# Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. XV. Iminyl Radicals[1]

D. Griller,[2] G. D. Mendenhall,[3] W. Van Hoof,[4] and K. U. Ingold*

Contribution from Division of Chemistry, National Research Council of Canada, Ottawa, Canada. Received March 11, 1974

Abstract: Five iminyl radicals, $R_2C=\dot{N}$ (R = t-Bu, 1-adamantyl, i-Pr, CF_3, and C_6H_5), have been generated by photolysis directly, in the cavity of an epr spectrometer, of solutions of the parent ketimines in di-*tert*-butyl peroxide. At $-35°$ the rate constants for the bimolecular self-reactions to form the corresponding azines are 4×10^2 (t-Bu), 5×10^4 (1-Ad), 4×10^7 (i-Pr), 2×10^8 (Ph), and 4×10^9 $M^{-1} sec^{-1}$ (CF_3). At temperatures above $-25°$ (t-Bu)$_2$-C=N undergoes a first-order decay. This reaction is a β scission and yields pivalonitrile and a *tert*-butyl radical. The rate of this β scission is compared with the rates of β scission of structurally analogous alkoxy radicals.

Iminyl radicals, $RR'C=\dot{N}$, have frequently been detected by epr spectroscopy when solids containing nitrogenous materials are subjected to high-energy irradiation.[5-13] Monoalkyliminyl radicals, $RHC=N\cdot$, have been formed from nitriles in solution both by their reaction with hydrated electrons, followed by protonation, and directly by their reaction with hydrogen atoms.[14,15] Diaryliminyl radicals have been observed during the thermal rearrangement of oxime thionocarbamates in solution.[16] However, no general method for the production of dialkyliminyls *in solution* has been reported. We have found that both dialkyliminyl and diaryliminyl radicals are readily produced and detected by photolyzing deoxygenated solutions of the appropriate ketimine in di-*tert*-butyl peroxide directly in the cavity of an epr spectrometer.

$$(CH_3)_3CO\cdot + R_2C=NH \longrightarrow (CH_3)_3COH + R_2C=N\cdot$$
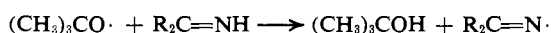
The frequent detection of iminyl radicals has been pointed out by Symons[13] and he has suggested possible reasons why these radicals are "stable."[17] However, in the majority of the examples quoted the iminyl radicals were generated in solid matrices at 77°K or colder. Under such conditions, radical–radical reactions become very slow because diffusion, if it occurs at all, is very slow. The observation of iminyls in such matrices means only that once they are formed at these temperatures they do not isomerize, nor do they attack the surrounding matrix.

In this paper we report a kinetic study of a selection of these radicals in solution. The radicals studied were chosen with a view to maximizing their lifetimes by decreasing the rates of their bimolecular self-reactions by all the usual means.[18,19]

Experimental Section

The general experimental procedure for kinetic studies of free radicals on our Varian E-3 epr spectrometer has been described previously.[1] The iminyl radicals were generated from the corresponding imines by photolysis of their solutions in di-*tert*-butyl peroxide, with addition of cyclopropane as a cosolvent when required. The precautions necessary to prevent generation of the corresponding iminoxy radical, $R_2C=NO\cdot$, were the same as those employed to prevent the formation of nitroxides from amino radicals.[20]

Materials. Di-*tert*-butyl ketimine, (t-Bu)$_2$C=NH, was in part a gift from Dr. H. D. Hartzler and was in part prepared by his procedure.[21] It was purified by preparative vpc and stored under argon. Di-(1-adamantyl) ketimine, (1-Ad)$_2$C=NH, was prepared by the same process and was purified by recrystallization from *n*-hexane, mp 140–143°, lit.[22] 113.5–6.1°. Diisopropyl ketimine, (i-Pr)$_2$C=NH, was prepared by the method of Pickard and Tolbert[23] and was purified by preparative vpc; nmr (in ppm from TMS) methyl 0.90; methine 1.66, J = 6.6 Hz; mass spectrum m/e 113, calcd mol wt for $C_7H_{15}N$ = 113.2. Diphenyl ketimine, $Ph_2C=$NH, was prepared by the method of Lachman.[24] Bistrifluoromethyl ketimine, $(CF_3)_2C=$NH, was a commercial sample that was purified before use by trap-to-trap distillation. Diisopropyl ketone azine, (i-Pr)$_2$C=NN=C(i-Pr)$_2$, was prepared from diisopropyl ketone and hydrazine hydrate by the method of Elguero, et al.[25]

