JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 5, 7–18 (1992)

# COMPARISON OF THE CLEAVAGE REACTIONS OF α-NITROCUMENE RADICAL ANION AND α,*p*-DINITROCUMENE RADICAL ANION

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**The rates of loss of $NO_2^-$ from the radical anions of 2-(4-nitrophenyl)-2-nitropropane (α,*p*-dinitrocumene) and 2-phenyl-2-nitropropane (α-nitrocumene) were compared by three different methods. The rate constant for the apparently heterolytic process ($D_N$) undergone by the radical anion of the dinitrocumene was measured by pulse radiolysis to be $2 \times 10^3\ s^{-1}$ in dimethylformamide at 25 °C. This value is in reasonable agreement with values estimated from an indirect chemical method and from cyclic voltammetry at low temperature. The rate for the formally homolytic dissociation process ($D_R$) undergone by the radical anion of the mononitrocumene could not be determined by pulse radiolysis but could be shown to be between 50 and 1000 times faster than the dinitro case using the other two methods. Possible reasons for the faster rate for the $D_R$ process are discussed with reference to related systems for which the $D_R$ process had been found to be unexpectedly slow.**

## INTRODUCTION

Cleavage of the radical anions of α-substituted *p*-nitrocumenes has been a reaction of critical significance in the development of present-day understanding of the class of mechanisms known as $S_{RN}1$ processes.[1] In 1966, it was recognized simultaneously by Kornblum *et al.*[2] and Russell and Danen[3] that the nucleophilic substitution reactions of some *p*-nitrobenzylic halides involved radical chain mechanisms subsequently named $S_{RN}1$.[4] Shortly thereafter, Kornblum and co-workers showed that one of the unique properties of such reactions is their facile occurrence at tertiary carbon[5] and that nitrite ion can function as a leaving group when present in α,*p*-dinitrocumene, **1**.[6] Later, Kornblum *et al.*[7] discovered that with nitrite as leaving group, the *p*-nitro substituent is not required if the nucleophilic reagent is the salt of a nitroalkane. The reaction is slower here, is more affected by bulky groups in the nucleophile and gives non-substitution byproducts, but is still viable. The beneficial effect of the *p*-nitro substituent is illustrated by comparing the conditions for reactions (1)[8] and (2).[7] (HMPA is hexamethylphosphoramide.)

$$\underset{\mathbf{1}}{O_2NC_6H_4C(CH_3)_2NO_2} + (CH_3)_2NO_2Li \xrightarrow[\text{HMPA }(25\ ^\circ C)]{h\nu/2h} \underset{90\%}{O_2NC_6H_4C(CH_3)_2C(CH_3)_2NO_2} \quad (1)$$

$$\underset{\mathbf{2}}{C_6H_5C(CH_3)_2NO_2 + (CH_3)_2NO_2Li} \xrightarrow[\text{HMPA }(25\ ^\circ C)]{h\nu/6\text{ days}} \underset{30\%}{C_6H_5C(CH_3)_2C(CH_3)_2NO_2} + \underset{48\%}{C_6H_5C(CH_3)_2C(CH_3)_2C_6H_5} + \underset{(22\%)}{\text{unreacted } \mathbf{2}} \quad (2)$$

The mechanism for reactions (1) and (2) is well established as involving three propagation steps: (1) cleavage of the radical anion of the substrate to give nitrite ion ($D_N$ or $D_R$)[9] and a benzylic radical, (2) reaction of the radical with the 2-nitropropyl anion ($A_N$ or $A_R$)[9] and (3) electron transfer from the resultant radical anion to another molecule of substrate (T).[8] Although any of these steps, and also whatever initiation step precedes this sequence, might be responsible for making reaction (2) slower than reaction (1), we were struck by the fact that both the cleavage reaction and the reaction of the nucleophile with the resultant radical are formally heterolytic processes ($D_N$ and $A_N$)[9] for reaction (1) and are formally homolytic ($D_R$ and $A_R$)[9] processes for reaction (2). This is represented schematically in reactions (3) and (4) for the cleavage components of reactions (1) and (2), respectively.

$$\underset{\mathbf{1}^{-\cdot}}{{}^{\cdot -}O_2NC_6H_4\overset{|}{\underset{|}{C}}-NO_2} \xrightarrow{D_N} O_2NC_6H_4\overset{|}{\underset{|}{C}}{}^{\cdot} + {}^{-}{:}NO_2 \quad (3)$$

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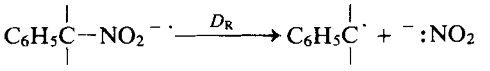
0894-3230/92/010007-12$06.00

*Received 22 July 1991*
*Revised 12 September 1991*



$$\underset{\mathbf{2}^{-\cdot}}{C_6H_5C{-}NO_2{}^{-\cdot}} \xrightarrow{D_R} C_6H_5C^{\cdot} + {}^{-}{:}NO_2 \qquad (4)$$

This distinction in the way electrons are apportioned is parallel to that noted earlier between reactions (5) and (6), in which reaction of (6) was at least $10^4$ times slower than reaction (5).[10]

$$\underset{\mathbf{3}^{-\cdot}}{{}^{\cdot -}O_2NC_6H_4CR_2OC_6H_5} \xrightarrow{D_N} O_2NC_6H_4CR_2^{\cdot} + {}^{-}{:}OC_6H_5 \qquad (5)$$

$$\underset{\mathbf{4}^{-\cdot}}{C_6H_5CR_2OC_6H_4NO_2^{-\cdot}} \xrightarrow{D_R} C_6H_5CR_2^{\cdot} + {}^{-}{:}OC_6H_4NO_2 \qquad (6)$$

As we shall discuss in greater detail later, a case can be made that the advantage in thermodynamic driving force for reaction (4) over reaction (3) is similar to that enjoyed by reaction (6) over reaction (5). With reactions (5) and (6), the thermodynamic advantage is overwhelmed by what we argued to be a kinetic advantage for $D_N$ processes over $D_R$ processes. If the same factors were at work in reactions (3) and (4), one might expect that reaction (3) would be faster than reaction (4) in spite of its thermodynamic disadvantage.

This paper describes experiments in which reactions (3) and (4) were isolated from the other chain components of reactions (1) and (2) in order to compare their rates. Three different approaches were employed, an indirect chemical method, pulse radiolysis and cyclic voltammetry. Our experiments show that the analogy to reactions (5) and (6) is not predictive in that reaction (4) is faster than reaction (3). This is important because it documents an exception to our previous generalization[10] that $D_N$ processes are faster than comparable $D_R$ processes. We shall discuss the difference in the cases after describing our results.

## RESULTS AND DISCUSSION

### Chemical approach

Compounds **1** and **2** were treated with solutions containing various stable radical anions and the reaction outcome was determined. When reaction occurred, the only observed product is the corresponding 1,2-diphenyl-1,2-dimethylbutane (bicumyl); the formation of this and the disappearance of **1** and **2** were assessed by NMR analysis. These results are summarized in Table 1.

For **1**, reaction occurred in dimethylformamide (DMF) when the anthraquinone radical anion, $AQ^{-\cdot}$ (potassium salt), was used, the reaction being essentially complete after 15 min at 25 °C.

