quenching by *tert*-butylamine of phosphorescence of benzophenone,[39] 7.0 × 10^7 M^{-1} sec^{-1}. That the value is lower than that for 2-butylamine may be due to a less favorable steric factor for interaction of the benzophenone triplet with the nonbonding electrons of N.

Acknowledgment. This work was supported by Fellowships under Title IV of the National Defense Education Act and from the Petroleum Research Fund, administered by the American Chemical Society, and by the National Science Foundation, GP 9247.

Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. II. Self-Reactions of *N*-Alkyl Nitroxides and *N*-Phenyl Nitroxide[1,2]

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Abstract: The self-reactions of methyl, isopropyl, *tert*-butyl, and phenyl nitroxides in solution have been examined by epr spectroscopy. The reaction is a disproportionation to yield a hydroxylamine and a nitroso compound: 2RNHO· → RNHOH + RNO. Rate constants for this reaction have been measured in several solvents. In benzene at 25° the rate constants are in the range 4 × 10^7 to 3 × 10^6 M^{-1} sec^{-1}. For R = phenyl and R = *tert*-butyl the reaction was shown to be reversible and the equilibrium constants were measured over a range of temperature. The measured enthalpy change for the reaction with R = *tert*-butyl is in good agreement with that calculated (for R = CH_3) from the heats of formation of the various species involved. Evidence is presented for hydrogen bonding of methyl nitroxide in methanol. The rate constant for the slow conversion of phenyl nitroxide to azoxybenzene has also been measured over a range of temperature in benzene.

It has been known for some time from qualitative observations made during the recording of the electron paramagnetic resonance spectra of nitroxide radicals that *N*-alkyl and *N*-aryl nitroxides are much less stable than the majority of *N,N*-dialkyl or *N,N*-diaryl nitroxides. The epr spectra of phenyl nitroxide[5-10] and several alkyl nitroxides (*e.g.*, MeNHO·,[11,12] *i*-PrNHO·,[13] *tert*-BuNHO·,[13,14] $PhCH_2NHO$·[15]) have been reported but there have been no quantitative studies of the stabilities or of the decay of any of these radicals. In Part I[2] we described an epr study of the kinetics and mechansim of the self-reaction of *N,N*-diethyl nitroxide in solution. The present paper describes a similar study of the self-reactions of methyl, isopropyl, *tert*-butyl, and phenyl nitroxides.

Experimental Section

The general experimental procedure has been described previously.[2] Nitroxide radicals were produced from the appropriate hydroxylamine in the cavity of a Varian E3 epr spectrometer. The hydroxylamine was oxidized to nitroxide by *tert*-butoxy radicals formed by the photolysis of di-*tert*-butyl peroxide (0.05–0.5 *M* generally)

$$tert\text{-BuOOBu-}tert \xrightarrow{h\nu} 2tert\text{-BuO}\cdot$$

$$tert\text{-BuO}\cdot + \text{RNHOH} \longrightarrow tert\text{-BuOH} + \text{RNHO}\cdot$$

When the light was cut off the decay of the signal due to RNHO· was rapid. The general procedure of Weiner and Hammond[16] was used to monitor the radical decays. That is, the light beam was chopped by a rotating sectored disc and a large number of identical decays were collected by a Fabri-Tek 1072 signal averager. In most cases the reactant solution flowed slowly through the cavity during an experiment. This prevented the build-up of nitroxide radicals which were more stable than the nitroxide under study, but did not interfere with the measurement of radical decays or of radical concentrations.

N-Methylhydroxylamine hydrochloride was obtained from Aldrich and was recrystallized from ethanol–ether. Neutralization of the dried salt with sodium glycolate yielded the free base which was distilled at reduced pressure under helium into receivers cooled in liquid nitrogen. This material was used immediately in the epr experiments without exposure to air.

