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Oxidation of N-Alkylhydroxylamines. IV.[1] Anodic Oxidation of N-Alkylhydroxylamines

Hiroteru Sayo, Shigeko Ozaki, and Masaichiro Masui

Faculty of Pharmaceutical Sciences, Osaka University[2]

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The anodic oxidation of N-monoalkyl and N,N-dialkylhydroxylamines in acetonitrile was studied. These hydroxylamines showed two anodic waves at glassy-carbon electrode. Controlled potential electrolysis of the hydroxylamines at the first wave consumed two electrons per molecule oxidized. N-Alkylhydroxylamines and N,N-dimethylhydroxylamine gave the corresponding nitroso compounds and a nitrone, $MeN(O)=CH_2$, respectively, while N,N-di-*t*-butylhydroxylamine gave *t*-nitrosobutane, *t*-butanol and isobutene. In the anodic oxidation the peak potentials were linearly related with the second order rate constants for oxidation of the hydroxylamines with DPPH, except in the case of N,N-di-*t*-butylhydroxylamine and di-*t*-butylnitroxide.

We investigated the oxidation of N-alkylhydroxylamines (hydroxylamines) with several one-electron oxidants and suggested a mechanism in which the nitroxide is formed by one-electron transfer from the nitrogen followed by a proton transfer from the hydroxyl group. We also showed that hydroxylamines are more susceptible to oxidation by one-electron oxidants than the corresponding amines.[1]

Electrochemical oxidation of hydroxylamines has received much less attention than that of amines and most studies on it have been to develop a quantitative method for analysis of hydroxylamines.[3] In the present study, we investigated the electrochemical oxidation of hydroxylamines in detail and compared the results with those on oxidation with one-electron oxidants.

Result

Cyclic Voltammetry

A preliminary experiment on *t*-butylhydroxylamine in aqueous buffer solution using cyclic voltammetry gave a single oxidation wave at pH 7 to 12. The value of E_p (peak potential) decreased linearly up to pH 9 and was not dependent on pH beyond pH 9, which corresponds closely to the pK_a value of the *t*-butylhydroxylammonium ion[4] (Table I).

Table I. Anodic Peak Potential of *t*-Butylhydroxylamine

pH	7.2	8.4	9.3	10.4	11.4	12.5
E_p V *vs.* SCE	0.95	0.80	0.70	0.70	0.70	0.70

However, other hydroxylamines did not show a distinct current peak in aqueous media. Next, anodic oxidation of hydroxylamines was studied in a nonaqueous solvent, acetonitrile. Results on the voltammetric behaviors of N-monoalkylhydroxylamines and N,N-dialkyl-

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[1] Part III: H. Sayo, S. Ozaki, and M. Masui, *Chem. Pharm. Bull.* (Tokyo), **21**, 415 (1973).

[2] Location: *1, Toneyama-6-chome, Toyonaka.*

[3] P.E. Iverson and H. Lund, *Anal. Chem.*, **41**, 1323 (1969).

[4] T.C. Bissot, R.W. Parry, and D.H. Campbell, *J. Am. Chem. Soc.*, **79**, 796 (1957).

hydroxylamines at a stationary glassy-carbon electrode in acetonitrile are summarized in Table II. Two oxidation waves were generally observed at a scanning rate of about 0.2 V sec^{-1}—0.05 V sec^{-1}, and both were irreversible. From its $i_p/CAv^{1/2}$ values, the first wave seems to correspond to one-electron transfer, except in the case of N,N-di-*t*-butylhydroxylamine.[5] The value of $E_p—E_p/2$ ($E_p/2$; half peak potential) for di-*t*-butylnitroxide shows that the slope of the current-potential curve is much steeper than that of the hydroxylamines.

Therefore, it is inappropriate to compare the value of $i_p/CAv^{1/2}$ of the nitroxide with those of the hydroxylamines.

