Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. 28. *N*-Alkoxy-*N*-alkylamino, *N*-Alkoxyamino, and *N*-Alkoxyanilino Radicals[1]

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Contribution from the Division of Chemistry, National Research Council of Canada, Ottawa, Canada K1A OR6. *Received April 1, 1976*

Abstract: Radicals of the types mentioned in the title have been generated and the kinetics and products of their decay have been examined. *N*-Alkoxy-*N*-alkylamino, $RO\dot{N}R'$, and *N*-alkoxyamino, $RO\dot{N}H$, radicals decay with second-order kinetics at about 10% of the diffusion-controlled rate. *N*-Alkoxyanilino radicals, $RO\dot{N}C_6H_5$, are much more persistent, they decay with first-order kinetics and exist in equilibrium with their dimers, $\Delta H \sim 13.5$ kcal/mol. *N*-Alkoxyaminos yield alcohols as the only organic products of decay, and *N*-ethoxyanilino yields only ethanol and *trans*-azobenzene. *N*-Alkoxy-*N*-alkylamino radicals generally yielded complex mixtures of products. However, *N*-benzyloxy-*N*-benzylamino gave approximately equimolar amounts of *O*-benzylbenzaldoxime, benzyl alcohol, benzaldehyde, and ω,ω'-azotoluene. The first of these products must arise by disproportionation. It is proposed that the other three products are formed via a Russell-type six-center concerted decomposition of an N–N coupled product. This type of decay appears to be confined to *N*-benzyloxy-*N*-alkylamino radicals, presumably because the benzylic hydrogens are activated by the adjacent phenyl group.

In this laboratory, we have been interested for many years in the rates and mechanisms of decay of alkylperoxy radicals, $ROO\cdot$,[3] alkyl nitroxides, $R_2NO\cdot$,[4] and alkylhydrazyl radicals, $R_2N\dot{N}R$.[5] These neutral, isoelectronic radicals have, as a common feature, one or more lone pairs of electrons on both the atom that formally bears the unpaired electron and on an adjacent atom. All three groups of radicals contain certain members that are relatively persistent[6] and many members that decay by complex and interesting reaction mechanisms.[3-5] In the present paper, we report on the kinetics, products, and mechanisms of decay of some *N*-alkoxy-*N*-alkylamino radicals, $RO\dot{N}R'$, *N*-alkoxyamino radicals, $RO\dot{N}H$, and *N*-alkoxyanilino radicals, $RO\dot{N}C_6H_5$, which constitute the fourth and final group of radicals in this isoelectronic class.

Danen and co-workers[7,8] were the first[9] to detect *N*-alkoxy-*N*-alkylamino and *N*-alkoxyanilino radicals by EPR spectroscopy. They paid relatively little attention to the lifetimes of these radicals, but did note[8] that certain *N*-alkoxyarylamino radicals were quite persistent. This last observation has been confirmed by others for quite a variety of alkoxyarylamino radicals,[11-14] and an exceptionally persistent *N*-alkoxy-*N*-vinylamino radical has also been reported.[15] *N*-Alkoxyamino radicals have not been detected previously.

Experimental Section

The general experimental procedures and the kinetic EPR technique have been described previously.[4,5]

Radical Production. The radicals were generated directly in the cavity of a Varian E-4 EPR spectrometer by Danen's procedures.[8] The *N*-alkoxy-*N*-alklyamino, *N*-alkoxyamino, and *N*-ethoxyanilino radicals were prepared by photolysis of the appropriate hydroxylamine and di-*tert*-butyl peroxide in isopentane or toluene, normally ca. 1:1:2 by volume. The *N*-ethoxyanilino radical could also be prepared by oxidation of the hydroxylamine with silver oxide. *N*-*tert*-Butoxyanilino was prepared by photolysis of aniline and di-*tert*-butyl peroxide in toluene.[8]

Materials. All the hydroxylamines used in this work are known compounds. *O*-Ethylhydroxylamine (Chemical Procurement Labs.), *O*-benzylhydroxylamine (Aldrich), and *N,O*-dimethylhydroxylamine (Aldrich) were liberated from their hydrochloride salts and used without further purification. *N*-Methyl-*O*-*tert*-butylhydroxylamine was prepared from ethyl azidoformate[16] by the procedure of Danen et al.[8] *N*-Methyl-*O*-benzylhydroxylamine and *N*-isopropyl-*O*-methylhydroxylamine were prepared from *N*-hydroxyurethane (Aldrich) by the procedure of Jones and Major.[17] *N*-Isopropyl-*1,1,1,3,3,3*-d_6-*O*-methylhydroxylamine was prepared by the same procedure using $(CD_3)_2CHBr$ (Merck Sharp and Dohme). *N,O*-Dibenzylhydroxlyamine was prepared from *N*-hydroxyurethane by the procedure of Jones and Fleck.[18] *N*-Phenyl-*O*-ethylhydroxylamine was prepared from 1,3-diphenylhydroxylurea.[19,20]

