[Chem. Pharm. Bull.
34(8)3079—3086(1986)]

Electrochemical Oxidation of *N*-Nitrosopiperidines: Dual Pathways for *N*-Nitramine Formation

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(Received January 16, 1986)

Electrochemical transformation of five *N*-nitrosopiperidines and *N*-nitrosodibutylamine to the corresponding *N*-nitramines has been investigated in acetonitrile at −30 °C. The nitramines are formed by the reaction of the radical cations, generated by one-electron transfer from the nitrosamines, either with dissolved oxygen (path 1) or with water which is contaminating or deliberately added to the medium (path 2): the former is an overall one-electron process, and the latter is a two-electron process. The radical cations derived from *N*-nitroso-2,2,6,6-tetramethylpiperidine and *N*-nitroso-2,2,6,6-tetramethyl-4-piperidone give the nitramines exclusively *via* path 2, while the reaction of those from *N*-nitroso-2-ethylpiperidine and *N*-nitrosodibutylamine proceeds *via* path 1. Contributions of both pathways are suggested for the radical cations from *N*-nitrosopiperidine and *N*-nitroso-2,6-dimethylpiperidine. It is proposed that path 2 becomes feasible when the radical cation exhibits a certain degree of stability as revealed by the observation of reversible character in the cyclic voltammetry of the parent nitrosamine.

Keywords——*N*-nitrosopiperidine; *N*-nitropiperidine; radical cation; electrochemical oxidation; cyclic voltammetry; controlled potential electrolysis; electron spin resonance spectrum; open circuit relaxation

Electrochemical oxidation of *N*-nitrosamines derived from symmetrical dialkylamines in acetonitrile with dissolved oxygen has been shown to give the corresponding nitramines [R_2N-NO_2] and β-ketonitrosamines [$R'COCH_2N(R)-NO$].[1,2] A mechanism involving the reaction of unstable nitrosamine radical cations formed by the initial one-electron transfer with dioxygen has been proposed for the product formation.[2] Neither the nitramine nor the β-ketonitrosamine was obtained without the oxygen. In these studies, although *N*-nitroso-2,2,6,6-tetramethylpiperidine (**1a**) gave the most stable radical cation among the *N*-nitrosodialkylamins examined,[3] formation of the nitramine **2a** (Chart 1) was not verified in the electrolysis at temperatures above 0 °C.[2] However, electrolysis of **1a** at a lower temperature has been found to afford **2a** even under deoxygenated conditions. Thus, the possibility of another reaction process is suggested for the electrochemical transformation of *N*-nitrosamines to *N*-nitramines, and seems worthy of further investigation.

This paper reports the results of cyclic voltammetry and controlled potential electrolysis of **1a** and related *N*-nitrosopiperidines **1b**—**e** in acetonitrile under various conditions. *N*-Nitrosodibutylamine (**1f**), a typical aliphatic acyclic nitrosamine,[2] was included in the study to compare its electrochemical behavior with those of cyclic nitrosamines. The nitramines **2a**—**f** and the β-ketonitrosamines **3e** and **3f** were formed in the electrolysis. The nature of the radical cation derived from **1b** was examined by electron spin resonance (ESR) spectroscopy. A reaction process involving the reaction of nitrosamine radical cations with water will be proposed in addition to that reported previously.[2]