A reasonable mechanism for cleavage under the conditions described above is

$$\mathbf{1} \text{ or } \mathbf{2} + D^{-\cdot} \underset{k_{-1}[D]}{\overset{k_1}{\rightleftharpoons}} \mathbf{1}^{-\cdot} \text{ or } \mathbf{2}^{-\cdot}$$

$$\xrightarrow{k_{\text{diss}}} \underset{\mathbf{1}^{\cdot} \text{ or } \mathbf{2}^{\cdot}}{XC_6H_5CR_2^{\cdot}} + NO_2^{-} \qquad (7)$$

The donor radical reacts with the nitro compound in an energetically uphill process to give the radical anion of the substrate, which then dissociates. The rate of conversion of **1** or **2** to products is given by rate $= k_1[D^{-\cdot}][\mathbf{1} \text{ or } \mathbf{2}]k_{\text{diss}}/(k_{-1}[D] + k_{\text{diss}})$. The equilibrium constant $k_1/k_{-1}$ may be estimated using electrochemical reduction potentials given in Table 1 and estimates of reduction potentials for **1** and **2**. For **1**, we assume that 4-nitrotoluene should be a valid model, suggesting $E_{1/2} = -1{\cdot}14$ V.[11] The threshold donor required to produce cleavage of **1** was anthraquinone radical anion, $AQ^{-\cdot}$. AQ is reduced at $E_{1/2} = -0{\cdot}84$ V, a potential 0·30 V more positive than estimated for **1**. From the Nernst equation, the equilibrium constant for the pre-equilbrium in reaction (7) is then $k_1/k_{-1} = 9 \times 10^{-6}$. Because $k_{-1}$ represents an energetically downhill electron-transfer process, it may be safely assumed to be close to the diffusion limit,[12] $k_{-1} = 10^{10}\ \text{l mol}^{-1}\text{s}^{-1}$. Thus, for the reaction of $AQ^{-\cdot}$ with **1**, it may be estimated that $k_1 = 1 \times 10^5\ \text{l mol}^{-1}\text{s}^{-1}$. It is immediately clear that $k_1$ cannot represent the rate-limiting step. An experiment carried out for 5 min at 0 °C with $[AQ^{-\cdot}] = [\mathbf{1}] = 0{\cdot}1$ M gave 26% cleavage (see Table I). This conversion corresponds to $k_{\text{obs}}$ (second order) $= 1{\cdot}2 \times 10^{-2}\ \text{l mol}^{-1}\text{s}^{-1}$, which is $10^7$ times less than the value of $k_1$ predicted from reduction potentials.

This means that cleavage must be rate limiting, and we are left with the more complicated rate expression, rate $= k_1k_{\text{diss}}[AQ^{\cdot}]\ [\mathbf{1} \text{ or } \mathbf{2}]/k_{-1}[AQ]$. Although we did not attempt a detailed kinetic study, reasonable estimates regarding the value of $[AQ^{-\cdot}]/[AQ]$ during the first 26% of reaction suggest that $k_{\text{diss}} = 6 \times 10^2\ \text{s}^{-1}$ at 0 °C or roughly $6 \times 10^3\ \text{s}^{-1}$ at 25 °C in DMF. (A problem with this analysis is that it would predict that reaction of **1** with the radical anion of 1,3-dinitrobenzene should have been observable; however, we could not detect product formation after 24 h at 25 °C.)

Interestingly, the threshold for reaction in tetrahydrofuran (THF), which gave apparently homogeneous solutions of the donor radical anions, occurs at a significantly more negative reduction potential. In THF, **1** gave a barely detectable reaction with the radical anion of 2,4-dinitroanisole ($E_{1/2} = -0{\cdot}92$ V) after 24 h and required 2,2-dinitrobiphenyl radical anion ($E_{1/2} = -0{\cdot}97$ V) for substantial conversion. Although reduction potentials appropriate to the circumstances of the THF reactions were not available, it seems unlikely that the difference between the THF and DMF reactions results from differences in the pre-equilibrium step. We would expect changes in solvation and ion pairing to affect $D^{-\cdot}$ and $\mathbf{1}^{-\cdot}$ similarly. A more likely hypothesis is that ion pairing retards the rate of cleavage through stabilization of both $D^{-\cdot}$ and $\mathbf{1}^{-\cdot}$ relative to the transition state for cleavage. Ion association at the transition state for cleavage of $\mathbf{1}^{-\cdot}$ might well be restricted for steric reasons.

The threshold potential for reaction with **2** occurs at $-1{\cdot}25$ V, which is the reduction potential of *N,N*-dimethyl-4-nitroaniline (DMNA). $\text{DMNA}^{-\cdot}$ reacts readily with **2** in both DMF and THF, as did several radical anions from compounds with more negative reduction potentials [2,4,6-tri-*tert*-butylnitrobenzene ($E_{1/2} = -1{\cdot}5$ V), benzophenone, fluoranthene, naphthalene and biphenyl). For **2**, $E_{1/2} = -1{\cdot}61$ V has been reported;[13] however, **2** was reduced irreversibly under the conditions of the experiment from which this value

Table 1. Reaction of various electron donors with **1** and **2**[a]

| Donor[b] | $-E^{c}_{1/2}$ | Solvent | Time (min) | Reaction of **1** (%)[d] | Reaction of **2** (%)[d] |
|---|---|---|---|---|---|
| $\text{2-MeNQ}^{-\cdot}$ | 0·66[e,f] | DMF | 15 | <5 | — |
| $\text{DQ}^{-\cdot}$ | 0·73[e,g] | DMF | 15 | <5 | — |
| $\text{1,3-DNB}^{-\cdot}$ | 0·77[e,h] | DMF | 1440 | <5 | — |
| | | THF | 1440 | <5 | — |
| $\text{AQ}^{-\cdot}$ | 0·84[e,i] | DMF | 15 | 84 ± 5 | — |
| | | DMF | 5[j] | 26 ± 3 | — |
| | | THF | 1440 | <5 | — |
| | | THF–DMF (2:1) | 1440 | <5 | — |
| $\text{4,4'-DNBP}^{-\cdot}$ | 0·88[e,k] | DMF | 60 | >90 | — |
| | | THF | 1440 | <5 | — |
| $\text{2,4-DNA}^{-\cdot}$ | 0·92[e] | THF | 1440 | 5 | — |
| | | THF–DMF (1:5) | 30 | 53 ± 5 | — |
| $\text{2,2-DNBP}^{-\cdot}$ | 0·97[e] | THF | 1440 | 41 ± 4 | — |
| | | THF–DMF (10:3) | 15 | >90 | |
| $\text{NB}^{-\cdot}$ | 1·10[e,l] | DMF | 15 | >80 | — |
| | | DMSO | 1200 | >95 | |
| | | DMF | 2880 | — | <5 |
| | | DMSO | 2880 | — | <5 |
| $\text{2-NA}^{-\cdot}$ | 1·17[e] | THF | 30 | 65 ± 6 | |
| | | THF–DMF (1:1) | 30 | >95 | |
| | | THF | 2520 | — | <5 |
| | | THF–DMF (1:1) | 1420 | — | <5 |
| $\text{DMNA}^{-\cdot}$ | 1·25[e] | DMF | 15 | — | >90 |
| | | THF | 1440 | — | >95 |
| | | DMF | 5[m] | — | 33 ± 3 |
| | | DMF | 5[n] | — | 16 ± 2 |
| $\text{TBNB}^{-\cdot}$ | 1.5[o] | THF | 60 | >80 | — |
| | | THF | 15 | — | >95 |

[a] **1** and **2** were present at concentrations of 25 to 100 mM and were treated with approximately 10% excess of radical anion solution at 25 °C unless stated otherwise.

