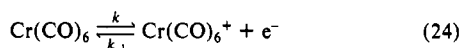


Figure 11. Variation of the anodic peak potential in cyclic voltammetry of $\text{Cr}(\text{CO})_6$ as a function of nucleophile concentrations. (●) $\text{RCO}_2^- =$ acetate and (○) trifluoroacetate as lithium salts. Recorded at a constant sweep rate of 20 mV sec^{-1} . $[\text{Cr}(\text{CO})_6] = 1.0 \times 10^{-3} \text{ M}$ and 0.1 M TEAP .

of $\text{Cr}(\text{CO})_6$ has been shown by cyclic voltammetry to be a reversible one-electron process in acetonitrile solutions²⁷ (see eq 24). However, in



the presence of added nucleophiles such as acetates and trifluoroacetate, the cyclic voltammogram becomes irreversible, owing to the facile anation of the resultant substitution-labile cation in eq 25.⁵⁸ The disappearance



of the reverse cathodic wave, even at low concentrations of lithium trifluoroacetate, is shown in Figure 10. At these low concentrations of nucleophile, the kinetically second-order reaction in eq 8 is sufficiently slow to render the electrochemical process as partially irreversible, as shown by the left side of Figure 11. Under these conditions, the anodic peak potential increases with the rate of the competing anation, in accord with standard electrochemical theory.²⁸ Importantly, above a critical concentration of nucleophile ($\sim 10^{-2} \text{ M}$), the anodic potential is independent of the nature and speed of the following chemical reaction. In other words, when the second-order disappearance of the cation $\text{Cr}(\text{CO})_6^+$ in eq 8 is faster than the reverse rate of electron transfer k_{-1} in eq 7, E_p becomes invariant. Under these conditions the electrochemical wave is considered to be totally irreversible, and the observed peak current i_p is independent of the complexity or the speed of the following chemical reactions.

Acknowledgments. We thank Dr. R. M. Wightman for many helpful discussions, Dr. C. L. Wong for his involvement in the early stages of this work, Dr. D. Peters for the loan of the rotated-disk electrode, and the National Science Foundation for financial support. J. K. Kochi also thanks Dr. R. A. Marcus for helpful discussions and advice.

(58) The facile replacement of carbon monoxide in the cation ion-radicals of metal carbonyls is generally applicable to nucleophiles.⁵ In this study we employed acetate and (at higher concentrations) trifluoroacetate since they yielded the most unambiguous results owing to their electroinactivity at the large positive potentials required to oxidize $\text{Cr}(\text{CO})_6$.

Intramolecular Electron Transfer in the Anion Radicals of Nitrobenzyl Halides¹

P. Neta* and D. Behar

Contribution from the Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana 46556. Received January 21, 1980

Abstract: One-electron reduction of nitrobenzyl halides produces the anion radicals which subsequently undergo intramolecular electron transfer and decompose into nitrobenzyl radicals and halide ions. The optical absorption spectra of the initial anion radicals ($\lambda_{\text{max}} \approx 300\text{--}310 \text{ nm}$) and the subsequently formed nitrobenzyl radicals ($\lambda_{\text{max}} = 350$ and 400 for the para and ortho, respectively) are quite intense ($\epsilon \approx 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ in most cases) and significantly different. This enables identification of the various species and measurement of the rates of intramolecular electron transfer or C-X bond scission. The rates are 4×10^3 , 1.7×10^5 , and $5.7 \times 10^5 \text{ s}^{-1}$ for *p*-nitrobenzyl chloride, bromide, and iodide, respectively. The ortho derivatives decomposed nearly twice as rapidly while the meta decomposed much more slowly. The anion radical of *p*-nitrobenzyl bromide has $\text{p}K_a = 2.8$, and the protonated form is found to undergo the intramolecular transfer ~ 60 times more slowly than the anion radical. The pattern of reactivity of the various anion radicals is rationalized in terms of spin density and charge distribution at the various positions on the ring and in terms of the electrophilicities of the halogens.

Introduction

Intramolecular electron transfer in biopolymers is an important process in many biological redox systems. The transport of an electron through large molecules has been experimentally studied in several systems, including peptides and redox proteins.² Detailed intramolecular electron-transfer mechanisms can be investigated in small model compounds.³⁻⁵ In several studies

utilizing complexes of Co(III) with aromatic or heterocyclic carboxylic acids an electron transfer from the ligand radical to the central metal ion has been observed.^{3,4} One-electron reduction of (nitrobenzoato)pentamminecobalt(III) complexes was found to produce initially the coordinated nitrobenzoate anion radicals. Subsequently, an intramolecular electron transfer took place from the reduced ligand to the Co(III). The rate constant of this transfer was found to depend strongly on the position of the nitro group relative to the coordinated carboxylate.