N-Isopropylhydroxylamine and *N*-*tert*-butylhydroxylamine were prepared by reduction of the corresponding nitro compounds using the method described by Meisenheimer and Chou.[17] The hydroxylamine hydrochlorides were treated in the same way as for the methyl compound. *N*-Phenylhydroxylamine was prepared by the method of Vogel.[18]

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(1) Issued as NRCC No. 12239.

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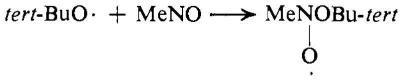
Results

(i) Alkyl Nitroxides. Although all four of the nitroxides studied in this work could be made to decay with clean second-order kinetics, some care was necessary to achieve this result. The photolysis of solutions of alkyl hydroxylamines containing di-*tert*-butyl peroxide for periods greater than ~0.1–1.0 sec resulted in the build up of secondary radicals which, of course, interfered with the decay measurements. Although these secondary radicals were not investigated in detail, the major component from methylhydroxylamine was tentatively identified as methyl *tert*-butoxy nitroxide (ten lines in benzene, $a_N \sim 29$ G, $a_H \sim 9.5$ G) and that from *tert*-butylhydroxylamine was identified as di-*tert*-butyl nitroxide (three lines in benzene, $a_N \sim 15.5$ G). The formation of the former radical can be ascribed to the trapping of *tert*-butoxy radicals by the nitrosomethane which is formed in the self-reaction of methyl nitroxide radicals. The complete reaction sequence could be represented as

$$\textit{tert}\text{-BuOOBu-}\textit{tert} \xrightarrow{h\nu} 2\textit{tert}\text{-BuO}\cdot$$

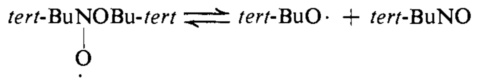
$$\textit{tert}\text{-BuO}\cdot + \text{MeNHOH} \longrightarrow \textit{tert}\text{-BuOH} + \text{MeNHO}\cdot$$

$$\text{MeNHO}\cdot + \text{MeNHO}\cdot \longrightarrow \text{MeNHOH} + \text{MeNO}$$



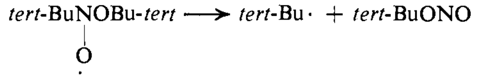
$$\textit{tert}\text{-BuO}\cdot + \text{MeNO} \longrightarrow \text{Me}\underset{\dot{\text{O}}}{\underset{|}{\text{N}}}\text{OBu-}\textit{tert}$$

Nitroso compounds are known to be good traps for alkoxy radicals[14,19,20] and it was therefore a surprise to find that the major secondary radical from *tert*-butylhydroxylamine was di-*tert*-butyl nitroxide rather than *tert*-butoxy *tert*-butyl nitroxide. However, the latter radical is known to be unstable[19] and to decompose. The products may be a *tert*-butoxy radical and 2-methyl-2-nitrosopropane[21]



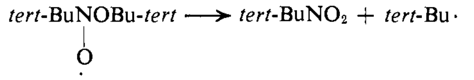
$$\textit{tert}\text{-Bu}\underset{\dot{\text{O}}}{\underset{|}{\text{N}}}\text{OBu-}\textit{tert} \rightleftharpoons \textit{tert}\text{-BuO}\cdot + \textit{tert}\text{-BuNO}$$

or a *tert*-butyl radical and *tert*-butyl nitrite[19,22]



$$\textit{tert}\text{-Bu}\underset{\dot{\text{O}}}{\underset{|}{\text{N}}}\text{OBu-}\textit{tert} \longrightarrow \textit{tert}\text{-Bu}\cdot + \textit{tert}\text{-BuONO}$$

or a *tert*-butyl radical and 2-methyl-2-nitropropane[23]



$$\textit{tert}\text{-Bu}\underset{\dot{\text{O}}}{\underset{|}{\text{N}}}\text{OBu-}\textit{tert} \longrightarrow \textit{tert}\text{-BuNO}_2 + \textit{tert}\text{-Bu}\cdot$$