Product Studies. Photolysis of a solution of 0.1 ml of (i-Pr)$_2$-C=NH in 0.3 ml of di-*tert*-butyl peroxide under argon in a quartz tube at $-35°$ for 1 hr yielded *tert*-butyl alcohol and diisopropyl ketone azine in a 2:1 mole ratio as the only products.

$$2(CH_3)_3CO\cdot + 2(i-Pr)_2C=NH \longrightarrow$$
$$2(CH_3)_3COH + (i-Pr)_2C=NN=C(i-Pr)_2$$
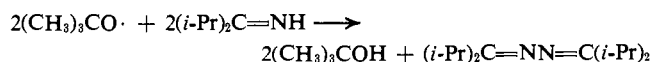
Photolysis of a solution of 0.1 ml of (t-Bu)$_2$C=NH in 0.3 ml of peroxide under argon in a quartz tube at 24° for 90 min yielded

(1) Issued as N.R.C.C. No. 14217. Part XIV: V. Malatesta and K. U. Ingold, *J. Amer. Chem. Soc.*, **96**, 3949 (1974).

(2) N.R.C.C. Postdoctoral Fellow, 1973–1974.

(3) N.R.C.C. Postdoctoral Fellow, 1971–1973.

(4) N.R.C.C. Summer Student, 1973.

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(16) R. F. Hudson, A. J. Lawson, and E. A. C. Lucken, *J. Chem. Soc., Chem. Commun.*, 807 (1971); 721 (1972). See also C. Brown, R. F. Hudson, and A. J. Lawson, *J. Amer. Chem. Soc.*, **95**, 6500 (1973).

(17) "Stability" has no universally accepted meaning to free-radical chemists,[18,19] though attempts have been made to define it.[18]

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tert-butyl alcohol, isobutane, isobutylene, 2,2,3,3-tetramethylbutane (8% based on tert-butyl alcohol), and pivalonitrile (75% based on tert-butyl alcohol). The isobutane and isobutylene were formed in approximately equal amounts but, because they are gases, were not analyzed quantitatively. It would appear that $(t\text{-Bu})_2C=N(t\text{-Bu})$ and $(t\text{-Bu})_2C=NN=C(t\text{-Bu})_2$ either are not formed or are unstable under the experimental conditions.

Results

Epr Spectra. The spectrum assigned to $t\text{-Bu}_2C=N$ could be obtained by photolysis of solutions containing $t\text{-Bu}_2C=NH$ or $t\text{-Bu}_2C=ND$ and di-tert-butyl peroxide or benzophenone (isopentane as solvent). In the presence of oxygen this radical is converted to di-tert-butyliminoxy, $(t\text{-Bu})_2C=N\dot{O}$.[26] These experiments confirm that the radicals observed arise by abstraction of the imino hydrogen rather than by a radical addition to the C=N bond.

The hyperfine splittings and g values of the radicals studied in this work are recorded in Table I. The epr

Table I. Epr Parameters for Some Iminyl Radicals in Di-tert-butyl Peroxide at $-30°$

Radical	g	a^N (G)	a^{other} (G)
$(t\text{-Bu})_2C=\dot{N}$	2.0032	10.31[a]	1.0[a] [(CH₃)₆]
$(1\text{-Ad})_2C=\dot{N}^b$	2.0030	10.28	c
$(i\text{-Pr})_2C=\dot{N}$	2.0028	9.53	0.62 [(CH₃)₄];[d] 0.93 [(CH)₂]
$Ph_2C=\dot{N}^e$	2.0033	10.13	c
$(CF_3)_2C=\dot{N}^f$	2.0037	9.13	4.56 [(CF₃)₂]

[a] Inadvertently given in MHz in ref 26 rather than the stated gauss. [b] 1-Ad represents the 1-adamantyl group. [c] H couplings not resolved. [d] Or 0.31. For comparison,[7] in an adamantane matrix $a^N = 9.7$, a^H [(CH₃)₂] = 1.33 for $Me_2C=\dot{N}$, and $a^N = 9.5$, a^H[(CH₂)₂] = 1.25 for $Et_2C=\dot{N}$. [e] Reported,[16] $g = 2.0033$, $a^N = 10$, $a^H = 0.4$. [f] Prolonged photolysis at 20° yielded a complex spectrum comprising signals from two or more "secondary" radicals.

