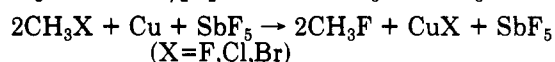
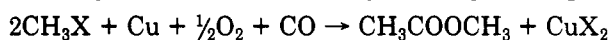
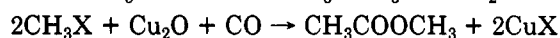
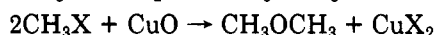
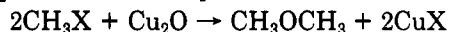


Table IV. Oxidative Carbonylation of MeBr with CO/Cu/O₂ over SbF₅-Graphite Catalyst (270 °C, 140 atm, CH₃Br/CO/O₂ = 1.5:44:1, Cu/SbF₅ = 2.4:1)

time (h)	yield, mol %		
	MeF	Me ₂ O	AcOMe
1	13	5	23
2	10	6	36
4	12	6	34
6	10	7	38
22	6	5	51
25	5	4	48

fluoride) reacts with carbon monoxide and copper oxides or copper and oxygen over SbF₅-graphite catalyst to give methyl acetate. The reaction is an oxidative carbonylation because it proceeds only when a copper oxide or copper and oxygen is present. The major byproduct of the reaction is dimethyl ether (as well as methyl fluoride formed by halogen exchange with the catalyst). When Cu₂O is used, AcOMe and Me₂O are formed in comparable amounts in competing reactions. With Cu and Cu/O₂, AcOMe becomes the major product. AcOMe was found not to be produced via prior formation of Me₂O. AcOMe and Me₂O are formed in parallel reactions.



The results of the studied reactions showed that the preferred system for oxidative carbonylation of methyl halides to AcOMe uses CO and CuO or Cu powder and molecular oxygen in conjunction with SbF₅-graphite catalyst. The optimum conditions of the reaction are at 270 °C and 140 atm pressure.

Experimental Section

Materials and Catalyst. Carbon monoxide of 99.5% minimum purity (Matheson) was used in all experiments without further purification. According to GC analysis carbon monoxide contained small impurities of methane ($\approx 0.1\%$) and ethane ($\approx 0.05\%$). Cuprous oxide, cupric oxide, and copper powder were as used previously.¹ Purified argon was used for flushing and blanketing the reactors. Oxygen used was extra dry (Matheson). Methyl halides (Matheson) were used as received. Intercalated SbF₅-graphite catalyst was obtained from Alfa Products.

General Experimental Procedure and Analysis. The pressure reactor, general procedures used, and analytical methods were described previously.¹

In typical runs 17.6 mmol of CH₃Br (1 mL) or 20 mmol of CH₃F or CH₃Cl was used together with 10 mmol of Cu₂O and 1.7 g of SbF₅-graphite catalyst. The molar ratio of MeBr/CO/Cu₂O in typical experiments was about 1.7:50:1 and the MeBr/SbF₅ catalyst ratio was 4.5. The results are summarized in the tables.

Acknowledgment. Our work was supported by the National Science Foundation and the Loker Hydrocarbon Research Institute.

Registry No. MeBr, 74-83-9; MeCl, 74-87-3; MeF, 593-53-3; CO, 630-08-0; Cu₂O, 1317-39-1; SbF₅, 7783-70-2; Me₂O, 115-10-6; AcOMe, 79-20-9; Cu, 7440-50-8.

Electrochemical Reduction of *p*-Nitrophenyl Azide: Evidence Consistent with the Formation of *p*-Nitrophenylnitrene Anion Radical as a Short-Lived Intermediate

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The electrochemical reduction of *p*-nitrophenyl azide in DMF, acetonitrile, and butyronitrile is initially a one-electron process that affords the corresponding anion radical as a transient intermediate. Although *p*-O₂NC₆H₄N₃⁻ is too short-lived to be observed by our methods, product studies are consistent with a reaction pathway in which *p*-O₂NC₆H₄N₃⁻ decomposes by loss of dinitrogen to give the corresponding nitrene anion radical, *p*-O₂NC₆H₄N⁻, as a short-lived intermediate. In the absence of added reagents, 4,4'-O₂NC₆H₄N=NC₆H₄NO₂²⁻ is formed as the principal product via dimerization of anion radicals. In DMF, hydrogen atom abstraction and carbonyl addition/radical β -fragmentation are observed also as reaction pathways and become increasingly important processes with decreasing current density and increasing temperature. The products of the two latter reaction pathways are *p*-O₂NC₆H₄NH⁻ and *p*-O₂NC₆H₄N⁻CON(CH₃)₂, respectively. In the presence of the weak oxygen acid (CF₃)₂CHOH, reduction of *p*-O₂NC₆H₄N₃ is a two-electron process that yields dinitrogen and *p*-O₂NC₆H₄NH₂ as products. In the presence of weak methylene carbon acids such diethyl malonate, a chain reaction involving diazo transfer ensues, producing the corresponding diazoalkane and *p*-O₂NC₆H₄NH₂ in high yields.

Introduction

Dissociative electron attachment to diazoalkanes (R₂C=N₂) has been shown to be a convenient and ready method for the preparation of certain carbene anion radicals (R₂C⁻) in the gas¹ and condensed phases.² In the

condensed phase, R₂C⁻ formation has only been observed from those R₂C=N₂⁻ where the negative charge has been stabilized by electron-withdrawing substituents (e.g., (EtO₂C)₂C⁻)^{2a} or where the carbene carbon center has been incorporated into a cyclopentadienyl ring.^{2d} In the few

(1) (a) McDonald, R. N.; Chowdhury, A. K.; Setser, D. W. *J. Am. Chem. Soc.* **1980**, *102*, 6491. (b) Zittle, P. F.; Ellison, G. B.; O'Neil, S. V.; Lineberger, W. C.; Reinhardt, W. R. *J. Am. Chem. Soc.* **1976**, *98*, 3731. (c) McDonald, R. N.; Chowdhury, A. K.; McGhee, W. D. *J. Am. Chem. Soc.* **1984**, *106*, 4112. (d) McDonald, R. N.; Gung, W. Y. *J. Am. Chem. Soc.* **1987**, *109*, 7328.

(2) (a) Van Galen, D. A.; Young, M. P.; Hawley, M. D.; McDonald, R. N. *J. Am. Chem. Soc.* **1985**, *107*, 1465. (b) Van Galen, D. A.; Hawley, M. D. *J. Electroanal. Chem.* **1987**, *218*, 227. (c) Bethell, D.; Parker, V. D. *J. Am. Chem. Soc.* **1986**, *108*, 7194. (d) Bethell, D.; Parker, V. D. *J. Chem. Res.* **1987**, 116. (e) McDonald, R. N. *Tetrahedron* **1989**, *45*, 3993. (f) Bethell, D.; Parker, V. D. *Acc. Chem. Res.* **1988**, *21*, 400.