Table II. Cyclic Voltammetric Data of N-Monoalkyl and N,N-Dialyklhydroxylamines in Acetonitrile 25°

No.	Compound	E_p, V *vs.* SCE 1st wave	2nd wave	$i_p/CAv^{1/2}$ [a]	($E_p-E_p/2$) V
1	EtNHOH	0.65[b]	1.45[b]	0.675	0.38
2	-NHOH	0.60[b]	1.45[b]	0.443	0.23
3	EtCH(CN)NHOH	1.40[c]	1.90[c]	[d]	0.23
4	*t*-BuNHOH	0.80[b]	1.55[c,b]	0.480	0.23
5	$Me_2CEtNHOH$	0.85[b]			0.30
6	$Me_2C(CN)NHOH$	1.50[c]	2.25[c]	[d]	0.20
7	$Me_2C(COOEt)NHOH$	1.05[b,c]	1.80[c]	0.580	0.30
8	$\{Pr^nCH(CN)\}_2NOH$	1.90[c]	2.45[c]	[d]	0.23
9	Me_2NOH	0.50[b]	1.25[b]	0.426	0.33
10	(t-Bu)$_2$NOH	1.00[b,c]	1.55[c]	0.892	0.22
11	(t-Bu)$_2\dot{N}O$	0.45[b]	1.55[c]	1.28	0.06

a) These values are for the first wave. i_p; the peak current in ampere, C; the bulk concentration in moles/liter, A; the area of electrode in cm^2, v; the scan rate in volts per second.
b) Sodium perchlorate was used as supporting electrolyte.
c) Ethyltri-*n*-butylammonium tetrafluoroborate was used as supporting electrolyte. The essentially same data were obtained when EtN (n-Bu)$_3BF_4$ was used instead of sodium perchlorate.
d) At the potentlai more positive than 1.5V, the appearance of a background current makes it difficult to measure the net current caused by electrolysis of the substrate.

From results by voltammetry on nitrosoethane, ethyl α-nitrosoisobutyrate, nitrosocyclohexane and *t*-nitrosobutane, the second wave was found to coincide with the oxidation wave of these compounds. In this work, mainly the first wave was examined.

As seen in Table II, hydroxylamines are in general more susceptible to electrochemical oxidation than the corresponding amines.[5] Dialkylhydroxylamine seems more easily oxidizable than monoalkylhydroxylamines, but the presence of a strongly electron-withdrawing group or a bulky group affects this. With primary or secondary groups, the peak potential is less positive than with tertiary alkyl groups which causes greater steric hindrance. (E_p for EtCH(CN)NHOH is less positive than that for $Me_2C(CN)NHOH$; E_p for Me_2NOH is less positive than that for (t-Bu)$_2$NOH.)

Results of cyclic voltammetry on hydroxylamines using platinum electrode were essentially identical with those using a glassy-carbon electrode. However, values for i_p showed poor reproducibility, probably because of the difficulty in obtaining an identical electrode surface in each measurement.

The observed values of E_p of the hydroxylamines investigated are more positive than those obtained by Iverson and Lund at a dropping mercury electrode.[6]

Differences between values obtained at mercury and at platinum electrodes are not uncommon.[7]

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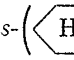
5) C.K. Mann, *Anal. Chem.*, **36**, 2424 (1964).
6) P.E. Iverson and H. Lund, *Acta Chem. Scand.*, **19**, 2303 (1965).
7) I.M. Kolthoff and J.J. Lingane, Polarography, 2nd ed. Vol. 2, Interscience Pub., 1952, p. 779.

Controlled Potential Electrolysis and Product Analysis

Controlled potential electrolysis of the compounds shown in Table III at a potential near that of first peak was carried out in acetonitrile containing sodium perchlorate at a glassy-carbon anode.

TABLE III. Oxidation products from N-Monoalkyl and N,N-Dialkylhydroxylamines in Acetonitrile

Compound	Pyridine present	Potential[a] applied	n	Product	Yield[b]
EtNHOH	no	0.7	0.54	*cis*-(EtN=O)$_2$	26%
	yes	0.7	1.64		[c]
-NHOH	no	0.7	0.70	*cis*-(-N=O)$_2$	33%
	yes	0.7	1.85		[c]
t-BuNHOH	no	0.80	0.66	*t*-BuN=O	35%
	yes	0.90	1.95	*t*-BuN=O	95%
Me$_2$CEtNHOH	no	0.85	0.62	Me$_2$CEtN=O	39%
	yes	0.95	1.54	Me$_2$CEtN=O	76%
Me$_2$NOH	no	0.60	0.65	MeN(O)=CH$_2$	34%
	yes	0.60	1.85		[c]
(*t*-Bu)$_2$NOH[d]	yes	1.05	2.10	*t*-BuN=O *t*-BuOH Me$_2$C=CH$_2$	91% 26% 6%
(*t*-Bu)$_2$N$\dot{\text{O}}$	no	0.6	0.48	*t*-BuN=O *t*-BuOH Me$_2$C=CH$_2$	49%, 49%[e] 42%, 51%[e] 8%, 5%[e]
	yes	0.6	0.95	*t*-BuN=O *t*-BuOH Me$_2$C=CH$_2$	90% 30% 17%

