deuterated analogs was determined to be 36.7% by a comparison of the standardized glpc calibration curve of VI and added *o*-dichlorobenzene.

The reaction and its product analysis were repeated using a 1:1:0.66:0.025 mol ratio mixture of reactants. A reaction carried out for 17 hr gave a 25% yield of chlorovinylation products. The analytical results are listed in Table V, reaction 23.

A control experiment carried out without added peroxide showed no exchange had taken place in the recovered starting materials and that no chlorovinylation products were formed.

The Reaction of Tetrachloroethylene with *n*-Hexane and Perdeuteriocyclohexane. A reaction mixture having a 1:1:0.33:0.017 mol ratio of *n*-hexane–perdeuteriocyclohexane–tetrachloroethylene–*tert*-butyl peroxide was allowed to react for 16 hr in the previously described manner. Glpc analysis with the added standard showed that for duplicate experiments a 25% yield (14% cyclohexyl substituted and 11% hexyl substituted) of substituted starting materials was produced. Preparative glpc (SE-30, 55°) of the reaction mixture allowed the isolation of the unsubstituted cyclohexanes and *n*-hexanes. The mass spectral analyses of these recovered materials are listed in Table VI.

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Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. VII. Self-Reactions of Iminoxy Radicals[1]

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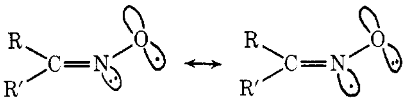
Abstract: The silver oxide oxidations of a number of oximes in benzene solution have been examined. The reaction probably involves the intermediate formation of iminoxy radicals. Rather complex mixtures of products are generally produced because of the instability of some of the initially formed iminoxy radical dimers. Iminoxy radicals can dimerize by N–N, N–O, and O–C coupling. The kinetics and rate constants for the decay of a wide variety of photochemically generated iminoxy radicals have been measured by epr spectroscopy. Under the conditions of the decay experiments the radicals are in equilibrium with "unstable" dimers. For unhindered dialkyliminoxy radicals the equilibrium is rapidly established and lies in favor of the dimers. Decay is first order. For the majority of diaryliminoxy, alkylaryliminoxy, and hindered dialkyliminoxy radicals the equilibrium favors the radicals or else is only slowly established and decay is second order. A unified reaction scheme is proposed but in view of the complexities of the iminoxy radical self-reactions the precise interpretation of the measured decay rate constants and activation parameters is uncertain.

Since their identification by Thomas[4] in 1964, a very large number of iminoxy radicals, RR′C=NO·, have been prepared by numerous workers using a variety of experimental techniques.[5–15]

Interest in these radicals has centered almost exclusively on their electron paramagnetic resonance (epr) spectra which are characterized by a large splitting, ~30 G, due to nitrogen. This indicates that there is significant spin density on nitrogen in an orbital with considerable s character. Calculations[11,12] have indicated that 41 ± 5% of the unpaired spin is on an orbital whose p/s ratio is 6.1 ± 0.7, the CNO angle being about 139°. The radicals are best represented by the canonical structures



The unpaired electron is in a π type orbital which lies in the nodal plane of the C–N π bond. Iminoxy radicals are therefore described as σ radicals to distinguish them from the more common class of π radicals in which the unpaired electron is in an orbital perpendicular to the nodal plane of the molecular π system. Frequently, both isomeric iminoxy radicals are observed, regardless of which of two geometrically isomeric oximes is oxidized. The configuration stability of the radical is therefore not as great as that of the parent oxime. The hyperfine splitting patterns for protons in iminoxy radicals show two types of effect. There is a long-range interaction which is greatest when the proton, the iminoxy group, and the intervening atoms are coplanar and there is a shorter range interaction that appears to occur directly across space, as opposed to through the bonds.

Despite the number of epr studies of iminoxy radicals there has been only one report on the kinetics of their self-reactions. Gilbert and Norman[8a] mixed equimolar concentrations of oxime and lead tetra-

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[1] Issued as NRCC No. 12815. Part VI: G. B. Watts and K. U. Ingold, *J. Amer. Chem. Soc.*, **94**, 2528 (1972).

[2] NRCC Postdoctorate Fellow 1969–1971.

[3] NRCC Postdoctorate Fellow 1970–1972.

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acetate in methylene chloride in the absence of oxygen and found first-order decay for the iminoxy radicals from biacetyl monoxime, fluorenone oxime, 4,4′-dinitrobenzophenone oxime, and benzophenone oxime. Our own results suggest that these kinetics may have been complicated by the simultaneous formation and decay of the radicals.

Our long-standing interest in the kinetics of free-radical reactions and our recent studies of the self-reactions of nitroxide radicals[16] prompted the present investigation into the self-reactions of iminoxy radicals. Both first- and second-order decay processes have been observed. The radical structure has a profound influence on the kinetics and for this reason we have investigated a much wider range of structures than was encompassed in the nitroxide work.

Experimental Section

Materials. The oximes were prepared from commercially available ketones[17] and aldehydes by standard methods.[18,19] Their physical characteristics agreed with those reported in the literature. Solvents were reagent grade materials that were deoxygenated before use. Silver oxide was commercial grade material which was used without further purification.

Kinetic Procedures. Our general experimental procedures for radical generation and for the measurement of radical concentrations and decay rates have been described in previous papers in this series.[1,16] The iminoxy radicals were generated in the cavity of the epr spectrometer by the photolysis of deoxygenated solutions of the oximes containing di-*tert*-butyl peroxide, BOOB.

$$\mathrm{BOOB} \xrightarrow{h\nu} 2\mathrm{BO}\cdot$$

$$\mathrm{BO}\cdot + \mathrm{RR'C{=}NOH} \longrightarrow \mathrm{BOH} + \mathrm{RR'C{=}NO}\cdot$$

In a few experiments iminoxy radicals were generated by the oxidation of oximes with ceric ammonium nitrate in methanol

$$\mathrm{Ce^{IV}} + \mathrm{RR'C{=}NOH} \longrightarrow \mathrm{Ce^{III}} + \mathrm{H^+} + \mathrm{RR'C{=}NO}\cdot$$

Decay kinetics were studied in a stop-flow apparatus. With equal concentrations of ceric and oxime the radical formation reaction could not be entirely separated from the decay process. With a fivefold excess of ceric the radicals decayed extremely rapidly which suggests that they themselves can be oxidized by ceric ion, *e.g.*

$$\mathrm{Ce^{IV}} + \mathrm{(CH_3)_2C{=}NO}\cdot \longrightarrow \mathrm{Ce^{III}} + \mathrm{CH_2{=}C(CH_3)N{=}O} + \mathrm{H^+}$$

The most suitable concentrations for stop-flow studies were found to be 10^{-4} *M* $\mathrm{Ce^{IV}}$ and 10^{-2} *M* oxime.

It is difficult to obtain "clean" epr spectra of iminoxy radicals, particularly unhindered dialkyliminoxy and alkylaryliminoxy radicals. This is because most methods of generating iminoxy radicals also produce varying amounts of secondary radicals (see below). This is, of course a much more critical problem in kinetic studies than in spectroscopic work. For kinetics the secondary radicals must be kept to the lowest possible level relative to the iminoxy concentration. In the photolytic experiments it was found necessary to change the reactant solution after each light pulse in order to prevent a build-up of rather stable secondary radicals.

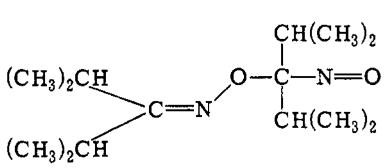
Products of the Oxidation of Oximes. The interpretation of the kinetic data for the self-reactions of iminoxy radicals would undoubtedly be assisted by a knowledge of the products of such reactions. While there have been a good many studies of the products formed when oximes are oxidized by presumed one-electron oxidizing agents such as lead tetraacetate,[9,20-23] potassium ferricyanide,[23,24] and ceric ion,[25,26] it is by no means certain that *all* of the identified products were formed *wholly* by the self-reactions of iminoxy radicals. In fact, the opposite appears to be firmly established for lead tetraacetate.[9,20-23] The suggestion[23c] that azine bis-*N*-oxides, $\mathrm{RR'C{=}N({\rightarrow}O)N({\rightarrow}O){=}CRR'}$ (which can be formed by the oxidation of fluorenone oxime and benzaldoxime with a variety of oxidizing agents[24,25]), are not produced by the coupling of iminoxy radicals because such products are not formed with lead tetraacetate, therefore appears unreasonable. Our own finding that ceric ion probably oxidizes some iminoxy radicals suggests that this oxidant is also unsatisfactory for product studies. For these reasons a few oximes were oxidized with silver oxide in the hope that this reagent would most closely duplicate the behavior of the radicals produced photochemically in the epr spectrometer.