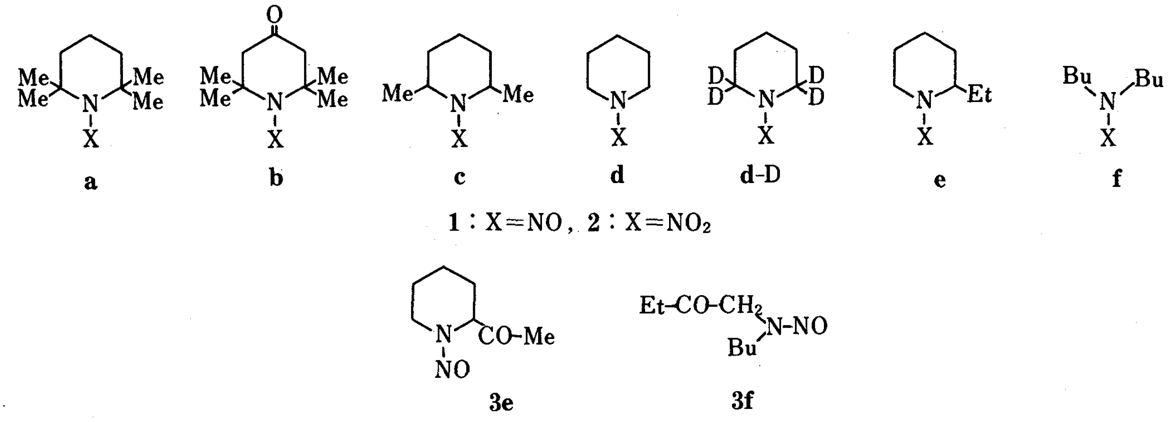

Chart 1

Results and Discussion

Figure 1 illustrates typical cyclic voltammograms of the nitrosamines **1b** and **1d** in acetonitrile. Potentials were measured against an Ag wire coated with AgCl. The voltammogram of **1b** at −30 °C (Fig. 1-A, solid line) was little affected by the presence or absence of dissolved oxygen in the medium or by adding a small amount of water to the medium. Essentially the same voltammetric behaviors were observed for the nitrosamines **1a**[4)] and **1c**: the anodic peak potentials were 1.68, 1.80, and 1.85 V for **1a**, **1b**, and **1c**, respectively. The apparently reversible nature of the voltammograms suggests that the anodic process is attributed to one-electron oxidation of these nitrosamines to the corresponding radical cations (**4**, see Chart 2), because generation of **4** from **1a**[3)] and **1b** (see below) under the voltammetric conditions has been confirmed by ESR spectroscopy. At room temperature, the oxidation of the three nitrosamines became irreversible (see Fig. 1-B).

At −30 °C voltammetry of **1d** also showed a cathodic peak due to the reduction of the radical cation **4d** (Fig. 1-C; the peak potential of the anodic wave, 1.98 V), but the smaller cathodic peak suggests that **4d** is less stable than **4a**—**c**. Deoxygenation of the medium enhanced the anodic peak (*ca.* 20%), and in the presence of added water (1%) the anodic peak increased by a factor of 1.4 and the cathodic peak disappeared (Fig. 1-D). The voltammetric

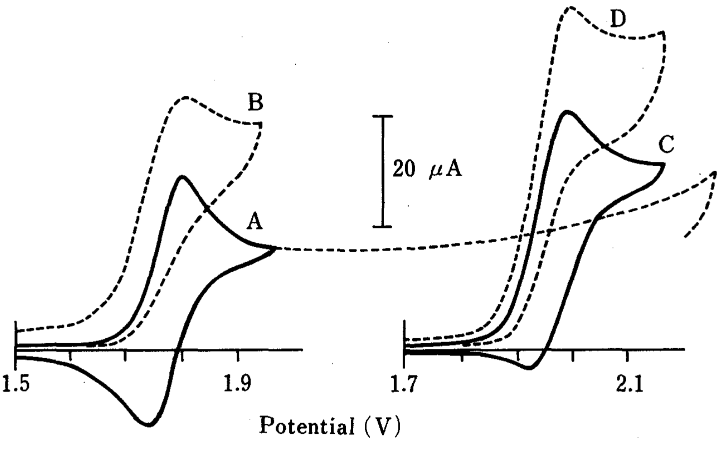

Fig. 1. Cyclic Voltammograms of **1b** (2.04 mM) and **1d** (2.18 mM) in Acetonitrile (0.1 M Et_4NBF_4)

A, **1b** at −30 °C; B, **1b** at room temperature; C, **1d** at −30 °C; D, **1d** at −30 °C in the presence of 1% water. Glassy carbon anode (area = 0.071 cm^2); voltage sweep rate, 50 mVs^{-1}. Potentials were measured against an Ag wire coated with AgCl.

TABLE I. Results of Controlled Potential Electrolysis of **1**[a]