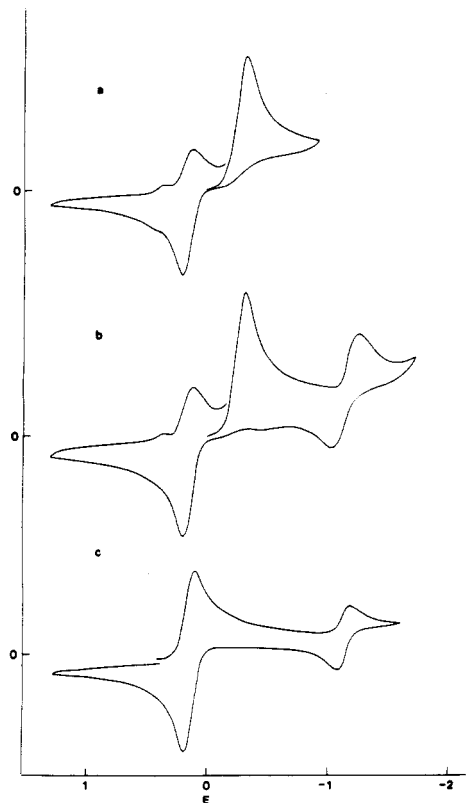


Figure 1. (a and b) Cyclic voltammetric behavior of a 2.88 mM solution of $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3$ in CH_3CN -0.1 M $n\text{-Bu}_4\text{NClO}_4$ at 22 °C. The scan was initiated in the negative-going direction from an initial potential of 0.0 V at a rate of 0.2 V/s. Working electrode: 0.20 cm² planar platinum button. Cathodic switching potential: -1.0 and -1.8 V for (a) and (b), respectively. (c) Cyclic voltammetric behavior of 4,4'-dinitroazobenzene in CH_3CN -0.1 M $n\text{-Bu}_4\text{NClO}_4$ at 22 °C. The scan was initiated in the negative-going direction from an initial potential of 0.4 V at a rate of 0.2 V/s. Working electrode: 0.20 cm² planar platinum button.

carbene anion radicals that have been prepared, reports of the chemical reactions of R_2C^- in the condensed phase have been limited thus far to those involving hydrogen atom abstraction from the solvent and protonation by added electroinactive Brønsted acids. In contrast, an impressive variety of chemical reactions have been reported for the carbene anion radicals in the gas phase.¹

As a part of our continuing study of carbene and nitrene anion radicals, the preparation of an aryl nitrene anion radical in the condensed phase was attempted. The experimental procedure is analogous to that used for the successful preparation of PhN^- in the gaseous phase, viz., the reductive elimination of N_2 from an aryl azide.³ In order to stabilize the initial aryl azide anion radical for possible kinetics studies and to facilitate the electrochemical study of the intermediates and products, a nitro substituent was placed as a reporter group in the *para* position of PhN_3 .

Results and Discussion

Acetonitrile. The product distribution that arises from the electrochemical reduction of $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3$ is a function of the solvent, rate of reduction of $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3$, temperature, and the nature and amount of an added electroinactive proton donor or carbonyl trapping agent. The simplest redox behavior is obtained in acetonitrile at

room temperature in the absence of an added proton donor or carbonyl trapping agent. When the cathodic switching potential is more positive than -1.0 V (Figure 1a), the cyclic voltammogram for the reduction of $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3$ in 0.1 F $n\text{-Bu}_4\text{NClO}_4\text{-CH}_3\text{CN}$ consists of a single cathodic peak near -0.32 V (vs $\text{CdCl}_2/\text{Cd}(\text{Hg})$; $E_{\text{CdCl}_2/\text{Cd}(\text{Hg})}$ vs SCE = -0.75 V) on the first negative-going scan. This process was shown by single potential step chronoamperometry to be diffusion controlled at a planar platinum electrode ($A = 0.20$ cm²) in the time range $3 \text{ ms} \leq t \leq 10 \text{ s}$ and to involve one electron per molecule of $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3$. The n value was ascertained by comparison of the chronoamperometric $it^{1/2}/CA$ value for the reduction of $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3$ with that for the known one-electron reduction of 1,4-dicyanobenzene to its stable anion radical.

Although the anion radical of $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3$ is too unstable to be reoxidized on the reverse, positive-going sweep at any scan rate $v \leq 100$ V/s and $T \geq -37$ °C, the single electroactive product arising from the decomposition of $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3^{\cdot-}$ affords two chemically reversible redox processes near 0.18 and -1.20 V (Figure 1b). By comparison of the cyclic voltammogram for $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3$ (Figure 1b) with that for an authentic sample of 4,4'-dinitroazobenzene, the redox couple near 0.18 V (Figures 1a and 1b) has been determined to be due to the reversible, two-electron reduction of $4,4'\text{-O}_2\text{NC}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4\text{NO}_2$ to its dianion while the reversible couple near -1.20 V arises from the reversible, one-electron reduction of $4,4'\text{-O}_2\text{NC}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4\text{NO}_2^{\cdot-}$ to its trianion radical. Evidence for the assignment of these several n values is found in the ratio of the cyclic voltammetric cathodic peak heights for the reduction of $4,4'\text{-O}_2\text{NC}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4\text{NO}_2$ to $4,4'\text{-O}_2\text{NC}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4\text{NO}_2^{\cdot-}$ and of $4,4'\text{-O}_2\text{NC}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4\text{NO}_2^{\cdot-}$ to $4,4'\text{-O}_2\text{NC}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4\text{NO}_2^{2-}$ (Figure 1c). The experimental value of 2.85 for this ratio is in excellent agreement with the predicted value of $(n_1/n_2)^{3/2} = (2/1)^{3/2} = 2.83$.⁴ Apparently, the reduction of $4,4'\text{-O}_2\text{NC}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4\text{NO}_2$ to $4,4'\text{-O}_2\text{NC}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4\text{NO}_2^{\cdot-}$ occurs in a single two-electron step because the *p*-nitrophenyl moieties in $4,4'\text{-O}_2\text{NC}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4\text{NO}_2$ are not conjugated in this solvent-electrolyte system at these temperatures.