The oxime was dissolved in deoxygenated benzene and flushed with nitrogen. The reaction system was arranged so that silver oxide could be added under nitrogen, while the gaseous products liberated during the reaction could be collected. The oxidation mixture was stirred at room temperature until gas evolution ceased and the products were then identified (insofar as was readily possible). The oxidation was repeated on a small scale to determine (by thin layer chromatography) which of the products was formed initially. The product yields given below are based on starting oxime. They were determined by normal procedures (*e.g.*, infrared spectroscopy and quantitative isolation by column or thick layer chromatography).

(i) **Acetoxime** (10.1 g, 0.138 mol) and silver oxide (32.1 g, 0.138 mol) in 500 ml of benzene gave 0.018 mol of gas (0.013 mol of nitrogen and 0.005 mol of nitrous oxide). Gas–liquid chromatography (glc) indicated that about 20% of the product was acetone. On concentration of the benzene solution a yellow, nonvolatile, oil (~32%) remained. This oil contained no significant amount of *N*-methylacetamide and no further characterization was attempted.

(ii) **Diisopropyl ketoxime** (13.1 g, 0.102 mol) and $\mathrm{Ag_2O}$ (0.102 mol) in 500 ml of benzene gave 0.0030 mol of gas (0.0027 mol of $\mathrm{N_2}$ and 0.0003 mol of $\mathrm{N_2O}$). The reaction mixture turned blue in the early stages of reaction and then gradually became green as the reaction progressed. Three major products were detected: diisopropyl ketone (2–5%), a blue liquid, and a yellow crystalline solid.

The blue compound was unstable decomposing slowly even at −20° at which temperature it was a semicrystalline blue syrup. Decomposition yielded, in part, the yellow compound and probably occurred *via* the diisopropyliminoxy radical since solutions of the blue compound at room temperature showed a fairly strong epr signal attributable to this radical. At room temperature the blue compound was quite unstable in $\mathrm{CCl_4}$ but it was stable enough in benzene for its nmr spectrum to be obtained (in $\mathrm{C_6D_6}$). The blue color and the infrared spectrum, which showed a strong band at 1560 cm^{-1} (as is found with $\mathrm{(CH_3)_3CNO}$), indicate that it is a nitroso compound. The nmr spectrum shows the presence of four isopropyl groups (2:1:1). The elemental analysis and molecular weight (vapor pressure osmometry) are consistent with structure **1**, a head-to-tail iminoxy radical dimer.



1

Anal. Calcd for $\mathrm{C_{14}H_{28}N_2O_2}$: C, 65.59; H, 11.01; N, 10.93; mol wt 256.4. Found: C, 65.41; H, 10.99; N, 11.05; mol wt 260.

The uv spectrum has a shoulder at 2700 Å (ϵ 180) and the blue color is due to an absorption with $\lambda_{\max}$ 7030 Å and ϵ 11. For com-

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[17] We are indebted to Professor J. Warkentin for a sample of 7-norbornenone which was hydrogenated on a Pd–C catalyst to 7-norbornanone.

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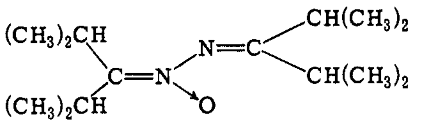
parison, $(CH_3)_3CNO$ has λ_{max} at 6700 and 6900 Å with ϵ 14.[27] The alternative formulation of this dimer as $Pr_2{}^iC{=}N({\rightarrow}O)C(Pr_2{}^i)NO$ is ruled out by the absence of a strong absorption (ϵ ~10,000) at 2800 Å.[28]

The nmr spectrum of the yellow compound (mp 66–73°) shows that it contains four nonequivalent isopropyl groups. The color, elemental analysis, and molecular weight (mass spectrometry) are consistent with structure 2.



2

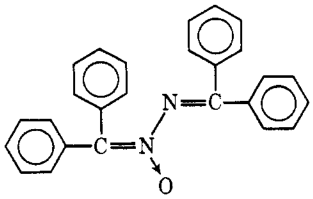
Anal. Calcd for $C_{14}H_{28}N_2O$: C, 69.95; H, 11.74; N, 11.65; mol wt 240.4. Found: C, 69.77; H, 11.90; N, 11.44; mol wt 240 (mass spectrometry), 246 (vapor pressure osmometry).

The uv spectrum has λ_{max} 2400 Å (ϵ 7000) with the absorption tailing to beyond 4000 Å.

In the initial stages of the silver oxide oxidation **1** is formed in ~75% yield, the balance being ketone and **2**.

(iii) **Di-*tert*-butyl Ketoxime.** The oxidation of this oxime to yield a moderately stable iminoxy radical has been described previously.[29]

(iv) **Benzophenone oxime** (10.2 g, 0.052 mol) and Ag_2O (0.052 mol) in 1 l. of benzene gave gas (presumably N_2 and N_2O), 0.013 mol; benzophenone, 60%; benzophenone azine *N*-oxide (**3**), 28%, yellow crystals, mp 155–160°; benzophenone oxime anhydride *N*-oxide (**4**), 12%, white crystals, mp 208–210°. Compounds **3** and **4** were identified by comparison with authentic samples prepared by potassium ferricyanide oxidation of benzophenone oxime at room temperature and at 0°, respectively, according to the procedure of Lauer and Dyer.[24] The oxime was also oxidized in carbon tetrachloride at 30° with *tert*-butoxy radicals generated thermally by the decomposition of *tert*-butyl hyponitrite. Both benzophenone and **4** were identified, but **3** could not be detected.



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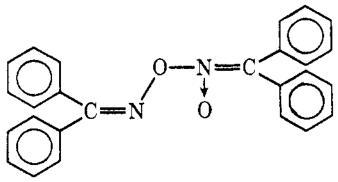

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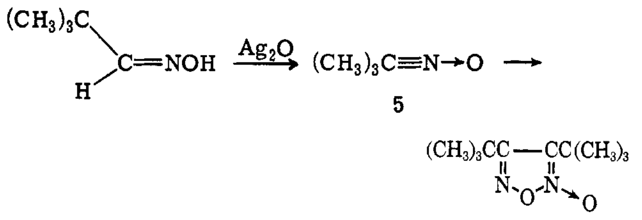
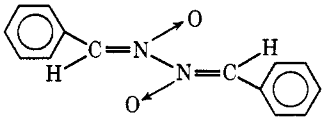
(v) **Pivaldoxime** (10.0 g, 0.099 mol) and Ag_2O (0.088 mol) in 500 ml of benzene gave no nitrogen or pivaldehyde. The initial product was identified as a nitrile oxide, **5**, by the infrared spectrum (strong bands at 2280 and 1175 cm^{-1}).[30] Over the course of several days these bands disappeared completely and the strongest band in the spectrum became one at 1550 cm^{-1}. This band is due to 3,4-di-*tert*-butylfuroxan (**6**) which was the principal product and was isolated by preparative tlc.



5

6

(vi) **Benzaldoxime** (12.0 g, 0.099 mol) and Ag_2O (0.099 mol) in 500 ml of benzene gave 0.0076 mol of gas (presumably N_2 and N_2O). The only initial product identifiable by tlc of the reaction mixture (R_f value) was benzaldazine bis-*N*-oxide (**7**). An authentic sample of **7** (mp 104–108°) was prepared by oxidation of benzaldoxime with ceric ammonium nitrate.[25] Compound **7** is unstable in solution[25] and breaks down in a few hours to yield nitrogen, benzaldehyde, benzonitrile, benzoic acid (presumably by the oxidation of the benzaldehyde), and several other products. A complex mixture of products is therefore present in the final oxidation mixture.



