

Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. XIV. 1,1-Dialkylhydrazyl Radicals¹

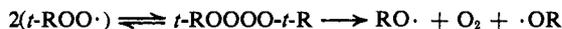
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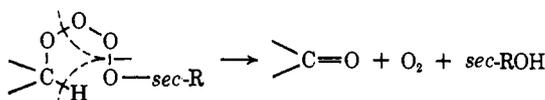
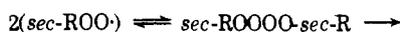
Abstract: The self-reactions of 1,1-dialkylhydrazyl radicals at ambient temperatures have been examined by kinetic epr spectroscopy. Dimethyl-, diethyl-, and dibenzylhydrazyls decay rapidly with bimolecular kinetics. The products suggest that the initial reaction is a dimerization but that the resulting tetrazane is unstable and decomposes to amine and nitrogen. Diisopropylhydrazyl and the hydrazyl derived from 1-amino-2,2,6,6-tetramethylpiperidine decay slowly with first-order kinetics. These radicals exist in equilibrium with their dimer. Decay involves a disproportionation reaction of the free radicals with the formation of the parent hydrazine and an *N*-nitrene. The dialkylaminonitrenes decompose to hydrocarbons and nitrogen. Arrhenius parameters for these decays and the heats of dimerization were determined. The results are discussed both in relation to classical studies of the oxidation of 1,1-dialkylhydrazines and in relation to the decay processes for the isoelectronic alkylperoxy radicals and dialkyl nitroxides.

In this laboratory we have been interested for many years in the rates and mechanisms of the bimolecular self-reactions of alkylperoxy radicals, ROO·.³⁻⁶ We have recently broadened our studies to cover the isoelectronic dialkyl nitroxides, R₂NO·.⁷⁻⁹ In this paper we extend our investigations to yet another group of isoelectronic radicals, the 1,1-dialkylhydrazyls, R₂NNH·.

All three of these groups of radicals contain certain members that are relatively long lived, but the mechanisms of their self-reactions are not identical. Thus, *tert*-alkylperoxy radicals exist in reversible equilibrium with a tetroxide that can decay irreversibly to oxygen and two alkoxy radicals³⁻⁵

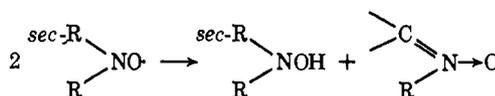


Secondary (and primary) alkylperoxy radicals are much shorter lived. Some of them react by the same mechanism⁶ but in the majority of cases the tetroxide decays to molecular products directly, *via* the six-membered cyclic transition state first proposed by Russell.¹⁰



With both tertiary¹¹ and secondary¹² alkylperoxy radicals the evolved oxygen comes from the terminal oxygen atoms of *two* radicals. Nitroxides also can

react reversibly to form a diamagnetic dimer.⁷⁻⁹ If both alkyl groups are tertiary the nitroxides are extremely stable, but if one alkyl group is secondary (or primary) the nitroxide can undergo a bimolecular self-reaction to form molecular products.

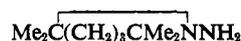


It is likely that a cyclic transition state is also involved in this reaction.^{7,8}

The 1,1-dialkylhydrazyl radicals show interesting similarities and differences when compared with their isoelectronic counterparts. As we have already shown¹³ these radicals can be generated by photolysis of the parent hydrazines in di-*tert*-butyl peroxide solutions directly in the cavity of an epr spectrometer. Kinetic and product data on these radicals are presented in this paper.

Experimental Section

Materials. Four of the hydrazines used in this work, Me₂NNH₂, Et₂NNH₂, *i*-Pr₂NNH₂, and 1-amino-2,2,6,6-tetramethylpiperidine



(hereafter referred to as TMPNH₂) were prepared by LiAlH₄ reduction of the nitrosoamines.¹⁴ The conversion of TMPNO to TMPNH₂ was increased from 44%¹⁴ to 85% by a longer reaction time (48 hr) at a lower temperature (95°). 1,1-Dibenzylhydrazine was prepared from benzyl chloride and hydrazine.¹⁵

Samples of diethylhydrazine and 1-aminotetramethylpiperidine were also prepared labeled with ¹⁵N in their NH₂ groups. These labeled compounds were prepared from the parent amines by the same routes as the unlabeled materials,¹⁴ except that the amines were *N*-nitrosated with Na¹⁵NO₂ (Merck Sharpe and Dohme) containing >97 atom % ¹⁵N, before reduction to the hydrazines. Adequate quantities of both materials were obtained using 0.5 g of Na¹⁵NO₂ for each nitrosation together with the appropriate quantity of amine. The labeled hydrazines were purified in the usual way and their chemical purity was checked by vpc. Mass spectrometry showed they contained 97 atom % ¹⁵N in the NH₂ group, as expected.

(13) V. Malatesta and K. U. Ingold, *J. Amer. Chem. Soc.*, **95**, 6110 (1973).

(14) J. R. Roberts and K. U. Ingold, *J. Amer. Chem. Soc.*, **95**, 3228 (1973), and references cited therein.

(15) M. J. S. Dewar and W. B. Jennings, *J. Amer. Chem. Soc.*, **95**, 1562 (1973).

(1) Issued as NRCC No. 13958. Part XIII: G. D. Mendenhall, D. Griller, D. A. Lindsay, T. T. Tidwell, and K. U. Ingold, *J. Amer. Chem. Soc.*, **96**, 2441 (1974).

(2) N.R.C.C. Postdoctoral Fellow, 1972-1973.