In the present work, intramolecular electron transfer within the anion radicals of nitrobenzyl halides is reported. Experiments⁶ have shown that one-electron reduction of nitrobenzyl halides produces initially the anion radicals, which then undergo an intramolecular electron transfer and decompose into halide ions and nitrobenzyl radicals. Such processes have been suggested previously as intermediate steps in several organic substitution reactions.⁷ In this work we report the direct observation of these

(1) The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-2088 from the Notre Dame Radiation Laboratory.

(2) See, e.g.: Faraggi, M.; Klapper, M. H.; Dorfman, L. M. *J. Phys. Chem.* **1978**, *82*, 508. Pecht, I.; Farver, O.; Goldberg, M. *Adv. Chem. Ser.* **1977**, *No. 162*, 1979. Simic, M. G.; Taub, I. A. *Faraday Discuss. Chem. Soc.* **1977**, *No. 63*, 270 and references therein.

(3) Hoffman, M. Z.; Simic, M. *J. Am. Chem. Soc.* **1972**, *94*, 1757. Simic, M. G.; Hoffman, M. Z.; Brezniak, N. V. *Ibid.* **1977**, *99*, 2166.

(4) Cohen, H.; Meyerstein, D. *J. Chem. Soc., Dalton Trans.* **1975**, 2477. Wiegardt, K.; Cohen, H.; Meyerstein, D. *Ber. Bunsenges. Phys. Chem.* **1978**, *82*, 388. Wiegardt, K.; Cohen, H.; Meyerstein, D. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 608.

(5) Prütz, W. A.; Land, E. *J. Int. J. Radiat. Biol. Relat. Stud. Phys., Chem. Med.* **1979**, *36*, 513 and references therein.

(6) Preliminary experiments were carried out in this laboratory by V. Madhavan.

processes and the measurement of the absolute rate constants for the decomposition of various nitrobenzyl halide anion radicals.

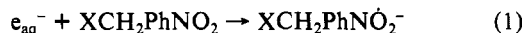
Experimental Section

o-Nitrotoluene was obtained from Eastman and was purified by distillation under reduced pressure. *p*-Nitrotoluene was also obtained from Eastman. *p*-Nitrobenzyl iodide and *m*-nitrobenzyl bromide were from K&K, *m*-nitrobenzyl iodide was from Adams Chemical Company, and the other nitro compounds were from Aldrich. Alcohols and inorganic compounds were Baker analyzed reagents. Water was purified by a Millipore Milli-Q system.

Solutions were prepared freshly before irradiation and were deoxygenated by bubbling with N_2 or N_2O . In the latter case the N_2O serves also as an electron scavenger ($N_2O + e_{aq}^- \rightarrow N_2 + OH^- + OH$). Optical absorption spectra of the solutions were recorded on a Cary 219 spectrophotometer. Irradiation was carried out by using an ARCO LP-7 linear accelerator supplying 5-ns pulses of 9-MeV electrons. Each pulse produces 2–4 μM of radicals. The transient absorption spectra and kinetics were measured by the computer-controlled pulse radiolysis apparatus described previously.^{8,9}

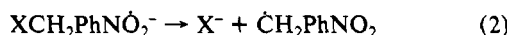
Results and Discussion

Aqueous solutions of nitrobenzyl halides containing *tert*-butyl alcohol were irradiated, and the transient absorption spectra were recorded at various times after the pulse. In these solutions, only the hydrated electrons (and the small yield of H atoms) react with the substrate (eq 1) while the OH radicals are scavenged by

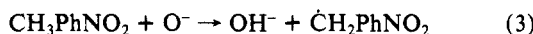


t-BuOH to produce the inert and weakly absorbing $\dot{C}H_2C-(CH_3)_2OH$ radical.¹⁰

Spectra. The spectra observed with the *p*-nitrobenzyl halides are presented in Figure 1. In all cases, the spectrum observed immediately after the pulse has an absorption maximum around 310 nm and is assigned to the corresponding nitro anion radicals. All these spectra changed with time to result in a 350-nm peak, which is identical for the three halides. This absorption is assigned to the *p*-nitrobenzyl radical produced by the intramolecular electron transfer and C–X bond scission (eq 2). The spectral



assignment is supported by comparison (Figure 1) with the spectrum of $\dot{C}H_2PhNO_2$ produced from *p*-nitrotoluene (Figure 1a) by reaction with O^- radicals at high pH (eq 3).¹¹ The yield



of $\dot{C}H_2PhNO_2$ from *p*-ClCH₂PhNO₂ (Figure 1b) is only ~75% of that obtained from the Br and I derivatives because reaction 2 in the former case is slower, resulting in the partial disappearance of ClCH₂PhNO₂⁻ by second-order decay.

The experimental points of the transient spectra represent the difference between the absorption of the product radical and that of the parent compound. After these points are corrected for the corresponding extinction coefficients of the parent compounds, the true spectra of the radicals are obtained. These are shown by the dotted and dashed lines for the nitro anion and benzyl radicals, respectively. The accuracy of the corrected spectra is less than that of the difference (experimental) spectra, since it is limited by the exact knowledge of the extinction coefficients and the yields of the radiolytic reactions.