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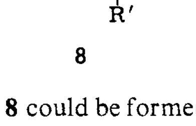
(vii) **Other Oximes.** Several ketoximes, including methylisopropyl, methyl-*tert*-butyl, benzylmethyl, dibenzyl, ethylphenyl, and isopropylphenyl ketoxime, yielded blue solutions of varying stability when oxidized with silver oxide in benzene. This is indicative of the formation of a nitroso compound, although not necessarily one similar in structure to compound **1**.

Results

(a) **Epr Spectra.** The hyperfine splittings of the iminoxy radicals studied in the present work are listed in Table I. Where comparison is possible the present data are in good agreement with the literature. The epr spectra of iminoxy radicals have been discussed in detail by numerous authors,[4–9] and only one of the new radicals in this work has any features of special interest. 7-Norbornyliminoxy shows hyperfine splittings due to three equivalent protons (presumably one bridgehead and two endo (or exo) protons). This equivalence must be fortuitous (just as is the equivalence of the three methyl and two ortho protons in methylphenyliminoxy radicals).

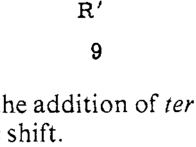
(b) **Secondary Radicals.** Most recorded spectra of iminoxy radicals show lines due to other nitrogen containing radicals.[5,6,8a,9,13] The nitrogen splittings of these secondary radicals are generally reported to be in the range 12–16 G, which suggests that they are nitroxides.

The oxidation of oximes with *tert*-butoxy radicals frequently yielded spectra indicating the presence of two (sometimes probably more) nitrogen-containing secondary radicals. One (or one group) had a_N ~ 13–15 G, and the other had a_N ~ 28 G. The radicals with the smaller a_N value are probably **8** and in some cases dialkyl nitroxides with structure **9** may also be present.



$$BO{-}\overset{R}{\overset{|}{C}}{-}\overset{H}{\overset{|}{\underset{\underset{R'}{|}}{N}}}{-}O\cdot$$

8



$$BO{-}\overset{R}{\overset{|}{\underset{\underset{R'}{|}}{C}}}{-}\overset{R''}{\overset{|}{N}}{-}O\cdot$$

9

Radical **8** could be formed by the addition of *tert*-butoxy to the oxime and a prototropic shift.

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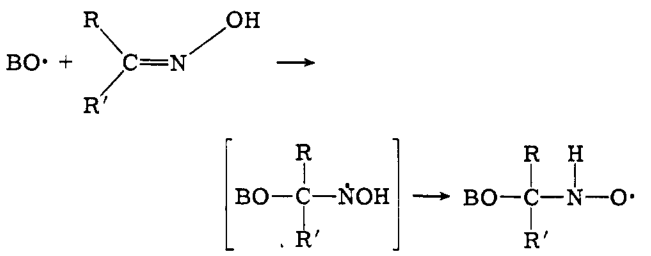
Table I. Coupling Constants (Gauss) of Iminoxy Radicals, $RR'C{=}NO\cdot$, in Benzene at ~25°

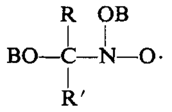
Iminoxy radical		This work			Literature			
R	R′	a_N	a_H	No. of H	a_N	a_H	No. of H	Ref
CH_3	CH_3	30.7	1.4	6	30.4	1.4	6	8c
CD_3	CD_3	31.6	*a*					
CH_3	CH_3CH_2	30.5	1.4	5				
CH_3	$CH_3CH_2CH_2$	30.7	1.4	5				
CH_3	$(CH_3)_2CH$	30.7	1.5	4				
CH_3	$(CH_3)_3C$	31.0	1.5	3	31.4	1.4	3	6b
CH_3	$(CH_3)_3CCH_2$	31.0	1.3	5				
CH_3	$C_6H_5CH_2$	31.6	1.5	5				
CH_3	$(C_6H_5)_2CH$	32.8	1.5	4				
$C_6H_5CH_2$	$C_6H_5CH_2$	31.6	1.3	4	29.3	1.25	4	5
$(CH_3)_2CH$	$(CH_3)_2CH$	30.7	1.2	14[b]				
$(CH_3)_3C$	$(CH_3)_3C$	32.2	0.4	*c*				
c-C_6H_{11}		30.7	2.8, 1.4	2, 2	31.0	2.9, 1.45	2, 2	8a
c-C_5H_9		32.2	*d*					
c-C_4H_7		31.6	*d*					
2,2,6,6-Me_4-*c*-C_6H_{11}		32.8	1.2	6				
7-Norbornyl		29.9	1.9	3				
CH_3	C_6H_5	32.2	1.5	5	31.6	1.4	5	8e
CH_3CH_2	C_6H_5	30.7	*d*					
$(CH_3)_2CH$	C_6H_5	32.2	*d*		31.6			9b
CF_3	C_6H_5	32.5	1.3	2	*e*	*e*	*e*	8e
CH_3	*p*-$NH_2C_6H_4$	31.9	1.4	5				
CH_3	*p*-$CH_3OC_6H_4$	32.2	1.3	5	31.7	1.4	5	6b
CH_3	*p*-$CH_3C_6H_4$	32.2	1.3	5	31.8	1.4	5	13
CH_3	*p*-BrC_6H_4	30.7	1.3	5	32.0			9b
CH_3	*p*-CNC_6H_4	31.6	1.5	5				
CH_3	*p*-$NO_2C_6H_4$	31.6	1.4	5	31.2	1.5		9b
α-Tetralyl		30.5	*d*					
C_6H_5	C_6H_5	32.8	1.4	2	31.4	1.4	2	8a
p-$CH_3OC_6H_4$	*p*-$CH_3OC_6H_4$	32.5	1.3	2	31.5	1.4	2	8a
p-$CH_3C_6H_4$	*p*-$CH_3C_6H_4$	32.5	1.3	2				
p-ClC_6H_4	*p*-ClC_6H_4	32.5	1.3	2				
9-Fluorenyl		30.7	2.3	2	30.85	2.7, 1.0	1, 1	8d
H	CH_3	*f*			32.5	5.2	1	4
H	$(CH_3)_3C$	*f*			*g*	*g*	*g*	8e
H	C_6H_5	*f*			*h*	*h*	*h*	4

[a] Deuterium splitting not resolved. [b] Spectrum temperature dependent, only 11 lines are resolvable at 70°. [c] Spectrum temperature dependent, 24 lines can be resolved from 24 to 42°, at 60° there are 16 lines, and at 75°, 14 lines. [d] Not resolved. [e] Two radicals, (i) $a_N = 32.2$, $a_H = 1.45$ (2), $a_F = 0.5$ (3) and (ii) $a_N = 31.6$, $a_F = 8.65$. [f] Radical concentration too low for a detailed examination of the spectrum to be worthwhile. [g] Two radicals, (i) $a_N = 32.2$, $a_H = 7.4$ (1), $a_H = 0.95$ (9) and (ii) $a_N = 30.5$, $a_H = 27.0$ (1). [h] Two radicals, (i) $a_N = 31.6$, $a_H = 6.2$ (1), $a_H = 1.4$ (2) and (ii) $a_N = 29.2$, $a_H = 26.9$ (1), see also ref 8b.



Other radicals which are known to add to oximes in a like manner include $\cdot OH$,[31-34] $\cdot NH_2$,[32,33] $\cdot CH_2OH$,[33] $\cdot CO_2H$,[35] and $\cdot CO_2^-$[35] but not $\cdot CH_3$.[33]

The secondary radicals with a_N ~ 28 G must be alkyl alkoxy nitroxides, **10**, since this nitrogen splitting is quite characteristic of such species.[36]



$$BO-\overset{R}{\underset{R'}{C}}-\overset{OB}{N}-O\cdot$$

10

10a, R = R′ = CH_3

The concentration of secondary radicals, relative to the concentration of the iminoxy radical, was highly dependent on oxime structure. In general, secondary radicals were more pronounced with unhindered dialkyl oximes and alkyl aryl oximes than with diaryl oximes and hindered dialkyl oximes. In static systems the relative importance of secondary radicals increased with the duration of the photolysis. As a rule, clean iminoxy spectra could be obtained under flow conditions.