(3) K. U. Ingold, *Accounts Chem. Res.*, **2**, 1 (1969).

(4) J. A. Howard, *Advan. Free-Radical Chem.*, **4**, 49 (1972).

(5) J. A. Howard in "Free Radicals," Vol. II, J. K. Kochi, Ed., Wiley, New York, N. Y., 1973, Chapter 12.

(6) D. Lindsay, J. A. Howard, E. C. Horswill, L. Iton, K. U. Ingold, T. Cobbley, and A. Li, *Can. J. Chem.*, **51**, 870 (1973).

(7) K. Adamic, D. F. Bowman, T. Gillan, and K. U. Ingold, *J. Amer. Chem. Soc.*, **93**, 902 (1971).

(8) D. F. Bowman, T. Gillan, and K. U. Ingold, *J. Amer. Chem. Soc.*, **93**, 6555 (1971).

(9) G. D. Mendenhall and K. U. Ingold, *J. Amer. Chem. Soc.*, **94**, 7166 (1972); **95**, 6390, 6395 (1973).

(10) G. A. Russell, *J. Amer. Chem. Soc.*, **79**, 3871 (1957).

(11) P. D. Bartlett and T. G. Traylor, *J. Amer. Chem. Soc.*, **85**, 2407 (1963); T. G. Traylor, *ibid.*, **85**, 2411 (1963).

(12) J. E. Bennett and J. A. Howard, *J. Amer. Chem. Soc.*, **95**, 4008 (1973).

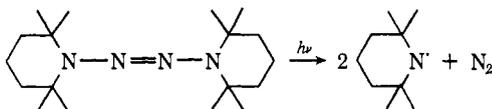
Kinetic Procedure. The epr kinetic technique has been described in previous papers in this series.^{1,7,8,14} The hydrazines (0.2 ml or 0.2 g) were dissolved in isopentane, cyclopentane, or benzene (0.6 ml) containing di-*tert*-butyl peroxide (0.2 ml) that had been freed from hydroperoxide by distillation from triphenylphosphine. The resulting solutions were carefully degassed by the freeze-thaw method and sealed off under vacuum. The radical concentrations and decay kinetics were monitored on a Varian E-3 epr spectrometer.

"Secondary" Radicals. In most experiments, a "clean" hydrazyl epr spectrum was obtained as soon as photolysis was begun (see Results). However, "secondary" radicals were sometimes a problem with *i*-Pr₂NNH₂ and TMPNH₂.

(i) *i*-Pr₂NNH₂. We only succeeded in generating the desired radical free from *i*-Pr₂NO· in a few preliminary experiments. In all subsequent work, despite using freshly prepared and carefully distilled hydrazine, the nitroxide was always present. It did not hinder the interpretation of the hydrazyl epr spectrum but it did have a serious effect on the kinetic studies (see below). We can only suppose that some diisopropylhydroxylamine was present as an impurity in the hydrazine as we prepared it.

On some occasions, and quite irreproducibly, another "secondary" radical was formed ($a^N = 14.5$ G, $a^N = 8.3$ G, $a_H(2H) = 0.95$ G, $g = 2.0044$ at -20°). The structure of this radical is unknown.

(ii) TMPNH₂. In contrast to *i*-Pr₂NNH₂, the spectrum of the 2,2,6,6-tetramethylpiperidin-*N*-oxyl, TMO, was never observed in degassed solutions of TMPNH₂. (This is somewhat surprising since TMO is a great deal more stable than *i*-Pr₂NO·.) However, after 5–10 min of photolysis at room temperature a second spectrum starts to appear which was unequivocally identified as tetramethylpiperidyl, TMP·, by its epr parameters.¹⁴ We believe it is formed by photolysis of the tetrazene¹⁴ which we deduce must be a reaction product. The TMP· could be very simply removed without dis-



turbing the hydrazyl concentration by cooling the sample to -78° and storing in the dark for a few days. On rewarming the sample the hydrazyl spectrum returns quite unaffected but the amino radical is gone, as we would expect from our kinetic studies of the latter radicals.^{14,16}

In the presence of air, TMPNH₂ solutions show a TMPNH signal in the absence of peroxide and of light. However, when oxygen was bubbled through the solution there was a progressive broadening of the epr lines and eventual disappearance of the TMPNH signal, no new signal appearing. The TMPNH signal was regenerated by removing most of the oxygen. If the oxygenated sample was photolyzed a strong signal due to TMO· appeared, presumably by reaction of oxygen with TMP·.^{14,17}

As with *i*-Pr₂NNH₂, on a few occasions a "secondary" radical of unknown structure was produced from TMPNH₂ ($a^N = 14.8$ G, $a^N = 6.6$ G, $g = 2.0044$ at -50°).

Product Studies. General Procedure. The dialkylhydrazine was allowed to react with approximately half its molar concentration of *tert*-butoxy radicals, generally in benzene as the solvent. The *tert*-butoxys were generated thermally, the preferred source being di-*tert*-butyl hyponitrite and the reaction temperature 50° .²⁰ The reaction was normally carried out in a nmr tube. The reactant solution was thoroughly degassed and the nmr tube was then sealed under vacuum. After 12–48 hr at 50° in the dark, the reaction mixture was analyzed first by nmr (without opening the tube) and then by vpc.²¹

(16) No amino radical signal was observed even on prolonged photolysis of the other hydrazines possibly because the corresponding dialkylamino radicals decay much more rapidly than tetramethylpiperidyl.¹⁴

(17) The absence of any signal attributable to the hydrazoxyl radical, TMPNHO, is surprising since such radicals are formed readily from oxygen and trialkylhydrazyls¹⁸ or 1,2-dicarboxyalkyl-1-alkylhydrazyls.¹⁹ We can only suppose that if hydrazoxyl radicals are formed they either disproportionate or react with the hydrazine.