No.	Compound (Amount/mmol)	Temp.[b] (°C)	E_{an}[c]	Conditions[d]	n-Value (F per mol)	Products identified[e] (Yield, %)
1	**1a** (0.29)	RT	1.65	O_2	2.6	**2a** (trace)
2	(0.29)	−30	1.65	O_2	2.2	**2a** (16), **1a** (6)
3	(0.26)	−30	1.65	N_2	2.4	**2a** (19), **1a** (10)
4	(0.27)	−30	1.65	N_2, H_2O	2.2	**2a** (78)
5	**1b** (0.28)	RT	1.79	O_2	3.8	**2b** (23)
6	(0.29)	0	1.79	O_2	3.2	**2b** (39)
7	(0.26)	−30	1.79	O_2	2.5	**2b** (92)
8	(0.29)	−30	1.79	O_2, H_2O	2.6	**2b** (96)
9	(0.30)	−30	1.79	N_2	2.5	**2b** (94)
10	(0.25)	−30	1.79	N_2, H_2O	2.8	**2b** (93)
11	**1c** (0.40)	−30	1.80	O_2	3.5	**2c** (49)
12	(0.35)	−30	1.80	N_2	3.7	**2c** (22), **1c** (25)
13	(0.35)	−30	1.80	N_2, H_2O	4.7	**2c** (22), **1c** (25)
14	**1d** (0.39)	RT	1.90	O_2	4.1	**2d** (21)
15	(0.39)	RT	1.90	N_2	6.2	**2d** (0)
16	(0.44)	RT	1.90	N_2, H_2O	5.7	**2d** (0)
17	**1d** (0.41)	−30	1.90	O_2	3.9	**2d** (31)
18	(0.46)	−30	1.90	N_2	4.0	**2d** (20)
19	(0.44)	−30	1.90	N_2, H_2O	4.2	**2d** (20)
20	**1d**-D (0.42)	−30	1.90	O_2	3.3	**2d**-D (39)
21	(0.40)	−30	1.90	N_2	3.7	**2d**-D (35)
22	(0.40)	−30	1.90	N_2, H_2O	3.8	**2d**-D (44)
23	**1e** (0.39)	RT	1.85	O_2	2.1	**2e** (42), **3e** (4)
24	(0.38)	RT	1.85	N_2	3.0	**2e** (0), **3e** (0)
25	(0.39)	RT	1.85	N_2, H_2O	3.6	**2e** (0), **3e** (0)
26	(0.35)	0	1.85	O_2	2.1	**2e** (49), **3e** (5)
27	(0.38)	−30	1.85	O_2	2.0	**2e** (32), **3e** (4)
28	(0.38)	−30	1.85	N_2	3.1	**2e** (0), **3e** (0)
29	(0.41)	−30	1.85	N_2, H_2O	4.1	**2e** (0), **3e** (0)
30	**1f** (0.49)	−30	1.84	O_2	2.3	**2f** (34), **3f** (38)
31	(0.49)	−30	1.84	N_2	3.0	**2f** (0), **3f** (0)
32	(0.48)	−30	1.84	N_2, H_2O	3.2	**2f** (trace), **3f** (trace)

a) In acetonitrile (20 ml) containing 0.1 M Et_4NBF_4. Sodium carbonate (400 mg) was suspended in the electrolysis solution except for the runs with **1e**. *b*) RT, room temperature. *c*) Anode potential, V *vs*. Ag wire coated with AgCl. *d*) O_2, saturated with oxygen; N_2, deoxygenated with N_2; H_2O, in the presence of 1% water. *e*) The yields of **2e**, **3e**, **2f**, and **3f** were determined by HPLC, and those of other products by GLC.

behavior of the nitrosamine **1e** was similar to that of **1d**, except that the oxidation of **1e** (peak potential, 1.91 V) was totally irreversible even in the presence of dissolved oxygen at −30 °C, indicating that the radical cation **4e** is unstable. The oxidation of the nitrosamine **1f** at −30 °C was also irreversible, as observed at room temperature.[2)]

The results of controlled potential electrolysis of **1** are summarized in Table I. The nitrosamines **1a** and **1b** are susceptible to denitrosation under acidic conditions. Since a proton is usually liberated in the electrochemical oxidation of organic compounds, sodium carbonate was suspended in the electrolysis solution of these nitrosamines to prevent acid-catalyzed decomposition. In fact, the yields of the nitramines **2a** and **2d** were very low (<2%) without the suspended base. In the electrolysis of **1c**, **1d**, and **1f**, sodium carbonate was also suspended to maintain constancy of the experimental conditions. However, the electrolysis of **1e** was carried out without the base, because the formation of the nitramine **2e** was disturbed by the suspended base: the reason for this is not yet clear.

Electrolysis of **1a** at room temperature in the presence of dissolved oxygen gave only a trace of the nitramine **2a** (Table I, run 1), while **1d** and **1e** afforded **2d** and **2e**, respectively, at the same temperature (runs 14 and 23). Although **2a** was produced at −30 °C, the yield was less than 20% and seemed to be independent of oxygen in the medium (runs 2 and 3). When water (1%) was added deliberately to the electrolysis solution, the yield of **2a** increased to *ca.* 80% (run 4). In the case of **1b** at −30 °C, dissolved oxygen and added water appeared to have no effect on the product formation, and **2b** was obtained almost quantitatively (runs 7—10). However, when the electrolysis was carried out in the presence of 1% $H_2{}^{18}O$ (99 atom%), the labeled oxygen atom was incorporated in 68% of **2b** produced. These results suggest that the oxygen atom in the nitro group of **2a** and **2b** comes from water in the medium. In the electrolysis without added water, the water contaminating the medium will be responsible for the product formation.[5] The lower yields of **2a** as compared to those of **2b** suggest that either the radical cation **4a** decomposes to unidentified products faster than **4b** or the reaction of **4a** with water is slower than that of **4b**. At present, no experimental evidence has been obtained to clarify this point. It is interesting to note that the *n*-value (Table I, the 6th column) to form