Several unsuccessful attempts were made to prepare *N,O*-di-*tert*-butylhydroxylamine. These included the general procedure used for *N,O*-dibenzylhydroxylamine,[18] an attempted coupling of monolithium *tert*-butylamide[21] with *tert*-butyl hypochlorite at low temperatures, and the reaction of di-*tert*-butyl nitroxide with bromine.[22]

Product Studies. In order to be able to propose a reaction mechanism for the decay of an alkoxyamino radical it is necessary to know both the kinetics for its decay and the products of its decay. The kinetics can almost always be determined much more easily than the products. It is difficult to obtain products derived solely from radical–radical reactions, and usually only a limited amount of product is available. The product is, moreover, often a mixture, some components of which are unstable or react with one another. In the present instance, several hydroxylamines were oxidized under conditions that, we hope, generated alkoxyamino radicals in a reasonably "clean" manner. Two principal oxidation procedures were employed.

A. The hydroxylamine (ca. 0.6 M) was allowed to react with ca. 50 mol % of thermally generated *tert*-butoxy radicals in degassed C_6H_6 or C_6D_6 in a sealed NMR tube for 48 h in the dark at 50 °C. The *tert*-butoxys were generated from *tert*-butyl hyponitrite (ca. 0.15 M), which would be fully decomposed in the 48 h.

B. The hydroxylamine (ca. 0.3 mmol) was shaken with Ag_2O (ca. 0.15 mmol) in degassed C_6H_6 or C_6D_6 for 24 h in the dark at 20 °C. The volatile components were then transferred on a high vacuum line to an NMR tube and sealed under vacuum. Oxidizing agents other than Ag_2O were sometimes employed.

Proton NMR spectra were recorded immediately before and after reaction. The presence, *or* absence, of a potential product was confirmed, whenever possible, by recording a new NMR spectrum following the addition of the requisite compound to the reaction mixture. The NMR spectroscopic data for the hydroxylamines that were oxidized and their oxidation product mixtures are available as supplementary material to this paper.

In so far as possible, the NMR results were confirmed and extended by VPC. However, combined VPC–mass spectrometry was less than satisfactory because many nitrogen-containing products were absorbed on the metal surfaces between the VPC detector and the mass spectrometer's ionization chamber. Mass spectrometry proved more successful when the oxidations were carried out in break-sealed vessels and the gases and vapors not condensable at liquid nitrogen, liquid nitrogen–chloroform, and room temperature were introduced directly into the spectrometer. For some reactions, a known quantity of argon was included in the break-seal to assist in determining the yields of the gaseous products.

Table I. EPR Parameters for *N*-Alkoxyamino Radicals[a]

Radical	g	a^N	$(a^H)_{NH}$	$(a^H)_{NCH}$	$(a^H)_{OCH}$
$CH_3CH_2O\dot{N}H$	2.0050	12.04	19.99		3.06
$CH_3CH_2O\dot{N}D$	2.0049	12.12	3.04 (D)[h]		3.04
$C_6H_5CH_2O\dot{N}H$	2.0049	12.18	20.06		3.23
$CH_3O\dot{N}CH_3$	2.0048[b]	14.30[b]		21.85[b]	2.62[b]
$CH_3O\dot{N}CH(CH_3)_2$	2.0046	13.95		18.80	2.56
$(CH_3)_3CO\dot{N}CH_3$	2.0048[b]	14.47[b]		21.51[b]	
$C_6H_5CH_2O\dot{N}CH_2C_6H_5$	2.0046	14.41		23.79	2.64
$C_6H_5CH_2O\dot{N}CH_3$	2.0048	14.15		21.7	2.27
$(CH_3)_3CO\dot{N}C_6H_5$	2.0044[c]	10.95[c]		*d*[c]	0.18[e]
$CH_3CH_2O\dot{N}C_6H_5$	2.0044	10.9[f]		*g*	1.6[f]

[a] Hyperfine couplings are in gauss and were measured at −60 °C unless otherwise noted. [b] From ref 8 at −90 °C. [c] From ref 8 at room temperature. [d] a^H (o) = 4.67, a^H(m) = 1.55, a^H(p) = 5.06. [e] $(CH_3)_3C$. Not resolved in ref 8. [f] Fitted by computer simulation. [g] a^H(o) = a^H(p) = 4.8,[f] a^H(m) = 1.6.[f] [h] Value calculated from the H/D magnetogyric ratios (6.51) equals 19.99/6.51 = 3.07 G. To form this radical, $CH_3CH_2ONH_2$ was exchanged with D_2O in situ.

