

Figure 7. Conformations of (a) dimer I and (b) dimer II in A-A type structure.

Figures 7, a and b, shows the conformations of dimer I ($\theta_{A-A} = \pm 75^{\circ}$) and dimer II ($\theta_{A-A} = \pm 30^{\circ}$) obtained for the A–A type structure.

Unfortunately, it is not possible to decide whether dimers I and II take an A-A or A-B structure because both the |D| and |E| values experimentally obtained can be well explained by those calculated for the above structures. However, the results of the calculation of the zfs parameters indicate that the trans conformation observed for the KI complex of native benzo-15-crown-5 by X-ray analysis⁶ is improbable for the present KI complex of 1 in ethanol rigid matrix. In a recent paper, we reported that the KI complex of the galvinoxyl-labeled B15C5 has a structure close to the cis conformation, in which the galvinoxyl skeletons stack over one another, based on the results of a calculation of the zfs parameters.¹⁰ It is probable that the van der Waals interaction between the two substituted galvinoxyl groups induces such a conformation. However, it is not clear at present why the two kinds of 2:1 complexes coexist in ethanol rigid matrix and take different conformations as described above.

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Registry No. 1, 84812-26-0; 1.LiI (1:1 complex), 84824-33-9; 1.LiI (2:1 complex), 84824-46-4; 1.NaI (1:1 complex), 84824-34-0; 1-NaI (2:1 complex), 84824-47-5; 1-KI (1:1 complex), 84824-36-2; 1.KI (2:1 complex), 84824-48-6; 1.RbI (1:1 complex), 84824-35-1; 1.RbI (2:1 complex), 84824-49-7; 1.MgCl₂ (1:1 complex), 84824-37-3; 1.MgCl₂ (2:1 complex), 84824-50-0; 1.CaCl₂ (1:1 complex), 84824-38-4; 1.CaCl₂ (2:1 complex), 84824-51-1; 1.SrCl₂ (1:1 complex), 84824-39-5; 1.SrCl₂ (2:1 complex), 84824-52-2; 1.BaI₂ (1:1 complex), 84824-40-8; 1-BaI₂ (2:1 complex), 84824-53-3; 1-KBr (1:1 complex), 84824-41-9; 1·KBr (2:1 complex), 84824-54-4; 1·KSCN (1:1 complex), 84824-43-1; 1.KSCN (2:1 complex), 84824-56-6; 1.KIO₄ (1:1 complex), 84824-44-2; 1.KIO₄ (2:1 complex), 84824-57-7; 1·K₂SO₄ (1:1 complex), 84824-45-3; 1·K₂SO₄ (2:1 complex), 84824-58-8; quinol-B15C5, 84812-24-8; phenol-B15C5, 84812-25-9; 4'-bromobenzo-15-crown-5, 60835-72-5; 2,6-di-tert-butyl-pbenzoguinone, 719-22-2.

Spin Trapping in Electrochemistry. Nonaqueous Electrochemical Behavior of Nitroso Spin Traps

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The oxidative and reductive behavior of 11 nitroso compounds has been characterized in *N*,*N*-dimethylformamide (DMF) and acetonitrile, in order to evaluate their utility as spin traps in electrochemical processes. The "potential windows" of these spin traps are reported as well as preliminary applications to the study of direct or indirect electrochemical reduction of alkyl halides.

Spin trapping is now recognized as a standard method to investigate reaction mechanisms.² This technique has recently been used to characterize radical intermediates arising from electrooxidations,³ photoassisted oxidations,⁴ and electroreductions of substrates⁵ in solution.

The characteristics of both nitrones and nitroso compounds, the most widely used spin traps, have been investigated and compared extensively.² The main advantage of nitroso spin traps over nitrones lies in their ability of forming nitroxides which give more direct information on the structure of the trapped radical. The electrochemical behavior of a large series of nitrones has recently been reported.⁶ The present paper is intended to describe