A brief investigation of the radical **10a** formed from acetoxime by a series of light flashes (spaced sufficiently far apart for its complete decay between flashes) showed that the initial rate of formation of **10a** was much lower than its rate of formation after a few flashes (which soon reached a constant value). This is consistent with the formation of **10a** from a nitroso compound **11** that rapidly reaches a steady-state concentration.

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(31) J. Q. Adams, *J. Amer. Chem. Soc.*, **89**, 6022 (1967).

(32) D. J. Edge and R. O. C. Norman, *J. Chem. Soc. B*, 182 (1969).

(33) P. Smith and W. M. Fox, *Can. J. Chem.*, 47, 2227 (1969).

(34) In the gas phase $\cdot OH$ are reported to abstract the aldehydic hydrogen from aldoximes: $\cdot OH + RC(H)NOH \rightarrow H_2O + R\dot{C}NOH \rightarrow RCN + \cdot OH$ (D. G. Horne and R. G. W. Norrish, *Proc. Roy. Soc., Ser. A*, **315**, 287 (1970)).

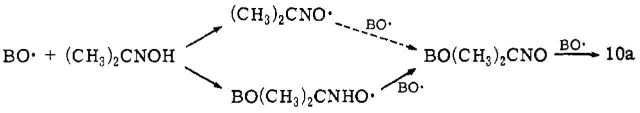
(35) D. J. Edge and R. O. C. Norman, *J. Chem. Soc. B*, 1083 (1970).

(36) (a) A. Mackor, T. A. J. W. Wajer, T. J. de Boer, and J. D. W. van Voorst, *Tetrahedron Lett.*, 385 (1967); (b) G. R. Chalfont, M. J. Perkins, and A. Horsfield, *J. Amer. Chem. Soc.*, **90**, 7141 (1968); (c) M. J. Perkins, P. Ward, and A. Horsfield, *J. Chem. Soc. B*, 395 (1970).

Table II. Rate Constants for the Decay of Dialkyliminoxy Radicals, RR′C═NO·, in Benzene at 25° ± 3° [a]

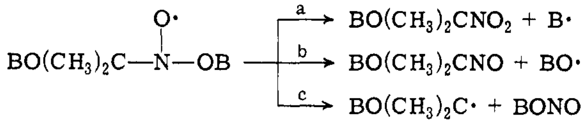
Iminoxy radical: R	Iminoxy radical: R′	Range in initial concn $[RR'C{=}NO\cdot]_0 \times 10^6$, M	$k^1_{epr} \times 10^2$, sec^{-1}	k^2_{epr}, M^{-1} sec^{-1}	$[R]_{ss} \propto h\nu^n$, $n \pm 0.1$
CH_3	CH_3	0.6–60	4[b]		0.5
CD_3	CD_3	0.7–7	4		
CH_3	CH_3CH_2	2–20	4		0.5
CH_3	$CH_3CH_2CH_2$	3–20	4		0.5
CH_3	$C_6H_5CH_2$	1–10	4		0.5
CH_3	$(CH_3)_3CCH_2$	2–10	3		0.5
CH_3	$(CH_3)_2CH$	0.2–30	5		0.5
CH_3	$(C_6H_5)_2CH$	2–20	4		0.5
CH_3	$(CH_3)_3C$	0.2 2–200	~0.3	 2000	Mixed
$C_6H_5CH_2$	$C_6H_5CH_2$	0.7–20	4[c]		0.5
$(CH_3)_2CH$	$(CH_3)_2CH$	0.2–10 100–1300	0.7[c]	 190	Mixed
$(CH_3)_3C$	$(CH_3)_3C$	1–10,000	Stable[d]		
c-C_4H_7		0.9–2	5		
c-C_5H_{11}		0.3–0.9	4		
c-C_6H_{11}		0.7–9	6		0.5
2,2,6,6-Me_4-c-C_6H_{11}		9–1900	0.08[c]		1
7-Norbornyl		0.5–5	32		1

[a] The importance of accurate temperature control (because of the high activation energy of the decay reaction) was not realized in the early work. [b] The rate constant is 2–3 times as large in CH_2Cl_2 and about 5 times as large in CH_3OH. [c] Decay is not clean first order. [d] A dimer analogous to **1** is formed over a period of several weeks (G. D. Mendenhall, unpublished results).



11

The decay of **10a** in benzene was first order, which is consistent with the various modes of decomposition that have been proposed for alkyl alkoxy nitroxides[16b, 36a,c, 37]



The *tert*-butyl radical formed in path a and the radical formed in path c (which will also be produced by the photolysis of **11**) can presumably add to **11** to yield nitroxides **9**, which should (to judge from their structure[16c]) be rather stable. This suggestion is consistent with the observation that extensive photolysis of oxime–peroxide mixtures yields rather stable nitroxides with $a_N \sim 15$ G.

(c) Kinetic Results. (i) Dialkyliminoxy Radicals. Dimethyliminoxy radicals decay with excellent first-order kinetics in benzene, chlorobenzene, toluene, methylene chloride, dichlorodifluoromethane, and methanol.[38] In benzene at ~25° the rate constant for this decay, k^1_{epr}

$$(CH_3)_2C{=}NO\cdot \xrightarrow{k^1_{epr}} \text{nonradical products}$$

was unaffected by the initial radical concentration (6×10^{-7}–6×10^{-5} M), by the concentration of acetoxime (0.04–0.8 M), or by the concentration of peroxide (7×10^{-3}–7×10^{-1} M). Furthermore, the rate constant did not change when the sample was extensively photolyzed so as to generate relatively large concentrations of products. There was only a small solvent effect on the reaction, the rate constant increasing somewhat with increasing solvent polarity. Under steady illumination the radical concentration was proportional to the *square root* of the light intensity (1–100% of full intensity).

The majority of the other dialkyliminoxy radicals studied behave in a similar manner to dimethyliminoxy. That is, decay is usually first order with reasonably "clean" kinetics. The k^1_{epr} values in benzene are similar to the value for dimethyliminoxy, as is shown in Table II. Moreover, under steady illumination the steady-state radical concentrations, $[R]_{ss}$, were found to be proportional to the square root of the light intensity in most of cases that were checked (see Table II).

Two dialkyliminoxy radicals, *tert*-butylmethyliminoxy and diisopropyliminoxy, decayed with clean second-order kinetics over most of the range of radical concentrations which could be obtained

$$2RR'C{=}NO\cdot \xrightarrow{k^2_{epr}} \text{nonradical products}$$

However both radicals decayed by a first-order process at very low concentrations. The rate constants for both first- and second-order processes were obtained.

A first-order radical decay with a rate constant independent of reactant and product concentrations and virtually independent of solvent, does not *of necessity* require that the decay process be a unimolecular radical reaction. The same kinetics can be obtained under certain conditions (see Discussion) if the radical is in equilibrium with a dimer.[39, 40] Proof that this was indeed the case was obtained by rapidly raising the temperature by about 10–20° during the course of a radical decay. In all cases examined (dimethyliminoxy, cy-

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(37) A. Mackor, T. A. J. W. Wajer, and T. J. de Boer, *Tetrahedron*, **24**, 1623 (1968).

(38) Photolysis in CH_3OH yields only the $\cdot CH_2OH$ radical. Iminoxy radicals were therefore generated by reaction of the oxime with Ce^{IV} in this solvent.

(39) L. R. Mahoney and S. A. Weiner, *J. Amer. Chem. Soc.*, **94**, 5029 (1972).

(40) J. R. Roberts and K. U. Ingold, *ibid.*, **93**, 6686 (1971).