a) volts *vs.* SCE
b) mole per cent of starting hydroxylamine
c) It is impossible to measure the yield of these nitrosoalkane dimer and the nitrone because they have the absorption in the ultra violet region, of which wave length are close to that of pyridine.
d) (*t*-Bu)$_2$NOH·HClO$_4$ was converted to free hydroxylamine in a deoxygenated electrolyte solution by adding excess pyridine.
e) Yield on the oxidation in acetonitrile containing 1% (v/v%) water.

Monoalkylhydroxylamines

Anodic oxidation of *t*-butylhydroxylamine gave an n value (the number of coulombs passed per mole of *t*-butylhydroxylamine) of 0.66 and *t*-nitrosobutane was obtained in 35% yield from the starting material. This suggests that about a third of the hydroxylamine was oxidized through two-electron oxidation to *t*-nitrosobutane while about two thirds was not oxidized, probably because of protonation. The yield of *t*-nitrosobutane and the n value increased up to 95% and 1.95, respectively, when excess pyridine was added to the solution just before electrolysis as an acceptor of the proton generated in the oxidation of *t*-butylhydroxylamine. The results of controlled potential oxidation of several hydroxylamines are summarized in Table III.

The other three monoalkylhydroxylamines examined had n values of 0.54—0.66 in the absence of pyridine and 1.64—1.95 in the presence of pyridine.

Product analysis showed that anodic oxidation of ethylhydroxylamine and cyclohexylhydroxylamine gave the *cis*-nitrosoethane and *cis*-nitrosocyclohexane dimer, respectively.

Their yields were close to those predicted from coulometric n values, and they isomerized slowly to the *trans* form. Oxidation of *t*-butylhydroxylamine and *t*-amylhydroxylamine gave the *t*-nitrosobutane and *t*-nitrosopentane monomer, respectively.

During controlled potential electrolysis of *t*-butylhydroxylamine, a weak electron spin resonance (ESR) signal assigned to *t*-butylnitroxide was detected by an internal generation technique.

Dialkylhydroxylamines

In the absence of pyridine, anodic oxidation of N,N-dimethylhydroxylamine showed an *n* value of 0.65 and gave a nitrone, N-methylmethyleneamine N-oxide, in 26% yield from the starting material. The *n* value increased to 1.85 on addition of excess pyridine. During controlled potential electrolysis of N,N-dimethylhydroxylamine, an ESR spectrum assigned to $Me_2N\dot{O}$, having six equivalent protons with 12.3G *h.f.s.* and a nitrogen atom with 15.2G *h.f.s.* was observed.

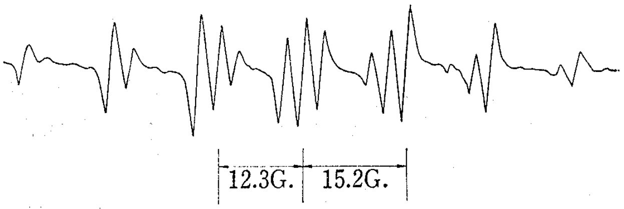


Fig. 1. The ESR Spectrum of $Me_2N\dot{O}$ obtained during the Controlled Potential Electrolysis of Me_2NOH

Anodic oxidation of N,N-di-*t*-butylhydroxylamine yielded *t*-nitrosobutane, *t*-butanol and isobutene but not di-*t*-butylnitroxide, although N,N-di-*t*-butylhydroxylamine has been reported to be oxidized easily to di-*t*-butylnitroxide by air.[8]

Anodic oxidation of di-*t*-butylnitroxide showed an *n* value of 0.48 and gave *t*-nitrosobutane, *t*-butanol and isobutene in 49%, 42% and 8% yield, respectively, from the starting material. Addition of an excess amount of water increased the yield of *t*-butanol and decreased that of isobutene. The total yield of *t*-butanol and isobutene was found to be nearly equal to that of *t*-nitrosobutane in both the above cases. The presence of excess pyridine during oxidation of di-*t*-butylnitroxide increased the *n* value to 0.95 and the yield of *t*-nitrosobutane up to 90%, but decreased the total yield of *t*-butanol and isobutene.