spectra of various other iminyl radicals have been discussed by numerous workers.[5-16] The major contribution to the orbital occupied by the unpaired electron is the nitrogen $2p_y$ atomic orbital. The isotropic ¹⁴N hyperfine splitting arises solely via polarization effects and is therefore of similar magnitude to that found in true π-electron nitrogen radicals, such as NH_2 (a^N ca. 10.3 G).[5,6,9,27]

Decay Kinetics. (i) Second-Order Decay. $(1\text{-Ad})_2C=\dot{N}$, $(i\text{-Pr})_2C=\dot{N}$, $(Ph)_2C=\dot{N}$, and $(CF_3)_2C=\dot{N}$ decay fairly rapidly. In the temperature range -40 to 20° the concentrations of these four radicals under steady illumination were proportional to (light intensity)$^{1/2}$, and the radicals decayed with second-order kinetics when the light was cut off. The bimolecular rate constants for decay, k^2_{epr}, at $-35°$ are listed in Table II. The products of these reactions are presumably the N–N coupled dimers in all cases, since this was the only product from diisopropyl ketimine.

$$2R_2C=\dot{N} \xrightarrow{k^2_{epr}} R_2C=NN=CR_2$$

The decay kinetics with $(t\text{-Bu})_2C=\dot{N}$ were more complicated. With radical concentrations in the range 10^{-4}–10^{-5} M decay was second order at temperatures

(26) G. D. Mendenhall and K. U. Ingold, J. Amer. Chem. Soc., **95**, 627, 2963 (1973).

(27) S. N. Foner, E. L. Cochran, V. A. Bowers, and C. K. Jen, Phys. Rev. Lett., **1**, 91 (1958).

Table II. Rate Constants (k^2_{epr}) for the Bimolecular Self-Reaction of Some Iminyl Radicals at $-35°$

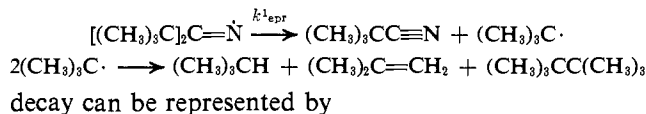| Radical	Initial concn[a] (M)	k^2_{epr} (M^{-1} sec^{-1})[a]
$(t\text{-Bu})_2C=\dot{N}$		$4 \times 10^{2\ b}$
$(1\text{-Ad})_2C=\dot{N}$	1×10^{-6}	5×10^4
$(i\text{-Pr})_2C=\dot{N}$	7×10^{-7}	4×10^7
$(Ph)_2C=\dot{N}$	1×10^{-7}	2×10^8
$(CF_3)_2C=\dot{N}$	1×10^{-7}	4×10^9

[a] Maximum concentration attained; measurements were also made using 30% of this concentration and the k^2_{epr} values were in good agreement. [b] Extrapolated see text.

from -100 to $-55°$ and, under steady illumination, the radical concentration was proportional to (light intensity)$^{1/2}$. The decay can be represented by

$$\log (k^2_{epr}/M^{-1}\ sec^{-1}) = (8.4 \pm 2.0) - (6.4 \pm 2.0)/\theta$$

where $\theta = 2.3\ RT$ kcal/mol. This equation yields $k^2_{epr} = 4 \times 10^2\ M^{-1}\ sec^{-1}$ at $-35°$.

(ii) First-Order Decay. At temperatures above $-25°$ decay of $(t\text{-Bu})_2C=\dot{N}$ is first order and the radical concentration under steady illumination is proportional to light intensity. This reaction was shown to be a β scission by isolating pivalonitrile and the usual products of tert-butyl radical self-reactions, from a room temperature photolysis of $(t\text{-Bu})_2C=NH$ in di-tert-butyl peroxide. In the temperature range -25 to 10° the

$$[(CH_3)_3C]_2C=\dot{N} \xrightarrow{k^1_{epr}} (CH_3)_3CC\equiv N + (CH_3)_3C\cdot$$

$$2(CH_3)_3C\cdot \longrightarrow (CH_3)_3CH + (CH_3)_2C=CH_2 + (CH_3)_3CC(CH_3)_3$$
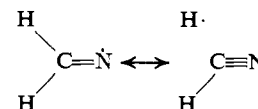
decay can be represented by

$$\log (k^1_{epr}/sec^{-1}) = (14.4 \pm 3.0) - (17.1 \pm 3.0)/\theta$$

and the half-life at 0° is ca. 0.1 sec.