Table III. Arrhenius Parameters for the Self-Reactions of Some Iminoxy Radicals

Iminoxy radical R	Iminoxy radical R′	Solvent	Temp range, °C	Log A^1_{epr}/ sec^{-1}	E^1_{epr}, kcal/mol	Log A^2_{epr}/ M^{-1} sec^{-1}	E^2_{epr}, kcal/mol
2,2,6,6-Me_4-c-C_6H_{11}		Benzene	25–60	11 ± 2	19 ± 3		
CH_3	CH_3	Benzene	10–50	11 ± 2	17 ± 3		
CD_3	CD_3	Benzene	25–50	13 ± 2	20 ± 3		
CH_3	CH_3	Toluene	5–50	12 ± 2	18 ± 3		
CH_3	CH_3	Chlorobenzene	5–50	10 ± 2	16 ± 3		
CH_3	CH_3	Dichloromethane	40–50	8 ± 2	12 ± 3		
c-C_6H_{11}		Benzene	10–50	14 ± 3	19 ± 4		
$C_6H_5CH_2$	CH_3	Benzene	25–50	13 ± 4	20 ± 5		
C_6H_5	CH_3	Benzene	25–40			9 ± 2	5 ± 3
C_6H_5	C_6H_5	Chlorobenzene	15–60			5 ± 2	2 ± 3
$(CH_3)_2CH$	$(CH_3)_2CH$	Benzene	25–55			5 ± 2	5 ± 3

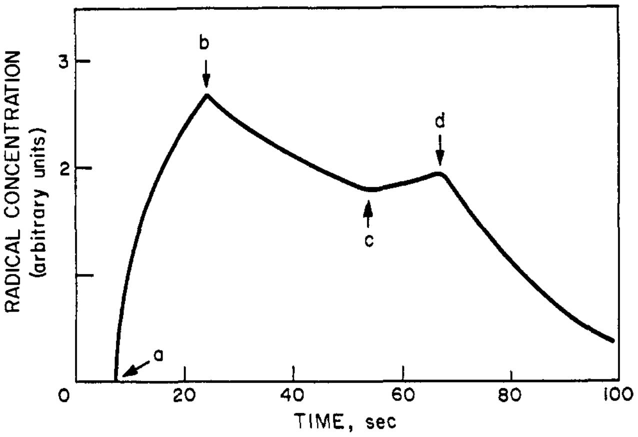


Figure 1. Effect of raising the temperature 10° during the decay of dimethyliminoxy radicals: (a) start of photolysis; (b) end of photolysis, temperature 10°; (c) temperature raised; (d) temperature 20°.

clohexyliminoxy, diisopropyliminoxy, dibenzyliminoxy, and diphenyliminoxy) there was a temporary rise in the radical concentration (see Figure 1). This occurred in spite of the fact that radical decay is faster at the higher temperature. Clearly there must be an equilibrium between radical and a dimer and the rise in temperature causes the dimer to decompose to radicals more rapidly than the radicals (or dimer) can decay to inert products. The existence of a dimer is also indicated by the observation that when the radicals were generated with a very brief flash of light there was initially a very rapid decay of the radicals to a lower "equilibrium" concentration. Decay from this equilibrium concentration occurred with the kinetics and rate constant obtained for radicals generated with a prolonged burst of light that allowed the equilibrium to be established before the decay was monitored.

Unstable intermediates have been identified in some other radical–radical reactions by low-temperature epr studies.[16] Attempts to examine the self-reactions of iminoxy radicals over a wide temperature range were hindered by the following factors. (i) Most of the oximes have low solubility in the solvents that might be used at low temperatures. (ii) The maximum iminoxy radical concentration that can be generated by the reaction

$$BO\cdot + RR'C{=}NOH \longrightarrow BOH + RR'C{=}NO\cdot$$

decreases rapidly as the temperature is lowered, presumably because this hydrogen abstraction has a fairly high activation energy. (iii) Some iminoxy radicals that decayed with clean second-order kinetics at room temperature were found to decay with first-order (or mixed-order) kinetics at higher temperatures. (iv) The relative concentration of secondary radicals increases as the temperature is lowered, presumably because the addition reaction

$$BO\cdot + RR'C{=}NOH \longrightarrow BO(RR')CNHO\cdot$$

has a lower activation energy than the abstraction.

In spite of these problems it was possible to obtain approximate Arrhenius parameters for the decay of some iminoxy radicals although the measurements had to be made over rather limited ranges of temperature (see Table III). The rate data used to calculate these parameters are based on measurements at the highest radical concentrations that were readily attainable at each temperature. Only decays that occurred with "clean" first- or second-order kinetics were used in the calculations. The accuracy of the activation parameters leaves a lot to be desired but it is difficult to see how they could have been significantly improved.

The radical–"unstable" dimer equilibrium was studied for a few iminoxy radicals. In the temperature range −30 to −80° the irreversible decay was sufficiently slow that the radical concentration could be reversibly increased or decreased by raising or lowering the temperature. Heats of dimerization, ΔH, were determined in toluene and are listed in Table IV. The entropy change for dimerization could not be deter-

Table IV. Enthalpies for the Radical–Dimer Equilibrium of Some Iminoxy Radicals in Toluene

Iminoxy radical R	Iminoxy radical R′	Equilibrium obsd in benzene	$\Delta H \pm 3$ in toluene, kcal/mol
CH_3	CH_3	Yes	20
CD_3	CD_3	Yes	*a*
$(CH_3)_2CH$	$(CH_3)_2CH$	Yes	15
$(CH_3)_3C$	$(CH_3)_3C$	No	
c-C_6H_{11}		Yes	*a*
CH_3	$C_6H_5CH_2$	Yes	17[b]
$C_6H_5CH_2$	$C_6H_5CH_2$	Yes	*a*
C_6H_5	CH_3	Yes	17
C_6H_5	C_6H_5	Yes[c]	*a*
C_6H_5	H	Yes	*a*
$(CH_3)_3C$	H	Yes	*a*

[a] Not determined. [b] At the higher temperatures some decay occurred and interfered with this measurement. The value given is a minimum value. [c] Studied in chlorobenzene.

mined because the equilibrium lies too far toward the dimer under the conditions of the experiments.

(ii) Aryl Ketoximes. Almost all iminoxy radicals having either one or two aryl groups decay with clean second-order kinetics. Values of k^2_{epr} in benzene[41] at ~25° for a variety of such radicals are listed in Table V

Table V. Rate Constants for the Decay of Alkylaryliminoxy and Diaryliminoxy Radicals in Benzene at 25 ± 2°

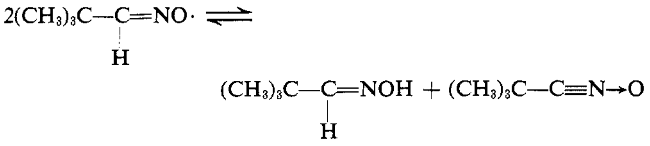
Iminoxy radical R	Iminoxy radical R′	Range in initial concn $[RR'C{=}NO\cdot]_0 \times 10^6$ M	$k^2_{epr} \times 10^{-3}$, M^{-1} sec^{-1}
CH_3	p-$NH_2C_6H_4$	0.7–4	500
CH_3	p-$CH_3OC_6H_4$	0.7–7	200[a]
CH_3	p-$CH_3C_6H_4$	5–20	50
CH_3	C_6H_5	2–80	30[b]
CH_3	p-BrC_6H_4	3–20	40
CH_3	p-CNC_6H_4	6	20[c]
CH_3	p-$NO_2C_6H_4$	0.6–2.0	30
α-Tetralyl		0.2–3	150
CH_3	C_6H_5	2–80	30[b]
CH_3CH_2	C_6H_5	0.3–0.8	30
$(CH_3)_2CH$	C_6H_5	6–200	0.2
p-$CH_3OC_6H_4$	p-$CH_3OC_6H_4$	1–20	30
p-$CH_3C_6H_4$	p-$CH_3C_6H_4$	2–50	5
C_6H_5	C_6H_5	3–100	2.5[d]
p-ClC_6H_4	p-ClC_6H_4	2–30	4
9-Fluorenyl		0.8–5	20
C_6H_5	C_6H_5	3–100	2.5[d]
CF_3	C_6H_5	4–350	First order

[a] In CH_2Cl_2, $k^2_{epr} = 8 \times 10^5$. [b] In n-pentane, $k^2_{epr} = 3 \times 10^4$; in chlorobenzene, $k^2_{epr} = 5 \times 10^4$; CH_2Cl_2, $k^2_{epr} = 4 \times 10^4$; methanol (generation with Ce^{IV}), $k^2_{epr} = 8 \times 10^5$. [c] First-order contribution to decay at lower radical concentrations. The maximum radical concentration obtained was 6×10^{-6} M. [d] In chlorobenzene, $k^2_{epr} = 3 \times 10^3$; CH_2Cl_2, $k^2_{epr} = 2 \times 10^4$; methanol (generation with Ce^{IV}), $k^2_{epr} = 2 \times 10^4$.