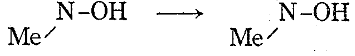
Discussion

Reaction Scheme

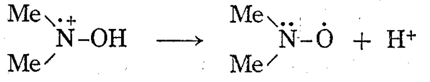
A reaction scheme for the oxidation of alkylhydroxylamines was formulated based on the oxidation products and the following experimental results; (1) both the electron density and the steric hindrance around the nitrogen atom of hydroxylamines affect the potential of the anodic waves, (2) the value of $i_p/CAv^{1/2}$ for the first wave corresponds to one-electron transfer except in the case of N,N-di-*t*-butylhydroxylamine, (3) the *n* value of 0.65 increases up to around 1.95 on addition of excess pyridine, (4) the nitroxide radicals $t\text{-BuNH}\dot{O}$ and $Me_2N\dot{O}$ can be observed during controlled potential electrolysis of *t*-butylhydroxylamine and N,N-dimethylhydroxylamine, respectively.

N,N-Dialkylhydroxylamines

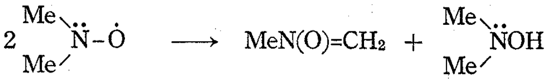
1) N,N-Dimethylhydroxylamine——The yield of $MeN(O){=}CH_2$ was close to that predicted from the *n* value and a radical, $Me_2N\dot{O}$, was detected during the oxidation. These results suggest the following reaction scheme.



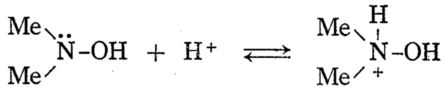
$$\mathrm{Me_2\ddot{N}{-}OH \xrightarrow{-e} Me_2\dot{N}^{+}{-}OH} \qquad (1)$$



$$\mathrm{Me_2\dot{N}^{+}{-}OH \longrightarrow Me_2\ddot{N}{-}\dot{O} + H^{+}} \qquad (2)$$



$$2\,\mathrm{Me_2\ddot{N}{-}\dot{O} \longrightarrow MeN(O){=}CH_2 + Me_2\ddot{N}OH} \qquad (3)$$



$$\mathrm{Me_2\ddot{N}{-}OH + H^{+} \rightleftharpoons Me_2\overset{H}{N}{}^{+}{-}OH} \qquad (4)$$

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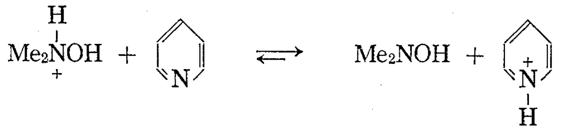
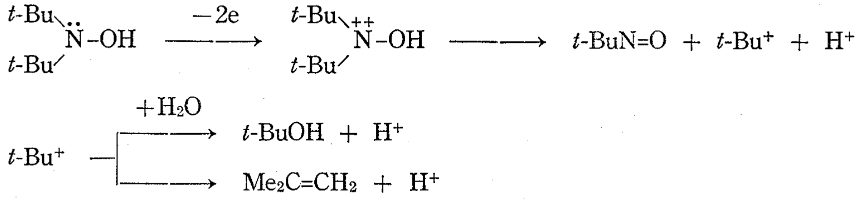
[8] A.K. Hoffman, A.M. Feldman, E. Gelblum, and W.G. Hodgson, *J. Am. Chem. Soc.*, **86**, 639 (1964).

In the above scheme $Me_2\dot{N}O$ undergoes disproportionation before being oxidized further at the anode. In the presence of pyridine, there may be an equilibrium which largely favors



formation of the pyridinium ion, so that substantial amount of N,N-dimethylhydroxylamine undergoes oxidation without being protonated.