[b] Abbreviations for donors: 2-MeNQ = 2-methylnaphthoquinone; DQ = duroquinone; 1,3-DNB = 1,3-dinitrobenzene; AQ = anthraquinone; 4,4′-DNBP = 4,4′-dinitrobiphenyl; 2,4-DNA = 2,4-dinitroanisole; 2,2′-DNBP = 2,2′-dinitrobiphenyl; NB = nitrobenzene; 2-NA = 2-nitroanisole; DMNA = *N,N′*-dimethyl-4-nitroaniline; TBNB = 2,4,6-tri-*tert*-butylnitrobenzene.

[c] Listed values are in DMF vs SSCE.

[d] Percentage reaction was determined by work-up and NMR analysis as described in the Experimental section.

[e] Value measured by us in DMF vs SSCE with $NaClO_4$ as electrolyte.

[f] $-E_{1/2} = 0{\cdot}69$ V (DMF–tetraethylammonium perchlorate).[38]

[g] $-E_{1/2} = 0{\cdot}76$ V (DMF–tetrapropylammonium perchlorate).[38]

[h] $-E_{1/2} = 0{\cdot}80$ V (DMF–tetrabutylammoniun iodide);[39] $-E_{1/2} = 0{\cdot}81$ V (DMF–tetrapropylammonium perchlorate).[40]

[i] $-E_{1/2} = 0{\cdot}83$ V (DMF–tetraethylammonium iodide).[41]

[j] Reaction of 33 mM **1** with 43 mM $\text{AQ}^{-\cdot}$ at 0 °C.

[k] $-E_{1/2} = 0{\cdot}89$ V (DMSO–tetrapropylammonium perchlorate).[39]

[l] $-E_{1/2} = 1{\cdot}08$ V (DMF–tetrapropylammonium perchlorate).[40]

[m] Reaction of 30 mM **2** with 36 mM $\text{DMNA}^{-\cdot}$ at 0 °C.

[n] Reaction of 30 mM **2** with 0·36 mM $\text{DMNA}^{-\cdot}$ and 0·15 mM DMNA.

[o] $-E_{1/2} = 1{\cdot}5$ V (MeCN–tetrapropylammonium perchlorate).[42]

was obtained. Nitro-*tert*-butane, for which the electrochemical reduction could be studied reversibly, gave $E_{1/2} = -1{\cdot}77$ V under similar conditions,[13] providing a sensible lower limit and suggesting that the reported value is reasonable. Thus, the threshold for reaction with **2** occurs at a potential difference of 0·36 V, suggesting that the corresponding pre-equilibrium of reaction (7) occurs with $k_1/k_{-1} = 5 \times 10^{-7}$. Rate constant estimation, using the fact that **2** reacts with DMNA$^{-\cdot}$ to give 33% conversion after 5 min at 0 °C, leads to an estimate for the cleavage rate constant of $2^{-\cdot}$ of $k_{\mathrm{diss}} \approx 2 \times 10^5\ \mathrm{s}^{-1}$ at 25 °C. This estimate should probably be viewed as a lower limit because of the uncertainty in the reduction potential of **2**.

In contrast to **1**, the threshold for reaction of **2** seemed to be insensitive to the change in solvent from DMF to THF. Possibly there is not much change in charge localization on going from $D^{-\cdot}$ to the transition state for the cleavage of $\mathbf{2}^{-\cdot}$.

### Pulse radiolysis approach

Radiolysis of **1** in either THF or DMF using a 50–500 ns pulse of 4 MeV electrons produced an initial transient which is believed to be the corresponding radical anion, $\mathbf{1}^{-\cdot}$. In THF the absorption maxima for this transient are 350, 470 and 560 nm, as can be seen in Figure 1. This is reasonably close to the spectrum reported by Buncel and Menon[14,15] for the radical anion of 4-nitrotoluene in THF with crown ether present. In THF the radical anion decays in a first-order process with a rate constant $k = 4{\cdot}7 \times 10^5\ \mathrm{s}^{-1}$.

In the DMF experiment, the maximum was at 340 nm and there was absorption extending out into the visible region, as seen in Figure 2. The curious aspect of the DMF case was the emergence of a peak at 440 nm, which corresponded to a stable product (up to 1·3 ms). We have tentatively assigned this absorption to the 4-nitrocumyl anion, $\mathbf{1}^{-}$, based on the observation of the 4-nitrobenzyl anion at 430–450 nm by Buncel and Menon[14,15] and others[16] and the fact that the only other logical product, the 4-nitrocumyl radical, would be expected to appear at 370 nm (based on the spectra of closely related radicals).[17] Also, this radical would be expected to disappear in a rapid second-order process, which is not what was observed. The spectral changes which occur after the pulse almost exactly match those reported by Maslak *et al.*,[18] who studied the cleavage of the lithium salts of radical anions of a series of 1-(4-nitrophenyl)-2-aryl-1,1,2,2-tetraethylethanes in dimethyl sulfoxide (DMSO). In these cases the nitroaryl radical anion showed maxima at 335 and 470 nm, with the latter, weaker band tailing to *ca* 500 nm. As in our case, fading of the 335 band was accompanied by the emergence of a band at 440 nm, which was shown to be the diethyl(4-nitrophenyl) carbanion. Irradiation of a DMF solution of **1** to a calculated dose of 1·5 Mrad gave a small conversion to several products as indicated by high-performance liquid chromatography (HPLC). One of these corresponded in retention time to 4-nitrocumene, but we were unable to identify the other products. It could be shown that they were not 4,4′-dinitrobicumyl or 2-(4-nitrophenyl)propene (*p*-nitro-α-methylstyrene).