(18) S. F. Nelsen and R. T. Landis, II, *J. Amer. Chem. Soc.*, **95**, 6454 (1973).

(19) V. Malatesta and K. U. Ingold, *Tetrahedron Lett.*, 3311 (1973).

(20) Di-*tert*-butyl peroxyoxalate, the other commonly used low-temperature thermal source of *tert*-butoxys, was found to react directly with 1,1-dialkylhydrazines.

Studies of the isotopic composition of the nitrogen evolved from the dialkylhydrazine oxidations were carried out in glass ampoules containing a break-seal. After reaction the ampoules were attached to the inlet of a mass spectrometer and the sample was cooled with liquid nitrogen before smashing the break-seal. In this way, only nitrogen entered the spectrometer.

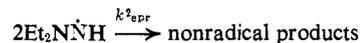
Results

Epr Spectra. The epr parameters for Me₂NNH, Et₂NNH, *i*-Pr₂NNH, TMPNH, and TMP¹⁵NH have been reported previously.¹³ Comparison of the hyperfine splittings (in di-*tert*-butyl peroxide at room temperature) for Et₂NNH ($a^H(\text{NH}) = 13.80$ G, $a^{15N} = 11.63$ G, $a^{14N} = 9.86$ G, $a^H(4H) = 6.05$ G)²² with those for Et₂N¹⁵NH ($a^H(\text{NH}) = 13.80$ G, $a^{14N} = 11.63$ G, $a^{15N} = 13.80$ G, $a^H(4H) = 6.05$ G) confirms our previous assignment¹³ of the nitrogen splittings in 1,1-dialkylhydrazyls.

The splittings for (PhCH₂)₂NNH ($a^H(\text{NH}) = 13.5$ G, $a^N = 11.6$ G, $a^H = 10.2$ G, $a^H(2H) = 6.5$ G, and $a^H-(2H) = 5.1$ G, in benzene: di-*tert*-butyl peroxide (3:1 by volume) at 0°) are of the expected magnitude (*cf.* Et₂NNH above) *except* for the presence of two pairs of magnetically nonequivalent methylene protons. This surprising result²³ suggests that there is either an interaction between the two phenyl rings which retards rotation about the C–N bonds²⁵ or that there is a strong interaction between one phenyl ring and the hydrazyl nitrogens.

Kinetics and Products of Hydrazyl Radical Decay.

The Unhindered Hydrazyls. (i) Kinetics. 1,1-Dimethyl-, diethyl-, and dibenzylhydrazyl decayed extremely rapidly when the light was cut off. The rate of decay could not be measured with Me₂NNH and (PhCH₂)₂NNH because of the poor signal to noise ratio which results from the very large number of individual lines in the epr spectra. However, Et₂NNH has fewer lines and it was possible to measure the rate. Decay occurs with second-order kinetics at (or close to) the diffusion-controlled limit, with $(k^2_{\text{epr}})\text{Et}_2\text{NNH} = (2.0 \pm 1.5) \times 10^9 M^{-1} \text{sec}^{-1}$ in isopentane at -70° .



Under similar experimental conditions, the concentrations of Me₂NNH, Et₂NNH, and (PhCH₂)₂NNH under steady illumination are approximately equal. Since the steady-state concentrations of all three radicals are proportional to the square root of the light intensity, it is safe to conclude that dimethyl- and dibenzylhydrazyl also decay bimolecularly at the diffusion-controlled limit.²⁷

(21) The vpc (silicone-rubber column and flame ionization detector) was surprisingly insensitive to aliphatic amines.

(22) These values differ slightly from those previously reported¹³ as a consequence of better spectra and more careful computer simulation.

(23) The methine hydrogens in *i*-Pr₂NNH are equivalent at -50° in cyclopentane. However, the amino hydrogens in H₂NNH, H₂NNMe, and H₂NNCH₂Ph are not equivalent at room temperature.²⁴

(24) V. Malatesta, D. Lindsay, E. C. Horswill, and K. U. Ingold, *Can. J. Chem.*, in press.

(25) The barrier to rotation is presumed to be greater than the barriers to inversion at nitrogen and to N–H flipping. However, the barrier would have to be much greater in (PhCH₂)₂NNH than the barriers found during nmr¹⁵ and esr²⁶ studies of analogous materials.

(26) S. F. Nelsen, private communication.

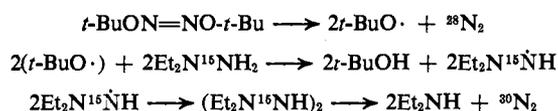
(27) In aqueous solution, Me₂NNH decays bimolecularly with $k^2 = 6 \times 10^8 M^{-1} \text{sec}^{-1}$.²⁸

(28) E. Hayon and M. Simic, *J. Amer. Chem. Soc.*, **94**, 42 (1972).

(ii) **Products.** (a) **Dimethylhydrazine** (0.63 mmol) and di-*tert*-butyl hyponitrite (0.15 mmol) in benzene (1 ml) containing some tetramethylsilane (TMS) as an internal standard were heated under vacuum in the dark for 13 hr at 50°. The only organic products detected (and quantitatively analyzed) by nmr and vpc were dimethylamine²⁹ (0.26 mmol), *tert*-butyl alcohol³⁰ (0.29 mmol), and di-*tert*-butyl peroxide (0.005 mmol). Unreacted Me₂NNH₂ (0.37 mmol) was also present. No tetramethyltetrazene (which is stable at 50°)³¹ could be detected.