The radicals have been arranged into groups according to whether the structural changes to the parent radicals, methylphenyliminoxy and diphenyliminoxy, could influence the decay process predominantly by a polar or by a steric effect.

A few aryliminoxy radicals give some indication of a first-order decay process at low concentrations and at low temperatures, but only one, ω-trifluoromethylphenyliminoxy, decays with first-order kinetics at all concentrations. The first-order rate constant for decay of this radical was $\sim 3 \times 10^{-3}$ sec^{-1} in benzene and was independent of the oxime concentration. Decay in cyclohexane was also first order but was much slower than in benzene. There was no evidence of any radical–dimer equilibrium. The radical concentration was proportional to the light intensity which suggests that the first-order decay results from a reaction of this radical with the solvent. This process was not examined further.

(iii) Aldoximes. *tert*-Butyliminoxy radicals decay with first-order kinetics, $k^1_{epr} = 1.0 \times 10^{-3}$ sec^{-1} at 25°. The steady-state radical concentration was proportional to the square root of the light intensity. The identification of *tert*-butylnitrile oxide as the initial oxidation product of pivaldoxime suggests that there must be a radical–radical disproportionation. During a decay the radical concentration could be increased by raising the temperature which implies that the disproportionation is reversible.[42]

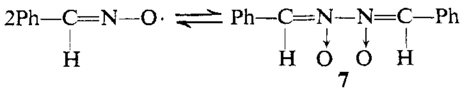


$$2(CH_3)_3C{-}\underset{\displaystyle H}{\underset{|}{C}}{=}NO\cdot \rightleftharpoons (CH_3)_3C{-}\underset{\displaystyle H}{\underset{|}{C}}{=}NOH + (CH_3)_3C{-}C{\equiv}N{\rightarrow}O$$

That nitrile oxides are capable of oxidizing oximes was confirmed by treating di-*tert*-butyl ketoxime with benzonitrile oxide, 4-methylbenzonitrile oxide, and the very stable[43] 2,4,6-trimethylbenzonitrile oxide. At room temperature the epr signal due to di-*tert*-butyliminoxy appeared immediately when solutions of any of these three nitrile oxides (~0.1 M benzene) were added to a solution of di-*tert*-butyl ketoxime (~0.02 M benzene).[44]

The decay kinetics for methyliminoxy radicals were not examined since the epr spectrum indicated that this radical could not be obtained sufficiently free from secondary radicals.

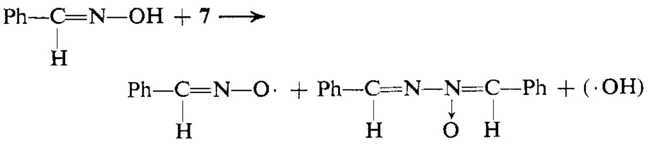
Phenyliminoxy radicals decay with first-order kinetics at 60° ($k^1_{epr} = 7 \times 10^{-2}$ sec^{-1}), but with second-order kinetics at 25° ($k^2_{epr} = 9 \times 10^7$ M^{-1} sec^{-1}). At both temperatures the steady-state radical concentration was proportional to the square root of the light intensity. If the sample was photolyzed at room temperature and the radicals were then allowed to decay completely, they could be temporarily regenerated by warming the sample by ~20°. The identification of benzaldazine bis-*N*-oxide (**7**) in the oxidation of benzaldoxime implies that phenyliminoxy radicals dimerize rather than disproportionate



$$2Ph{-}\underset{\displaystyle H}{\underset{|}{C}}{=}N{-}O\cdot \rightleftharpoons Ph{-}\underset{\displaystyle H}{\underset{|}{C}}{=}\underset{\displaystyle O}{\underset{\downarrow}{N}}{-}\underset{\displaystyle O}{\underset{\downarrow}{N}}{=}\underset{\displaystyle H}{\underset{|}{C}}{-}Ph$$

7

Our results suggest that this reaction is readily reversible at temperatures above ~30–40°. At these higher temperatures it is possible that some of the phenyliminoxy radicals are produced by a reaction such as



$$Ph{-}\underset{\displaystyle H}{\underset{|}{C}}{=}N{-}OH + \mathbf{7} \longrightarrow Ph{-}\underset{\displaystyle H}{\underset{|}{C}}{=}N{-}O\cdot + Ph{-}\underset{\displaystyle H}{\underset{|}{C}}{=}N{-}\underset{\displaystyle O}{\underset{\downarrow}{N}}{=}\underset{\displaystyle H}{\underset{|}{C}}{-}Ph + (\cdot OH)$$

since di-*tert*-butyliminoxy radicals are formed at room temperature in the reaction of **7** with di-*tert*-butyl ketoxime in benzene.

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[41] An increase in the solvent polarity tends to increase the decay rate constants (see footnotes *a*, *b*, and *d* in Table V).

[42] An analogous equilibrium is observed with $(CH_3)_3CNHO\cdot$.[16b]

[43] C. Grundmann and J. M. Dean, *J. Org. Chem.*, **30**, 2809 (1965).

[44] Epr signals from the appropriate radicals were also obtained when these nitrile oxides were allowed to react at room temperature or 60° with other good hydrogen donors capable of yielding stable radicals. Thus, *N*-hydroxypiperidine, 2,6-di-*tert*-butyl-4-methylphenol, and diphenylpicrylhydrazine yielded the corresponding nitroxide, phenoxy, and hydrazyl radicals, respectively. Epr signals were not obtained with good hydrogen donors yielding less stable radicals (*e.g.*, *tert*-butylthiol, 2,4,6-trimethylbenzenethiol, 3,5-di-*tert*-butylphenol, benzaldoxime, triphenylmethane, and 1,1-diisopropylhydrazine) presumably because the steady-state radical concentration is too low for detection. However, it is possible that a non-radical, 1,3-dipolar addition reaction can occur with some of these compounds.[45]

[45] C. Grundmann and H.-D. Frommeld, *J. Org. Chem.*, **31**, 157 (1966).

Discussion

There are two simple reaction schemes that can yield a first-order kinetic equation for the decay of a radical R· which exists in equilibrium with a dimer, R_2[39,40]

Scheme I

$$R_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2R\cdot \xrightarrow{k_2} \text{stable molecular products}$$

$$-d[R\cdot]/dt = k_1[R\cdot]^2 - 2k_{-1}[R_2] + k_2[R\cdot]^2$$

$$-2d[R_2]/dt = -k_1[R\cdot]^2 + 2k_{-1}[R_2]$$

That is

$$2d[R_2]dt + d[R\cdot]/dt = -k_2[R\cdot]^2 \qquad (1)$$

If $k_1 > k_2$, then

$$k_1[R\cdot]^2 \approx 2k_{-1}[R_2]$$

and therefore

$$2k_1[R\cdot]d[R\cdot]/dt = 2k_{-1}d[R_2]/dt$$

Substituting this expression into (1) yields

$$-d[R\cdot]/dt = k_2[R\cdot]^2/(1 + 2k_1[R\cdot]/k_{-1}) \qquad (2)$$

For values of $2k_1[R\cdot]/k_{-1} > 1$ decay will be first order with $k^1_{\text{epr}} = k_2k_{-1}/2k_1$, while for values of $2k_1[R\cdot]/k_{-1} < 1$ decay will be second order with $k^2_{\text{epr}} = k_2$. That is, decay will be first order at high radical concentrations and will be second order at low radical concentrations.

Scheme II

$$\text{stable molecular products} \xleftarrow{k_3} R_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2R\cdot$$

If $k_{-1} > k_3$ a similar kinetic procedure yields

$$-d[R\cdot]/dt = k_3(k_1/k_{-1})[R\cdot]^2/(1 + 2k_1[R\cdot]/k_{-1}) \qquad (3)$$

Once again, for values of $2k_1[R\cdot]/k_{-1} > 1$ decay will be first order but now $k^1_{\text{epr}} = k_3/2$, while for values of < 1 decay will be second order with $k^2_{\text{epr}} = k_3k_1/k_{-1}$. There is no obvious kinetic method for distinguishing between these two reaction schemes.