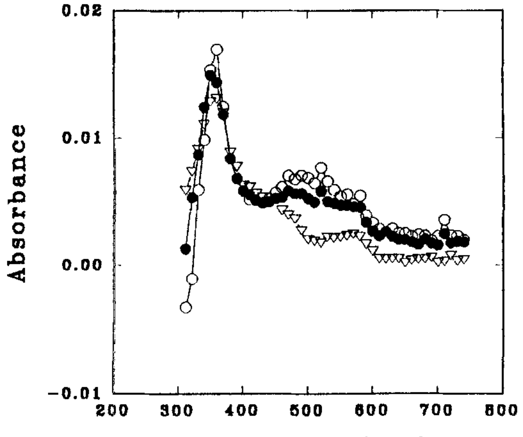


Figure 1. Pulse radiolysis of **1** in THF. ○, 0·1 μs; ●, 0·7 μs; ▽, 8·5 μs

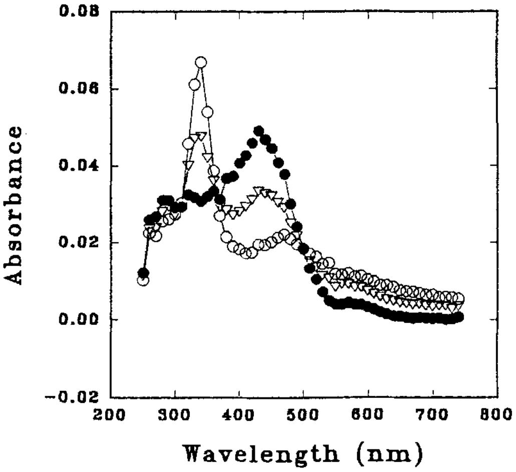


Figure 2. Pulse radiolysis of **1** in DMF. ○, 20 μs; ▽, 135 μs; ●, 472 μs

For radiolysis of **1** in DMF, the disappearance of the initial transient and the growth of the product at 440 nm can be fitted to a first-order decay curve and measured rate constants show no dose dependence in the range available. This is consistent with a unimolecular dissociation of $\mathbf{1}^{-\cdot}$. The rate constant for disappearance of the absorption assigned to the radical anion of the dinitrocumene is $k = 4\cdot3 \times 10^3$ s$^{-1}$. It seems very unlikely that the 4-nitrocumyl anion is a direct product of the dissociation of $\mathbf{1}^{-\cdot}$, because $NO_2$ plus 4-nitrocumyl anion should be unstable compared with $NO_2^-$ and 4-nitrocumyl radical. (In theory, a simple way to justify this statement is to determine the reduction potential of 4-nitrocumyl radical and the oxidation potential of $NO_2^-$. Unfortunately, neither of these measurements is straightforward. The reduction potential of $NO_2$ in acetonitrile is reported to be 0·07 V vs $Ag/AgNO_2$ in acetonitrile[19a] and an $E^0$ for the $NO_2/NO_2^-$ couple of 0·32 V has been calculated[19b] vs ferrocene/ferrocinium. This is at least 0·5 V positive of the potential at which we observe what is believed to be oxidation of the 4-nitrocumyl anion as discussed in the electrochemistry section of this paper.) It seems more probable that the dissociation process is sufficiently slow to allow the initially formed radical anion to serve as a one-electron reducing agent for the 4-nitrocumyl radical as it is generated. The peak at 440 nm grows at about the same rate as the disappearance of the peak at 340 nm, which is possible if the concentration of 4-nitrocumyl radical remains low relative to that of both the radical anion and the anion. The kinetics of such a first- and second-order reaction sequence can be treated analytically[20] to the extent that it is possible to show that $k_{diss}/k_3$ (where $k_3$ is the second-order rate constant for reduction of the radical by $\mathbf{1}^{-\cdot}$) is an upper limit for the concentration of the 4-nitrocumyl radical. Assuming that the rate constant for reduction of the 4-nitrocumyl radical by $\mathbf{1}^{-\cdot}$ is at the diffusion limit, $k_3 = 10^{10}$ l mol$^{-1}$ s$^{-1}$, then $k_1/k_3 = 4\cdot3 \times 10^{-7}$. We estimate the concentration of radical anion to be *ca* $10^{-5}$ M immediately after the pulse. Under these conditions, the kinetics for loss of $\mathbf{1}^{-\cdot}$ will be essentially first order for roughly two half-lives.

In our radiation product studies, which employed a $^{60}$Co source of radiation, the steady-state concentration of radical anion can be calculated to be much lower. This may explain why we observed other products in addition to 4-nitrocumene.

In aqueous solvents, it appears that the dinitrocumene radical anion is stable on the time scale of pulse radiolysis. In isopropanol–water (70:30, v/v) with NaOH present, the initially generated spectrum shows an absorption maximum at 330 nm and a broad band at *ca* 440 nm. This spectrum is stable to 4 ms, suggesting that the radical anion is responsible for the observed absorbance. The relatively small conversions observed in product studies carried out in this solvent are also explained by the hypothesis of a stable radical anion. Neta[17] has reported that the radical anion of a closely related compound does not undergo cleavage on this time scale in an aqueous medium. Also, Scher and Lichtin[21] reported the formation of a stable radical anion from **1** with an absorption maximum at 310 ± 5 nm. Scher and Lichtin's experiment was carried out in water which was 16 mM in KOH and 1 M in *tert*-butyl alcohol. The observed maximum shifts to slightly longer wavelengths in methanol and Scher and Lichtin measured the rate constant for the dissociation process at $k = 0\cdot5$ s$^{-1}$ in methanol. Moreover, they proved that the main product, which under these conditions is 4-nitrocumene, arises from the 4-nitrocumyl anion. This demonstrates that the reaction sequence that we propose to account for the absorbance at 440 nm in DMF is possible when the rate of dissociation is sufficiently slow. Our observed dissociation rate in DMF is $10^4$ times faster than the methanol reaction, but we suggest that it is still possible to produce the 4-nitrocumyl anion by this route. Of course, the anion is not protonated in DMF as it would be in aqueous or alcoholic solvents.

The overall conclusion for the dinitrocumene system as deduced from the pulse radiolysis data is that the radical anion is stable in water and aqueous solvents at least for a few microseconds, but dissociates at a measurable rate in DMF and in THF. It is interesting that the rate constant for dissociation of $\mathbf{1}^{-\cdot}$ is determined by pulse radiolysis to be faster in THF than in DMF, whereas the rate of reaction of **1** with a given donor radical anion is significantly slower in THF than in DMF. We suggest that this is due to the effect of ion pairing on $k_{diss}$ for this substrate, stabilizing the radical anion relative to the transition state for cleavage. In the radiolysis experiment, where alkali metal ions are not present to form ion pairs, it would appear that the free ion is less stable in THF than in DMF.

The situation with **2** is less clear. The pulse radiolysis experiment with **2** in isopropanol–water–NaOH showed a stable absorption at 295 ± 5 nm. It would seem that this must be the radical anion of **2**, for several reasons. First, neither $NO_2^-$ nor cumyl radical absorbs in this spectral region. $NO_2^-$ has a very weak absorption at 350 nm and an end absorption starting at *ca* 250 nm.[22] The cumyl radical has been reported by several investigators to absorb at 320–325 nm. In well resolved spectra, two peaks appear at *ca* 315 and 325 nm.[23] Moreover, the cumyl radical would disappear in a rapid, second-order process, which is not what we observe. The only possibility would seem to be that the 295 nm absorption is due to $\mathbf{2}^{-\cdot}$, which would mean that it is relatively stable in aqueous solution with NaOH present.

The data for the mononitrocumene **2** in organic solvents (THF and DMF) are interesting but fail to yield rate constants. In THF, the transient spectrum shows absorption maxima at 270 and 310 nm (see Figure 3). These absorptions decay in a second-order fashion. In DMF, the spectrum is not sufficiently different from that observed when DMF alone is irradiated to justify any conclusions. We tentatively assume that our observed transient spectra are due to the cumyl radical, based on the chemical and electrochemical experiments

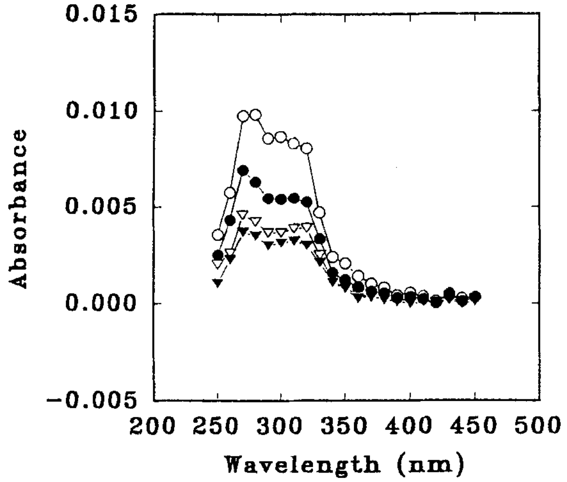


Figure 3. Pulse radiolysis of 2 in THF. ○, 2 μs; •, 11 μs; ▽, 32·3 μs; ▼, 57·3 μs

described in the other sections of this paper which indicate that $2^{-\cdot}$ dissociates more rapidly than $1^{-\cdot}$. Also, our product studies reported in the Experimental section show the clear signature of cumyl radicals. Unfortunately, the spectra taken by themselves are not definitive and could conceivably be due to $2^{-\cdot}$.