Discussion

Symons[13] suggested that the "stability" of iminyl radicals arises from two factors. (i) A powerful hyperconjugative interaction, the presence of which can be deduced from the large value of a^H (ca. 87 G) in $H_2C=\dot{N}$, i.e.

(ii) Dimerization of iminyls via N–N coupling will require a considerable readjustment of the orbitals around nitrogen, and this could contribute to weakness in the N–N bond of azines. Both factors only imply that N–X bonds in $R_2C=N-X$ compounds will be weak when compared with N–X bonds in many other nitrogen containing compounds,[28] and so iminyl radicals should be formed rather easily in a variety of systems. Such appears to be the case.[5-16] However, there is no reason to suppose that "stability" from such factors would have an effect on the rates of radical–radical reactions.

(28) Specifically, azines should undergo fairly facile N–N cleavage,[29-31] and iminyl radicals should be readily formed by hydrogen abstraction from imines and should themselves be poor hydrogen atom abstracting agents.

(29) See, e.g., J. F. Ogilvie, Chem. Commun., 359 (1965); R. W. Binkley, J. Org. Chem., **33**, 2311 (1968); M. Kamachi, K. Kuwata, and S. Murahashi, J. Phys. Chem., **75**, 164 (1971); W. J. Middleton, J. Amer. Chem. Soc., **93**, 423 (1971).

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(31) B. G. Gowenlock, R. M. Haynes, and C. F. Johnson, J. Chem. Soc. B, 1098 (1971).

Examination of the rate constants listed in Table II indicates that only steric factors have any significant effect on the rates of the bimolecular self-reactions of iminyl radicals. Neither potential polar effects (*e.g.*, $(CF_3)_2C\!=\!\dot{N}$) nor the presence of aromatic rings (*i.e.*, $Ph_2C\!=\!\dot{N}$) reduces the rate significantly below the diffusion-controlled limit. The latter observation may relate to the structure of these radicals which precludes substantial delocalization of the unpaired electron into the π system of the aromatic rings. It is also of interest in connection with reports[16] that iminyl radicals can be detected when certain alkaryl- and diaryloxime thionocarbamates, $RR'C\!=\!NOC(S)NMe_2$, are heated to temperatures where they rearrange to the corresponding thioxime carbamates, $RR'C\!=\!NSC(O)NMe_2$. The rates of radical generation in these experiments (so far as they can be ascertained) appear to be quite sufficient to account for the ready detection of the iminyl radicals even though they couple at close to the diffusion-controlled limit (see Table II).

As is usually the case,[19] only steric factors have a dramatic effect on the rates of the bimolecular self-reactions of iminyl radicals. The 6.4-kcal/mol activation energy for the dimerization of $(t\text{-Bu})_2C\!=\!\dot{N}$ causes the rate to be seven orders of magnitude slower than diffusion controlled at $-35°$. It indicates that the steric retardation is due principally to enthalpy rather than to entropy effects.

Reaction mechanisms involving the β scission of intermediate iminyl radicals have sometimes been suggested previously.[31,32] It is interesting to compare the rate constant for β scission of $(t\text{-Bu})_2C\!=\!\dot{N}$ with that for β scission of some structurally related alkoxy radicals, since the two types of radical are isoelectronic. Thus, for *tert*-butoxy[33]

$$(CH_3)_3CO\cdot \longrightarrow CH_3COCH_3 + \dot{C}H_3$$
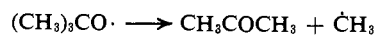
$\log (k/\text{sec}^{-1}) = 12.4 - 13.9/\theta$; $\tau_{1/2} = 3.4 \times 10^{-2}$ sec at $0°$

for *tert*-butyldimethylmethoxy[34]

$$(CH_3)_3C(CH_3)_2CO\cdot \longrightarrow CH_3COCH_3 + (CH_3)_3C$$
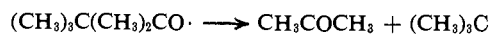
$\log (k/\text{sec}^{-1}) = 14.8 - 7.5/\theta$; $\tau_{1/2} = 1.1 \times 10^{-9}$ sec at $0°$

and for di-*tert*-butyliminyl

$$[(CH_3)_3C]_2C\!=\!\dot{N} \longrightarrow (CH_3)_3CN + (CH_3)_3\dot{C}$$
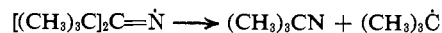
$\log (k/\text{sec}^{-1}) = 14.4 - 17.1/\theta$; $\tau_{1/2} = 1.4 \times 10^{-1}$ sec at $0°$