Results

EPR Spectra. The EPR parameters for the radicals studied in this work are listed in Table I. The spectra of *N*-alkoxy-*N*-alkylamino and of *N*-alkoxy-*N*-arylamino radicals have been discussed in some detail by Danen,[7,8] but *N*-alkoxyamino radicals have not previously been reported. The only noteworthy feature in the EPR spectra of the last named radicals is that their nitrogen hyperfine splittings (hfs) are about 2 G smaller than the nitrogen hfs in *N*-alkoxy-*N*-alkylamino radicals. This difference is in the same direction and is of similar magnitude as that observed for N(1) hfs in alkylhydrazyls.[23] For example,[23] for $H\dot{N}(1)N(2)H_2$ and $R\dot{N}(1)N(2)H_2$, the N(1) hfs are 11.7 and 13.8 G, respectively, and for $H\dot{N}(1)N(2)R_2$ and $R\dot{N}(1)N(2)R_2$, the N(1) hfs are 9.8 and 11.8 G, respectively. We have previously[23,24] explained such differences in nitrogen hfs in terms of inductive effects. That is, an electron-releasing R′ group (alkyl) will enhance the N hfs because it will stabilize canonical structure **1** relative to canonical structure **2.** In contrast, an electron-withdrawing R′ group (hydrogen or, to a greater extent, phenyl or, to an even greater extent,[8] an aromatic ring containing an electron-withdrawing substituent) will reduce the N hfs because it will stabilize **2** relative to **1.**

$$\underset{\mathbf{1}}{R-\ddot{O}-\dot{N}-R'} \longleftrightarrow \underset{\mathbf{2}}{R-\overset{+}{\dot{O}}-\overset{-}{\ddot{N}}-R'}$$

Kinetics of Radical Decay. The *N*-alkoxyamino and *N*-alkoxy-*N*-alkylamino radicals all decay with "clean" second-order kinetics at rates which are about 10% of the diffusion-controlled limit. Rate constants for the decay of these radicals at −60 °C are listed in Table II. The differences in the measured rate constants are larger than our reproducibility (±30%), but are probably within our true experimental error.

$$2RO\dot{N}R' \xrightarrow{k^2_{\text{epr}}} \text{products}$$

The *N*-alkoxy-*N*-anilino radicals decay relatively slowly. Under the conditions of our experiments, these radicals were sufficiently persistent that it could be shown, by raising and lowering the temperature, that they exist in equilibrium with a diamagnetic dimer:

$$2RO\dot{N}C_6H_5 \rightleftharpoons (RONC_6H_5)_2$$

Measurements of the equilibrium constant for *tert*-butoxyanilino over a temperature range from −63 to 74 °C gave ΔS = 21 ± 2 gibbs/mol and ΔH = 12.5 ± 0.5 kcal/mol. This radical decayed with "clean" first-order kinetics, but the measured rate constant increased with each successive regeneration of the radical. At 22 °C the radical, when first generated, had a half-life of ca. 40 min, but this rose to an eventual value of 8.9 h. We have encountered this kind of phenomenon on several occasions when studying the decay of persistent radicals. We attribute it to the reaction of the radical with impurities in the system that are slowly consumed. Whether the longest half-life represents the "true" limiting half-life can never be unequivocally determined.

The ethoxyanilino radical is much less persistent than the *tert*-butoxyanilino. This prevented the measurement of ΔS, but ΔH was determined to be 14.5 ± 0.5 kcal/mol in the temperature range −43 to −4 °C. This radical also decayed with first-order kinetics having a half-life of ca. 4 min at 12 °C. A detailed study of the decay kinetics was not undertaken because we were never able to obtain a completely "clean" EPR spectrum of this radical. Since the lifetime did not appear to change appreciably with time, we believe that the decay of this radical is not due to its reaction with impurities in the reactant mixture.