One extremely curious result is the formation of a relatively stable absorption centered at 285 nm which appears when 2 is subjected to radiolysis in THF saturated with $O_2$. This cannot be $2^{-\cdot}$, because it would have been oxidized during the pulse. The only (highly speculative) explanation we can offer is that this is the cumylperoxyl radical, $C_6H_5C(CH_3)_2OO^\cdot$, or some species derived therefrom. Simple peroxyl radicals absorb at about 250–260 nm, but tail out to 300 nm and above.[24] Considering that the starting compound absorbs out to about 300 nm, it seems possible that the difference spectrum would show a maximum at 280 nm if the cumylperoxyl radical was being generated. If this is the case, it would mean that an initially generated transient species produces cumyl radicals faster than it reacts with $O_2$. It seems clear from our other experiments that $2^{-\cdot}$ is not sufficiently short lived to meet this criterion. One possibility is that the solvated electrons are trapped by both the $NO_2$ group and the phenyl group and that this gives two different radical anions, $2^{-\cdot}$ and $2^{-\cdot\prime}$:

$$\underset{2^{-\cdot\prime}}{{}^{\cdot-}C_6H_5C(CH_3)_2NO_2} \quad \text{and} \quad \underset{2^{-\cdot}}{C_6H_5C(CH_3)_2NO_2^{-\cdot}}$$

In this scenario, both $2^{-\cdot}$ and $2^{-\cdot\prime}$ are formed from solvated electrons, but the latter dissociates faster than intramolecular electron transfer to the nitro group. Dissociation produces cumyl radicals.

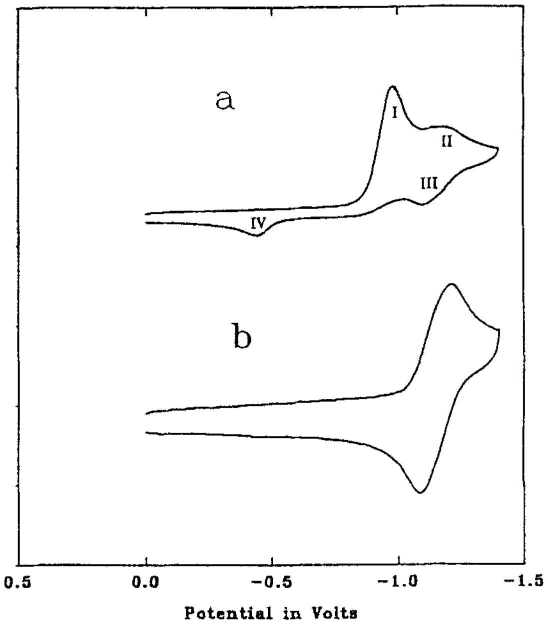


Figure 4. Cyclic voltammograms of (a) 1 at 50 mV $s^{-1}$ and (b) 5 at 200 mV $s^{-1}$ in DMF with 0·1 M TBAP vs SSCE with a glassy carbon working electrode at 25 °C

## Electrochemical approach

A cyclic voltammogram of 1 in DMF at 25 °C is shown in Figure 4(a). The first cathodic wave (I) appears at −0·98 V vs SSCE and no return wave is observed. The peak current is roughly proportional to the square root of the scan rate. However, the wave shifts to slightly more negative potentials with increasing scan rate. Moreover, the wave is sharper than would be expected for a simple one-electron process. Unfortunately, the proximity of a second cathodic wave (II), $E_{pc} = -1 \cdot 18$ V, precludes a more quantitative analysis of its behavior. The second reduction appears to be quasi-reversible at room temperature ($E_{pa} = -1 \cdot 09$ V, III) with $i_{pa}/i_{pc} = 1$ and $E_{pa} - E_{pc} = 90$ mV at a scan rate of 20 mV $s^{-1}$. This latter process apparently is due to reduction of 2,3-di(4-nitrophenyl)-2,3-dimethylbutane (4,4′-dinitrobicumyl), 5, formed by dimerization of $1^\cdot$:

$$2(1^\cdot) \rightarrow \underset{5}{O_2NC_6H_4C(CH_3)_2C(CH_3)_2C_6H_4NO_2} \qquad (8)$$

This was confirmed by cyclic voltammetry on an authentic sample of 5 [Figure 4(b)]. Compound 5 was isolated from bulk electrolysis in DMF. The cyclic voltammogram of 1 also showed a small anodic peak at −0·45 V (IV), which we believe is due to oxidation of the 4-nitrocumyl anion, $1^-$. This peak only appeared if the sweep included prior traversal of the first cathodic wave, suggesting that reduction of $\mathbf{1}^{\cdot}$ to $\mathbf{1}^{-}$ occurs at a potential more positive than $-1{\cdot}15$ V. At room temperature, the peak height of this anodic wave increases with increasing scan rate, suggesting that $\mathbf{1}^{-}$ reacts with adventitious water to an increasing extent as the scan rate is slowed. Wave IV disappears when water is added to the solvent. At low temperature, where it will be seen that the one-electron reduction of **1** becomes reversible, wave IV disappears as I becomes reversible. The cathodic partner of wave IV could not be detected under any conditions, even with repetitive cycling at rapid scan rates.

When the temperature of the electrolysis cell is lowered to $-40$ °C, the oxidation wave associated with peak I (oxidation of $1^{-\cdot}$) became clearly visible at a scan rate of 4015 $\mathrm{mV\,s^{-1}}$ (see Figure 5). At low temperature with rapid scanning, waves II and III disappear, allowing us to treat the remaining voltammogram as representative of a simple EC or ECE (E = heterogeneous electron transfer, C = chemical reaction) process. At 51 200 $\mathrm{mV\,s^{-1}}$, $i_{\mathrm{pc}}/i_{\mathrm{pa}}$ was nearly unity and wave IV had essentially disappeared. At $-40$ °C, the rate of cleavage of $\mathbf{1}^{-\cdot}$ can be readily calculated using the method of Nicholson and Shain,[25] in which the relationship between $i_{\mathrm{pc}}/i_{\mathrm{pa}}$ and scan rate is matched to a published working curve. Using this procedure, the cleavage rate constant for $\mathbf{1}^{-\cdot}$ was calculated to be $11 \pm 3\ \mathrm{s^{-1}}$ at $-40$ °C.

When the same cyclic voltammetric measurements were carried out on **2** in DMF, a single cathodic wave was observed at $-1{\cdot}6$ V vs a saturated sodium-calomel electrode (SSCE). A published $E_{1/2}$ value measured in dimethoxyethane is $-1{\cdot}61$ V.[14] The corresponding anodic wave for this couple is entirely absent even in scans carried out at the fastest available scan rates (51 200 $\mathrm{mV\,s^{-1}}$) at $-40$ °C. The temperature was further lowered by immersion of the electrochemical cell in a solid carbon dioxide–acetone bath. It was then possible to measure a weak anodic wave at a temperature estimated to be $-70$ °C (see Figure 6), but the kinetic analysis at this temperature was complicated by slow heterogeneous electron transfer. The ratio $i_{\mathrm{pc}}/i_{\mathrm{pa}}$ decreases with increasing scan speed, as expected for the EC or ECE mechanism with the chemical step being relatively fast. That the chemical step is dissociation of the initially formed radical anion to give cumyl radical is confirmed by bulk electrolysis studies described in the Experimental section.