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TABLE I: Electrochemical Reduction of Nitroso Compounds^a

		concu	monomer		dimer		other peaks		
compd	medium	mM	E_{p_1} , dV	$I_{p_1}, \mu A$	E_{p_2}, V	$I_{p_2}, \mu A$	$\overline{E_{p3}, V}$	E_{p_4}, V	E_{ps}, V
t-BuNO ^{g, 27}	DMF ^b	1.5	-0.98	1.28	-1.62	1.38	-2.16 ^e		
p-(Me ₂ N)NOBz	DMF^{b}	1.5	-0.69 (r)				-1.20^{f}	-1.60^{f}	-1.75^{e}
Me NÕBz	DMF^{b}	5.0	-0.66(r)	1.8	-1.11	2.6	-2.09 ^e		
$(t-Bu)_3NOBz$	DMF^{b}	1.0	-0.64 (r)				-1.98^{e}		
Me_4NOBz	DMF^{b}	1.5	-0.61 (r)	1.0	-1.10	1.5	-1.86^{e}		
o-MeNOBz	DMF^{b}	1.6	-0.39 (r)				-1.00^{t}	-1.40^{t}	-1.60^{e}
NOBz	DMF^{b}	1.5	-0.37 (r)				-0.83^{t}	-1.59^{t}	-1.68^{e}
Cl ₃ NOBz	DMF^{b}	5.0	-0.03 (i)	7.3	-0.34	0.4	-1.04		
F₅NOBz	DMF^{b}	5.0	+0.14 (i)				-0.21	-0.89	-1.05
t-BuNO	AN^c	5.0	-2.06 (i)						
$p-(Me_2N)NOBz$	AN^{c}	3.0	-1.55 (r)				-1.88	-2.06	-2.33
Me _s NOBz	AN^{c}	3.0	-1.49 (r)	5.0	-2.11	8.9			
$(t-Bu)_{3}NOBz$	AN^{c}	1.0	-1.55 (r)						
Me ₄ NÕBz	AN^{c}	1.8	-1.47 (r)	2.6	-2.05	5.0			
o-MeNOBz	AN^{c}	3.0	-1.33 (r)				-1.85	-1.93	-2.26
NOBz	AN^{c}	4.5	-1.24 (r)				-1.80	-1.98	
Cl ₃ NOBz	AN^{c}	5.0	-0.99 (i)	34.5	-1.50	1.0	-1.94	-2.15	
F _s NOBz	AN^{c}	3.5	-0.82 (i)				-1.63	-1.82	-2.20
(MeO) ₅ NOBz	AN^{c}	2.0	-1.40 (r)						
$tris(CO_2Me)NOBz$	AN^c	1.0	-0.75 (r)				-1.30	-1.52	-1.83

^a Cyclic voltammetry, $v = 50 \text{ mV s}^{-1}$. ^b Electrolyte: DMF/0.1 M N(C₄H₉)₄BF₄. Stationary Hg electrode. Reference: Ag/AgI/I⁻ (0.1 M), DMF. ^c Electrolyte: CH₃CN/0.1 M NEt₄ClO₄. Stationary Pt disk. Reference: Ag/AgNO₃ (0.01 M), CH₃CN. ^d r = reversible step. i = irreversible step in the given conditions. ^e Peak attributed to the formation of the dianion. ^f Peak attributed to the azoxy derivative. ^g Voltammogram drawn after 8 min.

some results of our extensive investigation on the electrochemical behavior of nitroso spin traps,⁷ and their ability to characterize free radicals, generated via electrochemical processes.

(CH₃)₃C-NO

o-MeNOBz

t-BuNO



tetra-MeNOB2





		Х = Н	NOBz
X C(CH ₃) ₃	tri-t-BuNOBz	X = CH3	penta-MeNOBz
X = CI	tri-chloroNOBz	X = OCH3	penta-MéONOBz
$X = CO_2CH_3$	tri-(CO ₂ Me)NOBz	X¤F	penta-fluoroNOBz

Results and Discussion

Reduction. The investigated spin traps and the results of their electroreduction in DMF and/or acetonitrile are listed in Table I. At the mercury electrode the cyclic



Figure 1. Cyclic voltammograms of Me₄NOBz. Variation of the switching potential. Reference electrode: Ag/AgI/I⁻ (0.1 M), DMF. Working electrode: stationary Hg electrode. Electrolyte: DMF/Bu₄NBF₄ (0.1 M). $c = 1.5 \times 10^{-3}$ M. v = 50 mV s⁻¹. t = 20 °C.

voltammograms exhibit several steps (Figure 1). The first step, which corresponds to the formation of the monomer radical anion, is reversible, except for the F_5 NOBz and the Cl₃NOBz. As expected, resonance stabilization of the reduced form makes the arylnitroso compounds easier to reduce than *t*-BuNO.