The spectra obtained with the ortho derivatives are shown in Figure 2. The spectra of the anion radicals observed immediately after the pulse exhibit maxima around 300 nm, somewhat similar to those of the para isomers. The spectra observed at longer times, which are assigned to the *o*-nitrobenzyl radical, are quite different than that of the para isomer. The *o*-nitrobenzyl radical has a broad

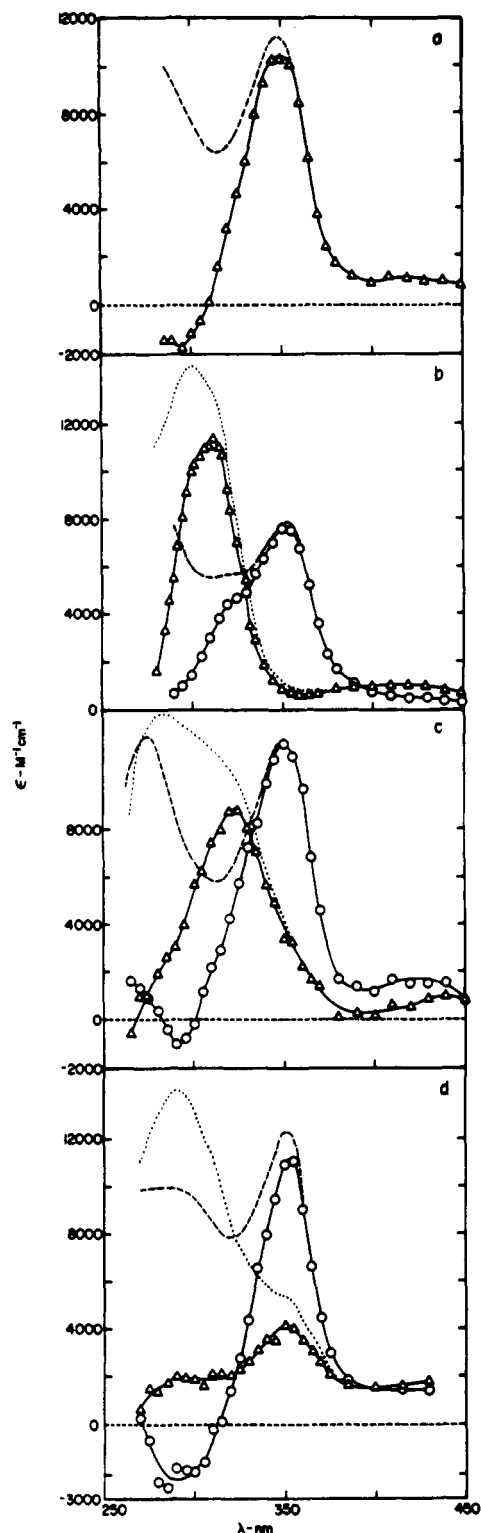


Figure 1. Absorption spectra of the radicals produced by reaction of e_{aq}^- with *p*-nitrobenzyl halides: (a) reference spectrum of *p*-nitrobenzyl radical produced by reaction of O^- with *p*-nitrotoluene in N_2O -saturated solution at pH 13.5 (ϵ was calculated by using $G(O^-) = 6.0$); (b) *p*-nitrobenzyl chloride (1×10^{-4} M) [(Δ) 1.5 μs after the pulse; (O) 700 μs later]; (c) *p*-nitrobenzyl bromide (2×10^{-4} M) [(Δ) 0.5 μs after the pulse; (O) 15 μs later]; (d) *p*-nitrobenzyl iodide (5×10^{-5} M) [(Δ) 0.2 μs after the pulse; (O) 10 μs later]. For b, c, and d all solutions were neutral and contained 0.1 M *t*-BuOH and were deoxygenated by bubbling with N_2 . The extinction coefficients were calculated by using $G = 2.8$ and thiocyanate dosimetry. The experimental points (difference spectra) were corrected for the bleaching of the parent compounds absorption. The dotted lines represent the corrected spectra of the initial electron adducts and the dashed lines the corrected spectra of the subsequently formed *p*-nitrobenzyl radical.

(7) See, e.g.: Kornblum, N.; Michel, R. L.; Kerber, R. C. *J. Am. Chem. Soc.* **1966**, *88*, 5660, 5662. Russell, G. A.; Danen, W. C. *Ibid.* **1966**, *88*, 5663. Russell, G. A.; Pecoraro, J. M. *Ibid.* **1979**, *101*, 3331 and references therein.

(8) Patterson, L. K.; Lilie, J. *Int. J. Radiat. Phys. Chem.* **1974**, *6*, 129.

(9) Schuler, R. H.; Neta, P.; Zemel, H.; Fessenden, R. W. *J. Am. Chem. Soc.* **1976**, *98*, 3825.