Products of Radical Decay. I. *O*-Benzylhydroxylamine oxidized by method A or B (see Experimental Section) gave benzyl alcohol as the sole organic product:

$$C_6H_5CH_2ONH_2 \xrightarrow[\text{A or B}]{\text{oxid}} C_6H_5CH_2OH(+\ N_2)$$

It has been reported[25] that *O*-alkylhydroxylamines can be oxidized to hyponitrites, RON=NOR, but the quoted examples refer to oxidations with bromine under basic conditions. Dibenzyl hyponitrite could not be detected under any of the conditions we explored. Of course, it would not survive method A since it decomposes thermally about ten times more rapidly than di-*tert*-butyl hyponitrite.[26] However, it could not be detected when the hydroxylamine was oxidized with Ag_2O in benzene for as little as 1 h at room temperature, and it should certainly have survived thermal decomposition under such mild conditions. Similarly, it did not appear to be formed when the hydroxylamine was oxidized with PbO_2 or MnO_2 at room temperature, the only organic product again being benzyl alcohol (together with a trace of benzaldehyde derived by further oxidation of the alcohol). The appropriate alcohol and/or the carbonyl compound derived from it have been reported to be the major products in the oxidation of a number of other *O*-alkylhydroxylamines by a variety of oxidizing agents.[27]

II. *N*-Phenyl-*O*-ethylhydroxylamine oxidized by method A or B gave only *trans*-azobenzene and ethanol in a molar ratio of 1:2:

$$C_6H_5NHOC_2H_5 \xrightarrow[\text{A or B}]{\text{oxid}} \underset{\text{trans}}{C_6H_5N{=}NC_6H_5} + 2C_2H_5OH$$

The same products were formed when solutions of this hydroxylamine were exposed to the air for a short period. In

Table II. Rate Constants for the Second-Order Decay of *N*-alkoxyamino and *N*-alkoxy-*N*-alkylamino Radicals at −60 °C

Radical	$k^2_{\mathrm{epr}} \times 10^{-8}$, $M^{-1}\ s^{-1}$ [a]
$CH_3CH_2O\dot{N}H$	4.2
$C_6H_5CH_2O\dot{N}H$	1.6
$CH_3O\dot{N}CH_3$	2.7
$CH_3O\dot{N}CH(CH_3)_2$	1.0
$(CH_3)_3CO\dot{N}CH_3$	3.4
$C_6H_5CH_2O\dot{N}CH_2C_6H_5$	5.8 [b]
$C_6H_5CH_2O\dot{N}CH_3$	1.0

[a] The measured rate constants are reproducible to ±30% in each case. [b] Measured at −20 °C.

separate experiments, it was shown that if *cis*-azobenzene[28] had been formed in method B it would have survived unchanged.

III. ***N,O*-Dibenzylhydroxylamine** oxidized by method A gave benzyl alcohol, benzaldehyde, *trans*-ω,ω′-azotoluene, and *O*-benzylbenzaldoxime in approximately equimolar amounts:

$$C_6H_5CH_2ONHCH_2C_6H_5 \xrightarrow[A]{\text{oxid}} C_6H_5CH_2OH + C_6H_5CHO + t\text{-}C_6H_5CH_2N{=}NCH_2C_6H_5 + C_6H_5CH_2ON{=}CHC_6H_5$$

Oxidation of the hydroxylamine by method B gave benzyl alcohol, benzaldehyde, and *O*-benzylbenzaldoxime, together with benzaldehyde azine instead of the azotoluene. In a separate experiment, it was shown that *trans*-ω,ω′-azotoluene[29] was oxidized to benzaldehyde azine under these conditions.[30]

$$t\text{-}C_6H_5CH_2N{=}NCH_2C_6H_5 \xrightarrow[B]{\text{oxid}} C_6H_5CH{=}NN{=}CHC_6H_5$$

Attempts to prepare the (unknown) *cis*-ω,ω′-azotoluene by photolysis of the trans compound[31] were unsuccessful. In benzene at room temperature bibenzyl and a trace of toluene were the only products. Even at −30 °C (in toluene) some bibenzyl was formed. It seems possible that the cis isomer is thermally very unstable.

IV. ***N*-Isopropyl-*O*-methylhydroxylamine** gave oxidation products that had very complex NMR spectra. These spectra could not be completely interpreted and so the product balances were very poor. The two oxidation methods gave generally similar, but not identical, spectra. Method A gave 20 mol % methanol (based on consumed hydroxylamine) and 3 mol % *O*-methylacetoxime. Method B gave 20 mol % methanol and 10 mol % *O*-methylacetoxime. In separate experiments, it was shown that methanol would not have been consumed under either of these experimental conditions.

By analogy with the *N,O*-dibenzylhydroxylamine oxidations we might expect methanol, formaldehyde, and azoisopropane (or acetone azine) to be formed in high, and equivalent, yields. However, neither formaldehyde nor azoisopropane could be detected. Free formaldehyde is, of course, so reactive[32,33] that its absence was not surprising. In the case of the azo compound, both the cis and trans isomers would have been difficult to identify by NMR. For this reason, $CH_3ONHCH(CD_3)_2$ was oxidized by method A. In this hydroxylamine, and its oxidation products, the methine H can be more easily observed since the normal septet pattern has collapsed to a single peak. Despite this simplification in the NMR spectrum neither *cis*- (CH, τ 6.02) nor *trans*- (τ 6.35) azoisopropane could be detected.