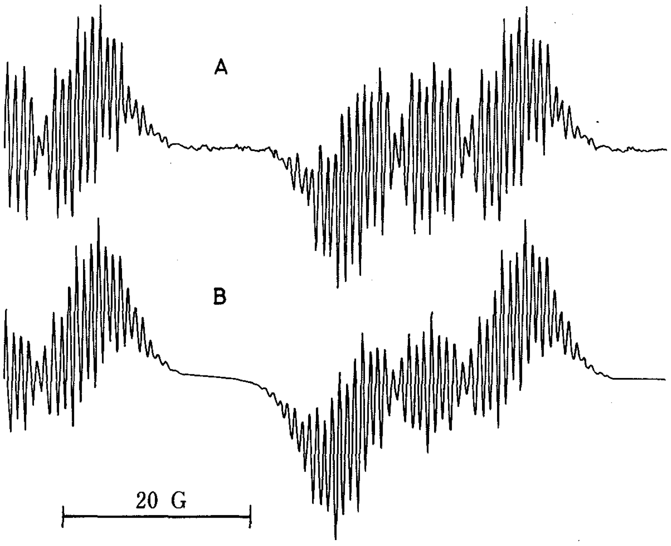

Fig. 2. ESR Spectrum of an *in Situ*-Electrolyzed Solution of **1b** (10 mM) in Acetonitrile (0.1 M Et_4NBF_4) at −30 °C (A) and Its Computer Simulation (B)

The higher-field half of the spectrum is shown. Computer simulation was performed by using the coupling constants given in the text and a line width of 0.5 G (Lorentzian line shape).

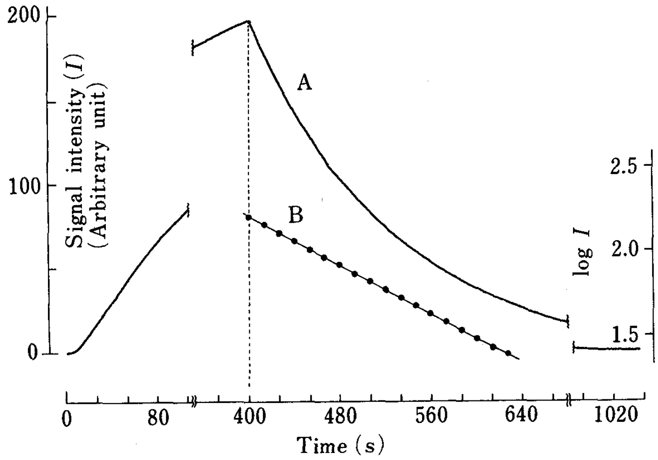

Fig. 3. Open Circuit Relaxation Experiment Following the ESR Signal Generated by *in Situ* Electrolysis of **1b**

In acetonitrile containing 0.1 M Et_4NBF_4 and 0.55 M water at −30 °C. A, signal intensity–time curve (left ordinate); B, plot of logarithm of the signal intensity against time (right ordinate). Initial concentration of **1b**, 10 mM. The pre-electrolysis was allowed to proceed for 400 s (dashed line).

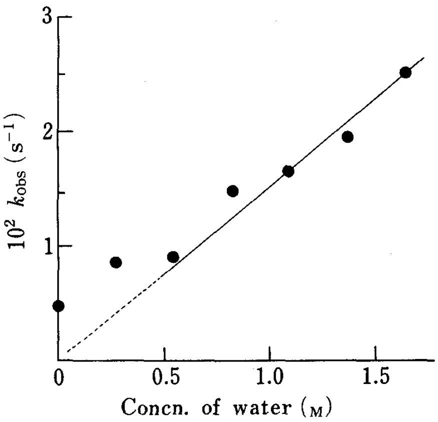

Fig. 4. Dependence of the Observed Pseudo-First-Order Rate Constant for the Decay of the Radical Cation **4b** on the Concentration of Water

The experimental conditions are the same as those in Fig. 3.