(10) Simic, M.; Neta, P.; Hayon, E. *J. Phys. Chem.* **1969**, *73*, 3794.

(11) Neta, P.; Hoffman, M. Z.; Simic, M. *J. Phys. Chem.* **1972**, *76*, 847; Neta, P.; Schuler, R. H. *Ibid.* **1973**, *77*, 1368.

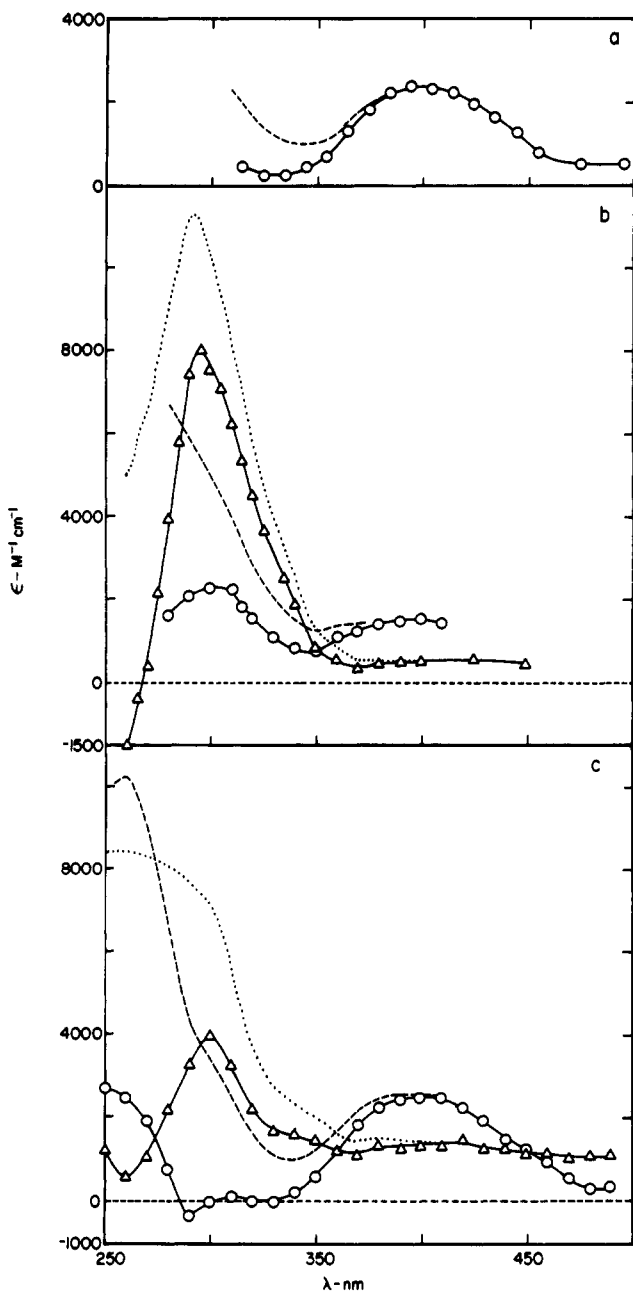


Figure 2. Absorption spectra of the radicals produced by reaction of e_{aq}^- with *o*-nitrobenzyl halides: (a) reference spectrum of *o*-nitrobenzyl radical produced by reaction of O^- with *o*-nitrotoluene in N_2O -saturated solution at pH 13.5; (b) *o*-nitrobenzyl chloride [(Δ) 2 μ s after the pulse; (\circ) 280 μ s later]; (c) *o*-nitrobenzyl bromide [(Δ) 2 μ s after the pulse; (\circ) 10 μ s later]. Both solutions contained 5×10^{-5} M substrate and 0.1 M *t*-BuOH at neutral pH and were bubbled with N_2 . The spectra corrected for the bleaching of the parent compound are shown by dotted (initial) and dashed (later) lines.

absorption peaking at 400 nm, which is much less intense than that of the para isomer (cf. Figures 1 and 2) at 350 nm. Both isomers have another strong absorption band at 260–270 nm.

The spectra of the anion radicals of *m*-nitrobenzyl bromide and iodide are shown in Figure 3. These spectra decay at longer times with no apparent formation in the 350–450-nm range. However, the *m*-nitrobenzyl radical, produced from *m*-nitrotoluene + O^- , is found to have only weak absorption between 300 and 550 nm with a broad peak ($\epsilon \approx 750 \text{ M}^{-1} \text{ cm}^{-1}$) at 430 nm. It is, therefore, impossible to monitor the buildup of the benzyl radical from the *m*-nitrobenzyl halide electron adduct.