First-order decay kinetics could also arise through a true unimolecular decay process[46]

Scheme III

$$2R\cdot \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R_2$$

$$R\cdot \xrightarrow[k_4]{} \text{stable molecular product}$$

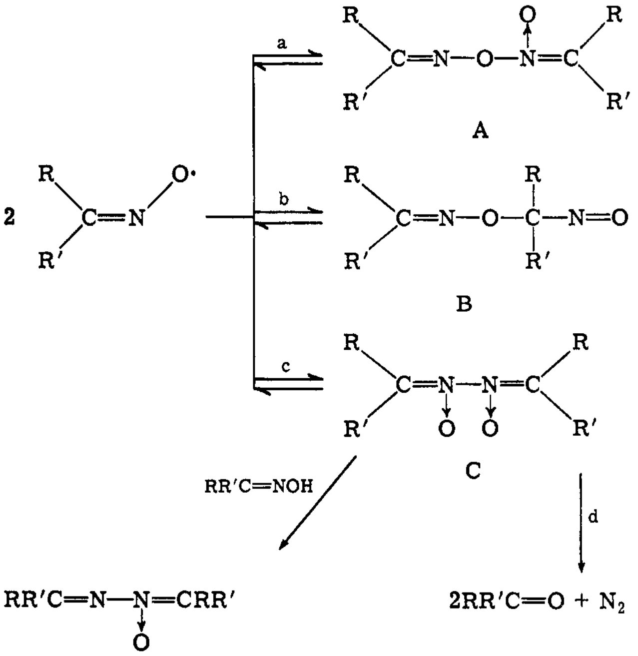
A similar kinetic procedure to that applied in Scheme I yields

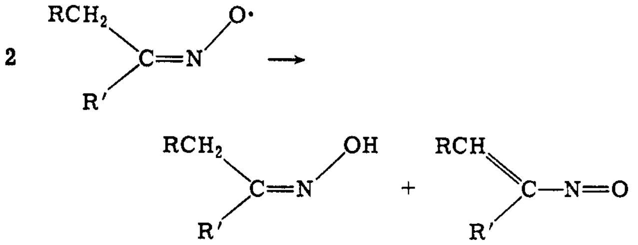
$$-d[R\cdot]/dt = k_4[R\cdot]/(1 + 2k_1[R\cdot]/k_{-1}) \qquad (4)$$

Under steady illumination $d[R\cdot]/dt = d[R_2]/dt = 0$ and simple kinetic analysis of Schemes I and II shows that the steady-state radical concentration, $[R]_{ss}$, will be proportional to the square root of the rate of radical formation, regardless of whether $2k_1[R\cdot]/k_{-1}$ is $>$ or < 1. In contrast, Scheme III predicts that the steady-state radical concentration will be directly proportional to the light intensity. Since the rate of radical formation must be proportional to the light intensity, the general dependence of the radical concentrations on the square root of the light intensity (Table II) implies that Scheme I or II is applicable to the majority of iminoxy radicals that decay with first-order kinetics. This conclusion is supported by the "temperature jump" experiments which indicated that dialkyliminoxy radicals are in equilibrium with dimer during their decay, in all the cases that were examined.

The principle self-reactions of the majority of iminoxy radicals are indicated in Scheme IV. The initial process is a dimerization and there are at least three dimers that may be formed. With the exception of the *tert*-butyliminoxy radical, disproportionation products were not observed. The potential reaction

Scheme IV





is, therefore, relatively unimportant unless the unsaturated nitroso compounds are responsible for the intractable residues which were formed during the silver oxide oxidations of some dialkyloximes. The source of the small quantities of nitrous oxide that were formed is uncertain.

Space-filling molecular models indicate that dimer C is sterically the most crowded of the three dimers and this is also indicated by the fact that it is isolated in large amounts only from phenyliminoxy radicals. When dimer C is formed from other iminoxy radicals it can presumably serve as a precursor for azine *N*-oxide, ketone, nitrogen, and possibly N_2O. It is likely that

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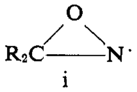
(46) Three possible first-order processes can be envisaged: (i) β scission (ring opening is known to occur when 2,2,6,6-tetramethylcyclohexanone oxime is oxidized with lead tetraacetate[21a,d]); (ii) intramolecular hydrogen atom abstraction; and (iii) rearrangement to an oxaziridyl radical i (improbable on energetic grounds).



i

dimer C, and probably dimers A and B as well, can in most cases decompose reversibly to re-form the starting iminoxy radicals.

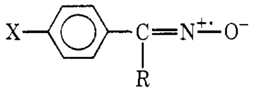
The majority of the dialkyliminoxy radicals listed in Table II probably undergo their self-reactions according to Scheme I or II. Although these two schemes cannot be kinetically distinguished it is possible to argue in favor of Scheme I on the basis of the similarity in the values of ΔH, the enthalpy for dimer formation, and E^1_{epr}, the activation energy for the unimolecular decay process.[40] On the other hand, the formation of ketone and nitrogen (and azine *N*-oxide) suggests that dimer C can decompose irreversibly. We therefore suggest that *both* schemes are in operation. For some iminoxy radicals k_3 will predominate over k_2 while for others the reverse will happen. The rate constants k_1, k_{-1}, k_2, and k_3 are all likely to be composite rate constants. Thus, $k_1 = k_a + k_b + k_c + \ldots$, while if one or two of the dimers are stable, for example A and B, then $k_{-1} = k_{-c} + \ldots$ and $k_2 = k_a + k_b$. Similarly, $k_3 = k_d + \ldots$. The measured rate constants and activation parameters for iminoxy radical self-reactions and the enthalpies for dimer formation therefore have no precise significance unless the initial products formed under the conditions of these experiments are known quantitatively.

Two partially hindered dialkyliminoxy radicals, methyl *tert*-butyliminoxy and diisopropyliminoxy, decay with second-order kinetics over most of the concentration ranges studied.[47] The oxidation of diisopropylketoxime yielded dimer B (**1**) together with diisopropyl ketone and the azine *N*-oxide (**2**). This suggests that Schemes I and II are still operable but that steric hindrance has reduced the stability and rate of formation of the dimers, so that $2k_1[\text{Pr}_2{}^{\text{i}}\text{CNO}\cdot]/k_{-1} < 1$. The enthalpy of formation of the unstable dimer is only −15 kcal/mol compared with −20 kcal/mol for the unstable dimer of dimethyliminoxy[48] (Table IV), and its formation may require an activation energy of ~5 kcal/mol (Table III).

The general behavior of diaryliminoxy and alkylaryliminoxy radicals resembles the behavior of diisopropyliminoxy radicals. That is, decay is second order (except for trifluoromethylphenyliminoxy) and has a low activation energy (2 kcal/mol for $\text{Ph}_2\text{CNO}\cdot$ and 5 kcal/mol for $\text{Ph(CH}_3\text{)CNO}\cdot$). The enthalpy of formation of the unstable dimer of $\text{Ph(CH}_3\text{)CHO}\cdot$ is −17 kcal/mol. The oxidation of benzophenone yielded dimer A (**4**) together with products indicating that dimer C was also probably formed.

Both steric and polar factors influence the magnitude of the bimolecular decay rate constants listed in Table V. The steric effect is obvious when diphenyliminoxy is compared with 9-fluorenyliminoxy. The "tying-back" of the phenyl rings increases k^2_{epr} by an order of magnitude. The steric effect is even better illustrated by the series, phenyliminoxy ($k^2_{\text{epr}} = 9 \times 10^7\ M^{-1}\ \text{sec}^{-1}$), α-tetralyliminoxy (1.5×10^5), methylphenyliminoxy (3×10^4), ethylphenyliminoxy (3×10^4), and isopropylphenyliminoxy (2×10^2). It seems probable that the magnitude of k^2_{epr} is determined primarily by the rate of formation of dimer. As has already been mentioned, azine bis-N-oxides are very crowded[49] and even with benzaldazine bis-*N*-oxide (**7**) it is not possible for the two phenyl rings and the $\text{C{=}N(\rightarrow O)N(\rightarrow O){=}C}$ group to lie wholly in one plane. It is not unreasonable therefore that the replacement of the benzaldehydic hydrogens of phenyliminoxy by larger groups should hinder this particular radical–radical coupling reaction.