2b, and probably **2a**, is not less than two, while the *n*-value for *N*-nitramine formation by the reaction of *N*-nitrosamine radical cation with dioxygen has been shown to be unity.[2]

In situ electrolysis of **1b** in actonitrile at $-30\,^{\circ}\mathrm{C}$ gave an ESR spectrum (Fig. 2), which is assigned to the radical cation **4b** with the following parameters: $g=2.0027$, $A_1=46.0$ (1N), $A_2=7.50$ (1N), $A_3=2.50$ (2H), $A_4=2.32$ (6H), $A_5=1.50$ (2H), and $A_6=0.88$ G (6H). This assignment is supported by the fact that the g-value and the large nitrogen hyperfine splitting of 46 G are close to those reported for other *N*-nitrosamine radical cations.[3] The pattern of the ESR spectrum was not affected by the presence of water at least up to 3%.

Open circuit relaxation experiments[6] on the ESR signal were conducted in order to characterize the reaction of the radical cation with water. A typical example is illustrated in Fig. 3. The rate of decay of the ESR signal decreased with an increase in the duration of electrolysis prior to the circuit opening. In each case, however, a good first-order decay of the radical cation was demonstrated over the period of at least two half-lives (see Fig. 3). As seen in Fig. 4, the observed pseudo-first-order rate constant (k_{obs}) obtained at an arbitrarily chosen period of pre-electrolysis (400 s) showed roughly first-order dependence on the amount of added water except for small water concentrations. Even in the absence of added water, the value of k_{obs} was considerable. At the pre-electrolysis period of 400 s, for example, $k_{\mathrm{obs}}=4.88\times10^{-3}\,\mathrm{s}^{-1}$ without added water, while $k_{\mathrm{obs}}=9.12\times10^{-3}\,\mathrm{s}^{-1}$ with 0.55 M water. The reason for this behavior will be discussed later. When D_2O was used in the place of H_2O, the rate of decay decreased to a small extent: $k_{\mathrm{obs}}(H_2O)/k_{\mathrm{obs}}(D_2O)=1.17$ at a water concentration of 0.55 M and at the pre-electrolysis period of 400 s.

The process (Eqs. 1—4) shown in Chart 2, which represents an overall two-electron oxidation of **1**, is proposed for the formation of the nitramines **2a** and **2b**.