Kinetics. The rate of reaction 2 for the para and ortho derivatives was determined by monitoring the rate of decay of the 310- or 300-nm absorption and the rate of the concomitant buildup

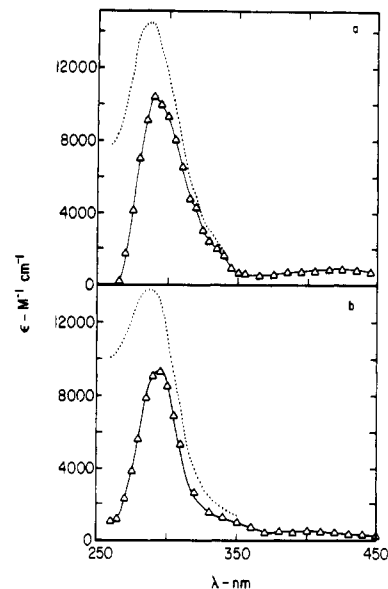


Figure 3. Absorption spectra of the radicals produced by reaction of e_{aq}^- with *m*-nitrobenzyl bromide (a) and iodide (b). The solutions contained 5×10^{-5} M substrate and 0.1 M *t*-BuOH at neutral pH and were bubbled with N_2 . The spectrum was recorded 5 μ s after the pulse. Similar spectra, with twice the yield, were obtained by using *i*-PrOH instead of *t*-BuOH.

Table I. Rate Constants for Intramolecular Electron Transfer in the Anion Radicals of Nitrobenzyl Halides^a

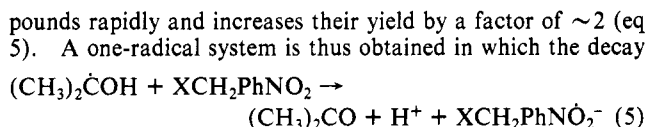
isomer	halogen		
	Cl	Br	I
para	$(4 \pm 1) \times 10^3$	$(1.7 \pm 0.2) \times 10^5$	$(5.7 \pm 0.9) \times 10^5$
ortho	$(1.0 \pm 0.2) \times 10^4$	$(4.0 \pm 0.6) \times 10^5$	
meta	<5	$(6 \pm 2) \times 10$	$(3 \pm 1) \times 10^3$

^a First-order rate constants in units of s^{-1} .

of the 350- or 400-nm absorption, respectively. The rates were found to be first order and independent of the concentration of the nitrobenzyl halide (over a range of 5×10^{-5} – 1×10^{-3} M *p*-nitrobenzyl chloride and 5×10^{-5} – 5×10^{-4} M *p*-nitrobenzyl bromide), thus confirming that the electron transfer is intramolecular as formulated in reaction 2. Only at the highest concentration of *p*-nitrobenzyl bromide examined (5×10^{-4} M) does a 10% increase in the rate appear to occur. This finding suggests an upper limit of $\leq 4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for the intermolecular reaction. Further confirmation was obtained from attempts to measure the rate of intermolecular electron transfer from *p*-nitrotoluene anion radical to benzyl halides. No experimental evidence for such a transfer was found. An upper limit of $k < 3 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ was determined by using *p*-cyanobenzyl bromide as a potential electron acceptor from the nitrotoluene anion radical. The measurement of this rate constant was limited by the self-decay of the radicals and the low solubility of the substrates. In any case, such a low rate constant will not contribute to the observed intramolecular transfer rates. The finding that nitrotoluene anion radical does not reduce cyanobenzyl bromide is not surprising in view of the expected lower electron affinity of the cyano vs. the nitro compound.

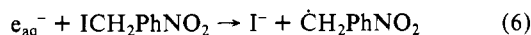
The rate of reaction 2 for the *m*-nitrobenzyl iodide is $3 \times 10^3 \text{ s}^{-1}$ slower than the rates for all the ortho and para derivatives (Table I). The *m*-nitrobenzyl bromide and chloride anion radicals were relatively long-lived, and their rate of undergoing reaction 2 was more difficult to determine. Following the rate of decay of the *m*-nitrobenzyl bromide electron adduct at 300 nm, the process appears to be mostly second order, attributed to radical-radical reactions. These reactions represent the mixed decay of the nitro anion radicals and the $\dot{C}H_2C(CH_3)_2OH$ radicals from *t*-BuOH. In order to extend the lifetime of $XCH_2PhNO_2^-$, we replaced *t*-BuOH by *i*-PrOH. The radical produced by reaction

of OH and H with *i*-PrOH (eq 4) reduces nitro aromatic compounds rapidly and increases their yield by a factor of ~ 2 (eq 5). A one-radical system is thus obtained in which the decay



is not accelerated by cross-reactions. Under these conditions, the anion radicals of *m*-nitrobenzyl bromide and chloride disappeared by processes which appear to be mostly second order. In order to further slow down this decay, we carried out experiments in alkaline solutions.¹² The decay of the *m*-nitrobenzyl bromide anion radicals was found to follow first-order kinetics with $k = 60 \text{ s}^{-1}$. With the *m*-nitrobenzyl chloride, however, the decay appeared to be strictly second order and an upper limit of 5 s^{-1} is estimated for reaction 2. The use of *i*-PrOH at pH 11 was also examined with *o*- and *p*-nitrobenzyl chloride and with *m*-nitrobenzyl iodide. In all these cases the rates of reaction 2 were found to be identical with those using *t*-BuOH in neutral solutions.