Throughout the series of investigated arylnitroso compounds, the changes in $E_{\rm p1}$ (Table I) could be tentatively rationalized in terms of both the electronic and steric effects of the ring substituents. An extensive electrochemical study of monomethyl- and polymethylnitrosobenzenes led us to conclude that the significant cathodic shift in reduction potentials of Me₄NOBz, $(t-Bu)_3$ NOBz, and Me₅NOBz relative to that of NOBz reflects mainly the inductive effects associated with the alkyl substituents.⁸ The large cathodic shift observed for the p-(Me₂N)NOBz relative to that of NOBz must be attributed to the strong π -electron-donor effect of the p-dimethylamino group. In the case of (MeO)₅NOBz⁹ the π -donating effect of the

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$$2 \operatorname{ArNO} (2M) \xrightarrow{\text{slow}} \operatorname{ArN} \xrightarrow{\text{Ar}} (D)$$
furst step (I_r): M + e \longrightarrow M⁻ (E₁)
second step (II_i): D + e \longrightarrow D⁻ (E₂)
D⁻ \longrightarrow M⁻ + M
 $\xrightarrow{\text{M} + e} \xrightarrow{\text{M}^-} (E_2)$
D + 2e \longrightarrow 2M⁻ (E₂)

methoxy groups is offset by their electron-wthdrawing effect, leading to a lower cathodic shift than the one observed for the p-(Me₂N)NOBz. Finally, the significant anodic shift observed for the Cl₃NOBz and the F₅ NOBz reflects the strong electron-withdrawing effect of the halogen substituents.

The nitroso compounds listed in Table I are isolated as crystalline dimers (except for the $(t-Bu)_3NOBz$ and F_5NOBz) which dissociate in solution to give the blue monomers.¹⁰ The apparent complexity of the observed I-E curves (Figure 1) is attributed to the existence of an equilibrium between the monomeric and dimeric forms of the nitroso compounds, which are both electroactive within the potential windows investigated here. For all the studied nitroso spin traps, the monomer reduction potential is more positive than the dimer reduction potential.

The general electroreductive behavior of the arylnitroso compounds can be illustrated through the discussion of the results obtained with the Me_4NOBz (in DMF at the mercury electrode). At moderate potential values, two main peaks are observed (Figure 1). The first step only is reversible; however, the observed anodic current is much larger than the cathodic part. The normal equality of cathodic and anodic currents is recovered when the potential scan is reversed before the second step. This observation led us to conclude that a transient species obtained from the second reduction step is oxidized at the first-step potential.

The second peak can then be attributed to the reduction of the dimer which is more difficult to reduce $(E_2 = -1.10)$ V) than the monomer $(E_1 = -0.61 \text{ V})$. The reduction of the dimer remains irreversible even at high (100 V s^{-1}) potential sweep rate, pointing to the very transient character of the dimer radical anion. The difference between the cathodic and anodic currents observed for the first step can then be explained by the decomposition of the dimer radical anion produced in the second step. This decomposition leads to the monomer radical anion and the neutral monomer which is immediately reduced (Scheme I). The monomer radical anion is the stable species accumulated at the electrode interface which can be reoxidized at the standard potential of the monomer. Additional experiments were carried out in order to definitively establish the link between the monomer-dimer equilibrium and steps I, and II_i.

Cyclic voltammograms were recorded at different temperatures. The intensity of the peak attributed to the monomer was shown to decrease as the temperature decreases (Figure 2), and at -15 °C the cathodic current was negligible. However, a significant anodic current still arises



Figure 2. Cyclic voltammograms (cathodic parts) of Me₄NOBz at different temperatures: (a) -12, (b) +22, (c) +42, (d) +60, and (e) +68 °C. Reference electrode: Ag/AgI/I⁻ (0.1 M), DMF. Working electrode: stationary Hg electrode. Electrolyte: DMF/Bu₄NI (0.1 M). $c = 4 \times 10^{-3}$ M. v = 100 mV s⁻¹.



Figure 3. Cyclic voltammogram of Me₄NOBz at low temperature. t = -15 °C. Reference electrode: Ag/AgI/I⁻ (0.1 M), DMF. Working electrode: stationary Hg electrode. Electrolyte: DMF/Bu₄NBF₄ (0.1 M). $c = 2 \times 10^{-3}$ M. v = 50 mV s⁻¹.

from the oxidation of the monomer radical anion formed during the reduction of the dimer (Figure 3, Scheme I).

As expected, the dimer concentration increases by varying the concentration from 5×10^{-4} to 6×10^{-3} M (calculated on the basis of the monomer molecular weight); this was followed by an increase of the dimer to monomer cathodic current ratio.