***N,N*-Dimethylformamide (DMF).** As in acetonitrile, the only discernible electroactive product arising from the reduction of $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3$ in 0.1 F $n\text{-Bu}_4\text{NClO}_4\text{-DMF}$ at a temperature of -51 °C is $4,4'\text{-O}_2\text{NC}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4\text{NO}_2^{\cdot-}$ (Figure 2a). In DMF, however, additional redox processes appear when the temperature is increased. For example, at room temperature (Figure 2b), the single two-electron reversible process that was observed near 0.20 V for the $4,4'\text{-O}_2\text{NC}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4\text{NO}_2/4,4'\text{-O}_2\text{NC}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4\text{NO}_2^{\cdot-}$ redox couple at -51 °C is seen now to consist of two closely spaced one-electron reversible processes for the stepwise reduction of $4,4'\text{-O}_2\text{NC}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4\text{NO}_2$ to $4,4'\text{-O}_2\text{NC}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4\text{NO}_2^{\cdot-}$ (Figure 2c). In addition, the irreversible reduction of $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3$ gives rise to two irreversible anodic peaks near 0.90 and 1.22 V on the reverse, positive-going sweep (Figure 2b). The relative magnitudes of these latter peaks increase at the expense of those arising from the oxidation of $4,4'\text{-O}_2\text{NC}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4\text{NO}_2^{\cdot-}$ with decreasing scan rate and increasing temperature. The anodic peaks at 0.90 and 1.22 V are attributed to the irreversible oxidation of $p\text{-O}_2\text{NC}_6\text{H}_4\text{NH}^-$ and $p\text{-O}_2\text{NC}_6\text{H}_4\text{N-CONMe}_2$, respectively. The assignments are based upon a comparison of the redox behavior that is shown in Figure 2b with those of authentic samples of $p\text{-O}_2\text{NC}_6\text{H}_4\text{NH}^-$ and $p\text{-O}_2\text{NC}_6\text{H}_4\text{N-CON}(\text{CH}_3)_2$. The latter species were prepared by the addition of Me_4NOH to so-

(3) (a) McDonald, R. N.; Chowdhury, A. K. *J. Am. Chem. Soc.* 1980, 102, 5118. (b) McDonald, R. N.; Chowdhury, A. K.; Setser, D. W. *J. Am. Chem. Soc.* 1981, 103, 6599.

Table I. Coulometric and Product Studies for the Reduction of *p*-Nitrophenyl Azide in *N,N*-Dimethylformamide^{a,b}

entry no.	concn (mM)	supporting electrolyte	added component	n (e ⁻)	product yield, %					
					ArNH ₂	ArN ₃	ArN ₂	ArNHCOCH ₃	ArN-HCON-Me ₂	ArNHN-(CONMe ₂)-Ar
1	8.24	<i>n</i> -Bu ₄ NClO ₄		0.96	39	6	6		27	15
2	4.93	<i>n</i> -Bu ₄ NClO ₄		0.91	40	4	6		29	16
3	3.85	<i>n</i> -Bu ₄ NClO ₄	(CF ₃) ₂ CHOH	2.40	100	trace				
4 ^c	2.94	<i>n</i> -Bu ₄ NClO ₄	(EtO ₂ C) ₂ CCH ₂	0.10	101					
5	2.33	LiClO ₄	(CH ₃ CO) ₂	0.92	41 (53)	22		37 (47)		
6	2.19	KClO ₄	(CH ₃ CO) ₂	0.32	32 (58)	45		21 (41)		
7	3.77	Me ₄ NPF ₆	(CH ₃ CO) ₂	0.74	67 (67)	trace		37 (37)		
8	3.12	<i>n</i> -Bu ₄ NClO ₄	(CH ₃ CO) ₂	0.86	75 (75)	trace		26 (26)		

^a Reductions were effected at a platinum gauze electrode at a potential of -0.30 V. The concentration of the supporting electrolyte is 0.1 M. The yields in parentheses are based upon the amount of *n*-nitrophenyl azide consumed. When (CH₃CO)₂ was added as an anion radical trap, [(CH₃CO)₂]/[*p*-O₂NC₆H₄N₃] was approximately 10. When (CF₃)₂CHOH was present as a proton donor, [(CF₃)₂CHOH]/[*p*-O₂NC₆H₄N₃] was approximately 6. ^b Abbreviation used: Ar = *p*-O₂NC₆H₄. ^c (EtO₂C)₂C=N₂ was also formed in 95% yield.

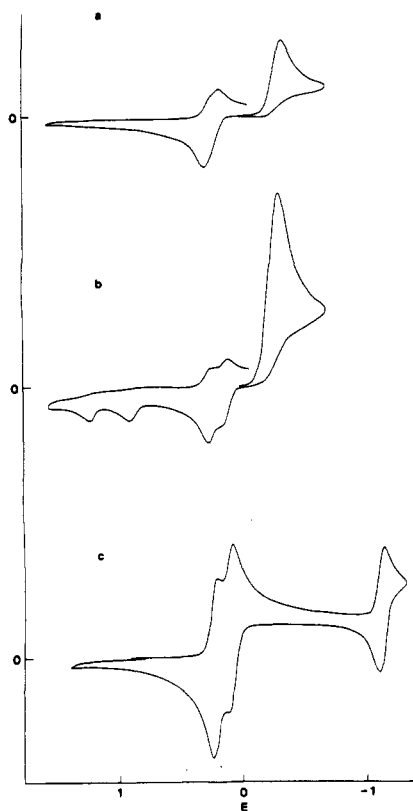


Figure 2. (a and b) Cyclic voltammetric behavior of a 3.0 mM solution of *p*-O₂NC₆H₄N₃ in DMF-0.1 M *n*-Bu₄NClO₄ at (a) -51 °C, (b) 22 °C. The scan was initiated in the negative-going direction from an initial potential of 0.0 V at a rate of 0.2 V/s. Working electrode: 0.20 cm² planar platinum button. (c) Cyclic voltammetric behavior of a 2.84 mM solution of 4,4'-dinitroazobenzene in DMF-0.1 M *n*-Bu₄NClO₄ at 22 °C. The scan was initiated in the negative-going direction from an initial potential of 0.8 V at a rate of 0.2 V/s. Working electrode: spherical platinum.

lutions of the corresponding conjugate acids.

Reverse current chronopotentiometry was used to identify several of the important steps in the pathways leading from reactants to products. First, theory predicts that the reverse transition time should equal the forward electrolysis time when $i_a = |0.414i_c|$ and the number of electrons in the forward and reverse steps is equal.⁴ With this ratio of current densities in the present experiment, the sum of the reverse transition times for the stepwise