In contrast, di-*tert*-butyl nitroxide is completely stable. Nitroso compounds are known to be photolytically unstable[24] and so the 2-methyl-2-nitrosopropane can serve both as a source and as a trap for *tert*-butyl radicals

$$\textit{tert}\text{-BuNO} \xrightarrow{h\nu} \textit{tert}\text{-Bu}\cdot + \text{NO}$$

$$\textit{tert}\text{-Bu}\cdot + \textit{tert}\text{-BuNO} \longrightarrow \textit{tert}\text{-Bu}_2\text{NO}\cdot$$

The different types of secondary nitroxide radicals formed from methyl- and *tert*-butylhydroxylamine can presumably be attributed to differences in the relative stabilities of the dialkyl and *tert*-butoxy alkyl nitroxides.

In the room temperature experiments the formation of the secondary nitroxide radicals was prevented by allowing the hydroxylamine solution to flow slowly through the cavity. Photolysis of the flowing solution gave clean alkyl nitroxide spectra similar to those reported by other workers. When the light was cut off the disappearance of the alkyl nitroxides followed accurate second-order kinetics provided the flow rate was slow compared with the decay rate. In experiments at other temperatures the solution was only passed through the cavity to replace a sample which had already been photolyzed. After the used sample had been flushed out the flow was stopped and the fresh sample was allowed to come to thermal equilibrium before the light was flashed on the sample and the radical decays were monitored. Each sample was used to generate 16 or 32 identical decays which were collected by the signal averager. At each temperature sufficient samples were used to generate smooth decay curves.

The results of the present work with alkyl nitroxides are summarized in Table I. This table lists the bimolecular rate constants, k_{epr}, for the rapid self-reactions

$$2\text{RNHO}\cdot \xrightarrow{k_{\text{epr}}} \text{RNHOH} + \text{RNO}$$

of methyl, isopropyl, and *tert*-butyl nitroxides at 25° in the various solvents employed. The rate constants are averages of not less than five separate experiments which generally covered a reasonable range in the initial nitroxide concentration. Measurements were also made over a range of temperatures with methyl nitroxide in methanol and with isopropyl and *tert*-butyl nitroxides in benzene. The activation parameters for the overall reactions are listed in these cases.

Wajer, *et al.*,[13] have shown that alkyl nitroxides can be produced by treating tertiary nitrosoalkanes with hydroxylamines. This suggested that the self-reaction of *tert*-butyl nitroxide might be reversible

$$2\textit{tert}\text{-BuNHO}\cdot \underset{k_{-\text{epr}}}{\overset{k_{\text{epr}}}{\rightleftharpoons}} \textit{tert}\text{-BuNHOH} + \textit{tert}\text{-BuNO}$$

Benzene solutions of *tert*-butylhydroxylamine and of 2-methyl-2-nitrosopropane (which is monomeric in solution) when mixed together gave low concentrations of *tert*-butyl nitroxide (see Table II). The equilibrium constant for this process is given by

$$(K_{\text{epr}})_{\textit{tert}\text{-BuNHO}\cdot} = \frac{(k_{-\text{epr}})_{\textit{tert}\text{-BuNHO}\cdot}}{(k_{\text{epr}})_{\textit{tert}\text{-BuNHO}\cdot}} = \frac{[\textit{tert}\text{-BuNHO}\cdot]^2}{[\textit{tert}\text{-BuNHOH}]_0[\textit{tert}\text{-BuNO}]_0}$$

where $[\textit{tert}\text{-BuNHOH}]_0$ and $[\textit{tert}\text{-BuNO}]_0$ are the concentrations of hydroxylamine and nitroso compound on mixing, there being no correction necessary for the very small amount of each that is converted to nitroxide. The variation of $(K_{\text{epr}})_{\textit{tert}\text{-BuNHO}\cdot}$ with temperature in benzene can be represented by the van't Hoff relation

