformamide.[24]

Since the supporting electrolyte is known to have a considerable effect upon the reaction constant, $\rho$,[25] the value of this constant was determined under our experimental conditions (Figure 8). From the value of this reaction constant ($\rho = 0.33$ V), appropriate substituent constants, and the half-wave potential of the unreactive nitrobenzene–nitrobenzene anion radical couple, the half-wave potentials for the other nitrobenzyl halides were readily calculated.

The stabilities of the anion radicals of the nitrobenzyl bromides and chlorides differ considerably, as evidenced by nearly nine orders of magnitude variation in rate constant. In comparison to the other anion radicals, the *m*-nitrobenzyl halide anion radicals are unusually stable. This exceptional stability has been noted[3,6] and discussed previously.[3] In the present case, the varying stability of the anion radicals is also reflected in the distribution of reduction products. When the anion radical decomposes rapidly, as in the *o*- and *p*-nitrobenzyl halide anion radicals, dimerization is favored by the high concentration of nitrobenzyl radicals. Steric considerations are of some importance, as shown by the slightly larger amounts of hydrogen abstraction product (Table I) with the *o*-nitrobenzyl halides. In contrast, the slow decomposition of *m*-nitrobenzyl anion radicals should give a higher concentration of *m*-nitrotoluene. A similar reaction pathway, abstraction of hydrogen atom, was observed in the electrochemical reduction of halogenated nitrobenzenes.[12]

## Experimental Section

**Instrumentation.** The cyclic voltammetric, chronoamperometric, and thin layer coulometric studies were performed on a transistorized, three-electrode potentiostat-galvanostat described previously.[12] Compensation of ohmic potential loss (uncompensated *iR*) was effected by the addition of a positive feedback loop from the output of the current follower to the input of the control amplifier.[26] The optimum amount of positive feedback was determined from a cyclic voltammetric examination of the electrochemical system. With the potential being scanned, the feedback current was increased slowly until loss of potential control resulted. Stability of the potentiostat was then restored by decreasing the feedback current slightly. The techniques suggested by Brown, Smith, and Booman[27] for stabilization of the potentiostat under 100% *iR* compensation were incorporated into this instrument.

A second potentiostat was employed for experiments requiring larger current and voltage capabilities. The control amplifier in this circuit[28] was a Harrison Model 6824A amplifier (±50 V, 1 A).

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The current and integrator circuits used Philbrick P85AU and P25AU operational amplifiers in standard configurations.

Readout in cyclic voltammetry experiments was to Moseley Model 7030A and 7035B X–Y recorders. For chronoamperometric studies of less than 1 sec duration, readout was to a Tektronix Model 564 oscilloscope equipped with Type 2A63 and 2B67 plug-ins and a Dumont Type 302 camera. The signal source was a Hewlett-Packard Model 3300–3302 function generator. Recording of current and measurement of coulombs in coulometric work were made with a Moseley Model 680 strip-chart recorder and a Fairchild Model 7050 digital voltmeter, respectively.

The gas chromatograph was a Hewlett-Packard Model 700 equipped with flame-ionization detection. The flame-ionization currents were measured with a Philbrick Model SP2A operational amplifier in a standard current-follower circuit and recorded on a Honeywell Model 19 strip-chart recorder. Optical spectra were recorded on Cary Model 11 recording spectrophotometer.

**Chemicals.** The nitrobenzyl halides, nitrotoluenes, and dinitrobibenzyls were commercially available samples. The purity of each was checked by gas chromatography, cyclic voltammetry, and melting point; impure samples were recrystallized repeatedly until at least 99% purity was obtained.

Tetraethylammonium perchlorate was prepared according to the method of Kolthoff and Coetzee;[29] tetraethylammonium bromide and chloride were Eastman White Label. (No effect was observed on the rate constants for the elimination of halide ion from the anion radicals of nitrobenzyl halides when the anion of the tetraethylammonium salt was changed from perchlorate to bromide.) All supporting electrolytes were stored in a vacuum desiccator prior to their use. Reagent-grade acetonitrile was dried over Linde Type 4A molecular sieves. All electrochemical experiments were performed in a glovebag under a nitrogen atmosphere at room temperature (22.5 ± 0.5°). Glove bags were purged by prepurified nitrogen gas. The nitrogen stream used to degas the solutions was passed first over hot copper wool and then through pure acetonitrile. The solutions were deaerated for at least 20 min prior to the electrochemical measurements.

**Cells and Electrodes.** The working electrode in the cyclic voltammetric and chronoamperometric experiments was a planar platinum button (Beckman No. 39273) with a geometric area of approximately 0.25 cm$^2$. The auxiliary electrode, a platinum foil, and the reference electrode, a saturated calomel electrode (SCE), were isolated from the working electrode compartment by means of porous Vycor glass (Corning No. 7930) and a bridge containing acetonitrile–0.1 *M* supporting electrolyte.

The working electrode for the spectral work was a piece of optically transparent gold minigrid having the following properties: 1000 lines/in. and $\%T = 45$ (Buckbee Mears Co.). The use of such an electrode in electrochemical studies has been described previously.[19] The gold electrode was held in place on one end of the optical cell by epoxy cement (Techkits E-63). Electrical connection to the gold electrode was made externally by means of an electrically conducting epoxy compound (Techkits CA-10). The platinum wire auxiliary and saturated calomel electrodes were separated from the working electrode compartment by glass frits and bridges of acetonitrile–0.1 *M* tetraethylammonium perchlorate. In order to obtain visible spectra of the reduction products of the nitrobenzyl halides, the working electrode potential was stepped sufficiently cathodic such that the concentration of any nitrobenzyl or dinitrobibenzyl species would be zero at the electrode surface. The electrochemical reduction of a 2 m*M* solution of nitrobenzyl halide for several seconds usually provided enough material for a good absorption spectrum. Wrinkling of the gold electrode with a consequent change in the effective path length of the cell across the surface of the electrode permitted only a qualitative study of the species produced electrochemically. Our attempt to use optically transparent thin layer electrodes[19] was unsuccessful because of the magnitude of the uncompensated *iR* and the concomitant variation of the concentration of the reduction products with distance along the electrode surface.

A large platinum gauze electrode was used as the working electrode in the large-scale coulometric work. The auxiliary (platinum gauze) and reference (SCE) electrodes were separated from the working electrode compartment by means of glass frits and bridges containing acetonitrile–0.1 *M* tetraethylammonium perchlorate. In a typical experiment, the potential of the working electrode was set sufficiently cathodic so as to reduce the nitrobenzyl halide but not so cathodic as to reduce either the corresponding nitrotoluene or dinitrobenzyl. The contents of the working electrode compartment were analyzed immediately after electrolysis by flame-ionization gas chromatography on SE-30 and UCW98 columns. Calibration curves for the nitrotoluenes and dinitrobibenzyls were constructed daily.

A thin layer electrode similar to the one described by McClure and Maricle[30] was constructed for the rapid determination of *n* values. The working electrode was a 3 mm length of 0.25 diameter platinum rod attached to a stainless steel spindle (L. S. Starrett Co.) by means of electrically conducting epoxy. The sides of the spindle and the platinum rod were covered with a thin layer of epoxy cement (Devcon WR-2) in order to render them electroinactive.

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