Polar effects on the rate constants for decay of aryliminoxy radicals can be ascribed to the influence of the para substituents on the radical dipole



This dipole will be reduced by an electron-donating para substituent so that there will be less electrostatic repulsion to be overcome in forming the azine bis-*N*-oxide and it should be more stable. As a consequence, electron-donating substituents should increase k^2_{epr} as is, in fact, observed. On the other hand, electron-withdrawing para substituents must increase the iminoxy radical dipole which should reduce the rate of N–N coupling. The measured decay rate constants do not show the expected effect. That is, the k^2_{epr} values found for electron-withdrawing substituents are similar to, or slightly larger than, those for the unsubstituted radicals. This suggests that the reduced rate of N–N coupling is compensated for by an increased rate of N–O and, perhaps, O–C coupling. That is, electron-donating substituents on the ring are expected to increase the yield, stability, and rate of formation of dimer C while electron-withdrawing substituents are expected to increase the yield of dimers A and B.

Summary

Dimers of at least three structurally different types can be formed by the self-reactions of iminoxy radicals. The products of this reaction are generally a rather complex mixture of these dimers and their decomposition products.

The decay of iminoxy radicals may occur with first- or second-order kinetics. Under the conditions of the decay experiments the radicals are probably in equilibrium with unstable dimers. When the equilibrium lies in favor of dimer, decay is first order; when it

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[47] For these two radicals the k^1_{epr} values cannot result from a radical–dimer equilibrium. That is, according to Schemes I and II the *kinetics should become second order, not first, at low radical concentrations* (which means that for these two radicals the kinetics should have remained second order). The dependence of $[\text{R}]_{\text{ss}}$ on the light intensity indicates that the 7-norbornyliminoxy and 2,2,6,6-tetramethylcyclohexyliminoxy radicals also decay by first-order processes which may be true unimolecular reactions.[46]

[48] If we assume ΔS_1 in the Van't Hoff relation is −38 gibbs/mol (which is a fairly typical value for radical–dimer equilibria), then at 300°K

$$2k_1[\text{Pr}_2{}^{\text{i}}\text{CNO}\cdot]/k_{-1} \approx 2 \times 10^{-38/4.6} \times 10^{15{,}000/4.6 \times 300}[\text{Pr}_2{}^{\text{i}}\text{CNO}\cdot] \approx 8 \times 10^2[\text{Pr}_2{}^{\text{i}}\text{CNO}\cdot]$$

and decay should be second order at radical concentrations below $\sim 10^{-3}\ M$. Second-order kinetics are observed in the concentration range 1×10^{-4}–$1.3 \times 10^{-3}\ M$ (Table II). Similarly

$$2k_1[(\text{CH}_3)_2\text{CNO}\cdot]/k_{-1} \approx 3 \times 10^6[(\text{CH}_3)_2\text{CNO}\cdot]$$

and decay should be first order at radical concentrations above $\sim 3 \times 10^{-7}\ M$ as is observed.

[49] Relatively few azine bis-*N*-oxides are known (L. Horner, L. Hockenberger, and W. Kirmse, *Chem. Ber.*, **94**, 290 (1961); M. M. Trojmovic and G. Just, *Can. J. Chem.*, **46**, 3719 (1968)).

favors the radicals, decay is second order. In view of the complexities of the reaction, the precise meaning of the measured decay rate constants is uncertain.

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Studies of Stable Free Radicals. X.[1] Nitronyl Nitroxide Monoradicals and Biradicals as Possible Small Molecule Spin Labels

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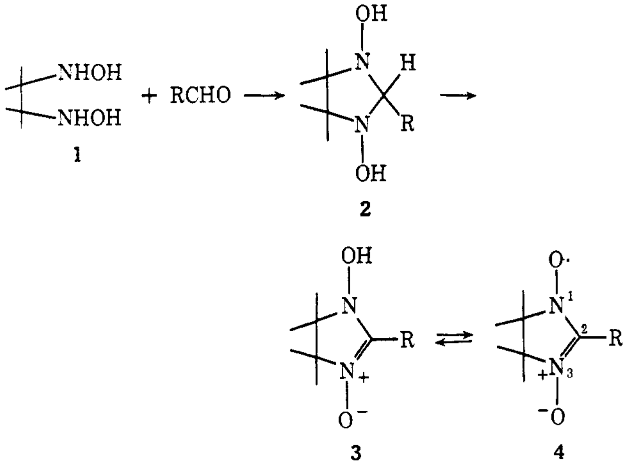
Contribution No. 43 from Syva Research Institute,
Palo Alto, California 94304. *Received March 8, 1972*

Abstract: The preparation, chemistry, and spectra of nitronyl nitroxides, a versatile new class of stable radicals, are described. The compounds are readily prepared from most aldehydes. Their esr spectra may have use in determining the extent of α substitution of the aldehyde where only small amounts of the aldehyde are available. Reaction of α-haloalkyl nitronyl nitroxides with amines proceeds readily, and the esr spectra of the resulting amino radicals may serve to distinguish between primary and secondary amines. Both conjugated and unconjugated biradicals have been prepared. The zero-field splitting data suggest that the conjugated biradicals exist in several possible planar conformations.

Stable free radicals that can undergo reactions at sites of high spin density are useful in the spin labeling of small molecules. By the attachment of such a radical to a host molecule spin density is distributed to the host. The electron spin resonance spectrum can then yield information concerning the site of attachment. Utilization of this technique has primarily been confined to spin labeling with semidiones.[4] Spin trapping experiments with nitroso compounds or nitrones in which reaction of a reactive radical yields a nitroxide is also a form of spin labeling, although these experiments are generally designed to give esr information about the reactive radical rather than the diamagnetic trap.[5]

In the course of studies to develop spin-labeling techniques for small molecules, a new class of stable radicals called nitronyl nitroxides was discovered.[6] These compounds can be readily prepared from many aldehydes by simple test tube reactions and their esr spectra yield direct information concerning the substitution of the aldehyde. In this and subsequent papers, the chemistry of nitronyl nitroxides will be discussed together with spectral data which can yield structural information concerning the starting aldehyde.

Aliphatic Nitronyl Nitroxides. Aliphatic aldehydes react rapidly with 2,3-dimethyl-2,3-bis(hydroxylamino)-butane (**1**). Although it is usually possible to isolate an anhydro adduct **2**, direct treatment of the reaction mixture with sodium periodate or lead dioxide gives an instantaneous color due to the formation of a nitronyl nitroxide **4**. Nitronyl nitroxides derived from saturated aldehydes are generally red whereas unsaturated aldehydes yield violet or blue radicals depending on whether the solvent is polar or nonpolar. When desired, the initial dihydro adducts **2** can be obtained as stable diamagnetic white solids. If sodium periodate or lead dioxide is added in limited amount to these compounds it is possible to obtain the highly air-sensitive intermediates **3**. Catalytic hydrogenation of the nitronyl nitroxides regenerates **3**, though rapid catalytic reoxidation occurs if the catalyst is not completely separated. The radicals when isolated are quite stable and in most cases can be stored at 0° for months without decomposition.



α hydrogens of 2-alkyl groups on nitronyl nitroxides are weakly acidic. Deuterium exchange of the 2-methyl hydrogens of **4**, R = CH_3, in alkaline deuterium oxide occurs without loss of the esr signal. Strong bases such as potassium *tert*-butoxide in DMSO cause

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(1) For paper IX, see E. F. Ullman, L. Call, and J. H. Osiecki, *J. Org. Chem.*, **35**, 3623 (1970).

(2) Synvar Postdoctoral Fellow, 1967–1969.

(3) Synvar Postdoctoral Fellow, 1967–1968.

(4) G. A. Russell, E. T. Strom, E. R. Talaty, K. Y. Chang, R. D. Stephans, and M. C. Young, *Rec. Chem. Progr.*, **27**, 3 (1966).

(5) E. G. Jansen, *Accounts Chem. Res.*, **4**, 31 (1971).

(6) For preliminary communications describing portions of this work, see J. H. Osiecki and E. F. Ullman, *J. Amer. Chem. Soc.*, **90**, 1078 (1968); D. G. B. Boocock, R. Darcy, and E. F. Ullman, *ibid.*, **90**, 5945 (1968).

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