$$(K_{\text{epr}})_{\textit{tert}\text{-BuNHO}\cdot} = e^{(\Delta S_{\text{epr}})_{\textit{tert}\text{-BuNHO}\cdot}/R}e^{-(\Delta H_{\text{epr}})_{\textit{tert}\text{-BuNHO}\cdot}/RT}$$

with $(\Delta S_{\text{epr}})_{\textit{tert}\text{-BuNHO}\cdot} = -8.2$ gibbs/mol and $(\Delta H_{\text{epr}})_{\textit{tert}\text{-BuNHO}\cdot} = 10.4$ kcal/mol. That is, the conversion of two *tert*-butyl nitroxide radicals into *tert*-butyl-

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Table I. Bimolecular Rate Constants and Activation Parameters for Fast Nitroxide Radical Decay

Nitroxide	Solvent	[Nitroxide]$_0$^{a} × 10^6, M	$(k_{epr})_{25°}$ × 10^{-6}, M^{-1} sec^{-1}	Temp range, °C	E_{epr}, kcal/mol	Log A_{epr}, M^{-1} sec^{-1}
MeNHO·	Isopentane	b				
	Benzene	0.7–5.0	36 ± 16			
	1-Propanol	2.0–3.5	3.5 ± 0.2			
	Methanol	2.9–7.5	1.5 ± 0.2	−77 to +25	−4.2	3.1
i-PrNHO·	Benzene	1.5–7.0	12 ± 3	8 to 68	2.5	8.9
tert-BuNHO·	Isopentane	0.5–0.7	66 ± 19			
	Benzene	0.8–3.6	6.7 ± 0.8	10 to 72	2.5	8.7
PhNHO·	Benzene	2.0–6.0	3.4 ± 0.3			

^{a} Range of initial nitroxide concentration at 25°. ^{b} Methylhydroxylamine was too insoluble in isopentane to give a usable MeNHO· signal.

Table II. The Equilibrium of *tert*-Butyl Nitroxide in Benzene

Temp, °C	[*tert*-BuNO]$_0$ × 10^3, M	[*tert*-BuNHOH]$_0$ × 10^3, M	[*tert*-BuNHO·] × 10^7, M	K × 10^{10}
24	50	7	3.5	3.4
24	7	50	4.0	4.4
24	29	29	5.6	3.8
24	29	29	5.7	3.9
44	29	29	10	12
63	29	29	16	30
77	29	29	22	59

Table III. The Equilibrium and Slow Decay of Phenyl Nitroxide in Benzene

Temp, °C	[PhNO]$_0$ × 10^3, M	[PhNHOH]$_0$ × 10^3, M	[PhNHO·]$_i$ × 10^5, M	K × 10^5	k_{azo}, M^{-1} sec^{-1}
22	6.6	5.8	2.1	1.2	1.0
22	6.6	29	6.7	2.4	1.5
22	33	5.8	7.3	2.8	1.8
22	33	29	12	1.5	1.8
41	33	29	21.5	4.7	2.2
60	33	29	24	6.0	6.0
80	33	29	37	15	15

hydroxylamine and 2-methyl-2-nitrosopropane is exothermic by 10 kcal/mol in benzene.

The rate constant for the self-reaction of *tert*-butyl nitroxide in benzene at 25°, $(k_{epr})_{tert\text{-BuNHO}\cdot}$, is 6.7 × 10^6 M^{-1} sec^{-1} (Table I). At this temperature the equilibrium constant is 4.4 × 10^{-10} and hence $(k_{-epr})_{tert\text{-BuNHO}\cdot} = 3 \times 10^{-3}\ M^{-1}\ \text{sec}^{-1}$. The variation with temperature of the forward reaction (see Table I) is given by

$$(k_{epr})_{tert\text{-BuNHO}\cdot} = 10^{8.7} \exp(-2500/RT)\ M^{-1}\ \text{sec}^{-1}$$