2) N,N-Di-*t*-butylhydroxylamine and di-*t*-Butylnitroxide——The E_p value of di-*t*-butylnitroxide was much less positive than that of N,N-di-*t*-butylhydroxylamine and the value of $i_p/CAv^{1/2}$ was considerably larger than the value corresponding to one-electron transfer (Table I). These findings support the following reaction scheme.

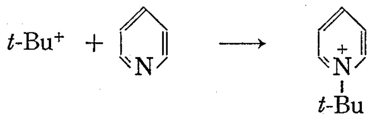


$$(t\text{-Bu})_2\ddot{N}\text{-OH} \xrightarrow{-2e} (t\text{-Bu})_2\overset{++}{N}\text{-OH} \longrightarrow t\text{-BuN=O} + t\text{-Bu}^+ + H^+$$

$$t\text{-Bu}^+ \xrightarrow{+H_2O} t\text{-BuOH} + H^+ \qquad t\text{-Bu}^+ \longrightarrow Me_2C{=}CH_2 + H^+$$

In oxidation of either N,N-di-*t*-butylhydroxylamine or di-*t*-butylnitroxide, the transient intermediate, *t*-butyl cation should undergo further reaction in a similar way, since the oxidation products are identical in the two reactions and the coulometric n value of the former is twice that of the latter.

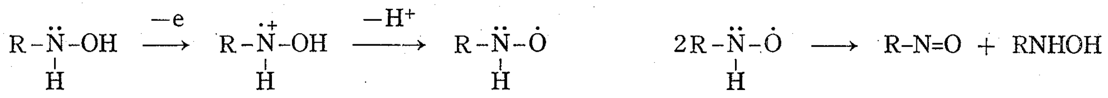
The *t*-butyl cation formed reacts with a trace of water present in acetonitrile or is deprotonated to form isobutene as above. Thus addition of water to the reaction medium increases the yield of *t*-butanol and decreases that of isobutene (Table III). Probably nucleophilic attack of pyridine on *t*-butyl cation caused the decreased yield of *t*-butanol observed in the



experiment with excess pyridine.[9]

Monoalkylhydroxylamines

The possible reaction scheme for anodic oxidation of monoalkylhydroxylamines is as follows:



$$R\text{-}\underset{H}{\ddot{N}}\text{-OH} \xrightarrow{-e} R\text{-}\underset{H}{\overset{\cdot+}{N}}\text{-OH} \xrightarrow{-H^+} R\text{-}\underset{H}{\ddot{N}}\text{-}\dot{O} \qquad 2R\text{-}\underset{H}{\ddot{N}}\text{-}\dot{O} \longrightarrow R\text{-N=O} + RNHOH$$

The intermediate, N-alkylnitroxide probably undergoes disproportionation rather than further oxidation. This seems likely because monoalkylnitroxides undergo disproportionation about 1000 times faster than dimethylnitroxide,[10] and the latter was found to undergo disproportionation only in the present study. ESR measurements showed only a weak signal, which is in accord with the much lower stability of the monoalkylnitroxide than that of dimethylnitroxide.

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[9] *a*) J.J. O'Conner and I.A. Pearl, *J. Electrochem. Soc.*, **111**, 335 (1964); *b*) V.D. Parker and L. Everson, *Chem. Commun.*, **1969**, 451.

[10] *a*) D.F. Bowman, T. Gillan, and K.U. Ingold, *J. Am. Chem. Soc.*, **93**, 6551 (1971); *b*) *Idem, ibid.*, **93**, 6555 (1971).

Correlation between Chemical and Electrochemical Oxidation

1) Products——In the present study, anodic oxidation of hydroxylamines was found to give essentially the same products as those obtained by DPPH oxidation except with an isomerized dimeric nitroso compound. Anodic oxidation of ethylhydroxylamine and cyclohexylhydroxylamine selectively gave the *cis*-nitrosoethane dimer and *cis*-nirosocyclohexane dimer, respectively.

Oxidation with DPPH or bromine gave the corresponding *trans*-nirosoalkane dimer.[1,11] However, in DPPH or bromine oxidation, it is not certain whether the *trans*-dimer was formed exclusively or whether a mixture of the *trans* and *cis* dimer was formed since the *cis*-dimer can isomerise to the *trans*-dimer which is thermodynamically more stable during the process of separation and recrystallization.