The rate constants for reaction 2, are, in most cases, sufficiently slow so that the process is well separated from the initial formation (reaction 1), which is diffusion controlled.¹³ Only in the case of *p*-nitrobenzyl iodide were the initial reaction with e_{aq}^- and the subsequent rearrangement not sufficiently separated in time. This overlap with the rapid reaction 2 is a result of the limited solubility of the compound, which slows down the occurrence of reaction 1. The "initial" spectrum observed 0.2 μs after the pulse (Figure 1d) already contains a small contribution from the *p*-nitrobenzyl radical. It is conceivable that part of this contribution is from a direct reaction



Direct attack of e_{aq}^- on the C-I site may be expected since iodo compounds react with e_{aq}^- nearly as rapidly as do nitroaromatic compounds. The results indicate that such a direct reaction (6) may occur with $\leq 30\%$ of the e_{aq}^- .

The rates of intramolecular electron transfer (Table I) are found to change with the halide. In the case of the ortho and para derivatives ratios of 1:40:140 are observed for Cl:Br:I, respectively. The increase in reactivities is in the same direction as that observed for reactions of haloaliphatic compounds with e_{aq}^- and in the opposite direction to the increase in electronegativity of the halogen. As has been argued for the case of $e_{\text{aq}}^- + \text{RX}$,¹⁴ the rate-determining step in these processes is the addition of an electron to the halogen atom which acts as an electrophilic center. The electrophilicity of X in RX increases in the order Cl, Br, I. The RX^- , initially formed, is assumed to have a very short but finite lifetime¹⁴ and breaks down into $\text{R} + \text{X}^-$. Although the reactivity increases with decreasing C-X bond strength, the breakage of the bond was suggested not to take place in the rate-determining step and thus to have no direct effect on the observed rates.¹⁴ This latter argument may not hold for the intramolecular electron transfer observed in the present work. If the electron is transferred from the nitro group to the halogen, as long as the C-X bond does not break, the electron may find its way back to the nitro group (or other sites in the molecule). As a result, the scission of the C-X bond may be the rate-determining step. It is noted that the ratio of reactivities observed here is surprisingly similar to the ratio of 1:40:110 for Cl:Br:I

observed in the rates of solvolysis of aliphatic halides.¹⁵

The position of the nitro relative to that of the CH_2X group has a strong effect on the rate of dehalogenation (Table I). The ortho isomer undergoes reaction 2 about 2.4 times more rapidly than the para isomer, while the meta undergoes reaction 2 at least two orders of magnitude more slowly. This order of reactivities is the same as that found in the intramolecular electron transfer in the anion radicals of (nitrobenzoato)pentamminecobalt(III).³ In both systems, the spin density distribution in the various ring positions of the nitro anion radical has a major effect on the rate of electron transfer. The fact that in the meta isomer the electron transfer is very slow compared with the other isomers results from the very low spin density at the meta position.¹⁶ An increased spin density should facilitate the transfer of the electron through the CH_2 group to the halide. According to this trend, the ortho isomer should decompose slightly more slowly than the para. The results, however, show an opposite trend, both in our work and in the Co(III) complexes. The latter finding has been rationalized³ in terms of direct electron transfer from the ortho-nitro anion group to the Co(III) center without the intermediacy of the carboxyl group. A similar mechanism may account for the present findings as well. Quantitatively, however, the present results show that the ratio of reactivity ortho to para is 2.4, while in the (nitrobenzoato)cobalt(III) case the ratio is ~ 150 . This increased relative rate of direct transfer from the NO_2^- group to the Co(III) results most probably from the larger difference in redox potentials between the nitrobenzoate and the Co center. In the nitrobenzyl halides, the electron transfer appears to be thermodynamically less favorable, and thus only a slight increase in the rate is found for the ortho vs. para. Furthermore, the direct approach of the NO_2^- group to the Co(III) or halide is geometrically different. The redox potential differences also account for the higher ratio between the reactivity of para vs. meta (>200) observed here as compared with that (17) in the Co(III) complexes.³ In other words, the same spin density ratio between para and meta causes a higher reactivity ratio when the reaction is driven by a lower difference in potential.

Similar arguments can be advanced for the effect of the distribution of the negative charge on the rate of reaction 2. Although the charge density is highest on the nitro group oxygens, a certain amount can be expected on the ortho and para carbons. This negative charge is then channeled through the CH_2 group to the halogen. Similar considerations on charge distribution have been discussed previously in rationalizing the rates of protonation of isomeric hydroxyphenyl radicals to phenoxyl radicals.⁹ It should be pointed out, however, that the hydroxyphenyl are σ radicals, i.e., that the spin is localized at the radical site.