Combining this with the equilibrium constant gives

$$(k_{-epr})_{tert\text{-BuNHO}\cdot} = 10^{6.9} \exp(-12{,}900/RT)\ M^{-1}\ \text{sec}^{-1}$$

The concentration of *tert*-butyl nitroxide present in equilibrium with the hydroxylamine and nitroso compound did not change noticeably over several days at room temperature nor over 10–15 min at 77°, the highest temperature studied. Given sufficient time the radical signal would presumably decay with the formation of azoxyisobutane

$$tert\text{-BuNHOH} + tert\text{-BuNO} \longrightarrow tert\text{-BuN{=}N}(\rightarrow \text{O})\text{Bu-}tert + H_2O$$

This compound is a stable liquid (bp 50° (20 mm)) which has been prepared by oxidizing azoisobutane with peracetic acid.[25] There seems no reason to suppose that this compound could not be formed in the above reaction since methylhydroxylamine and 2-methyl-2-nitrosobutane when heated in the absence of solvent to 85–110° react to give MeN=N(→O)-*tert*-Bu. Presumably the rate of formation of azoxyisobutane in solution is quite small.

(ii) Phenyl Nitroxide. Under flow conditions and with light flashes of short duration so that each flash fell on a fresh sample of the reactant solution, up to 70–80% of the phenyl nitroxide radicals decayed rapidly with second-order kinetics provided the phenylhydroxylamine concentration was not more than ~4 × 10^{-3} M. However, even under these conditions a small residual concentration of phenyl nitroxide always remained after the initial rapid decay and this disappeared only very slowly. With higher concentrations of phenylhydroxylamine or in static systems with photolysis for periods of a second or longer only a small part of the nitroxide decays rapidly and the main bulk of the radicals disappears extremely slowly. These results are consistent with the report of Russell, *et al.*,[10] that mixtures of nitrosobenzene and phenylhydroxylamine in benzene (and in a number of other solvents) give rise to low concentrations of phenyl nitroxide. These workers found that the concentration of radicals decreased slowly over a period of hours, after which an essentially quantitative yield of azoxybenzene was isolated. It is clear that the initial, fast, bimolecular reaction between phenyl nitroxide radicals must be reversible.

$$2\text{PhNHO}\cdot \underset{k_{-epr}}{\overset{k_{epr}}{\rightleftharpoons}} \text{PhNHOH} + \text{PhNO}$$

The equilibrium constant for this process was measured in benzene over a range of temperature. Known concentrations of phenylhydroxylamine and nitrosobenzene (which is monomeric in solution) were mixed and the initial concentration of phenyl nitroxide, [PhNHO·]$_i$, was determined. The equilibrium constant is given by

$$(K_{epr})_{\text{PhNHO}\cdot} = \frac{(k_{-epr})_{\text{PhNHO}\cdot}}{(k_{epr})_{\text{PhNHO}\cdot}} = \frac{[\text{PhNHO}\cdot]_i^{\,2}}{([\text{PhNO}]_0 - [\text{PhNHO}\cdot]_i)([\text{PhNHOH}]_0 - [\text{PhNHO}\cdot]_i)}$$

The values of this equilibrium constant are given in Table III. The variation with temperature can be represented by the van't Hoff relation, with $(\Delta S_{epr})_{\text{PhNHO}\cdot}$ = 2.9 gibbs/mol and $(\Delta H_{epr})_{\text{PhNHO}\cdot}$ = 7.2 kcal/mol.