The formation of the *cis*-dimer only in the present anodic oxidation suggests that the *cis*-dimer is formed after pre-orientation of the monomer at the surface of the electrode.

However, it seemes unlikely that all of the monomer is formed at the surface of the electrode, since in the present oxidation the nitroxide radicals was observed, showing that some disproportionation to form the nitroso compound must occur in the bulk of the solution as well as at the surface of the electrode. It has already been reported that formation of the *cis*-isomer from two monomers is kinetically preferred.[12]

Thus the detection of the *cis*-dimer only in the present oxidation can be explained by assuming that two monomeric molecules dimerize selectively towards the kinetically favored *cis*-dimer which isomerizes to *trans*-form on a time scale that is longer than the time required for electrolysis at room tempeature.[13]

2) Reaction Mechanism——The second order rate constants for the oxidation of hydroxylamines with DPPH[1] are plotted against the peak potential for the anodic oxidation in Fig. 2. A fairly good linear relationship is obtained for all the hydroxylamines except N,N-di-*t*-butylhydroxylamine and di-*t*-butylnitroxide.

This indicates that the reaction rate of DPPH oxidation and the E_p of the anodic oxidation show similar systematic changes with change in structure of the hydroxylamine. Thus the reaction mechanisms for the two oxidation must be similar and involve one of the lone-pair of electrons at the nitrogen in the initial reaction step of electron transfer, which is the rate determining step.[1] The deviation of N,N-di-*t*-butylhydroxylamine and di-*t*-butylnitroxide from this linear relation may be explained as follows. N,N-Di-*t*-butylhydroxylamine, which is the most susceptible of the compounds to DPPH oxidation, shows an anodic wave at a more positive potential than that expected, probably because steric hindrance around the nitrogen atom makes it difficult for an electron to be abstracted from the nitrogen by a rigid and bulky electrode. *t*-Butylnitroxide is most easily oxidized at the electrode, because it has a system

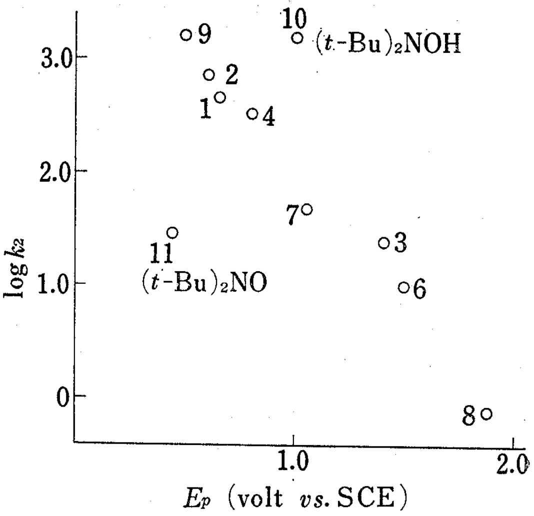

Fig. 2. Correlation of the Peak Potentials with the Second Order Rate Constants

k_2: second order rate constants for the oxidation of hydroxylamines with DPPH at 25° in ethanol

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[11] E. Muller and H. Metzger, *Chem. Ber.*, **88**, 165 (1955).

[12] *a*) A. Mackor, Th.A.J.W. Wajer, and Th.J. de. Boer, *Tetrahedron Letters*, **1967**, 2757; *b*) Th.A.J.W. Wajer and Th.J.de. Boer, *Rec. Trav. Chim.*, **91**, 565 (1972).

[13] T. Emery and J.B. Neilands, *J. Am. Chem. Soc.*, **82**, 4903 (1960).

of three electrons distributed between the nitrogen and oxygen and the electron can be abstracted from the nitrogen or oxygen side.

Hence its structure seems favorable for oxidation even by a rigid and bulky electrode. However, a nitroxide is less reactive towards chemical oxidation than expected. Thus the reactivity of oxidants with a substrate may be governed by the electron density at the reaction site of the substrate rather than by the geometrical structure.

Experimental

Materials——Acetonitrile was purified by the method of Mann.[14]

cis-Nitrosoethane dimer was prepared by the method of Emery.[13] Other nitrosoalkanes and hydroxylamines were prepared as described previously.[1] The supporting electrolyte, ethyltri-*n*-butylammonium tetrafluoroborate was prepared by the method of House.[15] Sodium perchlorate was recrystallized from ethanol–water, dried and stored *in vacuo* over P_2O_5.