Recent experiments with 5-chloro-1-methyl-4-nitroimidazole have shown that the anion radical is relatively long-lived but Cl^- is ultimately formed.¹⁷ This finding shows an example of delayed dehalogenation even when both NO_2 and Cl are attached directly to the same ring. Experiments with various halonitrobenzenes failed to show dehalogenation under the pulse radiolysis conditions probably due to the stronger C-X bonds in these compounds as compared with those in nitrobenzyl halides.¹⁸ This comparison suggests that the C-X bond scission may be the rate-determining step in reaction 2.

Effect of pH. The results discussed above dealt with the decomposition of nitrobenzyl halide anion radicals in neutral and alkaline solutions. In the acid region, however, the nitro group protonates and the rate of the intramolecular electron transfer is expected³ to decrease. Experiments with *p*-nitrobenzyl bromide between pH 2.3 and 0 indeed showed that the rate decreases. These experiments cannot be carried out with *t*-BuOH as an OH scavenger, since in the acid region e_{aq}^- is efficiently scavenged by H^+ to produce H atoms which may add to the ring rather than reduce the nitro group.¹⁹ This problem is overcome by the use

(12) The second-order decay of RNO_2^- becomes more rapid as the pH decreases since $\text{RNO}_2^- + \text{RNO}_2^-$ is very slow but $\text{RNO}_2^- + \text{RNO}_2\text{H}$ is much faster. Although the $\text{p}K_a$ of RNO_2H is $\sim 3-4$, the contribution of the protonated radical to the decay extends well into the high pH region. (Wardman, P., to be submitted for publication.)

(13) Nitroaromatic compounds react with e_{aq}^- with rate constants of $2-3 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$; see compilation by: Anbar, M.; Bambenek, M.; Ross, A. B. *Natl. Stand. Ref. Data Ser. (U. S., Natl. Bur. Stand.)* **1973**, No. 43. The rate constants for *p*-nitrobenzyl chloride and bromide were also estimated in this work and found to be $3 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$.

(14) Anbar, M.; Hart, E. J. *J. Phys. Chem.* **1965**, *69*, 271; Anbar, M. *Adv. Phys. Org. Chem.* **1969**, *7*, 115.

(15) Streitwieser, A. *Chem. Rev.* **1956**, *56*, 571 (Table 36).

(16) See, e.g.: Eiben, K.; Fessenden, R. W. *J. Phys. Chem.* **1971**, *75*, 1186.

(17) Clarke, E. D.; Wardman, P. *Int. J. Radiat. Biol. Relat. Stud. Phys., Chem. Med.* submitted for publication.

(18) Behar, D.; Neta, P., to be submitted for publication.

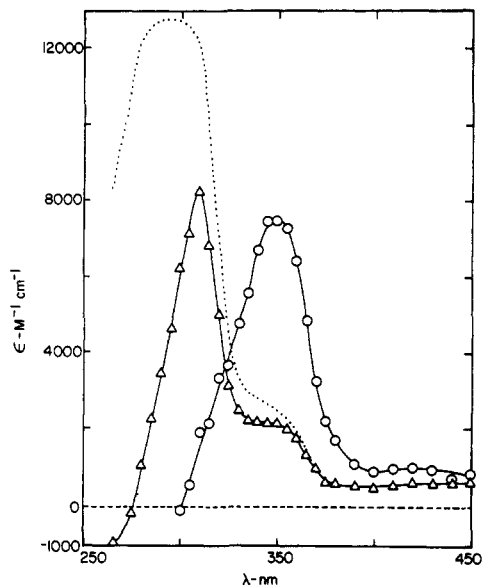


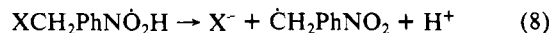
Figure 4. Absorption spectra of the radicals produced by reaction of $(\text{CH}_3)_2\text{COH}$ with *p*-nitrobenzyl bromide at pH 2. The solution contained 1×10^{-4} M substrate and 0.7 M *i*-PrOH and was bubbled with N_2O . The spectra were recorded 10 μs after the pulse (Δ) and 150 μs later (O). The dotted line is the initial spectrum corrected for the bleaching of the parent compound.

of *i*-PrOH which scavenges both OH and H to produce $(\text{CH}_3)_2\text{COH}$ (reaction 4), which then reduces the nitro compound (reaction 5). The rate constant of this one-electron reduction of *p*-nitrobenzyl bromide was determined to be $2.6 \times 10^9 \text{M}^{-1}\text{s}^{-1}$, i.e., in the same range as those of several other nitro aromatic compounds.²⁰ The spectra observed with this system at pH 2 are shown in Figure 4. The initial spectrum is mostly that of the

protonated radical $\text{BrCH}_2\text{PhNO}_2\text{H}$, with some contribution from the anion $\text{BrCH}_2\text{PhNO}_2^-$. The pK_a for such a radical (eq 7) is



expected to be ~ 3 .²¹ The spectrum observed at later times is that of the nitrobenzyl radical (eq 8).