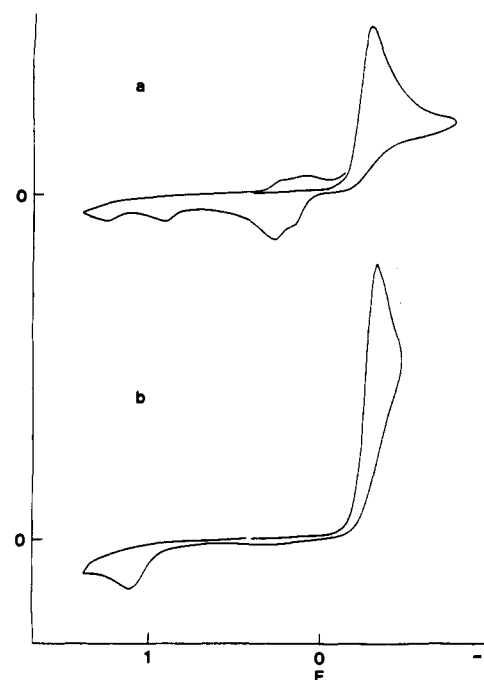
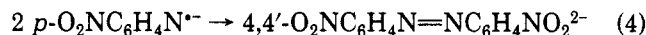
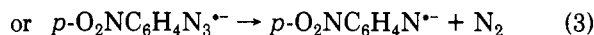
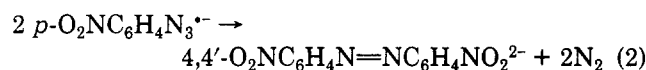
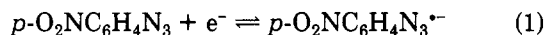


Figure 3. Cyclic voltammetric behavior of a 3.1 mM solution of *p*-O₂NC₆H₄N₃ in DMF-0.1 M *n*-Bu₄NClO₄ in the (a) absence and (b) presence of 33.4 mM 2,3-butanedione. Scan rate: 0.2 V/s; working electrode: spherical platinum.

oxidation of 4,4'-O₂NC₆H₄N=NC₆H₄NO₂²⁻ to 4,4'-O₂NC₆H₄N=NC₆H₄NO₂ and the oxidations *p*-O₂NC₆H₄NH⁻ and *p*-O₂NC₆H₄N-CON(CH₃)₂ to unidentified products equals the forward electrolysis time for the reduction of *p*-O₂NC₆H₄N₃. The result demonstrates that 4,4'-O₂NC₆H₄N=NC₆H₄NO₂²⁻, *p*-O₂NC₆H₄NH⁻, and *p*-O₂NC₆H₄N-CON(CH₃)₂ account for all electroactive products that arise under these reaction conditions from the reduction of *p*-O₂NC₆H₄N₃ and the subsequent rapid decomposition of *p*-O₂NC₆H₄N₃⁻.

Second, for a constant electrolysis time for the reduction of *p*-O₂NC₆H₄N₃ to *p*-O₂NC₆H₄N₃⁻ (eq 1), the reverse transition time for the oxidation of 4,4'-O₂NC₆H₄N=NC₆H₄NO₂²⁻ to 4,4'-O₂NC₆H₄N=NC₆H₄NO₂ decreases significantly with decreasing current density while the transition times for the oxidation of *p*-O₂NC₆H₄NH⁻ and *p*-O₂NC₆H₄N-CON(CH₃)₂ show concomitant increases. Because the concentration of electrogenerated *p*-O₂NC₆H₄N₃⁻ is proportional to the current density, the increase in the fraction of 4,4'-O₂NC₆H₄N=NC₆H₄NO₂²⁻ with increasing current density suggests that the dimeric dianion most probably arises by dimerization of either

(4) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; John Wiley and Sons, Inc.: New York, 1980.



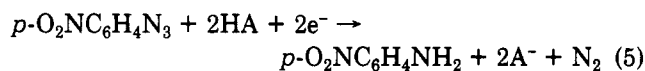
$p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3^{\cdot-}$ (eq 2) or the nitrene anion radical, $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}^{\cdot-}$ (eq 4). Importantly, this result excludes a process by which $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3^{\cdot-}$ or $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}^{\cdot-}$ reacts with unreduced $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3$ to form $4,4'\text{-O}_2\text{NC}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4\text{NO}_2^{\cdot-}$, followed by the subsequent reduction of $4,4'\text{-O}_2\text{NC}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4\text{NO}_2^{\cdot-}$ to $4,4'\text{-O}_2\text{NC}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4\text{NO}_2^{\cdot-}$ at the applied potential. The increases in the fractions of $p\text{-O}_2\text{NC}_6\text{H}_4\text{NH}^-$ and $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}^{\cdot-}\text{CON}(\text{CH}_3)_2$ that are formed with decreasing current density suggest that these products arise by first-order or pseudo-first-order reaction pathways (vide infra).

Butyronitrile. Cyclic voltammetric results in acetonitrile at -37°C and in DMF at -51°C have shown that $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3^{\cdot-}$ is too short-lived to give an anodic peak for its reoxidation to $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3$ at our maximum scan rate of 100 V/s. In an attempt to stabilize $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3^{\cdot-}$ with respect to subsequent chemical reaction, the cyclic voltammetric behavior of $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3$ was examined briefly in butyronitrile-0.1 *N*-Bu₄NClO₄ at -84°C . At $v = 100$ V/s, the only discernible anodic process that arises from the reduction of $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3$ was that for the chemically reversible two-electron oxidation of $4,4'\text{-O}_2\text{NC}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4\text{NO}_2^{\cdot-}$ to $4,4'\text{-O}_2\text{NC}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4\text{NO}_2$. The absence of an anodic peak for the reoxidation of $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3^{\cdot-}$ indicates that the lifetime of $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3^{\cdot-}$ does not exceed 1 ms under these reaction conditions.

Controlled-Potential Electrolysis. The results for the controlled-potential electrolytic reduction of $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3$ under a variety of conditions are shown in Table I. In the absence of an added proton donor or carbonyl trapping agent, the four principal products that were obtained after acidification and workup of the electrolyzed solution are $p\text{-O}_2\text{NC}_6\text{H}_4\text{NH}_2$; $p\text{-O}_2\text{NC}_6\text{H}_4\text{NHCONMe}_2$; $4,4'\text{-O}_2\text{NC}_6\text{H}_4\text{N}(\text{CONMe}_2)\text{NHC}_6\text{H}_4\text{NO}_2$, which is the formal product, minus dinitrogen, of the condensation of $p\text{-O}_2\text{NC}_6\text{H}_4\text{NHCONMe}_2$ with $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3$; and $4,4'\text{-O}_2\text{NC}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4\text{NO}_2$ (entries 1 and 2, Table I). When allowance is made for the amount of unreacted starting material that remains, the overall n value is approximately 1.0 electron per molecule of $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3$.