Oxidation of the normal hydroxylamine by method B gave N_2 in 50 mol % yield (i.e., 1 mol of N_2 for every 4 mol of hydroxylamine oxidized), CO_2 (30 mol %), propane (23 mol %), and propylene (3 mol %). None of these compounds were formed from the hydroxylamine by method A oxidation. The formation of N_2 implies that an N-N coupled species must be produced in the B oxidation, and, in fact, some nitrogen was formed when *trans*-azoisopropane was oxidized by method B. However, in this last reaction neither CO_2, nor propane, nor propylene was produced in significant quantities.

In a search for any thermally unstable products, the hydroxylamine (0.6 M) was photolyzed with di-*tert*-butyl peroxide (0.2 M) in cyclopropane at −80 °C for 5 h directly in the EPR cavity. The NMR spectrum recorded at −80 °C before allowing the sample to warm up was no different from that recorded after heating the sample to 50 °C for 48 h.

None of the following potential products were detected in either A or B oxidations: 2,3-dimethylbutane,[34] isopropylamine, 2-nitrosopropane, *O*-methylacetaldoxime, and acetone azine.

V. ***N,O*-Dimethylhydroxylamine** oxidized by method A gave methanol (ca. 50 mol %) and *O*-methylformaldoxime (ca. 5 mol %). A number of other compounds must be produced since the NMR spectra were very complex. However, neither *cis*- nor *trans*-azomethane was present. This was proven by adding a cis/trans mixture to the oxidation products and re-recording the NMR spectrum. Gaseous products included N_2 and a trace of CH_4. The amount of N_2 corresponded approximately to the amount of di-*tert*-butyl hyponitrite decomposed.

Oxidation by method B gave a much simpler NMR spectrum. Methanol was the only major organic product. The oxime, *cis*- and *trans*-azomethane, and formaldehyde were not present in detectable amounts. All of the nitrogen in the oxidized hydroxylamine appeared as nitrogen gas, i.e., the yield of N_2 was 100 mol %. Carbon dioxide (30% of the N_2) and methane (8% of the N_2) were also formed. In a separate experiment, it was found that *trans*-azomethane was oxidized by silver oxide to nitrogen containing ca. 3% methane but no CO_2.

VI. ***N*-Methyl-*O*-benzylhydroxylamine** (0.75 M) was oxidized by method A with 0.30 M *tert*-butoxy radicals. The amount of hydroxylamine consumed was 0.26 M, and the major products identified and quantitatively analyzed by NMR and VPC were: benzyl alcohol, 0.14 M; benzaldehyde, 0.11 M; and *trans*-azomethane, ≳0.06 M (this yield was based on NMR and not all the compound would be in solution). There did not appear to be any other major products, and, in particular, there was no *cis*-azomethane. Oxidation of the hydroxylamine by method B gave benzyl alcohol (0.21 M) and benzaldehyde (0.12 M) as the only identified nonvolatile products and, in the volatile products, a trace of *trans*-azomethane (ca. 0.01 M):

$$C_6H_5CH_2ONHCH_3 \xrightarrow[\text{A or B}]{\text{oxid}} C_6H_5CH_2OH + C_6H_5CHO + \underset{\text{trans}}{CH_3N{=}NCH_3}$$

Discussion

The fast second-order decay of *N*-alkoxyamino radicals is not surprising since these radicals are not sterically protected at the radical center.[6,36] The kinetics and the products from *O*-benzylhydroxylamine are consistent with an initial dimerization. This must be followed either by an intramolecular 1,2- or 1,3-hydrogen transfer or by a multistep, intermolecular process:

$$2RO\dot{N}H \xrightarrow{k^2_{\mathrm{epr}}} RONHNHOR \longrightarrow 2ROH + N_2$$

The overall reaction is exactly analogous to the reaction by which unhindered 2,2-dialkylhydrazyl radicals, $R_2N\dot{N}H$, decay to give dialkylamine, R_2NH, and nitrogen.[5a] Under certain conditions, it may be possible to oxidize the intermediate *N,N'*-dialkoxyhydrazine to the corresponding hyponitrite before it decomposes to the alcohol and nitrogen.[25,27]