The cyclic voltammetric curves allowed the estimation of the rate constant for dissociation of $\mathbf{2}^{-\cdot}$ as *ca* $100\ \mathrm{s^{-1}}$ at $-70$ °C. It was also possible to measure the

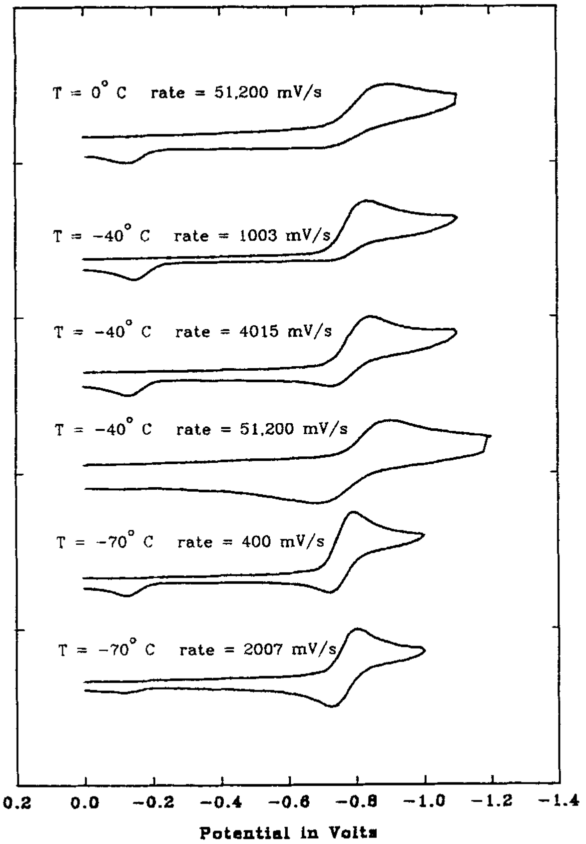


Figure 5. Cyclic voltammograms of **1** at reduced temperature as described in the Experimental section

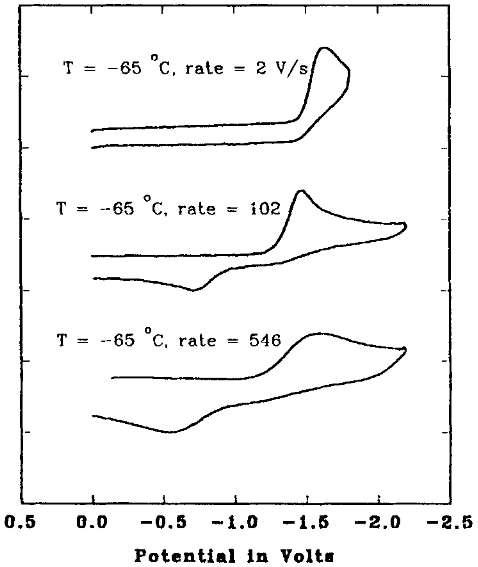


Figure 6. Cyclic voltammograms of **2** at reduced temperature as described in the Experimental section

dissociation rate constant for $\mathbf{1}^{-\cdot}$ under the same conditions at $1{\cdot}8 \pm 0{\cdot}4\ \mathrm{s}^{-1}$. Hence it would appear that the dissociation of $\mathbf{2}^{-\cdot}$ is roughly 50 times faster than the dissociation of $\mathbf{1}^{-\cdot}$ at −70 °C.

With data at two different temperatures for the dissociation rate of $\mathbf{1}^{-\cdot}$, it is possible, in principle, to carry out an Arrhenius extrapolation to obtain a room-temperature value for the dissociation rate constant; however, such a calculation is rendered imprecise by the uncertainty in the temperature and conditions for the lowest temperature electrochemical experiments. Using electrochemical data alone and reasonable error assumptions, the value of the rate constant for the dissociation of $\mathbf{1}^{-\cdot}$ can be calculated to be between 50 and $3 \times 10^3\ \mathrm{s}^{-1}$ at 25 °C.

### Comparison of results from different methods

Direct measurement of the rate constant for the dissociation of $\mathbf{1}^{-\cdot}$ was possible by pulse radiolysis at room temperature and from cyclic voltammetry at −40 °C. The value of $k_{\mathrm{diss}}$ is half of the observed loss of absorbance and therefore $k_{\mathrm{diss}} = 2{\cdot}1 \times 10^3$ at 25 °C in DMF. This falls at the upper edge of the range of values extrapolated from low-temperature electrochemical data and is reasonably close to the estimate made from the rate of reaction of **1** with $\mathrm{AQ}^{-\cdot}$. Even given the uncertainties inherent in these other techniques, the fact that this value is consistent with values estimated from the chemical and electrochemical experiments offers assurance that the process measured by pulse radiolysis is in fact the dissociation of $\mathbf{1}^{-\cdot}$.

Pulse radiolysis offers little help in measuring the rate of dissociation of $\mathbf{2}^{-\cdot}$. However, the electrochemical experiments carried out at −70 °C demand that $k_{\mathrm{diss}}$ for $\mathbf{2}^{-\cdot}$ in DMF is at least a factor of 50 larger than that for $\mathbf{1}^{-\cdot}$ at this temperature. The chemical experiments suggest that this factor is roughly 100, increasing our confidence that the weak oxidation wave seen in the cyclic voltammogram of **2** is in fact that for $\mathbf{2}^{-\cdot}$. This would put the dissociation rate constant for $\mathbf{2}^{-\cdot}$ at $k_{\mathrm{diss}} = 10^5\text{–}10^6\ \mathrm{s}^{-1}$ at 25 °C in DMF. A dissociation with a rate constant of this magnitude should have been observable by pulsed radiolysis in DMF, but $\mathbf{2}^{-\cdot}$ could not be detected above solvent background in this medium.

### Relationship to previous studies

Although we cannot measure $k_{\mathrm{diss}}$ for $\mathbf{2}^{-\cdot}$ at room temperature, we feel safe in saying that it is between 50 and 1000 times greater than that for $\mathbf{1}^{-\cdot}$. We had earlier estimated a free energy advantage for reaction (6) over reaction (5) of $10\ \mathrm{kcal\,mol}^{-1}$ (1 kcal = 4·184 kJ) due to the advantage in stability of 4-nitrophenoxide ion over phenoxide ion. Differences in reduction potential make $\mathbf{4}^{-\cdot}$ slightly less stable than $\mathbf{3}^{-\cdot}$, producing an additional *ca* $1\ \mathrm{kcal\,mol}^{-1}$ advantage for reaction (6). From this $11\ \mathrm{kcal\,mol}^{-1}$ advantage must be subtracted any stability advantage of 4-nitrobenzyl radical over benzyl radical. The magnitude of this stabilization is not known with certainty, but work by Creary *et al.*[26] in which the effect of substituents on cyclopropane ring opening to give benzylic radicals was determined shows that the 4-nitro-substituted system undergoes ring opening *ca* four times faster than the unsubstituted system. This factor is not large and, moreover, whatever its magnitude, we would expect it to offer the same advantage for reaction (3) over reaction (4) as it does for reaction (5) over reaction (6). In comparing reaction (3) with reaction (4), the main difference in thermodynamic driving force is the more negative reduction potential of **2** compared with **1**. This difference of *ca* 0·5 V favoring reaction (4) over reaction (3) is essentially equal to the advantage of reaction (6) over reaction (5), yet our previous studies showed that reaction (5) is at least $10^4$ times faster than reaction (6). The present study shows that reaction (4) is 50–1000 times faster than reaction (3). Why do the electron apportionment restrictions which were suggested to account for the slowness of the $D_{\mathrm{R}}$ mode in the first study not have the same effect on the $D_{\mathrm{R}}$ mode in the present study?