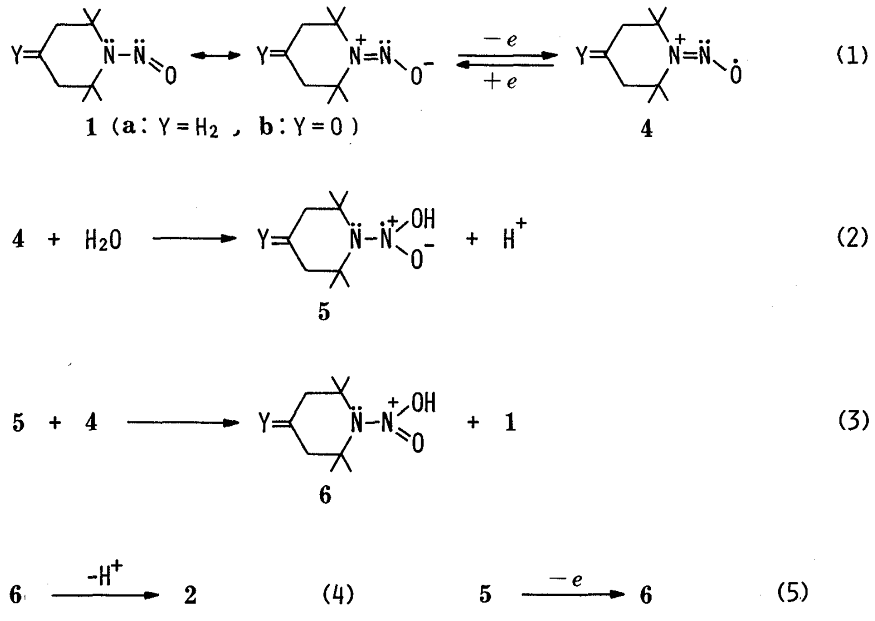

Chart 2

Rate-determining nucleophilic attack of water on the radical cation **4** (Eq. 2) results in the observed kinetics for the decay of **4** in the open circuit experiments, that is, first-order with respect to **4** and water. A similar reaction process, a so-called half-regeneration mechanism, with the same kinetics has been reported for the hydration of 9,10-diphenylanthracene radical cation.[7] The product of reaction of **4** with water is a neutral radical (**5**), and its oxidation potential must be less positive than that of **4**; hence a rapid electron transfer between **4** and **5** seems reasonable (Eq. 3). Homogeneous electron transfer reactions of this type have been well documented in the reactions of relatively stable radical cations with various nucleophiles.[8)] Direct electron transfer from the radical **5** at the electrode to give the cation **6** (Eq. 5) might be considered as an alternative to the homogeneous electron transfer (Eq. 3). However, the absence of any oxidation peak due to the nitramine **2b** in the cyclic voltammetry of **1b** (Fig. 1-A, dashed line) together with the anodic and cathodic peak ratio of close to unity (0.94) (Fig. 1-A, solid line) suggests that the contribution of such electron transfer to the overall process is negligible at least under the present experimental conditions:[9)] the nitramine **2b** showed an irreversible oxidation peak at 2.6 V. The value of $k_{obs}(H_2O)/k_{obs}(D_2O)$ for the decay of the radical cation **4b** (1.17) is in the range expected for solvent isotope effects and cannot be regarded as a result of primary isotope effect. Thus, a mechanism is ruled out which involves rate-determining hydrogen abstraction by **4** from water to give the protonated nitrosamine and hydroxyl radical followed by coupling of the hydroxyl radical with another molecule of **4** to form the cation **6**.

In the open circuit relaxation experiments on **4b**, the decrease in the rate of decay with the duration of the pre-electrolysis can be explained as follows. As seen in Chart 2, two protons are liberated in the formation of each molecule of **2b**. Since no base stronger than water is present in the system,[10)] the proton must be trapped by the water to reduce the concentration of water available for the reaction with **4b**. The half-life of **4b** in the presence of, for example, 0.55 M water is not larger than 80 s as judged from the value of k_{obs}, indicating that during the pre-electrolysis the reaction of **4b** to **2b** proceeds to a considerable extent simultaneously with its generation. The longer the electrolysis is continued, the more protons will be liberated to decrease the rate of decay after the circuit opening. When the water content in the system is very small (*e.g.*, in the absence of added water), the extent of the reaction to **2b** in the pre-electrolysis, and hence the amount of proton release, will be small and the rate of decay will be larger than that expected from the rates obtained at high water concentrations. In the hydration of 9,10-diphenylanthracene radical cation, decay of the radical cation faster than expected has been also observed at low water concentrations.[7)]

Electrolysis of the nitrosamine **1d** at room temperature gave the nitramine **2d** only in the presence of dissolved oxygen and without added water[11)] (Table I, runs 14—16). At −30 °C, however, **2d** was produced in the absence of oxygen, though the yield was higher in the presence of oxygen (runs 17—19). The possibility that the formation of **2d** under a nitrogen atmosphere is due to incomplete deoxygenation of the medium is ruled out from the results obtained on **1f** under the same conditions (runs 30—32). These results suggest that in the electrolysis of **1d** at −30 °C the reactions of the radical cation **4d** with oxygen[2)] and water take place concurrently to form the nitramine **2d**. The low yield of **2d** with added water (run 19) is probably due to the contribution of another reaction of **4d** to the overall process, that is, the decomposition of **4d** initiated by deprotonation from the α-carbon followed by further oxidation of the resulting neutral radical to unidentified products,[12)] as supported by the enhanced voltammetric peak of **1d** in the presence of added water (Fig. 1-D) and by the increased yields of the nitramine **2d**-D, as compared to those of **2d**, in the electrolysis of the α-deuterated *N*-nitrosopiperidine **1d**-D under a nitrogen atmosphere (runs 21 and 22).

In the time-scale of the controlled potential electrolysis, the process for the oxidation of the nitrosamine **1c** seems to be essentially the same as that of **1d** (runs 11—13), though the voltammetric results suggest that the radical cation **4c** is more stable than **4d**. On the other hand, in the electrolysis of the nitrosamines **1e** and **1f**, which showed no reversible character in the voltammetry at −30 °C, the nitramines **2e** and **2f** were formed only from the reaction of the radical cations **4e** and **4f** with dissolved oxygen (runs 27—32) as observed in the electrolysis of **1d** (runs 14—16) and **1f**[2)] at room temperature.

In summary, the following generalizations may be derived from the present observations together with the results reported previously.[2)] First, the electrochemical transformation of *N*-

nitrosodialkylamine to the corresponding *N*-nitramine proceeds *via* the reaction of the *N*-nitrosamine radical cation with dioxygen and/or with water. The former reaction is an overall one-electron process, while the latter is a two-electron process. Secondly, the reaction with water becomes appreciable under conditions where the radical cation exhibits a certain degree of stability as revealed by the observation of reversible character in the cyclic voltammetry of the parent nitrosamine.