(b) **Diethylhydrazine** in a similar reaction to the above, but without the TMS, gave 0.029 mmol of both *tert*-butyl alcohol and diethylamine. No tetraethyltetrazene was formed.

Reaction of 0.2 mmol of Et₂N¹⁵NH₂ with 0.05 mmol of hyponitrite in 1 ml of benzene at 50° for 20 hr in the dark gave nitrogen with the following isotopic composition: ²⁸N₂, 57.2; ²⁹N₂, 3.4; ³⁰N₂, 39.4. It seems reasonable to suppose that the ²⁸N₂ comes virtually entirely from the hyponitrite and that two *tert*-butoxy radicals are required to oxidize the hydrazine to the stage where it yields molecular nitrogen. The nitrogen must come from the terminal position of two hydrazyl radicals,³² as in the following scheme.



The Hindered Hydrazyls. (i) **Kinetics.** (a) **Tetramethylpiperidin-1-aminyl (TMPNH)** radicals are very much longer lived than the three unhindered hydrazyls discussed above. Decay of TMPNH occurs with reasonably "clean" first-order kinetics. The decay rate constants in neat di-*tert*-butyl peroxide and in peroxide: isopentane (1:3) were virtually identical and were also independent of the radical concentration (10⁻⁴ to 3 × 10⁻⁶ M) and of the initial hydrazine concentration (0.2 to 2.0 M). From -33 to 61° the decay rate constants can be approximately³⁵ (Figure 1) represented by

$$(k_{\text{epr}}^1)_{\text{TMPNH}} = 10^{9.2 \pm 2.0} e^{-(13000 \pm 2500)/RT} \text{ sec}^{-1}$$

If the temperature of an epr sample was raised rapidly during the course of a fairly slow radical decay, the concentration of radicals increased temporarily but they subsequently decayed more rapidly.^{14, 36} At temperatures below -30°, where the decay is extremely slow, the radical concentrations could be increased or decreased reversibly by raising and lowering the temper-

(29) This is also the only product found on electrochemical oxidation of Me₂NNH₂ in dimethyl sulfoxide: M. Michlmayr and D. T. Sawyer, *J. Electroanal. Chem.*, **23**, 375 (1969).

(30) The yield of *tert*-butyl alcohol was somewhat greater than the yield of amine probably because of *tert*-butoxy attack on the TMS.

(31) See, e.g., C. J. Michejda and W. P. Hoss, *J. Amer. Chem. Soc.*, **92**, 6298 (1970); S. F. Nelsen and R. Fibiger, *ibid.*, **94**, 8497 (1972).

(32) For comparison, the oxidation of hydrazine containing ¹⁵N₂H₄ by [Fe^{III}(H₂O)₆]³⁺ (N₂H₄ → 1/2 N₂ + NH₃ + H⁺ + e) yields molecular nitrogen, 50% of which is derived from the same hydrazine molecule and 50% from separate hydrazine molecules.^{33, 34}

(33) W. C. E. Higginson and D. Sutton, *J. Chem. Soc.*, 1402 (1953).

(34) J. W. Cahn and R. E. Powell, *J. Amer. Chem. Soc.*, **76**, 2568 (1954).

(35) There may be some curvature in the Arrhenius plot, but it is worth noting that although the experiments were done at different times and under different conditions none of the rate constants deviate by more than a factor of 2-3 from the line drawn in Figure 1.

(36) J. L. Brokenshire, J. R. Roberts, and K. U. Ingold, *J. Amer. Chem. Soc.*, **94**, 7040 (1972).

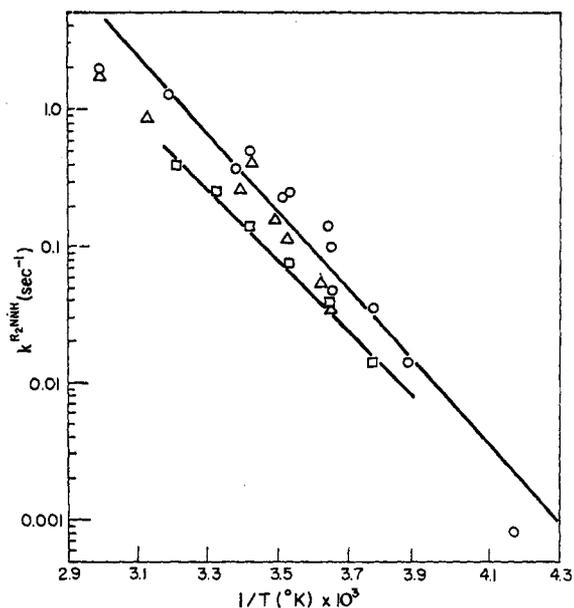


Figure 1. Arrhenius plot for the first-order decay of *i*-Pr₂N[•]NH (□), TMPNH (○), and TMPND (Δ).

ature. Both of these results indicate that under our experimental conditions the radicals exist in equilibrium either with a diamagnetic dimer^{3-5,7,8,14,36} or with diamagnetic disproportionation products.³⁷