Finally, the peak attributed to the reduction of the dimeric form is lacking¹¹ for those nitroso compounds which either are monomeric in solution (NOBz, p-(me₂N)NOBz, o-MeNOBz) or are isolated as crystalline monomers ((t-Bu)₃NOBz, F_5 NOBz).

A third irreversible step, III_i, is observed at more negative potentials ($E_p < -1.5$ V) and is probably associated with an electron transfer to the monomer anion radical, which is the only stable species accumulating on the electrode surface. The large potential difference between

⁽⁹⁾ The synthesis and trapping properties of this new spin trap have been studied in our laboratory, and the results will appear in a forthcoming paper.

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⁽¹¹⁾ In the case of pentamethoxynitrosobenzene oxidation, variabletemperature studies suggest that the peak observed at +1.30 V could be assigned to the dimeric form. However, during the reduction, no peak corresponding to the dimer was observed.



Figure 4. Electrochemical oxidation of (a) $(t-Bu)_3NOBz$ ($c = 1.5 \times 10^{-3}$ M) and (b) Me₄NOBz ($c = 1.5 \times 10^{-3}$ M). Reference electrode: Ag/AgNO₃ (0.01 M), CH₃CN. Working electrode: stationary Pt disk. Electrolyte: CH₃CN/Bu₄NBF₄ (0.1 M). Cyclic voltammetry. v = 50 mV s⁻¹. t = 20 °C.

the first step and the third one $(\Delta E_{\rm p} \simeq 1.3 \text{ V})$ supposes a rather difficult electron transfer to the monomer anion radical and consequently suggests a strong negative charge localization on the system electrophore, i.e., the nitroso group.

The general electroreductive behavior described above for the Me₄NOBz is also exhibited by its perdeuterated homologue, t-BuNO, Me₅NOBz, and Cl₃NOBz. At room temperature, the cyclic voltammograms of Cl₃NOBz and F₅ NOBz exhibit an irreversible first step. However, in the case of the former, the step becomes reversible at high sweep rates ($v \ge 500 \text{ mV s}^{-1}$) or at low temperature (T =-15 °C). The loss of chloride¹² from the Cl₃NOBz radical anion would account for the lack of reversibility. the appearance of a chloride oxidation peak provides evidence that chloride has been released into the solution.

Azoxybenzene has been reported to be formed during the electroreduction of nitrosobenzene.¹³ Accordingly the peaks observed at -0.83 and -1.59 V (Table I) were assigned to the reduction of the azoxy derivative. A similar behavior has been observed with *p*-(Me₂N)NOBz and *o*-MeNOBz. The rate of azoxydurene formation should be very low, and as expected no peak attributable to its reduction was detected. However, azoxydurene was isolated from a preparative electrolysis of Me₄NOBz.

Oxidation. Similarly, the nitroso derivatives which exhibit the monomer/dimer equilibrium give rise to two oxidation steps (Table II, Figure 4). The first step may be reversible while the second step, corresponding to the dimer, is never reversible. However, we emphasize, in agreement with a previous report of Blount et al.,⁶ that, in the case of t-BuNO, the monomer is oxidized at more positive potential than the dimer. On the other hand, for this same compound, the peak due to the monomer oxidation remains detectable even at low temperature. This result can be explained by the formation of the monomeric form, during the dimer oxidation process.



Figure 5. Position of the reduction peak potentials of the studied halides, relative to the reduction peak potential of Me₄NOBz. Working electrode: stationary Pt disk. Electrolyte: DMF/NEt₄ClO₄ (0.1 M). Cyclic voltammetry, v = 50 mV s⁻¹.

Moreover, we point out that the *t*-BuNO oxidation occurs more readily than that of NOBz. The result agrees with ESR results,¹⁴ which clearly demonstrate that arylnitroso radical cations are of the σ type and thus are not resonance stabilized. Consequently, the influence of the ring substituents on the oxidation potentials is not as clear as in the case of the electroreduction. Nevertheless, the oxidation potential is reduced by the alkyl groups and increased by the electron-withdrawing groups. The very low oxidation potential observed in the case of p-(Me₂N)NOBz corresponds to the oxidation of the parasubstituent-nitrogen lone pair, to give rise to an anilinium radical cation.¹⁵

Spin-Trapping Applications. Our first use of nitroso spin traps to study electrochemical processes was devoted to the well-known electroreduction of organic halides.¹⁶ Me₄NOBz and $(t-Bu)_3$ NOBz were used, and two kinds of organic halides were tested: those like *p*-nitrobenzyl bromide which are reduced before the scavengers, and those like benzyl bromide or methyl iodide which are reduced after the scavenger (Figure 5).