The almost negligible and the low yields of the nitramines **2a** and **2b**, respectively, in the electrolysis at room temperature (Table I, runs 1 and 5; see also run 6) suggest the contribution of some other mode of decomposition of the radical cations **4a** and **4b**, which is in a sense similar to that suggested for **4d**. Since the α-carbon atoms of **1a** and **1b** are quaternary, the possibility of C–N bond fission in the radical cations to give carbocations cannot be ruled out, as reported in the electrochemical oxidation of *N*,*N*-di-*tert*-butylformamide in methanol.[13] The activation energy of the decomposition must be larger than that of the reaction in Eq. 2, as evidenced by the increased yields of **2a** and **2b** at lower temperatures. However, the products of the decomposition are still uncertain. The reason for the negligible reactivity of the radical cations **4a** and **4b** toward oxygen is not clear either. Further studies on these points are in progress.

Experimental

Materials——The nitrosamine **1b** was prepared according to the method of Heintz[14] and recrystallized from water, mp 67 °C. Other nitrosamines including **1d-D** were prepared as described previously,[2] and gave the expected analytical results. The mass spectrum of **1d-D** showed that it is composed of **1d**-d_2 (3%), **1d**-d_3 (21%), and **1d**-d_4 (76%). Acetonitrile was purified as described previously.[15] Tetraethylammonium tetrafluoroborate was prepared from Et_4NBr and HBF_4, recrystallized from EtOH, and stored over P_2O_5 under reduced pressure. $H_2{}^{18}O$ (99 atom%) was obtained from CEA, France. Oxygen and nitrogen of more than 99.99% purity were used without any pretreatment.

Apparatus——Cyclic voltammetry and controlled potential electrolysis were carried out as described previously.[15] Infrared (IR), nuclear magnetic resonance (NMR), and mass spectra were obtained on JASCO A-202, Hitachi R-20A, and JEOL JMS-D300 spectrometers, respectively. Gas liquid chromatography (GLC) was performed using a JEOL JGC-20K gas chromatograph connected with a Takeda Riken TR-2215A digital integrator: Silicon DC 550 or PEG 20M was used as the packing. High performance liquid chromatography (HPLC) was carried out using a Waters 6000-A solvent delivery system and a Shimadzu SPD-2A spectrophotometric detector: Bondapack C_{18}-Corasil and 50—80% aqueous methanol were used. ESR spectra were recorded on a JEOL JES-FE 1X spectrometer equipped with 100 kHz field modulation and a ES-UCT-2AX variable-temperature accessory. The electrolysis cell used for internal generation of a nitrosamine radical cation and the procedure for obtaining its ESR spectra were as described previously.[3] A typical example of the open circuit relaxation experiments on **4b** is as follows. A solution of **1b** (10 mM) in acetonitrile containing 0.1 M Et_4NBF_4 and 0.55 M water was deoxygenated and introduced into the electrolysis cell.[3] After thermal equilibrium was attained (−30 °C), the solution was subjected to constant current electrolysis at 20 μA: the same procedure was used to obtain the full spectrum (Fig. 2). The electrolysis was discontinued after 400 s and the generated radical cation **4b** was allowed to decay. The change of intensity of the ESR signal, obtained with a modulation width of 5 G, was monitored continuously from the beginning of the electrolysis at an appropriate magnetic field (Fig. 3).

Identification and Determination of Products from Controlled Potential Electrolysis——Electrolyses were carried out in an H-type cell with 20 ml capacity (anode compartment). A glassy carbon plate and a stainless steel plate were used as the anode and the cathode, respectively. Typical examples of the procedures are described below.

The nitrosamine **1b** (46 mg) was subjected to electrolysis in acetonitrile (20 ml) containing 1% water, 0.1 M Et_4NBF_4, and 400 mg of suspended Na_2CO_3 at 1.79 V at −30 °C until the value of the current became <2% of the initial value. Before electrolysis the anolyte was deoxygenated with nitrogen at room temperature, and during the course of electrolysis a slow stream of nitrogen was passed over the anolyte. From the current–time curve, 67.8 C, which corresponded $n=2.8$, was found to have been consumed. The anolyte was adjusted to 50.0 ml by addition of acetonitrile in a volumetric flask. The resulting solution was subjected to GLC analysis. In a separate run with a larger amount of the substrate (192 mg), the electrolyzed solution was evaporated under reduced pressure, and the residue was extracted with ether (3 x 50 ml). The ether, after being dried with $MgSO_4$, was removed under reduced pressure, and the residue was subjected to preparative thin layer chromatography on neutral alumina with hexane–ethyl acetate (9 : 1) as the developing solvent. *N*-Nitro-2,2,6,6-tetramethyl-4-piperidone (**2b**, 164 mg) was isolated and recrystallized from hexane, mp 103 °C. *Anal.* Calcd for $C_9H_{16}N_2O_3$: C, 53.99; H, 8.05; N, 13.85. Found: C, 54.14; H, 8.17; N, 13.97. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1720 (C=O), 1515 (N–NO_2). NMR ($CDCl_3$) δ: 1.65 (12H, s), 2.75 (4H, s). The nitrosamine **1b** was electrolyzed similarly in the presence of $H_2{}^{18}O$ (99 atom%). The nitramine **2b** was analyzed by mass spectroscopy to determine the ^{18}O content in the nitro group.