The rate of the intramolecular transfer at pH 2 was only $2 \times 10^4 \text{s}^{-1}$, as compared with $1.7 \times 10^5 \text{s}^{-1}$ in neutral solution. This decrease must be due to the protonation of the nitro group. From the rates observed at pH 2.3, 1.9, 1.6, 1.4, 1.2, 0.9, and 0.6 (3.3 , 2.0 , 1.3 , 1.0 , 0.7 , 0.6 , and $0.3 \times 10^4 \text{s}^{-1}$, respectively) the pK_a of the nitro group is determined to be 2.8 ± 0.1 and the rate of intramolecular electron transfer in the protonated radical is estimated as $(3 \pm 1) \times 10^3 \text{s}^{-1}$. It was difficult to determine the kinetics of the latter process accurately at high acidities because second-order decay of the radicals overlapped the slow intramolecular reaction. The decrease in rate upon protonation of the nitro group is by a factor of 56, comparable to the ratio of 42 found for the (*o*-nitrobenzoato)cobalt(III) complex.³ This trend may be rationalized by the lack of negative charge in the protonated form or by changes in redox potentials,²² i.e., that the nitro anion radical is a stronger reductant than its protonated form.

Conclusion

It has been demonstrated that anion radicals of nitrobenzyl halides undergo intramolecular electron transfer and decompose into halide ions and nitrobenzyl radicals. This process takes place with rates varying from 0 to 10^6s^{-1} and is governed by the nature of the halide and the relative position of the nitro to the CH_2X group on the ring. The relative rates for the ortho and para derivatives are 1:40:140 for Cl:Br:I. The ortho decompose twice as rapidly as the para, while the meta decompose much more slowly. Protonation of the nitro group in the radical slows down the electron transfer and decomposition considerably.

(19) Whillans, D. W. *Radiat. Phys. Chem.* 1977, 10, 335.
 (20) Asmus, K. D.; Wigger, A.; Henglein, A. *Ber. Bunsenges. Phys. Chem.* 1966, 70, 862. Adams, G. E.; Willson, R. L. *J. Chem. Soc., Faraday Trans. 1* 1973, 69, 719. Neta, P.; Meisel, D. *J. Phys. Chem.* 1976, 80, 519.

(21) See review by: Neta, P. *Adv. Phys. Org. Chem.* 1976, 12, 223 and references therein.

(22) Meisel, D.; Neta, P. *J. Am. Chem. Soc.* 1975, 97, 5198.

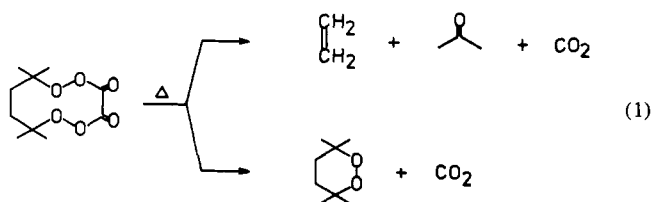
Fluorescer-Enhanced Chemiluminescence of a Cyclic Peroxalate via Electron Exchange

Waldemar Adam,^{*1} Carmen Cadilla,² Omar Cueto, and Luis O. Rodriguez²

Contribution from the Department of Chemistry, University of Puerto Rico, Rio Piedras, Puerto Rico 00931. Received November 19, 1979

Abstract: The direct and fluorescer-enhanced chemiluminescence of the cyclic peroxalate 7,7,10,10-tetramethyl-1,2,5,6-tetroxocane-3,4-dione is reported. That enhancement by 9,10-diphenylanthracene was much less effective than that by 9,10-dibromoanthracene and that triplet quenchers such as O_2 and piperylene did not alter significantly the rubrene-enhanced emission intensities suggested that the enhanced chemiluminescence was not derived via energy transfer from triplet-state products. At high fluorescer concentration the fluorescer catalyzes the decomposition of the cyclic peroxalate, but this catalysis is chemiluminescent. The logarithmic dependence between the enhanced chemiluminescence intensity and the oxidation potential of the fluorescer confirms that the dominant mechanism of light enhancement is via electron exchange.

The cyclic peroxalate in eq 1 was shown³ to decarboxylate



thermally into ethylene and acetone (major products) and into

3,3,6,6-tetramethyl-1,2-dioxane (minor product). The interesting observation about this cyclic peroxalate was its significantly higher activation energy ($\Delta H^\ddagger = 30 \pm 1 \text{kcal/mol}$) toward decarboxylation than its acyclic congener di-*tert*-butyl peroxalate ($\Delta H^\ddagger = 22 \pm 1 \text{kcal/mol}$). This was surprising, especially since thermochemical measurements revealed that the cyclic peroxalate

(1) NIH Career Development Awardee (1975-1980).

(2) Graduate Research Fellows in the Support for Biomedical Education (SUBE) Program sponsored by NIH-MBS.

(3) Adam, W.; Sanabia, J. *J. Chem. Soc., Chem. Commun.* 1972, 74.