The electroreduction of *p*-nitrobenzyl bromide in the presence of Me₄NOBz leads to corresponding *p*-nitrobenzyl duryl nitroxide ($a_N = 13.8 \text{ G}$, $a_H (2 \text{ H}) = 9.1 \text{ G}$, g = 2.0059), whose formation can be rationalized according to Scheme II. This scheme corresponds to a direct reduction of the Scheme II

$$p \text{-NO}_2(C_6H_4)CH_2Br + e \rightarrow [p \text{-NO}_2(C_6H_4)CH_2Br]^{-1}$$

$$1^{-1} \rightarrow p \text{-NO}_2(C_6H_4)\dot{C}H_2 + Br^{-1}$$

$$2 2 \cdot \rightarrow [p \text{-NO}_2(C_6H_4)CH_2]_2$$

$$2 \cdot + ArNO \rightarrow p \text{-NO}_2(C_6H_4)CH_2N(\dot{O})Ar$$

$$(ArNO = Me_4NOBz)$$

halide, giving 1⁻, which dissociates very quickly¹⁷ to produce the bromide anion, and the *p*-nitrobenzyl radical 2. Subsequent trapping of this radical by Me₄NOBz is fast enough¹⁸ to compete with its dimerization. The corresponding alkyl duryl nitroxides were also observed when the electroreduction of benzyl bromide or methyl iodide was carried out in the presence of Me₄NOBz. However, for these halides which are reduced after the scavenger, at least two mechanisms could account for the formation of the alkyl duryl nitroxides.

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In the first one, an indirect reduction of the organic halide is promoted by the nitroso radical anion, which plays the role of an electron carrier (Scheme III).

Scheme III

$$RNO + e \rightleftharpoons RNO^{-}$$
$$RNO^{-} + R'X \rightleftharpoons RNO + R'X^{-}$$
$$R'X^{-} \rightarrow R' + X^{-}$$
$$R' + RNO \rightarrow R'N(\dot{O})R$$

In the second one, the formation of the observed nitroxide can also be explained by a nucleophilic displacement,¹⁹ according to

$$RN^{-}$$
 + R'X - R-N-R' + X
 O_{\bullet}

The occurrence of both possibilities was clearly established by using the 2,4,6-tri-tert-butyl-3,5-dideuterionitrosobenzene 20 as a spin trap. The trapping of a methyl radical by this sterically crowded spin trap gives rise to the corresponding nitroxide.²¹ However, the nucleophilic attack on methyl iodide by the 2,4,6-tri-tert-butyl-3,5-dideuterionitrosobenzene radical anion only gives rise to the corresponding N-methoxyanilino radical, 19 which is easily identified by ESR. When methyl iodide is reduced in the presence of this trap (ArNO), the corresponding hydronitroxide ArN(O)H,²¹ resulting from the protonation of the nitroso radical anion by the residual water, is first observed during the early stages of the electroreduction. Then, the spectrum of the hydronitroxide disappears and is replaced by a complex spectrum, which is attributed to a mixture of the nitroxide, $ArN(O)CH_3$, generated by the trapping of methyl radicals, and the N-methoxyanilino, ArNOCH₃, generated by a nucleophilic substitution (Figure 6, Scheme ĨV).

Scheme IV

$$ArNO + e \rightleftharpoons ArNO^{-}$$

$$ArNO^{-} + H^{+} \rightarrow ArN(\dot{O})H$$

$$ArNO^{-} + CH_{3}I \rightleftharpoons ArNO + CH_{3}I^{-} (CH_{3^{*}} + I^{-})$$

$$ArNO + \cdot CH_{3} \rightarrow ArN(\dot{O})CH_{3}$$

$$Ar\dot{N}O^{-} + CH_{3}I \rightarrow Ar\dot{N}OCH_{3} + I^{-}$$

$$(ArNO = (t-Bu)_{3}NOBz)$$

On the other hand, when p-nitrobenzyl bromide is reduced at low potential in the presence of ArNO, the only nitroxide observed is $ArN(O)CH_2(C_6H_4)$ -p-NO₂, generated by the trapping of p-nitrobenzyl radicals. At higher potential, both $ArN(O)CH_2(C_6H_4)$ -p-NO₂ and the six-line spectrum of the hydronitroxide ArN(O)H were detected but we never observed any lines corresponding to the N-(p-nitrobenzyloxy)anilino radical, ArNOCH₂(C₆H₄)-p- NO_2 (Figure 7, Scheme V).