N-Nitro-2,2,6,6-tetramethylpiperidine (**2a**) was obtained by essentially the same procedure, mp 84 °C (from MeOH–H_2O). *Anal.* Calcd for $C_9H_{18}N_2O_2$: C, 58.04; H, 9.74; N, 15.04. Found: C, 58.04; H, 9.93; N, 14.89. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1510. NMR ($CDCl_3$) δ: 1.55 (12H, s), 1.6—1.9 (6H, m).

N-Nitro-2,6-dimethylpiperidine (**2c**) was obtained similarly by the electrolysis of **1c** under an oxygen atmosphere, mp 84 °C (from hexane). *Anal.* Calcd for $C_7H_{14}N_2O_2$: C, 53.15; H, 8.92; N, 17.71. Found: C, 53.13; H, 9.21; N, 17.59. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1500. NMR ($CDCl_3$) δ: 1.30 (6H, d), 1.5—2.0 (6H, m), 4.6—5.1 (2H, m).

An authentic sample of *N*-nitro-2-ethylpiperidine (**2e**) was prepared by the oxidation[16] of **1e** with H_2O_2–$(CF_3CO)_2O$, bp 122 °C (8 mmHg). *Anal.* Calcd for $C_7H_{14}N_2O_2$: C, 53.15; H, 8.92; N, 17.71. Found: C, 53.08; H, 9.24; N, 17.70. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1510. NMR ($CDCl_3$) δ: 1.0 (3H, t), 1.3—2.1 (8H, m), 2.8—3.5 (1H, m), 4.4—5.0 (2H, m).

N-Nitroso-2-acetylpiperidine (**3e**) was separated from the electrolyzed solution of **1e** as described above. Since **3e** is unstable and was obtained only in a small amount, elemental analysis could not be performed. However, the following spectral data support its structure. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1720, 1430. NMR ($CDCl_3$) δ: 1.4—2.0 (6H, m), 2.00 (*Z*-isomer) and 2.15 (*E*-isomer) (3H, two s, $C\underline{H}_3$) (*E*/*Z* = 1/3), 3.4—4.0 (1H, m, N–C$\underline{H}$–CO), 4.5—5.0 (2H, m, N–C$\underline{H}_2$).

The nitramines **2d** and **2f** and the β-ketonitrosamine **3f** were obtained from previous work.[2]

Acknowledgement This work was supported in part by a Grant-in-Aid for Scientific Research (60571017) from the Ministry of Education, Science and Culture.

References and Notes

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4) The cyclic voltammogram of **1a** in acetonitrile at −30 °C has been reported previously (ref. 3).
5) Acetonitrile is known to contain a small amount of water if it is not purified and treated with special care to avoid absorption of atmospheric moisture [see, for example, H. Kiesele, *Anal. Chem.*, **53**, 1952 (1981) and references cited therein]. Actually the yield of **2b** decreased to 64% when the electrolysis of **1b** was performed in freshly distilled acetonitrile, containing well-dried Et_4NBF_4 and Na_2CO_3, under a nitrogen atmosphere which was introduced into the electrolysis cell through a drying tube (*cf.* run 9).
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9) In the nitramine formation *via* the reaction of a nitrosamine radical cation with oxygen, an oxidation peak due to the nitramine has been observed in the cyclic voltammetry of the parent nitrosamine (ref. 2).
10) The voltammetric peak of **1f** is unaffected by the presence of a 2-fold excess of $HClO_4$, indicating that **1** is not protonated under the experimental conditions.
11) The yield of **2d** at room temperature in the presence of oxygen was lower than that reported previously (ref. 2). This is probably due to the change in the supporting electrolyte from Et_4NClO_4 (previous work) to Et_4NBF_4 (present work). The affinity of $ClO_4{}^-$ to water is suggested to be larger than that of $BF_4{}^-$ (S. Torii, "Yuki Denkai Gosei," Kodansha, Tokyo, 1981, pp. 20—22), and hence the effect of contaminating water in the medium on the product formation will be larger when Et_4NBF_4 is used as the supporting electrolyte; water has been shown to inhibit the formation of **2d** at room temperature (ref. 2).
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