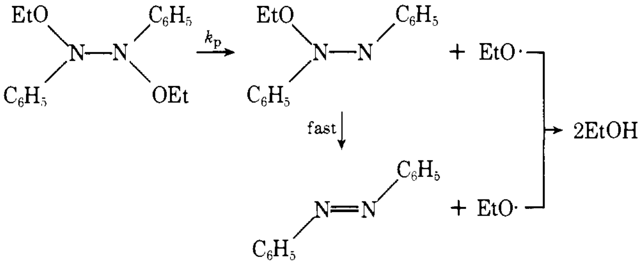
The *N*-ethoxy-*N*-anilino radical provides yet another example of a radical that decays slowly and with first-order kinetics *because* the radical is in equilibrium with its dimer *and* the dimer is present in higher concentration than the radical.[5a,37,38] The same kinetic phenomenon has been observed previously with certain phenoxy,[37] iminoxy,[38] and 2,2-dialkylhydrazyls.[5a] The reaction scheme can be represented either by

$$2\dot{R} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R_2 \xrightarrow{k_p} \text{products}$$

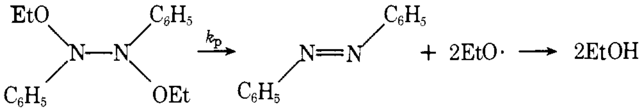
in which case, the measured rate constant for decay $k^1{}_{\text{epr}}$ is given by $k_p/2$, or by

$$\text{products} \xleftarrow{k_p} 2\dot{R} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R_2$$

in which case, $k^1{}_{\text{epr}} = k_pk_{-1}/2k_1$. Although these two schemes cannot be distinguished kinetically, in the present instance, the formation of *trans*-azobenzene and ethanol as the only products from *N*-ethoxy-*N*-anilino radicals leaves little doubt that the first scheme applies. That is, the products are probably formed directly from the dimer either in a two-step process:



or in a concerted reaction:

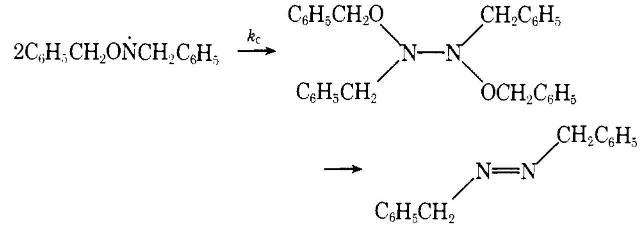


The greater persistence of the *tert*-butoxyanilino may be due to steric factors which make it more difficult for the dimer to attain a geometry favorable for a concerted decomposition. The initial coupling of the alkoxyanilino radicals probably occurs at a rate that is within one or two orders of magnitude of the diffusion-controlled limit.[39]

The measurements of the radical–dimer equilibria show that 1,2-dialkoxy-1,2-diphenylhydrazines have N-N bond strengths of 13.5 ± 1.0 kcal/mol. These bonds are, therefore, considerably weaker than the 30.5 kcal/mol N-N bond in tetraphenylhydrazine.[41,42] The increased dissociation of tetraarylhydrazines containing electron-donating (+M) ring substituents, such as *para*-methoxy, was discovered by Wieland over 60 years ago[44] and has been amply confirmed by subsequent work.[45,46] It is no real surprise to discover that the elimination of intervening aromatic rings makes dialkoxydiarylhydrazines even less stable than the ring substituted tetraarylhydrazines. The value of 21 gibbs/mol obtained for ΔS for the equilibrium of the *tert*-butoxyanilino radical with its dimer is smaller than the values found for most analogous radical–dimer equilibria.[47]

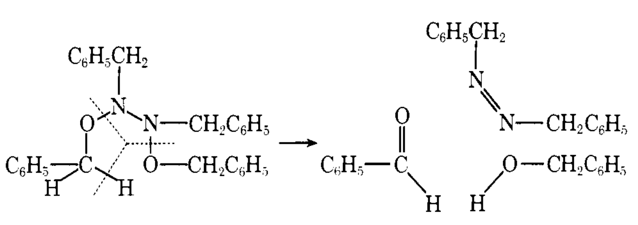
The mechanism by which *N*-alkoxy-*N*-alkylamino radicals decay is both the most interesting and the most frustrating to pin down precisely. The rapid second-order decay of these radicals indicates an initial dimerization and/or disproportionation. For *O*-benzyl-*N*-benzylamino radicals these two decay routes appear to be of approximately equal importance since, when *N*,O-dibenzylhydroxylamine was oxidized, the observable disproportionation product, *O*-benzylbenzaldoxime, was formed in about the same yield as *trans*-ω,ω'-azotoluene, a compound which must be formed from a dimer.

$$2C_6H_5CH_2O\dot{N}CH_2C_6H_5 \xrightarrow{k_d} C_6H_5CH_2ONHCH_2C_6H_5 + C_6H_5CH_2ON{=}CHC_6H_5$$