Scheme V

low potential

$$p-NO_2(C_6H_4)CH_2Br + e \rightarrow p-NO_2(C_6H_4)CH_2Br^- (p-NO_2(C_6H_4)CH_2 + Br^-)$$

 $p-NO_2(C_6H_4)CH_2 + ArNO \rightarrow p-NO_2(C_6H_4)CH_2N(\dot{O})Ar$
high potential

$$ArNO + e \Rightarrow ArNO^{-} \xrightarrow{+H^{+}} ArN(\dot{O})H$$

Conclusion

The voltammetric characterizations of 11 nitroso spin traps has been carried out. 2-Methyl-2-nitrosopropane is reduced at the most negative potential. Both steric and electronic effects have an important influence on the potential windows for the arylnitroso series. Bulky ortho substituents and electron-donating para substituents make the reduction potentials more negative in agreement with a π structure of the corresponding radical anions. Pentafluoronitrosobenzene is oxidized at the most positive potential, and the steric and electronic substituent effects on the oxidation potentials agree with a σ structure of the corresponding radical cations.

For some of the studied nitroso spin traps, the existence of a monomer/dimer equilibrium has a great influence on the electrochemical behavior, since both the monomeric and dimeric forms are electroactive. Preliminary applications of our study have been devoted to the electroreduction of organic halides. When the nitroso spin trap is reduced with more difficulty than the organic halide, the nitroso compound behaves only as a free-radical scavenger. When the nitroso spin trap is reduced more readily than the organic halide, the corresponding nitroso radical anion can behave as an electron carrier and reduce the halide. The ensuing alkyl radical is subsequently trapped by the excess of scavenger.

On the other hand, a nucleophilic attack of the halide by the nitroso radical anion leads to the corresponding nitroxide, or N-alkoxyanilino radical. Using the tri-tertbutylnitrosobenzene gives strong support for the occurrence of these two pathways.

A knowledge of the spin-trap redox behaviors is particularly important when the spin-trapping technique is applied to investigate electrochemical processes, or processes including monoelectronic transfer steps. Our study should be helpful in obtaining more confident results in these fields. The synthesis of new nitroso spin traps, which should be reduced at very negative potentials, is now in progress in our laboratories. Detailed electrochemical behaviors of different nitroso spin traps, as well as the ESR study of the nitroso radical anions and cations, will be published in forthcoming papers.

Experimental Section

Instrumentation. Voltammetric curves were recorded with Tacussel PRT 20-2X and PRT 30-0.1 potentiostats, on Sefram TGM 164 and Luxytrace X-Y recorders. A stationary mercury drop or a polished platinum disk (diameter = 2 mm) was used as a working electrode. The reference electrodes are described in the footnotes of Tables I and II.

ESR spectra were recorded on Bruker ER200D and Varian E 109 X band spectrometers.

Electrolysis in situ were performed with a cylindrical cell fitted with two coaxial electrodes or with a two-electrode flat quartz cell. Either voltage or current control was used during electrogeneration experiments. All the solutions were carefully degassed, and all the experiments were conducted under argon atmosphere.

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TABLE II: Electrochemical Oxidation of Nitroso Compounds^a

compd	concn, mM	$E_{\mathbf{p}_1}, \mathbf{V}$	E_{p_2}, V	E_{p_3}, V	E_{p_4}, V	
 t-BuNO	5	1.10 (i, d)	1.50 (m)	1.68 (w)	1.90 (w)	
p-(Me,N)NOBz	1.5	0.57				
Me NÔBz	2.0	1.03 (r, m)	1.40 (d)			
(t-Bu), NOBz	1.0	1.08(r)	• •			
Me₄ŃŎBz	1.8	1.15(r, m)	1.57 (d)			
o-MeNOBz	1.5	1.40	. ,			
NOBz	4.5	1.55 (i)	2.20			
Cl ₃ NOBz	5.0	1.61(i, m)	1.95 (d)			
F,NOBz	3.5	>1.90 (b)				
(MeO),NOBz	2.0	0.90(i, m)	1.30 (d)	1.80		
$tris(CO_2Me)NOBz$	1.0	(1.38)(w)	2.05			

^{*a*} Cyclic voltammetry, $v = 50 \text{ mV s}^{-1}$. Electrolyte: CH₃CN/0.1 M NET₄ClO₄. Reference electrode: Ag/AgNO₃ (0.01 M). Working electrode: Pt disk. i = irreversible step. r = reversible step. m = monomer. d = dimer. w = weak peak. b = broad peak, lost in the electrolyte discharge.