Effect of an Added Proton Donor. The products and the n value that are obtained when $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3$ is reduced electrolytically in the presence of a proton donor are a function of the proton donor type. When the proton donor is the electroinactive alcohol $\text{CF}_3\text{CH}_2\text{OH}$ ($\text{p}K_a^{\text{DMSO}} = 23.45$),⁵ the chronoamperometric n value for the reduction of $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3$ at a potential of -0.5 V is exactly twice that which was obtained in the absence of the added proton donor. When $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3$ was exhaustively reduced by controlled-potential electrolysis in the presence of the electroinactive proton donor $(\text{CF}_3)_2\text{CHOH}$, the only discernible product, $p\text{-O}_2\text{NC}_6\text{H}_4\text{NH}_2$, was formed quantitatively in an overall two-electron process (entry 3, Table I). The nominal n value of 2 requires that intermediate anion radicals which react by forming nitrogen-hydrogen bonds do so by proton abstraction rather than by hydrogen-atom abstraction. Without specifying the order of nitrogen-hydrogen bond formation and nitrogen-nitrogen

bond cleavage, $p\text{-O}_2\text{NC}_6\text{H}_4\text{NH}^{\cdot}$, the radical that is formed directly or subsequently after protonation of the precursor anion radical, would be reduced to its anion in a one-electron step at the applied potential. When these reactions are combined with the initial one-electron reduction of $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3$ to $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3^{\cdot-}$, the overall result is a two-electron process for the electrochemical conversion of $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3$ to $p\text{-O}_2\text{NC}_6\text{H}_4\text{NH}_2$ (or its conjugate base, $p\text{-O}_2\text{NC}_6\text{H}_4\text{NH}^-$, if the proton donor is incapable of protonating $p\text{-O}_2\text{NC}_6\text{H}_4\text{NH}^-$) (eq 5). The formation of 1 mol

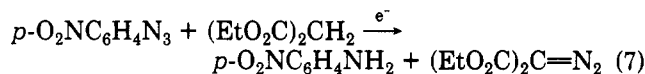


of gaseous product, which is assumed to be N_2 , for each mole of $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3$ that was reduced was established in separate experiments.⁶

If the anion radical that is the precursor to $p\text{-O}_2\text{NC}_6\text{H}_4\text{NH}^-$ were to react instead by hydrogen-atom abstraction, the expected n value is one as long as the solvent-derived radical, S^{\cdot} , is electroinactive (eq 6). In $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3 + \text{SH} + e^- \rightarrow p\text{-O}_2\text{NC}_6\text{H}_4\text{NH}^- + \text{N}_2 + \text{S}^{\cdot}$ (6)

the solvent-electrolyte systems employed in this study, there is no evidence from previous work in this laboratory that solvent-derived radicals which are known to be formed by hydrogen-atom abstraction are reduced electrochemically.^{2a,b}

Diazo Transfer. When a weak methylene carbon acid such as diethyl malonate is used as the electroinactive proton donor, a chain reaction is initiated by the reduction of $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3$ that results in diazo transfer from $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3$ to the methylene carbon acid (eq 7). The



reaction proceeds reasonably rapidly on the coulometric time scale at room temperature ($k = 5.6 \times 10^1 \text{ M}^{-1}\text{s}^{-1}$ for the rate-determining attack of $(\text{EtO}_2\text{C})_2\text{CH}^-$ on $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3$),⁷ affords $p\text{-O}_2\text{NC}_6\text{H}_4\text{NH}_2$ and $(\text{EtO}_2\text{C})_2\text{C}=\text{N}_2$ in nearly quantitatively yield (entry 4, Table I) and consumes 0.1 or less electron per molecule of $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3$ for complete reaction in coulometric reductions.

Although the details of this electrochemically induced diazo transfer reaction have been reported elsewhere,⁷ one of the results is germane to the present study. A nonintegral, limiting chronoamperometric n value of approximately 1.5 was obtained for $t < 100$ ms when $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3$ is reduced in the presence of an excess of $(\text{EtO}_2\text{C})_2\text{CH}_2$. Because the effect of the propagation cycle on the instantaneous chronoamperometric n value is negligible when $t \leq 100$ ms,⁷ the limiting n value of 1.5 indicates that hydrogen-atom abstraction (eq 6) competes with the reaction channel where the intermediate anion radical, which is either $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3^{\cdot-}$ or an anion radical that arises from the decomposition of $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3^{\cdot-}$, is protonated and the resulting neutral radical is subsequently reduced (eq 5). The emergence of hydrogen-atom abstraction as an important reaction pathway when $(\text{EtO}_2\text{C})_2\text{CH}_2$ is substituted for $\text{CF}_3\text{CH}_2\text{OH}$ is attributed to the relatively slow rate(s) of proton transfer from $(\text{EtO}_2\text{C})_2\text{CH}_2$ to the intermediate anion radical(s) and the relatively rapid rate of hydrogen-atom abstraction by either

(6) Herbranson, Dale E. Ph.D. Dissertation, Kansas State University, Manhattan, KS, 1983.

(7) Herbranson, D. E.; Hawley, M. D. *J. Electroanal. Chem.* **1983**, *144*, 423.

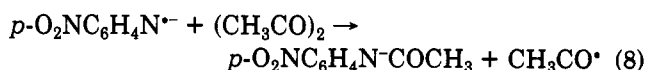
$p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3^{*-}$ or $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}^{*-}$. Interestingly, the carbene anion radical that is formed by the reductive elimination of dinitrogen from diazodimedone has also been reported to react by both the protonation and the hydrogen-atom abstraction pathway when diethyl malonate is the added proton donor.^{2b}

Effect of Carbonyl Trapping Agents. In order to test the propensity of the electrogenerated radical intermediates $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3^{*-}$, $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}^{*-}$, or $p\text{-O}_2\text{NC}_6\text{H}_4\text{NH}^*$ to undergo the carbonyl addition/radical β -fragmentation reaction, controlled-potential electrolysis of $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3$ was effected in the presence of a 10-fold excess of 2,3-butanedione, $(\text{CH}_3\text{CO})_2$. 2,3-Butanedione was selected as a potential radical trapping agent because of its electro-inactivity at the applied potential, its nearly collision-limited rate of reaction with PhN^{*-} in the gas phase ($k^{\text{C}=\text{O}}(\text{CH}_3\text{CO})_2 = 6.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$),⁸ and, as shown in separate control experiments,⁶ the absence of carbonyl addition/ β -fragmentation reaction with 4,4'- $\text{O}_2\text{NC}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4\text{NO}_2$, 4,4'- $\text{O}_2\text{NC}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4\text{NO}_2^{*-}$, 4,4'- $\text{O}_2\text{NC}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4\text{NO}_2^{2*-}$, $p\text{-O}_2\text{NC}_6\text{H}_4\text{NH}^*$, and $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}^-\text{CON}(\text{CH}_3)_2$. As ascertained from a comparison of Figure 3a with Figure 3b, the addition of 2,3-butanedione shuts down the reaction pathways that lead to 4,4'- $\text{O}_2\text{NC}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4\text{NO}_2^{2*-}$ ($E_{\text{p,a}} = 0.14 \text{ V}$), 4,4'- $\text{O}_2\text{NC}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4\text{NO}_2^{*-}$ ($E_{\text{p,a}} = 0.25 \text{ V}$), $p\text{-O}_2\text{NC}_6\text{H}_4\text{NH}^*$ ($E_{\text{p,a}} = 0.95 \text{ V}$), and $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}^-\text{CON}(\text{CH}_3)_2$ ($E_{\text{p,a}} = 1.22 \text{ V}$) and opens a reaction channel that leads to a product that is oxidized irreversibly at 1.12 V. By comparison of the observed cyclic voltammetric behavior with that for $\text{CH}_3\text{COCOCH}_2^-$, the anodic peak at 1.12 V is attributed to the irreversible oxidation of the conjugate base of 2,3-butanedione, $\text{CH}_3\text{COCOCH}_2^-$. The latter species is formed *inter alia* by the addition of the strong base Me_4NOH to a solution of 2,3-butanedione.