In order to distinguish between these two types of equilibria a mixture consisting of TMPNH₂ (0.1 ml), peroxide (0.1 ml), and cyclopentane (0.3 ml) was degassed and then photolyzed at -50° under argon to generate ca. 1 × 10⁻⁶ M TMPNH. The light was turned off and to the stable TMPNH radical solution a further 0.4 ml of neat TMPNH₂ was added without the sample being removed from the epr cavity. The liquids were mixed by bubbling argon through the solution. The signal due to the TMPNH *decreased* and by the amount expected because of a simple diluting action by the added hydrazine. The TMPNH radicals must therefore exist in equilibrium with their tetrazene.

$$K = [\text{TMPNH}]^2/[(\text{TMPNH})_2]$$

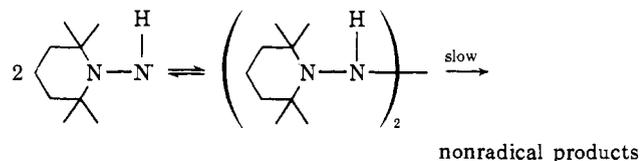
The variation in radical concentration with temperature in the range -35 to -85° was fitted to the van't Hoff relation, $K = e^{\Delta S/R} e^{-\Delta H/RT}$. (In this temperature range radical decay is negligible compared with the time required to determine the radical concentration.) A value for $\Delta H = 13.5 \pm 2.0$ kcal/mol was obtained but ΔS can only be estimated to be ≤ 32 gibbs/mol since the radicals were too short lived for the samples to be warmed sufficiently for most of the dimer to dissociate.

Under conditions where a radical is in equilibrium with a dimer and the latter is present in the higher concentration, the decay of the radicals will follow first-order kinetics *even when the radicals are actually destroyed in a bimolecular radical-radical reaction or when the dimer itself decays by some slow intramolecular process*.^{14, 36, 38} (These kinetics arise because the radical concentration serves merely to monitor the dimer concentration.) Such a possibility must be distin-

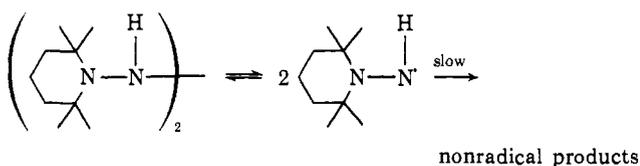
(37) D. F. Bowman, J. L. Brokenshire, T. Gillan, and K. U. Ingold, *J. Amer. Chem. Soc.*, **93**, 6551 (1971).

(38) S. A. Weiner and L. R. Mahoney, *J. Amer. Chem. Soc.*, **94**, 5039 (1972).

guished from the situation in which the first-order decay kinetics arise because the radicals decay by a process that is truly first order in radical concentration, e.g., a β scission. The two possibilities can be distinguished by the dependence of the radical concentration, under steady illumination, on the light intensity.³⁶ If the radicals are destroyed in a radical-radical reaction, their steady-state concentration will be dependent on the square root of the light intensity. On the other hand, if the radicals are destroyed by a true unimolecular process, or by a pseudounimolecular process such as a radical-molecule reaction, their concentration will be directly proportional to the light intensity. The steady-state concentration of TMPNNH was found to be proportional to the *square root* of the light intensity over the temperature range in which their decay kinetics were studied. The decay process can, therefore, be represented as either



or



Addition of a five- to tenfold molar excess of D_2O to solutions containing 1,1-dialkylhydrazines results in the virtually complete replacement of the amino hydrogens by deuterium.³⁹ Photolysis in the presence of di-*tert*-butyl peroxide then yields R_2NND radicals.¹³ The first-order rate constants for the decay of TMPND are not significantly different from those of the normal radical (see Figure 1).

(b) 1,1-Diisopropylhydrazyl radicals were generated in some preliminary experiments without the concomitant formation of diisopropyl nitroxide. They were then found to behave very similarly to TMPNH . That is, in di-*tert*-butyl peroxide the radicals decayed with "clean" first-order kinetics and the decay rate constant was independent of the radical concentration (2×10^{-5} to 10^{-6} M) and of the hydrazine concentration (0.2 to 2.0 M). The rate constants for decay are essentially the same as those for the decay of TMPNH (see Figure 1) and from -8 to 38° can be represented by

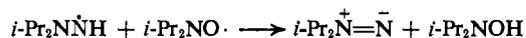
$$(k^1_{\text{ep}})_{i\text{-Pr}_2\text{NNH}} = 10^{8.1 \pm 1.0} e^{-(12000 \pm 1300)/RT} \text{ sec}^{-1}$$

These radicals existed in equilibrium with a dimer. This equilibrium was again shown not to be with disproportionation products since the addition of hydrazine had no effect (other than its diluent action) on an equilibrium hydrazyl concentration at -50° . For this equilibrium, from -40 to 0° , $\Delta H = 9.5 \pm 3.0$ kcal/mol and ΔS could not be determined. Under steady illumination the radical concentration was proportional to the square root of the light intensity and so

(39) Infrared spectroscopy showed that this exchange was essentially instantaneous in CCl_4 , in benzene, and in cyclohexane at 24° .

the decay mechanism involves a radical-radical reaction.

In subsequent experiments which were intended to determine k^1_{ep} and ΔH more accurately, we never succeeded in generating $i\text{-Pr}_2\text{NNH}$ free from $i\text{-Pr}_2\text{NO}\cdot$. Under these conditions, the hydrazyl decayed rapidly even at -80° and there was no sign of any hydrazyl-tetrazane equilibrium. The nitroxide decayed much more slowly than the hydrazyl when the light was cut off. It was not destroyed even by prolonged photolysis. We tentatively suggest that our initial experiments represent the "true" behavior of $i\text{-Pr}_2\text{NNH}$ radicals and that in the presence of the nitroxide there is a rapid cross reaction.