Figure 6. ESR spectrum obtained by in situ electroreduction of 2,4,6-tri-*tert*-butyl-3,5-dideuterionitrosobenzene in the presence of methyl iodide. Working electrode: platinum (area ca. 4 cm²). Electrolyte: DMF/NEt₄ClO₄ (0.1 M). Concentrations: Halide, c = 0.01 M; spin trap, c = 0.01 M. Electrogeneration at controlled current. (a) Experimental. (b) Simulated, using the following set of parameters: nitroxide radical (63.7%): $a_N = 13.10$ G, $a_H = 12.45$ G (3 H), line width = 0.5 G; anilino radical (36.3%): $a_N = 12.45$ G, $a_H = 2.45$ G (3 H), line width = 1.0 G, offset = 2.81 G toward high field.

Chemicals. Tetraethylammonium perchlorate was prepared by the addition of perchloric acid to tetraethylammonium hydroxide. The precipitate was recrystallized 3 times in water and vacuum dried at 60 °C. Commerical tetrabutylammonium tetrafluoroborate (Fluka) was used without further purification. N,N-Dimethylformamide was stored over sodium sulfate and then distilled under reduced pressure. Freshly distilled DMF was passed through a 10-cm column of Woelm activated alumina before each experiment. Acetonitrile was purified



Figure 7. ESR spectrum obtained by in situ electroreduction of *p*-nitrobenzyl bromide in the presence of 2,4,6-tri-*tert*-butyl-3,5-dideuterionitrosobenzene (ArNO): (•) ArN(O)CH₂(C₈H₄)NO₂, (∇) ArN(O)H. Working electrode: platinum (area ca. 4 cm²). Electrolyte: DMF/ NEt₄ClO₄ (0.1 M). Concentrations: halide, *c* = 0.01 M; spin trap, *c* = 0.01 M. Electrogeneration at controlled overall voltage.

according to ref 22. 2-Methyl-2-nitrosopropane, nitrosobenzene, o-methylnitrosobenzene, and p-(dimethylamino)nitrosobenzene were commercially available. The preparation and purification procedures of the others were performed as described in the literature: 2.3.5.6-Tetramethylnitrosobenzene, pentamethylnitrosobenzene. and pentamethoxynitrosobenzene were prepared by the action of butyl nitrite in acidic medium on the corresponding acetoxy mercuric compounds.²⁴ 2,4,6-Tri-tert-butylnitrosobenzene was prepared by oxidation of the corresponding aniline with 3-chloroperbenzoic acid.²⁰ Pentafluoronitrosobenzene²⁵ and 2,4,6-tris(methoxycarbonyl)nitrosobenzene²³ were prepared by the oxidation of the corresponding anilines with performic acid in dichloromethane. 2,4,6-Trichloronitrosobenzene was prepared by the action of 30% hydrogen peroxide in acetic acid on trichloroaniline as described by Holmes and Bayer.²⁶

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⁽²⁷⁾ In agreement with the results of Blount et al.⁶ only one peak is observed ($E_p = -1.77$ V vs. SCE) during the reduction of *t*-BuNO in acetonitrile. However, two peaks attributed to the monomer and the dimer were consistently observed when the reduction was carried out in DMF. The time-dependent behavior of these two voltammetric waves is consistent with the dissociation of the dimer to the monomer. It could be shown that the process is first order with respect to the dimer concentration and, at 20 °C, proceeds with a rate constant of $0.89 \times 10^{-3} \, \text{s}^{-1}$ (A rate constant of $1.51 \times 10^{-3} \, \text{s}^{-1}$ was calculated by Blount et al. from the time-dependent behavior of the two oxidation peaks observed in acetonitrile at 25 °C.)