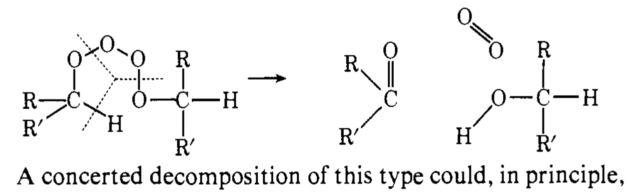


The interesting question is, of course, by what mechanism does the dimer decay? In the first place, it is not immediately obvious why the dimer should not survive unchanged in solution at room temperature. Although *N,N'*-dialkoxy-*N,N'*-dialkylhydrazines are rare, they are not entirely unknown. In 1974, Barton and co-workers[51] prepared two dialkoxydi(trifluoromethyl)hydrazines, $RO(CF_3)NN(CF_3)OR$, which, to judge from their melting points (150 °C for R = 1-adamantyl, and 188 °C for R = cholestan-3β-yl), are perfectly stable. *N,N'*-Dialkoxy-*N,N'*-dicarbalkoxyhydrazines,[52] $[R'OC(O)(RO)N\text{-}]_2$, and *N,N'*-dialkoxy-*N,N'*-diacylhydrazines,[53,54] $[R'C(O)(RO)N\text{-}]_2$, are also known compounds, with the former being somewhat more stable than the latter. We suggest that these three classes of *N,N'*-dialkoxyhydrazines owe their stability to the presence of the electron-withdrawing CF_3, $R'OC(O)$, and $R'C(O)$ groups. The stabilization of tetraarylhydrazine by electron-withdrawing ring substituents is well known.[44-46]

The formation of azobenzene from *N,N'*-diethoxy-*N,N'*-diphenylhydrazine, which was referred to above, can be readily understood since the development of conjugation between the two aromatic rings will provide a driving force for this reaction. This particular driving force is, of course, absent in the formation of azotoluene from *N,N'*-dibenzyloxy-*N,N'*-dibenzylhydrazine. Moreover, we believe we can rule out decomposition of this hydrazine to azotoluene and two benzyloxy radicals because this would be expected to yield *two* moles of alcohol per mole of azotoluene, rather than one (see above). The formation of azotoluene, benzyl alcohol, and benzaldehyde in equimolar quantities provides strong evidence in favor of a concerted decomposition via a six-membered cyclic transition state, i.e.,



Such a reaction mechanism is clearly analogous to the "Russell Mechanism"[3,55,56] for the decomposition of di-*sec*-alkyl tetroxides, i.e.,

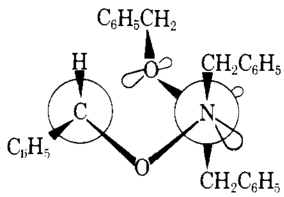


A concerted decomposition of this type could, in principle, yield azotoluene as the cis or the trans isomer, or even as a mixture of the two. The formation of only the trans isomer can be explained in three possible ways:

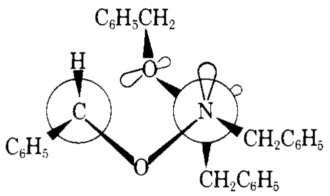
(i) The cis is actually produced, but is thermally unstable at room temperature and so inverts[57-59] to the trans isomer.[60]

(ii) The cis is produced in an electronically excited state and inverts to the trans isomer before losing this excess energy. That is, since the overall reaction will be quite exothermic, some of the excess energy could appear as electronic energy. A somewhat analogous situation obtains in the concerted[3i] decomposition of *sec*-alkyl tetroxides in which, for reasons of spin conservation, the oxygen is produced in an electronically excited singlet state.[3e,61]

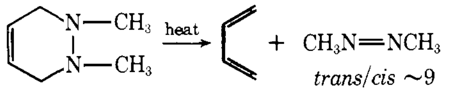
(iii) The trans isomer is produced simply because the transition state leading to this isomer is the most favored energetically (i.e., the Curtin-Hammett principle[62] is in operation). Formation of the trans isomer should be favored for two reasons. In the first place, the ground-state energy for sterically unhindered *cis*-azoalkanes is 7-8 kcal/mol higher than that for the trans isomer.[59,63] Secondly, the conformation of the transition state seems most likely to be of the chair type with the two *N*-benzyl groups both pseudoaxial, i.e., **3**, or one pseudoaxial and one pseudoequatorial, i.e., **4**. Reaction via transition-state **3** would lead directly to *trans*-azotoluene. This transition state should be energetically favored relative to **4** since steric repulsion between the *N*-benzyl groups will be minimized. Reaction via transition-state **4** might yield *cis*-azotoluene. However, it is worth noting that the retro-Diels-Alder reaction of 1,2,3,6-tetrahydropyridazine, which is obviously closely related to the reaction under consideration, has been shown by Nelsen[64] to yield mainly *trans*-azomethane, i.e.,



3



4



This result is of particular significance since the starting pyridazine prefers a conformation in which one methyl is pseudoaxial and one is pseudoequatorial (i.e., a conformation like **4**).