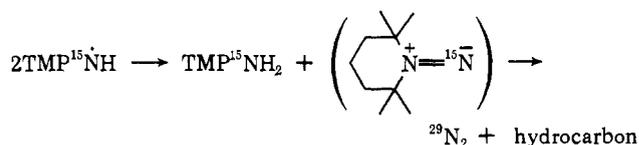
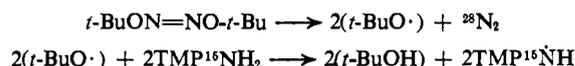


The nitroxide is not permanently destroyed by this reaction, since it will be generated on a subsequent photolysis.

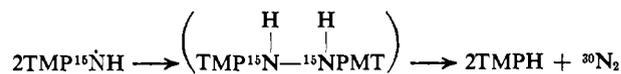


A trace of the hydroxylamine would therefore last a long time and would completely change the lifetime and decay kinetics of the hydrazyl.

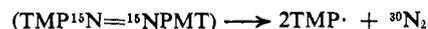
(ii) **Products.** (a) TMPNH_2 . Reaction of 0.17 mmol of $\text{TMP}^{15}\text{NH}_2$ (97 atom % ^{15}N in the NH_2 group) with 0.05 mmol of di-*tert*-butyl hyponitrite in 1 ml of benzene under vacuum at 50° in the dark gave nitrogen of the following isotopic composition: $^{28}\text{N}_2$, 49.6; $^{29}\text{N}_2$, 49.3; $^{30}\text{N}_2$, 1.1% after 4 hr. In a separate experiment the composition was: $^{28}\text{N}_2$, 54.0; $^{29}\text{N}_2$, 45.0; $^{30}\text{N}_2$, 1.0% after 48 hr. The $^{28}\text{N}_2$ again presumably comes virtually entirely from the hyponitrite and two *tert*-butoxy radicals must again be required to oxidize a molecule of the hydrazine to molecular nitrogen. The nitrogen evolved from the hydrazine must be formed from a single hydrazine molecule, as in the following scheme.



The small quantity of $^{30}\text{N}_2$ that is formed implies that there is a *minor* reaction pathway *via* either the tetrazane (though we did not detect any of the expected amine, 2,2,6,6-tetramethylpiperidine, TMPH)



or the tetrazene (perhaps the *cis* isomer¹⁴ since the normal *trans*-tetrazene should be stable at 50° in the dark).



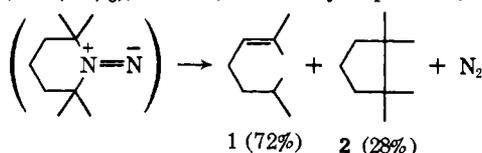
The only organic products from this, and from similar reactions using unlabeled TMPNH_2 , were *tert*-butyl alcohol and two hydrocarbons 1 and 2 which had rather similar vpc retention times. The mass spectra of these hydrocarbons indicated that they both had the empirical formula C_9H_{18} . Comparison with authentic 2,6-

dimethylheptene-1 (3) (Chemical Samples Co.) showed that neither hydrocarbon was this material. The mass spectra (Table I) suggested that the principal hydro-

Table I. Relative Intensities of the Principal Peaks in the Mass Spectra of Three C₈H₁₈ Hydrocarbons

<i>m/e</i>	1	2	3
126	1.0	1.0	1.0
111	0.1	0.9	0.1
98	0.1	0.5	0.1
83	0.4	1.7	0.3
70	1.4	2.5	1.5
69	3.8	2.7	1.9
64	0.4	0.9	0
56	2.9	4.3	5.3
55	1.8	2.7	2.1
43	7.1	4.3	1.5
41	2.9	2.1	1.8

carbon, 1 (72%), was 2,6-dimethylheptene-2, and the

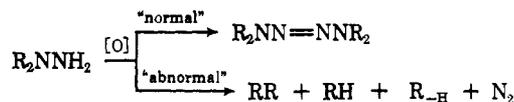


minor hydrocarbon, 2 (28%), was 1,1,2,2-tetramethylcyclopentane. The structure of 1 was confirmed by showing that it was identical with the major product produced by photodecarbonylation of 2,2,6,6-tetramethylcyclohexanone.⁴⁰ The total yield of 1 + 2 was equal to the yield of *tert*-butyl alcohol.

(b) Diisopropylhydrazine (45 mg) dissolved in 1 ml of di-*tert*-butyl peroxide and heated at 135° for 16 hr was analyzed by mass spectrometry and vp chromatography. The products were *tert*-butyl alcohol and acetone, together with a small amount of 2,3-dimethylbutane. There was no detectable amount of propane or propylene (mass spectrometry of vapors) or of diisopropylamine (vpc).