One factor which must be kept in mind is the greater driving force for both reactions (3) and (4) compared with reactions (5) and (6). The greater stability of nitrite ion compared with phenoxide ion may be estimated from the relative $\mathrm{p}K_{\mathrm{a}}$ values of nitrous acid ($\mathrm{p}K_{\mathrm{a}} = 3{\cdot}3$)[27] and phenol ($\mathrm{p}K_{\mathrm{a}} = 10{\cdot}0$)[28] in aqueous solution. For substituted phenols, we have found that a difference of about 2 $\mathrm{p}K_{\mathrm{a}}$ units produces a factor of roughly 25 in rate constant for reaction (5). Hence a very rough kinetic prediction may be made by multiplying our observed rate constant for loss of phenoxide in reaction (5) ($k = 1{\cdot}7 \times 10^{-4}$ in DMSO)[10] by $25^{6\cdot 7/2}$ for the change to nitrite and by 20 for the change from primary to tertiary to give $k_{\mathrm{est}} = 10^2\ \mathrm{s}^{-1}$. (Meot-Ner *et al.*[29] showed that one methyl group increases the rate of dissociation of α-substituted 4-nitrobenzyl halides by a factor of 20. Additional alkyl groups slowed the reaction, but the alkyl groups used were bulky.) Some additional allowance must be made for the fact that the alkyl group is attached to nitrogen rather than the oxygen of the leaving group. Given the uncertainty in these various assumptions, it would seem that our observed $k_{\mathrm{diss}}$ for $\mathbf{1}^{-\cdot}$ of $2{\cdot}1 \times 10^3\ \mathrm{s}^{-1}$ is about what would be expected, based on the structural differences between $\mathbf{1}^{-\cdot}$ and $\mathbf{3}^{-\cdot}$. Of course, $\mathbf{2}^{-\cdot}$ and $\mathbf{4}^{-\cdot}$ cannot be compared in the same way because the cleavage of $\mathbf{4}^{-\cdot}$ was too slow to measure, but it is clear that the observed $k_{\mathrm{diss}}$ for $\mathbf{2}^{-\cdot}$ is closer to what would be expected on thermochemical grounds than is the behavior of $\mathbf{4}^{-\cdot}$.

The reasons for this are far from clear, but several differences between the two cases warrant exploration. One factor which may be exerting an effect is the change from cleavage of a C—O bond in $\mathbf{3}^{-\cdot}$ and $\mathbf{4}^{-\cdot}$ to a C—N bond in $\mathbf{1}^{-\cdot}$ and $\mathbf{2}^{-\cdot}$. The bond polarization effect discussed[10] in connection with $\mathbf{3}^{-\cdot}$ and $\mathbf{4}^{-\cdot}$ would be lessened for $\mathbf{1}^{-\cdot}$ and $\mathbf{2}^{-\cdot}$. It is also possible that the fact that **4** contains an ether oxygen attached to the electron-accepting ring uniquely confers some special stability to $\mathbf{4}^{-\cdot}$ or destabilizes the transition state through which *it* undergoes cleavage. Lazana *et al.*[30] have shown that the preferred conformation for R—O—Ar$^{-\cdot}$ is that with the R—O bond in the plane of the aromatic ring. However, the energy difference between this and an orthogonal conformation is small. The fact that nitroanisole has a more negative reduction potential than nitrotoluene[31] and that this increased difficulty of reduction extends even to unsubstituted aryl ethers[32] would seem to indicate that bonding interactions between the aromatic ring and the non-bonded electrons on oxygen are substantially diminished after adding an electron to the ring. It seems unlikely to us that the residual interaction would be strong enough to explain the preferences we have observed for $D_N$ cleavage in ether radical anions.

Another, particularly intriguing, difference between the ethers and the nitrocumenes is that the thermochemical advantage for $\mathbf{2}^{-\cdot}$ over $\mathbf{1}^{-\cdot}$ is on the precleavage side of the equation for the cleavage reaction rather than in the product as for $\mathbf{4}^{-\cdot}$ vs $\mathbf{3}^{-\cdot}$. We have previously suggested that for the cleavage of $\mathbf{4}^{-\cdot}$, product stability is not 'felt' at the transition state as effectively for $D_R$ type reactions because the interaction between the extra electron in the $\pi$ system and its potential partner in the $\sigma$ bond has not developed at the transition state. It seems possible to us that the activation energy would be lowered more by raising the energy of the radical anion, which is what happens in going from $\mathbf{1}^{-\cdot}$ to $\mathbf{2}^{-\cdot}$, than by increasing the stability of the product anion as involved in the comparison of reaction (5) with reaction (6). We plan to examine cases related to reaction (6) in which the substituent on the phenoxyl moiety is changed in such a way as to make its reduction potential comparable to that of **2**.

## EXPERIMENTAL

*Solvents and reagents. N,N*-Dimethylformamide (DMF) was refluxed with calcium hydride at 15–20 Torr (1 Torr = 133·3 Pa) for 2 h, fractionally distilled at this pressure and stored under argon. Tetrahydrofuran (THF) was distilled from a solution of benzophenone ketyl under argon and stored under argon. Donor compounds were of the best grade commercially available. *N,N*-Dimethyl-4-nitroaniline[33] and 2,3-dimethyl-2,3-diphenylbutane[14] were prepared by published procedures.

$\alpha$,*p*-Dinitrocumene (**1**) was prepared as described by Kornblum *et al.*[34] and its physical properties and spectral characteristics were identical with those reported.

$\alpha$-Nitrocumene (**2**) was prepared as described by Kornblum and co-workers[7,35] and its physical properties and spectral characteristics were identical with those reported.

*Preparation of solutions of radical anion donors.* The appropriate amount of radical anion precursor, usually 1–2 mmol, and a PTFE-coated stirring bar were placed in a round-bottomed flask protected by a Mininert valve (Wilmad Glass). The flask was repeatedly evacuated and filled with argon through a high-vacuum, screw-valve PTFE stopcock. Small pieces of freshly cut potassium metal were added under an argon flow and finally solvent (10–20 ml) was added through the Mininert valve using a gas-tight syringe. The mixture was stirred at *ca* 25 °C for about 12 h, by which time the potassium metal had disappeared and the color of the radical anion was evident in the solution. Solutions which were used appeared homogeneous. In some cases, particularly with 1,3-dinitrobenzene, heating was required to effect complete reaction. For 2,4-dinitroanisole and 2-nitroanisole, the direct preparation using potassium metal was unsatisfactory and the radical anion solutions were prepared by treating a solution of the nitro compound in the desired solvent with a solution of the potassium salt of naphthalene radical anion in THF. Samples of all donor radical anion solutions were tested by bubbling in oxygen gas followed by the work-up described below. In cases where the donor precursor was not recovered by this procedure, the donor solution was not used.