Cyclic Voltammetry——Cyclic voltammetry was done with a three electrode system employing a linear scanning unit (Hokuto Denko Co, Model HB-101) equipped with a potentiostat (Hokuto Denko Co., Model PS-500B).

The electrode system consisted of a glassy-carbon indicator electrode (G.C.E.), a glassy-carbon counter electrode, and a saturated calomel electrode (S.C.E.). The S.C.E. was separated from the solution (acetonitrile) by a sintered disk and agar plug containing 0.1M sodium perchlorate. The G.C.E. was prepared by cutting glassy-carbon (GC-20, Tokai Electrode Manufacturing Co.) into a cylinder and coating its side with epoxy resin. Measurements were made at 25° with hydroxylamine concentration of 2—5 mM and a concentration of supporting electrolyte of about 0.1M. The scanning rate was $0.2\,V\,sec^{-1}$ $-0.05\,V\,sec^{-1}$ and current-potential curves were recorded using a Toa Model XYR-2A X–Y recorder.

Controlled Potential Electrolysis——Apparatus and Procedure: Electrolysis were performed with a potentiostat (Yanagimoto Manufacturing Co., Model V-8) and current was recorded with a Toa Electronics EPR-10A recorder. The quantity of electricity consumed in the electrolysis was calculated by integration from a current-time curve. An H-cell was used. The electrolysis solution in the anode was separated from the cathode by a sintered disk and methyl cellulose 400 plug containing 1M sodium perchlorate. The concentration of substrate was generally $1—2 \times 10^{-2}$M and that of the supporting electrolyte (sodium perchlorate) was about 0.1M. Solutions were deoxygenated by bubbling nitrogen gas through them and pre-electrolysis was run at the potential used for oxidation. The reactant and pyridine were introduced after pre-electrolysis and then electrolysis was carried out with mechanical stirring.

When isobutene was formed during electrolysis, it was prevented from escaping by sealing the anodic compartment with a cap. When monomeric nitroso compounds were formed, electrolysis was carried out in the dark to prevent photo-decomposition of these compounds.

Product Analysis——a) Monomeric and Dimeric Nitroso Compounds: The monomeric nitroso compounds, *t*-nitrosobutane and *t*-nitrosopentane were estimated by measuring their absorbancy in the visible region, at 680 mμ. The *cis*-dimeric nitroso compounds, nitrosoethane and nitrosocyclohexane, were estimated by measuring their ultraviolet absorption at 267 mμ and 278 mμ,[16] respectively.

b) *t*-Butanol and Isobutene: *t*-Butanol and isobutene were measured by gas chromatographic analysis in a JEOL JGC-750 gas chromatograph using 10 μl of the solution after electrolysis. The columun was packed with $AgNO_3$–benzylcyanide on 60—80 mesh NEOPAK 1A and maintained at 40°.

c) N-Methylmethyleneamine N-Oxide: $MeN(0)=CH_2$ was estimated by measuring the absorption at 243 mμ. The absorption in this region was well separated from that of nitrosomethane dimer and was essentially identical with that of $MeN(0)=CH_2$ prepared by a known method.[17] The apparent molar coefficient of $MeN(0)=CH_2$ was calculated to be 9800 assuming that, since $MeN(0)=CH_2$ could not be isolated,[18] the reaction proceeded to completion. The nitrone was also hydrolyzed to formaldehyde and methylhydroxylamine in 2N HCl and identified as the 2,4-dinitrophenylhydrazone of formaldehyde (80% yield, mole per cent of the starting hydroxylamine). The hydrazone was recrystallized from methanol (mp 166—168°).

ESR Measurements——The ESR spectrum of the free radicals formed during electrolysis were recorded with a JEOL P-10 spectrometer. The *h.f.s.* was measured using potassium peroxylamine disulfonate as a standard. The radicals were prepared in a electrolysis cell inserted into the cavity of the spectrometer.

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A platinum wire was used for the anode and the other electrode was essentially the same as that used in cyclic voltammetry. During electrolysis the flow rate of solutions containing hydroxylamines ($2—5\times10^{-2}$M) and sodium perchlorate (0.1M) was 15 ml hr^{-1}.

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