Discussion

The oxidation of 1,1-dialkylhydrazines by various reagents has been studied fairly extensively.⁴¹⁻⁴⁷ The reaction can yield either a tetrazene (the so-called "normal" oxidation product) or nitrogen may be evolved with the formation of coupled, and in some cases also olefinic, hydrocarbons (the "abnormal" oxidation).⁴¹⁻⁴⁷

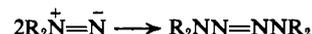


The relative importance of these two processes is dependent on the nature of the hydrazine and on the ex-

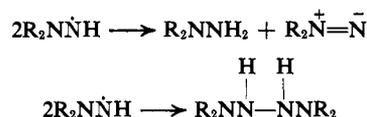
- (40) J. E. Starr and R. H. Eastman, *J. Org. Chem.*, **31**, 1393 (1966).
 (41) M. Busch and B. Weiss, *Chem. Ber.*, **33**, 2701 (1900).
 (42) (a) C. G. Overberger and L. P. Herin, *J. Org. Chem.*, **27**, 417 (1962); (b) *ibid.*, **27**, 2423 (1962), and the many references cited therein.
 (43) C. G. Overberger and S. Altscher, *J. Org. Chem.*, **31**, 1728 (1966).
 (44) C. G. Overberger, M. Valentine, and J. P. Anselme, *J. Amer. Chem. Soc.*, **91**, 687 (1969), and references cited therein.
 (45) L. A. Carpino, A. A. Santilli, and R. W. Murray, *J. Amer. Chem. Soc.*, **82**, 2728 (1960).
 (46) L. A. Carpino, *J. Amer. Chem. Soc.*, **84**, 2196 (1962); **85**, 2144 (1963); *J. Org. Chem.*, **30**, 321 (1965).
 (47) I. Bhatnagar and M. V. George, *J. Org. Chem.*, **33**, 2407 (1968), and references cited therein.

perimental conditions including the nature of the oxidizing agent and even the speed of mixing of the reagents. For example,^{42a} dropwise addition of 1-amino-2-phenylpiperidine to a mercuric oxide slurry in ethanol gave no tetrazene, 77% N₂, and 79% of a hydrocarbon mixture (38% phenylcyclopentane, 26% 5-phenylpentene, and 15% 1-phenylpentene). In contrast, rapid addition gave 58% tetrazene, 32% N₂, and 17% of the same hydrocarbon mixture.

These oxidations have generally been interpreted in terms of *N*-nitrene (diazene) intermediates, R₂N⁺=N⁻,⁴⁸ particularly since McBride and coworkers⁴⁹⁻⁵¹ showed that oxidations with halogens or alkali halates in aqueous acid yielded protonated *N*-nitrenes, R₂N⁺=NH, which were remarkably stable. On neutralization, or presumably if the oxidation is carried out in neutral or basic solutions, the *N*-nitrenes immediately dimerize to tetrazene.

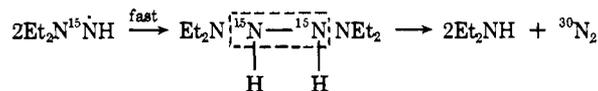


The intermediacy of *N*-nitrenes is not unreasonable for *true* two-electron oxidizing agents. However, as McBride and Kruse have pointed out,⁴⁹ with one-electron oxidizing agents hydrazyl radicals must be involved, and these can, in principle, either disproportionate or combine to give a tetrazene.⁵²



The present kinetic and product studies suggest that 1,1-dialkylhydrazyls can both dimerize and disproportionate and that the relative importance of these two processes (so far as the final products of reaction are concerned) is dependent on the degree of steric hindrance of the alkyl substituents.

The relatively unhindered hydrazyls, Me₂NNH, Et₂NNH, and (PhCH₂)₂NNH, react bimolecularly at rates close to the diffusion-controlled limit. The final products of reaction are dialkylamine and nitrogen gas which is derived from the terminal nitrogen atoms of the radicals. The initial product must, therefore, be the tetrazene⁵² and this must decompose by either a 1,2- or a 1,3-intramolecular hydrogen transfer (or perhaps by a proton-catalyzed process), *e.g.*



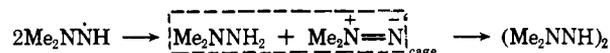
(48) The chemistry of *N*-nitrenes has been reviewed recently: B. V. Ioffe and M. A. Kuznetsov, *Russ. Chem. Rev.*, **41**, 131 (1972).

(49) W. R. McBride and H. W. Kruse, *J. Amer. Chem. Soc.*, **79**, 572 (1957).

(50) W. H. Urry, H. W. Kruse, and W. R. McBride, *J. Amer. Chem. Soc.*, **79**, 6568 (1957).

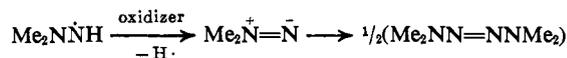
(51) W. R. McBride and E. M. Bens, *J. Amer. Chem. Soc.*, **81**, 5546 (1959).

(52) (a) Tetrazanes unsubstituted at the 2 and 3 positions have now been isolated by oxidation of *N*-aminolactams, see: D. J. Anderson, T. L. Gilchrist, and C. W. Rees, *Chem. Commun.*, 800 (1971). (b) A less probable route to tetrazene involving insertion of the *N*-nitrene into an N-H bond of the hydrazine is really equivalent to writing the dimerization as a two-step process.⁵³

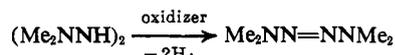


(53) See also W. C. E. Higginson, *Chem. Soc., Spec. Publ.*, No. 10, 95 (1957).

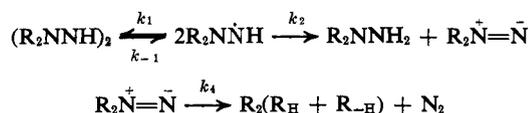
For these radicals dimerization must be faster than disproportionation as would appear to be the case for hydrazyl itself.^{28,54,55} It should perhaps be added that tetrazene could, in principle, be a major product of one-electron oxidation of these hydrazines provided the one-electron oxidizing agent was present in relatively high concentrations. Under such conditions it might oxidize the hydrazyl radical directly,⁵⁶ e.g.



or the intermediate tetrazene, e.g.