We attempted to check at least the first of these three possibilities by examining the products formed by oxidation of *N*-isopropyl-*O*-methylhydroxylamine and of *N,O*-dimethylhydroxylamine since both *cis*-azoisopropane[31,58,65] and *cis*-azomethane[31,65] are known to be reasonably stable at room temperature. Unfortunately, neither hydroxylamine gave detectable yields of the appropriate *cis*- or *trans*-azoalkane. A variety of products were formed, relatively few of which could be identified (see Results). However, the virtual absence of the disproportionation products (*O*-methyl oximes) and the high yields of N_2 in the silver oxide oxidations make it extremely probable that these two *N*-methoxyalkylamino radicals react principally by coupling to form *N,N'*-dimethoxy-*N,N'*-dialkylhydrazines. It would appear that these hydrazines do not decompose to any appreciable extent[66] by a Russell type of mechanism. However, the complexity of the NMR spectra of the oxidation products of the *N*-methoxy-*N*-alkylamines suggests that these hydrazines decompose by other routes such as N-C or N-O bond homolysis. In the presence of silver oxide these hydrazines, or their decomposition products, are converted to N_2, CO_2, and the appropriate alkane.

The only apparent reason for the different behavior of the *N*-benzyloxy-*N*-benzylamine and the *N*-methoxy-*N*-alkylamines is the strength of the C-H bond that must be broken. That is, the concerted decomposition of *N,N'*-dibenzyloxy-*N,N'*-dibenzylhydrazine might be facilitated by the bond weakening effect of the phenyl in the *O*-benzyl group. This possibility is, we believe, confirmed by our experiments with *O*-benzyl-*N*-methylamine. Oxidation of this hydroxylamine with *tert*-butoxy radicals gave benzyl alcohol, benzaldehyde, *and trans*-azomethane in comparatively high yields. These three products were also formed using silver oxide as the ozidizing agent, though in this case only a trace of *trans*-azomethane was produced. In neither reaction was there any *cis*-azomethane which indicates that the trans isomer is formed directly from the hydrazine.

Finally, we note that the varied behavior exhibited by *N*-alkoxy-*N*-alkylamino radicals is not without precedent since we have shown previously[3i] that not all *sec*-alkylperoxy radicals decay by a Russell mechanism. The main route for the decay of certain *sec*-alkylperoxys appears to be decomposition of the tetroxide to two alkoxy radicals and oxygen (rather than to alcohol, ketone, and oxygen).

The variety of self-reactions undergone by alkoxyamino radicals makes these species as interesting as their three isoelectronic counterparts referred to in the Introduction. To summarize, we have identified the following four types of bimolecular self-reaction:

$$2\mathrm{RO\dot{N}H} \rightarrow (\mathrm{RONH})_2 \rightarrow 2\mathrm{ROH} + \mathrm{N}_2 \qquad (1)$$

$$2\mathrm{RO\dot{N}C_6H_5} \rightleftharpoons (\mathrm{RONC_6H_5})_2 \rightarrow t\text{-}\mathrm{C_6H_5N{=}NC_6H_5} + 2\mathrm{RO}\cdot \rightarrow 2\mathrm{ROH} \qquad (2)$$

$$2\mathrm{RO\dot{N}CHR_2'} \rightarrow \mathrm{RONHCHR_2'} + \mathrm{RON{=}CR_2'} \qquad (3)$$

$$2\mathrm{C_6H_5CH_2\dot{O}NR'} \rightarrow (\mathrm{C_6H_5CH_2ONR'})_2 \rightarrow \mathrm{C_6H_5CHO} + \mathrm{C_6H_5CH_2OH} + t\text{-}\mathrm{R'N{=}NR'} \qquad (4)$$

In addition, the bimolecular self reaction of $\mathrm{CH_3O\dot{N}R}$ radicals would appear to follow yet a different course. It is also worth noting that West and Boudjouk[69] have observed that certain silicon and germanium containing alkoxyamino radicals undergo an interesting unimolecular self-reaction, e.g.,

$$\mathrm{Me_3SiO\dot{N}SiMe_3} \longrightarrow (\mathrm{Me_3Si})_2\mathrm{NO}\cdot$$

Acknowledgment. We should like to thank Professor W. C. Danen for encouraging us to embark on this work with a gift of chemicals.

Supplementary Material Available: A listing of proton NMR spectroscopic data for the hydroxylamines used in this work and for their oxidation products (17 pages). Ordering information is given on any current masthead page.

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