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The rate constant for the fast self-reaction of phenyl nitroxide in benzene at 25° is $3.4 \times 10^6\ M^{-1}\ \text{sec}^{-1}$ (Table I). At this temperature $(K_{\text{epr}})_{\text{PhNHO}\cdot} = 2.3 \times 10^{-5}$ and hence $(k_{-\text{epr}})_{\text{PhNHO}\cdot} = 78\ M^{-1}\ \text{sec}^{-1}$ in benzene. If it is assumed that the activation energy for the self-reaction of phenyl nitroxide is 2.5 kcal/mol (as is the case for isopropyl nitroxide and *tert*-butyl nitroxide in benzene) then $A_{\text{epr}} = 2 \times 10^8\ M^{-1}\ \text{sec}^{-1}$. For the back reaction then we have

$$(k_{-\text{epr}})_{\text{PhNHO}\cdot} = 10^{8.9} \exp(-9700/RT)\ M^{-1}\ \text{sec}^{-1}$$

The slow decay of phenyl nitroxide (to yield azoxybenzene eventually[10]) was monitored by epr at each temperature at which the equilibrium constant was measured. The decays were accurately second order in phenyl nitroxide

$$\text{PhNHO}\cdot + \text{PhNHO}\cdot \xrightarrow{k_{\text{azo}}} \text{PhN{=}N({\to}O)Ph} + \text{H}_2\text{O}$$

The measured rate constants for this slow decay, k_{azo}, are given in Table III. From 22 to 80° this rate constant can be represented by

$$k_{\text{azo}} = 2.2 \times 10^6 \exp(-8300/RT)\ M^{-1}\ \text{sec}^{-1}$$

with $(k_{\text{azo}})_{25°} = 1.8\ M^{-1}\ \text{sec}^{-1}$ in benzene. There would seem to be no way of determining whether azoxybenzene is actually produced in a reaction involving two phenyl nitroxide radicals or whether the reaction occurs directly between nitrosobenzene and phenylhydroxylamine, the measured nitroxide concentration serving merely to monitor the change in concentration of these species. Other possibilities also exist, for example, the coupling of the isomeric Ph$\dot{\text{N}}$OH radicals or some condensation reaction involving $\text{PhNO}\cdot^-$, the nitrosobenzene radical anion.[10,26–28]

Discussion

The rate constants for the fast self-reactions of the three alkyl nitroxides and of phenyl nitroxide in benzene at 25° differ by only a factor of ~10 which indicates that the overall reaction is not particularly subject to steric or resonance effects. This result contrasts with the very pronounced influence of steric and resonance factors on the rate constants for the self-reactions of dialkyl and diaryl nitroxides. For example, in benzene at 25°, k_{epr} for dimethyl nitroxide is $2.1 \times 10^4\ M^{-1}\ \text{sec}^{-1}$,[29] and for diisopropyl nitroxide it is $5\ M^{-1}\ \text{sec}^{-1}$ [29] while di-*tert*-butyl nitroxide is completely stable[30] and diphenyl nitroxide would decay only very slowly.[30] The preexponential factors, A_{epr}, for the isopropyl and *tert*-butyl nitroxide self-reactions in benzene are somewhat smaller than the values generally found for simple radical–radical reactions in solution which is consistent with the small (2.5 kcal/mol) activation energies observed for both reactions. It is possible that a part of this activation energy arises from the energy required to desolvate the radicals prior to their self-reaction. That is, the rate data in benzene are consistent with a simple bimolecular disproportionation between two nitroxide radicals with, possibly, a prior desolvation of the radical centers.

$$\text{RNHO}\cdot + \text{C}_6\text{H}_6 \rightleftharpoons (\text{RNHO}\cdot)_{\text{solv}}$$

$$2\text{RNHO}\cdot \longrightarrow \text{RNHOH} + \text{RNO}$$

The rate constants for the self-reactions of methyl and *tert*-butyl nitroxide decrease as the polarity of the solvent increases. The magnitude of this effect appears to be more pronounced than that observed previously for the self-reaction of diethyl nitroxide[2] which probably reflects the more exposed nature of the radical center in the monoalkyl nitroxides.