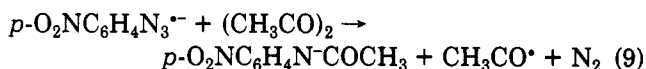
In the controlled electrolysis of $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3$ in the presence of a 10-fold excess of 2,3-butanedione, the potential of the platinum gauze electrode was made sufficiently negative to reduce $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3$ but insufficiently negative to reduce 2,3-butanedione ($E_{\text{p,c}} = -0.71 \text{ V}$, irreversible), $p\text{-O}_2\text{NC}_6\text{H}_4\text{NH}_2$ ($E_{\text{p,c}} = -0.70 \text{ V}$, reversible), or $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}^-\text{COCH}_3$ ($E_{\text{p,c}} = -0.84 \text{ V}$).⁶ As shown by entries 5–8, Table I, the yield of the carbonyl addition/radical β -fragmentation product varies from a low of 26%, when $n\text{-Bu}_4\text{NClO}_4$ is the supporting electrolyte, to a high of 47%, when LiClO_4 is the supporting electrolyte. The formation of $p\text{-O}_2\text{NC}_6\text{H}_4\text{NHCOCH}_3$ demonstrates that addition of an electrogenerated radical to the carbonyl group of $(\text{CH}_3\text{CO})_2$ competes with other decomposition modes of this radical in this solvent–electrolyte system.

The three most plausible radicals that could be involved in the carbonyl addition/radical β -fragmentation reaction to form $p\text{-O}_2\text{NC}_6\text{H}_4\text{NHCOCH}_3$ are $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3^{*-}$; the corresponding nitrene anion radical, $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}^{*-}$; and $p\text{-O}_2\text{NC}_6\text{H}_4\text{NH}^*$. In order to determine whether $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}^-\text{COCH}_3$ or its conjugate acid might be formed under these solution conditions by reaction of $p\text{-O}_2\text{NC}_6\text{H}_4\text{NH}^*$ with 2,3-butanedione, $p\text{-O}_2\text{NC}_6\text{H}_4\text{NH}^*$ was generated *inter alia* in the presence of 2,3-butanedione via the electrochemical oxidation of $p\text{-O}_2\text{NC}_6\text{H}_4\text{NH}^*$. No discernible formation of $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}^-\text{COCH}_3$ was observed, which suggests that $p\text{-O}_2\text{NC}_6\text{H}_4\text{NH}^*$ does not lie in the principal product-forming channel. Unfortunately, because $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3^{*-}$ is too short-lived to allow the kinetics of its reactions to be examined by our methods (*vide infra*), it cannot be ascertained whether it is $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3^{*-}$

and/or $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}^{*-}$ that must react with 2,3-butanedione. If $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}^{*-}$ is the reactive intermediate in question, then the overall pathway for adduct formation is described by eq 8. On the other hand, if



$p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3^{*-}$ is the reactive intermediate, then the adduct anion radical must undergo a second radical β -fragmentation reaction, one of which involves the elimination of dinitrogen (eq 9).



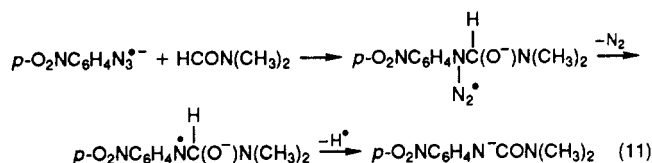
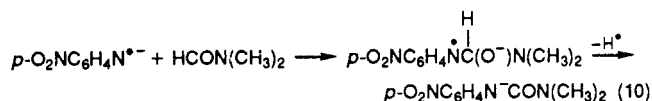
The absence of an anodic peak for the oxidation of $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}^-\text{COCH}_3$ near 1.35 V and the appearance of an anodic peak for the oxidation of $\text{CH}_3\text{COCOCH}_2^-$ near 1.12 V (Figure 3b) is consistent with rapid proton transfer from $(\text{CH}_3\text{CO})_2$ to $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}^-\text{COCH}_3$. That the anodic peaks for the cyclic voltammetric oxidations of $p\text{-O}_2\text{NC}_6\text{H}_4\text{NH}^*$ and $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}^-\text{CON}(\text{CH}_3)_2$ would disappear upon addition of an excess of 2,3-butanedione was demonstrated in separate control experiments.⁶

Other Reaction Pathways Involving 2,3-Butanedione. Cyclic voltammetric and coulometric results also suggest two additional competing modes of reaction between 2,3-butanedione and $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3^{*-}$ and/or $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}^{*-}$. First, the cyclic voltammetric peak height for the reduction of $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3$ in the presence of 2,3-butanedione is approximately 60% larger than that for the same peak in the absence of 2,3-butanedione. This result is consistent with 2,3-butanedione functioning also as a proton donor for $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3^{*-}$ and/or $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}^{*-}$. As shown above, protonation of all anionic intermediates would afford a maximum n value of 2 (eq 5), whereas hydrogen-atom abstraction by all anion radical intermediates would be expected to give an n value of 1 (eq 6). Second, the coulometric n values for the reduction of $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3$ in the presence of 2,3-butanedione are all less than the sum of the fractions of products $p\text{-O}_2\text{NC}_6\text{H}_4\text{NH}_2$ and $p\text{-O}_2\text{NC}_6\text{H}_4\text{NHCOCH}_3$ (entries 6–8, Table I). Because the overall n values are less than 1 when 2,3-butanedione is present, this suggests that $\text{CH}_3\text{COCOCH}_2^-$, which would be formed if transfer of a proton from $(\text{CH}_3\text{CO})_2$ to either $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3^{*-}$ or $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}^{*-}$ were to occur, may be participating in a diazo transfer reaction in the same manner as methylene carbon acids. As demonstrated by the result for diethyl malonate (entry 4, Table I), diazo transfer is an electrochemically induced chain reaction in which n approaches 0 and $p\text{-O}_2\text{NC}_6\text{H}_4\text{NH}_2$ is afforded quantitatively as one product.⁷ The validity of this suggestion was demonstrated in the following manner: the addition of a catalytic amount of Me_4NOH to a solution of $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3$ and an excess of $(\text{CH}_3\text{CO})_2$ resulted in the complete transformation of $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3$ into $p\text{-O}_2\text{NC}_6\text{H}_4\text{NH}_2$ and a concomitant, equal-molar reduction in the concentration of $(\text{CH}_3\text{CO})_2$. No attempt was made to identify or quantitate the second assumed product of this reaction, $\text{CH}_3\text{COCOCH}=\text{N}_2$.