The loss of *tert*-butyl from the iminyl occurs at a rate comparable to the loss of methyl from *tert*-butoxy, but is much slower than the loss of *tert*-butyl from *tert*-butyldimethylmethoxy. These rate differences are related to the differences in the exothermicities of the β scission. Thus, from the heats of formation of methyliminyl (34.4 kcal/mol)[35] and acetonitrile (19 kcal)[36] and of ethoxy (-4.9 kcal)[35] and acetaldehyde (-39.7 kcal)[36] the heats of the reactions $CH_3CH\!=\!\dot{N} \rightarrow CH_3C\!\equiv\!N + H\cdot$ and $CH_3CH_2O\cdot \rightarrow CH_3CH\!=\!O + H\cdot$ are estimated to be endothermic by 36.7 and 17.3 kcal/mol, respectively.

(32) See, *e.g.*, G. L. Pratt and J. H. Purnell, *Proc. Roy. Soc., Ser. A*, 260, 317 (1961); *Trans. Faraday Soc.*, 58, 692 (1962); J. Kalvoda, *Helv. Chim. Acta*, 51, 267 (1968); T. P. Forshaw and A. E. Tipping, *Chem. Commun.*, 816 (1969); M. L. Poutsma and P. A. Ibarbia, *J. Org. Chem.*, 34, 2848 (1969); L. J. Winters, J. F. Fischer, and E. R. Ryan, *Tetrahedron Lett.*, 129 (1971).

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(34) D. Griller and K. U. Ingold, *J. Amer. Chem. Soc.*, 96, 630 (1974).
(35) H. E. O'Neal and S. W. Benson, "Free Radicals," Vol. 2, J. K. Kochi, Ed., Wiley, New York, N. Y., 1973, Chapter 17.
(36) Estimated from data given in ref 37.
(37) S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, 69, 279 (1969).

A Complete Kinetic Analysis of the A-SE2 Mechanism of Acid-Catalyzed Addition of Methanol to an Olefinic Double Bond

Claude F. Bernasconi*[1] and William J. Boyle, Jr.

Contribution from the Thimann Laboratories of the University of California, Santa Cruz, California 95064. Received August 24, 1973

Abstract: In 80% methanol–water 1,1-bis(*p*-dimethylaminophenyl)ethylene (1) undergoes slow, general acid catalyzed protonation at the double bond to form a carbonium ion (2) which is rapidly converted to the methyl ether (3) upon reaction with methanol or methoxide ion. This system is unique in that 1, 2, and 3 coexist at detectable concentration in acidic solution; it thus provides the first example of an A-SE2 addition to an olefinic double bond in which a complete kinetic and equilibrium analysis of the component steps has been accomplished. Rate constants for protonation of 1 by lyonium ion and for deprotonation of 2 by the solvent are 23 M^{-1} sec^{-1} and 4.8×10^{-2} sec^{-1}, respectively. These are rather low even for carbon bases and acids. Rate constants for nucleophilic attack on the cation 2 by methoxide ion and methanol are 4.9×10^4 M^{-1} sec^{-1} and 2.5 sec^{-1}, respectively, ratio $\sim 2 \times 10^4$. This ratio is considerably lower than expected on the basis of Ritchie's N_+ value.

T he mechanism of hydration (or alcoholation) of olefins[2] has been the subject of some controversy since the hypothesis of Taft[3] that the acid-catalyzed hydration of simple olefins involves rapid, reversible

(1) Alfred P. Sloan Fellow, 1971–1973.
(2) P. B. D. De La Mare and R. Bolton, "Electrophilic Additions to Unsaturated Systems," Elsevier, New York, N. Y., 1966, p 25.

(3) (a) R. W. Taft, Jr., *J. Amer. Chem. Soc.*, 74, 5372 (1952); (b) R. W. Taft, Jr., E. L. Purlee, P. Riesz, and C. A. DeFazio, *ibid.*, 77, 1584 (1955).