The very low value of the preexponential factor and the existence of a negative activation energy for the self-reaction of methyl nitroxide in methanol was completely unexpected since diethyl nitroxide behaves quite normally in methanol.[2] The negative activation energy can be qualitatively accounted for by assuming that hydrogen-bonded nitroxide radicals[31] do not react with one another and that the strength of the hydrogen bonds that they form with the solvent is less than the strength of the hydrogen bonds formed in bulk methanol. The overall process can be represented as

$$(\text{MeOH})_m + (\text{MeOH})_n \rightleftharpoons (\text{MeOH})_{m+n} \tag{1}$$

$$\text{MeNHO}\cdot + (\text{MeOH})_n \rightleftharpoons \text{MeNHO}\cdot(\text{MeOH})_n \tag{2}$$

$$\text{MeNHO}\cdot + \text{MeNHO}\cdot \longrightarrow \text{MeNHOH} + \text{MeNO} \tag{3}$$

where $(\text{MeOH})_n$, etc., represent the long chains of hydrogen-bonded methanol molecules which are present in liquid methanol, and $\text{MeNHO}\cdot(\text{MeOH})_n$ represents a hydrogen-bonded nitroxide radical. Since each $(\text{MeOH})_n$ chain contains one nonbonded OH group the concentration of such groups is given by

$$k_1[\text{nonbonded OH}]^2 = k_{-1}[\text{nonbonded OH}]$$

that is

$$[\text{nonbonded OH}] = k_{-1}/k_1 = K_1$$

A hydrogen bond to the nitroxide requires a nonbonded OH group. The concentration of nonbonded nitroxide is therefore given by

$$[\text{MeNHO}\cdot] = \frac{K_2[\text{MeNHO}\cdot(\text{MeOH})_n]}{[\text{nonbonded OH}]} = \frac{K_2}{K_1}[\text{MeNHO}\cdot(\text{MeOH})_n]$$

Since most of the nitroxide radicals will by hydrogen bonded, the rate of nitroxide decay measured by epr spectroscopy is given by

$$\frac{-\text{d}[\text{NO}\cdot]}{\text{d}t} = k_3[\text{MeNHO}\cdot]^2 = k_3\left|\frac{K_2}{K_1}\right|^2[\text{MeNHO}\cdot(\text{MeOH})_n]^2$$

The measured rate constant, k_{epr}, is therefore equal to $k_3K_2{}^2/K_1{}^2$ and the measured activation energy

$$E_{\text{epr}} = -4.2\ \text{kcal/mol} = E_3 + 2\Delta H_2 - 2\Delta H_1$$

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(26) The decay curve for $\text{PhNO}\cdot^-$ is second order in radical anion and has a rate constant of $140\ M^{-1}\ \text{sec}^{-1}$ at 23° in ethanol containing sodium hydroxide.[10,27] The product is azoxybenzene.

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(31) The involvement of methyl nitroxide in hydrogen bonding is also indicated by the fact that the coupling constants (a_{N}, etc.) are larger in methanol than in isopentane or benzene.[30]

The hydrogen bond strength in bulk methanol, ΔH_1, is about 5 kcal/mol.[32] The activation energy for reaction 3 is probably $\sim$2.5 kcal/mol to judge from the results with isopropyl nitroxide and *tert*-butyl nitroxide in benzene. Hence, the negative activation energy for the overall process can be accounted for if the strength of the hydrogen bond formed between the nitroxide and methanol, ΔH_2, has a value of $\sim$2 kcal/mol, which seems not unreasonable.

The preexponential factor for the overall reaction is

$$A_{\mathrm{epr}} = 10^{3.1} = A_3 e^{2(\Delta S_2 - \Delta S_1)/R}\ M^{-1}\ \mathrm{sec}^{-1}$$

Since the preexponential factor for reaction 3 is probably $\sim 10^{8.8}\ M^{-1}\ \mathrm{sec}^{-1}$ (Table I), the experimental data indicate that $\Delta S_2 - \Delta S_1 \approx -13$ gibbs/mol. This result is consistent with the general observation that entropy differences accompanying reversible associations decrease as the size of the species involved increases.