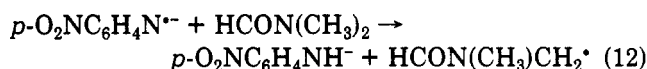
Plausible Pathways for the Formation of $p\text{-O}_2\text{NC}_6\text{H}_4\text{NH}^*$ and $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}^-\text{CON}(\text{CO}_3)_2$ in DMF. The electrogeneration of $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3^{*-}$ in relatively low concentration was shown by reverse current chronopotentiometric experiments (*vide supra*) to favor the formation of products $p\text{-O}_2\text{NC}_6\text{H}_4\text{NH}^*$ and $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}^-\text{CON}(\text{CH}_3)_2$, both of which are believed to arise by first-order or pseudo-first-order reaction pathways. The formation of $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}^-\text{CON}(\text{CH}_3)_2$ is proposed to occur

(8) McDonald, R. N.; Chowdhury, A. K. *J. Am. Chem. Soc.* 1983, 105, 198.

either by the carbonyl addition of $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}^{\bullet-}$ /radical β -fragmentation process described by eq 10 or by the carbonyl addition of $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3^{\bullet-}$ /radical double β -fragmentation process described by eq 11.



The formation of $p\text{-O}_2\text{NC}_6\text{H}_4\text{NH}^-$ presumably occurs via hydrogen-atom abstraction from the solvent, DMF, by either $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3^{\bullet-}$ (eq 6) or $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}^{\bullet-}$ (eq 12) and



should afford a solvent-derived radical as the second product of this reaction. Because the coulometric and chronoamperometric n values in the absence of an added proton donor are nominally 1, the results suggest that none of the radicals produced in the formation of either $p\text{-O}_2\text{NC}_6\text{H}_4\text{NH}^-$ or $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}^-\text{CON}(\text{CH}_3)_2$ is electroactive. The occurrence of hydrogen-atom abstraction from DMF but not acetonitrile and the suggestion that the solvent-derived radical is $\text{HCON}(\text{CH}_3)\text{CH}_2^{\bullet}$ are consistent with the several carbon-hydrogen bond energies that have been reported for these materials: $D^\circ(\text{NCCH}_2-\text{H}) = 92.9 \pm 2.5$,⁹ $D^\circ((\text{CH}_3)_2\text{NC}(=\text{O})-\text{H}) = 95.3$,¹⁰ and $D^\circ(\text{HC}(=\text{O})-\text{N}(\text{CH}_3)\text{CH}_2-\text{H}) = 85$ kcal/mol.¹¹

Order of Bond Breaking and Making. The formation of $p\text{-O}_2\text{NC}_6\text{H}_4\text{NH}^-$ from $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3^{\bullet-}$ requires the making of a nitrogen-hydrogen bond and the cleavage of a nitrogen-nitrogen bond. Attempts were made to study the kinetics of the decomposition of $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3^{\bullet-}$ at subambient temperatures in order to determine whether bond breaking precedes or follows bond making. Unfortunately, the absence of a cyclic voltammetric anodic peak for the oxidation of $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3^{\bullet-}$ at all $v \leq 100$ V/s and $T \geq -84$ °C permits us only to conclude that the maximum lifetime of $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3^{\bullet-}$ is 1 ms. If it could have been ascertained, for example, that the rate of the reaction of $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3^{\bullet-}$ is the same in the presence and absence of electroinactive proton donors such as $\text{CF}_3\text{CH}_2\text{OH}$, then unequivocal evidence for $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3^{\bullet-}$ undergoing rate-determining loss of dinitrogen to give $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}^{\bullet-}$ as an unobserved intermediate would have been obtained.^{2a}

We strongly favor the rate-determining loss of dinitrogen in all reactions of $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3^{\bullet-}$ and the formation of the corresponding nitrene anion radical as an unobserved intermediate. Nevertheless, our results do not permit us to exclude the possibility that it is the aryl azide anion that is the reactive intermediate in one or more of the hydrogen-atom abstraction, protonation, and carbonyl addition/radical β -fragmentation reactions. The evidence for the intermediacy of the nitrene anion radical in the electroreduction of $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3$ is largely circumstantial. First, to our knowledge there is no documented example of any initially generated nitroaromatic anion radical that undergoes rate-determining hydrogen atom abstraction in

the presence of relatively strong proton donors such as diethyl malonate. Second, a carbonyl addition/double radical β -fragmentation, which would be required if the azide anion radical were the reactive intermediate, has no precedent to our knowledge. And third, extremely rapid loss of dinitrogen from phenyl azide anion radical and the formation of phenylnitrene anion radical has been observed in the gas phase. Moreover, with the exceptions of tetrazene formation and the dimerization of the phenylnitrene anion radical, which is precluded in the gas phase, the principal reaction pathways that have been reported for $\text{PhN}^{\bullet-}$ in the gas phase have also been observed here in the electrochemical reduction of $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_3$.³ This result parallels the behavior of carbene anion radicals ($\text{R}_2\text{C}^{\bullet-}$) where similar chemical behavior is observed in both the gas and condensed phases.^{1,2}

Experimental Section

Electrochemical Instrumentation. Cyclic voltammetric, chronoamperometric, and chronopotentiometric experiments were performed with three-electrode potentiostats-galvanostats. When the instruments were used in the potentiostat mode, ohmic potential loss between the reference and working electrodes was corrected electronically.¹² Control of the potentiostats and the acquisition and processing of the rapid-scan cyclic voltammetric and chronoamperometric data were performed with a laboratory digital computer (ADAC Model 2000, LSI 11/2).

Cell, Electrodes, and General Procedures. All electrochemical experiments were performed on an all-glass vacuum line. For all non-coulometric experiments, approximately 30 mL of solvent was transferred by trap-to-trap distillation into an un-compartmentalized electrochemical cell that had been loaded previously with the supporting electrolyte. A positive pressure of helium was maintained when the reference electrode and compounds were transferred into the cell. Traces of oxygen, if present either before or after the addition of the electroactive species, were removed by several freeze-pump-thaw cycles. Helium was used to bring the cell up to atmospheric pressure. Slush baths, which were prepared from liquid nitrogen and the appropriate liquid,¹³ were used to maintain the cell at constant, subambient temperature.