*Reaction of radical anion solutions with 1 and 2.* In the same type of reaction vessel as described above, the appropriate amount of a stirred solution of **1** or **2** in the reaction solvent was treated with the radical anion solution using a gas-tight syringe. After the required reaction time, the reaction mixture, usually about 10 ml, was poured into 30 ml of water and extracted with 30 ml of dichloromethane, adding a small amount of saturated aqueous sodium chloride. For DMF reactions, the dichloromethane solution was washed with three 20 ml portions of water. The dichloromethane solution was dried with anhydrous sodium sulfate and the solvent removed under reduced pressure. Products from reaction mixtures involving **2** were then analyzed by NMR spectrometry. The residues from work-up of reactions with **1** were treated with a small amount of benzene and the white solid precipitate collected by centrifugation. This solid proved to be 2,3-bis(4-nitrophenyl)-2,3-dimethylbutane (**5**). When recrystallized from acetone, its m.p. was 285–286 °C, which is somewhat higher than that reported (lit.[36] m.p. 265 °C, decomp.), but its spectral characteristics showed clearly that the structure was that assigned. $^1$H NMR ($CDCl_3$): $\delta$ 8·082, 8·037, 7·203, 7·157 (8 H), 1·38 ppm (s, 12H). IR (KBr): 2987, 1513, 1085, 1015, 854 cm$^{-1}$. This compound was very insoluble in most solvents.

For reactions of **1**, the product yield was calculated from the weight of precipitated **5** plus the small amount of this compound evident in the NMR spectrum of the mixture. The product from the reaction of **2** with the various electron donors was 1,1,2,2,-tetramethyl-1,2-diphenylethane (bicumyl), as shown by comparison with authentic material prepared following the procedure of Hoffmann *et al.*[13] No products other than the bicumyl type were detected by NMR in any of the reaction mixtures and yields calculated from the loss of starting nitro compound were in reasonable agreement with the amount of bicumyl produced.

*Electrochemical experiments.* These were performed using either an EG&G PAR Model 273 potentiostat/galvanostat or a Bioanalytical Systems Model 100A electrochemical analyzer. Electrolytes were of electrometric grade from Southwestern Analytical. They were recrystallized from methanol and dried in a vacuum oven prior to use in kinetic runs. The working electrode was a freshly polished platinum or glassy carbon disk, while a platinum coil and a saturated sodium calomel electrode (SSCE) served as counter and reference electrodes, respectively.

The low-temperature kinetic runs were carried out under similar conditions except that a platinum microelectrode (10 $\mu$m diameter) was employed as a working electrode in some instances. Also, a silver wire was used as a (pseudo) reference electrode at low temperature in order to avoid freezing of the SSCE. The silver wire was fully insulated by heat-shrinkable PTFE tubing except for the tip, and the uninsulated portion was placed within 1–2 mm of the working electrode surface to minimize cell resistance. IR compensation was utilized for all kinetic experiments. In addition, it was found that an *in situ* pretreatment of the platinum working electrode (several excursions to the cathodic solvent limit) greatly enhanced the heterogeneous electron-transfer rate, thus allowing faster scan rates to be employed.

*Pulse radiolysis.* Pulse radiolysis was carried out at the Center for Fast Kinetics Research using a system described previously.[37] Solutions were normally 2 mM and were bubbled with argon gas for at least 0·5 h before use. Pulses of 4 MeV electrons of 50–500 ns were employed in the radiolysis studies of **1** and **2**.

*Products from radiolysis.* Product identification studies were carried out after radiation of **1** and **2**. Solutions of **1** (10–15 mM) in either DMF, THF or isopropanol–water (1:1, v/v) given a dose of 1·5 Mrad from a $^{60}$Co source gave only very small amounts of several products, as judged from UV (250 nm)-detected peak intensities. In the DMF run, one of these corresponded in retention time to 4-nitrocumene, but neither 4-nitro-$\alpha$-methylstyrene nor **5** was present. Other small peaks were not identified. In THF, no significant amount of 4-nitrocumene or any of the other suspect compounds was produced. The main observed peak may have been from coupling of solvent radical with the 4-nitrocumyl radical, as could be expected based on results obtained with **2**. However, it was not possible to confirm this because **1**, which was the preponderant compound in all reaction mixtures, was unstable under gas chromatographic conditions.

In the case of **2**, a 20 mM solution in THF was given a dose of 64 Mrad in 1600 800 ns pulses (shaking after every 400 pulses). The starting **2** was reduced to about 20% of its initial concentration. HPLC on a $C_{16}$ column with UV detection at 260 nm showed peaks corresponding in retention time to cumene, $\alpha$-methylstyrene and bicumyl. Two other substantial peaks appeared and these are believed to correspond to peaks assigned by gas chromatographic–mass spectrometric (GC–MS) analysis to cumyltetrahydrofuran and 4-methyl-2,4-diphenylpentene (probably the 2-isomer). The former shows a parent ion at $m/z$ 190 with major fragments at $m/z$ 119 (cumyl cation) and 71 (tetrahydrofurfuryl cation). The latter showed an apparent parent ion at $m/z$ 236 with significant ions at $m/z$ 221 ($M - CH_3$), 143, 128 and 91. A number of what appeared to be dimers of tetrahydofurfuryl radical were also evident by GC–MS. Analysis of data obtained by GC with flame ionization detection in combination with HPLC information indicates approximate relative yields of the five major products of cumene, bicumyl, $\alpha$-methylstyrene, cumyl-THF and diphenylmethylpentene of 2·1:1·3:1·0:1·0:0·25. The same products, with the exception of the cumyl-THF, were observed on radiolysis in DMF with less cumene and more bicumyl. For low-dose runs in both of these solvents, relatively less diphenylmethylpentene was observed. In high-dose runs carried out in isopropanol–water, the conversion of nitro compound was lower than in DMF or THF and the only significant product evident by HPLC was the strongly UV-absorbing $\alpha$-methylstyrene. For runs with a dose of 1·5 Mrad using $^{60}$Co, the amount of $\alpha$-methylstyrene and diphenylmethylpentene was about the same for reactions run in all three solvents, but bicumyl was not observed using isopropanol–water.

*Products from electrolysis.* Electrolysis of a 10 mM solution of **1** in DMF with tetrabutylammonium perchlorate (TBAP) (0·1 M) at 1·0 V vs. SCE gave a white precipitate. HPLC analysis showed that both the precipitate and the material remaining in solution were pure **5**. The precipitate after washing with methanol melted at about 295 °C, with some discoloration preceding melting. The melting point was not reproducible, seeming to depend on heating rate.

After electrolysis of a 10 mM solution of **2** in DMF with TBAP (0·1 M) at 2·0 V vs. SCE with total charge passed equivalent to 1·3 electrons per molecule of **2**, slightly less than half of **1** was converted to bicumyl, half to cumene and *ca* 10% to α-methylstyrene.

## ACKNOWLEDGMENTS

The authors thank the Research Corp. for a Research Opportunity Award to R. D. G. which helped to support this research. Additional support came from BRSG SO7 RRO7114-21 awarded by the Biomedical Research Support Grant Program, Division of Research Resources, National Institute of Health. Pulsed radiolysis experiments were carried out at the Center for Fast Kinetics Research, supported by NIH (RR 00886) and by the University of Texas at Austin. Technical assistance and help with data interpretation from Drs E. Gaillard, S. J. Atherton and other members of the CFKR staff were invaluable.

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