While the above picture of the mechanism of the self-reaction of methyl nitroxide in methanol is undoubtedly oversimplified, it does account qualitatively for the observed results. Furthermore, it suggests that similar unusual Arrhenius parameters may be found for other bimolecular reactions in hydrogen bonding media, provided the reactants can form a weak hydrogen bond to give unreactive species, whereas the nonbonded reactants can react together rapidly and with little activation energy.

Thermochemistry of Nitroxide Self-Reactions. Benson and coworkers[33] have recently summarized the heats of formation of a number of compounds of interest in connection with the present work. Thus, $\Delta H_f°(\mathrm{CH_3NHOH}) = -12$ kcal/mol, $\Delta H_f°(\mathrm{CH_3NO}) = 16$ kcal/mol, and since $\Delta H_f°(\mathrm{H}\cdot) = 52$ kcal/mol the overall reaction

$$\mathrm{CH_3NHOH} \longrightarrow \mathrm{CH_3NO} + \mathrm{H}\cdot + \mathrm{H}\cdot$$

is endothermic by $12 + 16 + 2 \times 52 = 132$ kcal/mol in the gas phase. If we make the reasonable assumption that the O–H bond strength in methylhydroxylamine, D(CH$_3$NHO–H), is the same as that in 2,2,6,6-tetramethyl-*N*-hydroxypiperid-4-one (*viz.*, 71 kcal/mol[34]) it follows that $\mathrm{D(CH_3N(\dot{O})\text{–}H)} = 132 - 71 = 61$ kcal/mol. The reaction

$$2\mathrm{CH_3NHO}\cdot \longrightarrow \mathrm{CH_3NHOH} + \mathrm{CH_3NO}$$

is therefore exothermic by 10 kcal/2 mol of radical in the gas phase. This value is in excellent agreement with the value of 10 kcal/mol found in this work for the analogous self-reaction of *tert*-butyl nitroxide in benzene. The low activation energies found for these self-reactions are consistent with exothermic processes. The lower rate constant for phenyl nitroxide compared with the alkyl nitroxides is probably related to the lower exothermicity found for this reaction, *viz.*, 7.2 kcal.

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Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. III. Self-Reactions of Dialkyl Nitroxide Radicals[1,2]

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Abstract: Bimolecular rate constants and activation parameters have been measured for the self-reactions of several dialkyl nitroxides in a number of solvents. It has been shown that there is a large deuterium isotope effect on the reaction if the hydrogens on the α-carbons are replaced by deuterium. The results are consistent with a mechanism involving the reversible formation of a diamagnetic nitroxide dimer and its slow decomposition to a hydroxylamine and a nitrone. The equilibrium constant for dimer formation has been determined with $(\mathrm{CH_3CD_2})_2\mathrm{NO}\cdot$ in isopentane and in $\mathrm{CF_2Cl_2}$. The analogy between the self-reactions of nitroxides and of peroxy radicals is pointed out.

The first paper in this series[5] described a study of the self-reaction of diethyl nitroxide in solution. The second-order rate constants for decay of the radicals were measured by epr spectroscopy over a range of temperature in a variety of solvents. Studies at low temperatures (−100 to −150°) indicated that the nitroxide radicals exist in equilibrium with a diamagnetic dimer

$$2\mathrm{Et_2NO}\cdot \rightleftharpoons (\mathrm{Et_2NO})_2$$

Dimer was identified in isopentane and in $\mathrm{CF_2Cl_2}$ and, in the latter solvent, the irreversible decay of the radicals was just slow enough to obtain a very rough estimate of the equilibrium constant and the heat and en-

[1] Issued as N.R.C.C. No. 12295.

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