All chronoamperometric experiments that were conducted in the absence of an added proton donor were performed on either a planar platinum or a vitreous carbon electrode that had a geometric area of 0.20 cm²; generally, a vitreous carbon planar electrode was used when an added proton donor was present. The auxiliary electrode was a piece of platinum foil (ca. 1 cm²) that was parallel to and approximately 1 cm away from the working electrode. All potentials listed were measured with respect to a cadmium amalgam reference electrode which is in contact with a DMF solution that is saturated with both sodium chloride and cadmium chloride (Type A-III).¹⁴ The potential of this electrode is -0.75 V vs SCE. Dual reference electrodes were used in all cyclic voltammetric and chronoamperometric experiments.¹⁵ The second reference electrode, which was a platinum wire in series with a 0.1 μF capacitor, was placed in parallel with the cadmium amalgam electrode.

The anode and cathode compartments in all controlled-potential electrolyses were separated by means of a glass frit. A large platinum gauze cylinder and a planar platinum flag ($A \approx 1$ cm²) served as the cathode and anode electrodes, respectively. The degree of electrolysis was monitored periodically by cyclic voltammetry. In certain experiments, the change in the gas pressure in the cathode compartment was also monitored as a function of the n value. Details for the construction and operation of the

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electrolysis cell have been described.⁶

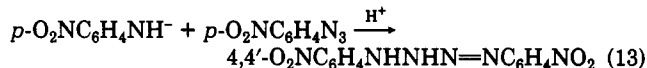
Chemicals. One-liter aliquots of DMF (Burdick and Jackson) were purified by passage through a column of alumina (500 g, 80–200 mesh, Brockman activity 1, activated at 600 °C overnight) and were collected over a mixture of Davison 4-Å molecular sieves and alumina. This procedure was carried out in a dry, nitrogen-filled glovebag. After purification, the solvent was transferred immediately to the vacuum line. Acetonitrile (Burdick and Jackson) and butyronitrile (Eastman Kodak) were purified according to the procedure of Walter and Ramaley, method B.¹⁶ This procedure involves four reflux–distillation steps using, successively, anhydrous Al₂Cl₆, KMnO₄/Li₂CO₃, KHSO₄, and CaH₂. The purified solvent was then stored over CaH₂ on the vacuum line.

p-O₂NC₆H₄N₃¹⁷ and *p*-O₂NC₆H₄NHCONMe₂¹⁸ were synthesized according to standard literature procedures; the remaining chemicals were purchased from commercial sources. The purity of each compound was verified by a melting point determination and/or HPLC. When necessary, further purification was accomplished by standard distillation or recrystallization procedures. Heat- and light-sensitive reagents were refrigerated or stored at 0 °C in well-sealed glass bottles. Tetrabutylammonium perchlorate (Southwestern Analytical Chemicals), tetramethylammonium hexafluorophosphate (Aldrich), lithium perchlorate, and potassium perchlorate were used as supporting electrolytes. These salts were stored in a vacuum oven at 60 °C with phosphorus pentoxide as the desiccant.

Chromatography. The products of the electrolyzed solutions were separated by HPLC (Beckman Scientific Model 332 with a Model 420 controller) using a 6.35-mm diameter by 25-cm length stainless steel columns packed with Partisil 2 ODS, LiChrosorb RP-18, Vydac RP, Alltech 600 RP, or LiChrosorb RP-8, 10-μm mean particle size. The eluting solvent was a mixture of methanol–water, which, depending upon the separation, varied in composition from 90/10 to 50/50. All solvent mixtures were used at a flow rate of 1.0 mL/min. The wavelength used in all absorbance measurements was 254 nm. Calibration curves for standards of all products were constructed daily.

Products Arising from the Controlled-Potential Electrolysis in DMF. In the absence of added reagents, the cyclic voltammetric reduction of *p*-O₂NC₆H₄N₃ in DMF affords 4,4'-O₂NC₆H₄N=NC₆H₄NO₂²⁻, *p*-O₂NC₆H₄NH⁻, and *p*-O₂NC₆H₄N⁻CON(CH₃)₂ as relatively long-lived intermediates. On the coulometric time scale, however, *p*-O₂NC₆H₄NH⁻ and possibly *p*-O₂NC₆H₄N⁻CON(CH₃)₂ are unstable with respect to subsequent

reaction with *p*-O₂NC₆H₄N₃. For example, dissolution of *p*-O₂NC₆H₄NH₂ in DMF –0.1 M *n*-Bu₄NClO₄ and addition of an equimolar amount of Me₄NOH converted *p*-O₂NC₆H₄NH₂ to its orange-colored conjugate base, *p*-O₂NC₆H₄NH⁻. Subsequent addition of *p*-O₂NC₆H₄N₃ resulted in a relatively rapid color change to give a dark blue-green solution that exhibited complex cyclic voltammetric behavior. Quenching the reaction with acetic acid and subsequent analysis by HPLC yielded a large number of reaction products, one of which was 1,4-bis(*p*-nitrophenyl)-tetrazene (eq 13).¹⁹ The tetrazene afforded a major cathodic peak



at 0.2 V, which indicates that it would be reduced at the potentials at which *p*-O₂NC₆H₄N₃ is reduced. No attempt was made to identify the products that arise from the reduction of either 1,4-bis(*p*-nitrophenyl)tetrazene or its corresponding conjugate base.

A compound that is tentatively identified as the tetrasubstituted urea, *N,N*-dimethyl-*N'*-(*p*-nitroamino)-*N'*-(*p*-nitrophenyl)urea, was also isolated from preparative-scale electrolyses of *p*-O₂NC₆H₄N₃, which were conducted in DMF. After the completion of an electrolysis, the reaction mixture was protonated with acetic acid, diluted with water, and extracted with benzene. After evaporation of the benzene on a rotary evaporator, the extract was separated by preparative scale thin layer chromatography on silica gel with methanol–benzene (1:9 by volume) as the developing solvent. The desired compound was then extracted from the silica gel with acetone; the latter was subsequently removed by rotary evaporation. The isolated compound was recrystallized from ethanol/water and its purity verified by HPLC. Experimental data: mp 183.5–184.5 °C; MS, *m/z* = 345.1, (*M* + 1)/*M* = 0.193 (theoretical for C₁₅H₁₅N₅O₅, 0.189); ¹³C NMR (*d*₆-DMSO) δ 39.8 (CH₃), 111.2 and 118.4 (C1 and C1'), 125.3 and 126.4 (C2 and C2'), 139.5 and 142.4 (C3 and C3'), 149.8 and 153.1 (C4 and C4'), and 157.4 (C=O). Attempts to prepare the tetrasubstituted urea nonelectrochemically by reaction of *p*-O₂NC₆H₄N⁻CON(CH₃)₂ with *p*-O₂NC₆H₄N₃ were unsuccessful.

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