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Registry No. *t*-BuNO, 917-95-3; *p*-(Me₂N)NOBz, 138-89-6; Me₅NOBz, 65594-36-7; (t-Bu)₃NOBz, 24973-59-9; Me₄NOBz, 38899-21-7; o-MeNOBz, 611-23-4; NOBz, 586-96-9; Cl₃NOBz, 1196-13-0; F₅NOBz, 1423-13-8; (MeO)₅NOBz, 84802-28-8; tris-

 $(CO_2Me)NOBz$, 49838-52-0; t-BuNO=NOBu-t, 31107-20-7; Me₅NOBz=BzNOMe₅, 84802-30-2; Me₄NOBz=BzNOMe₄, 84802-31-3; Cl₃NOBz=BzNOCl₃, 84802-32-4; (t-Bu)₃BzN(O)-CH₂(C₆H₄)NO₂, 84802-33-5; (t-Bu)₃BzN(O)H, 40489-75-6; pnitrobenzyl bromide, 100-11-8; p-nitrobenzyl duryl nitrodide, 84802-29-9; methyl iodide, 74-88-4; N-methyl-N-tris(tert-butyl)phenyl nitroxide radical, 33721-34-5; N-methoxy-N-tris-(tert-butyl)phenyl anilino radical, 64191-72-6; benzyl bromide, 100-39-0.

Study of NO₃ by Laser-Induced Fluorescence

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The nitrate radical, NO_3 , was directly detected by the laser-induced fluorescence method. The band structure of the fluorescence excitation spectrum was consistent with that of the absorption spectrum. The fluorescence spectrum excited at 662 nm corresponding to the 0–0 transition showed progressions with 1060- and 1480-cm⁻¹ intervals, which were assigned to the symmetric stretching (ν_1) and degenerate antisymmetric stretching (ν_3) modes of the ground state NO_3 , respectively. The fluorescence lifetime excited at the 0-0 band was estimated to be 2.8 μ s from the Stern-Volmer plots in the pressure region of 0.04–0.6 torr.

Introduction

The nitrate free radical, NO₃, has recently received increasing interest in connection with atmospheric chemistry due to the recognition of its role in chemical cycles involving oxides of nitrogen and ozone.^{1,2} The reaction

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \tag{1}$$

is the principal source of NO_3 in the atmosphere and its existence in ambient polluted air³ and the stratosphere⁴ has been observed by the optical absorption.

The absorption spectrum of NO₃ consists of approximately 20 diffuse bands in the region of 665-400 nm.^{5,6} Even though the spectrum at longer wavelengths was photochemically inactive,^{5,7} fluorescence has not been observed.⁸ The purpose of this paper is to report the detection of NO₃ by the laser-induced fluorescence technique, which is a satisfactory method for detecting free radicals in many cases. Very recently, McDonald⁹ also detected NO_3 by the same technique in the pulsed photolysis system. Here, we derive the vibrational frequencies of NO_3 in the ground state from the fluorescence spectrum and also discuss the fluorescence lifetime of NO₃ in the excited state.

Experimental Section

Excitation of NO_3 was achieved by pumping with a pulsed tunable dye laser. Radiation from a dye laser entered and left the fluorescence cell (4 cm in diameter) through horizontal side arms having a set of antiscatter baffles. The emission was detected at right angles to the laser beam by a photomultiplier (Hamamatsu TV R-928). Glass filters were used in front of the photomultiplier to reduce the scattered light. The fluorescence signal was fed to a boxcar integrator (NF Circuit Design Block, BX-531/BP-10) and was subsequently digitized and stored. The output was printed out or plotted on a chart recorder.

A nitrogen laser (4 mJ/pulse, 5-10 Hz) pumped dye laser (Molectron DL 14) was used for following the fluorescence decay and measuring the fluorescence excitation spectrum. The duration of the laser pulse was about 8 ns and the bandwidth was about 0.01 nm. The dyes Rh-610, Rh-640, and Ox-725/Rh-610 (Exciton Chemical Co.) covered the wavelength region between 595 and 677 nm. The output power was monitored by a photodiode. In order to measure the fluorescence spectrum, we used a flash lamp pumped dye laser with a duration of 0.6 μ s and a bandwidth of 0.1 nm as the excitation source. The fluorescence was dispersed by a monochromator (Nikon G-500, 1200 grooves/mm, blazed at 500 nm).

The NO₃ radical was formed from the reaction of nitrogen dioxide with ozone at room temperature by using a flow reactor in order to avoid the accumulation of products in photochemical reactions. Ozone generated by a commercial ozonizer was collected on silica gel at 195 K and was purified by a bulb-to-bulb distillation prior to each experiment. The purity of ozone stored in a large bulb was determined to be more than 95% by optical absorption at 254 nm. Nitrogen dioxide was prepared by oxidizing nitric oxide with an excess amount of oxygen overnight and purified by freeze-pump-thaw cycles until a white solid was obtained. These gases were handled in a conventional greaseless vacuum system and the flow rates were controlled by needle valves. The pressure was measured by an MKS capacitance manometer.

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