Quite different behavior is observed with the sterically hindered hydrazyls, TMPN $\dot{\text{H}}$ and *i*-Pr₂N $\dot{\text{N}}\text{H}$. Decay of these radicals is slow and follows first-order kinetics. The principal products are those of an "abnormal" oxidation, that is, hydrocarbons and gaseous nitrogen which is derived from a single molecule of hydrazine. Our results leave no doubt that these radicals exist in equilibrium with the corresponding tetrazanes. While the slow, first-order decay could, in principle, be due to a slow irreversible decay of the tetrazane,^{14,35,37} the products make it much more likely that the radicals undergo a slow disproportionation. The *N*-nitrene formed in the disproportionation must be the source of the final products. The over-all process can be represented as



There is probably also some dimerization of the *N*-nitrene since the formation of tetramethylpiperidyl on prolonged photolysis of TMPNH₂ samples implies that the tetrazene is a minor product. At sufficiently low temperatures it is possible that the tetrazene would be oxidized to tetrazene (*i.e.*, "normal" oxidation products would be formed). Some tetrazene may also decay intramolecularly to form amine and nitrogen. (This process may be the source of the small quantity of ³⁰N₂ found in the TMP¹⁵NH₂ oxidation.)

According to the above reaction scheme, the decay kinetics will be first order provided $2k_1[\text{R}_2\text{N}\dot{\text{N}}\text{H}]/k_{-1} > 1$ and will be given by³⁵

$$\frac{-d[\text{R}_2\text{N}\dot{\text{N}}\text{H}]}{dt} = k^1_{\text{epr}}[\text{R}_2\text{N}\dot{\text{N}}\text{H}] = \frac{k_2k_{-1}}{2k_1}[\text{R}_2\text{N}\dot{\text{N}}\text{H}]$$

The measured activation energy for decay, E^1_{epr} , will be equal to $E_2 + \Delta H_1$. Since E^1_{epr} is found to equal ΔH_1 within experimental error, it must be concluded that the disproportionation of hydrazyl radicals is a fairly facile process that has no more than a small activation energy. However, the disproportionation must still be

(54) W. C. E. Higginson and P. Wright, *J. Chem. Soc.*, 1551 (1955).

(55) F. H. Pollard and G. Nickless, *J. Chromatog.*, **4**, 196 (1960).

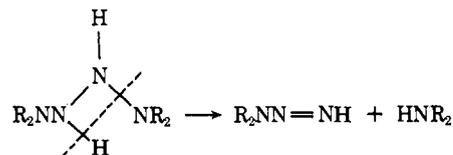
(56) See ref 34 and 53 for evidence that this can occur during the oxidation of hydrazine.

slower than the dimerization. Thus, the difference between hindered and unhindered 1,1-dialkylhydrazyls, so far as kinetics and products go, is simply that the hindered tetrazanes decay reversibly which gives the hindered hydrazyls a lifetime sufficient for them to disproportionate.

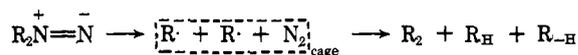
The similarity in the k^1_{epr} values for *i*-Pr₂N $\dot{\text{N}}\text{H}$ and TMPN $\dot{\text{H}}$ (see Figure 1), while certainly a rather surprising coincidence, is not wholly unreasonable. That is, molecular models suggest that steric hindrance toward dimerization in these two radicals should not be too dissimilar and so values of k_{-1}/k_1 should be similar. In addition, it seems likely that k_2 should be virtually independent of the nature of the alkyl groups. Perhaps, therefore, even more bulky alkyl groups would yield shorter lived (larger k^1_{epr}) 1,1-dialkylhydrazyl radicals since the equilibrium concentrations of tetrazane would be even lower. There would seem to be little likelihood of discovering a 1,1-dialkylhydrazyl that is "stable" at room temperature.

The enthalpies for the dimerization (in saturated hydrocarbon solvents) of 1,1-dialkylhydrazyl radicals, *viz.*, ~ 13.5 kcal/mol, are significantly greater than for dimerization of the isoelectronic alkylperoxy radicals (~ 9 kcal/mol)³⁻⁵ and dialkyl nitroxides (~ 8 kcal/mol).⁹ As expected, this behavior parallels the bond strengths of related compounds. For example, $DH^\circ[\text{Me}_2\text{NNMe}_2] \approx 54$ kcal/mol⁵⁷ and $DH^\circ[\text{MeOOMe}] \approx 37$ kcal/mol,⁵⁸ each of these bond strengths being about four times as great as for the corresponding N₄ and O₄ compounds.

The mechanism of the intramolecular decomposition of the unhindered tetrazanes is uncertain, but it is known that they can yield amine and nitrogen.^{52a} In the absence of an acid catalyst it is tempting to propose an initial 1,3-hydrogen shift to yield first the triazene.²⁸ This process is analogous to the 1,5-hydrogen shift in the Russell mechanism for the decomposition of di-*sec*-alkyl tetroxides.



The decomposition of the hindered *N*-nitrenes could, in principle, be a wholly concerted ionic type of process. However, many studies of the products of the "abnormal" oxidation of carefully chosen 1,1-dialkylhydrazines make a free radical generating reaction with a strong cage effect appear much more probable.^{42b,43-45,47,48,59}



(57) D. M. Golden, R. K. Solly, N. A. Gac, and S. W. Benson, *Int. J. Chem. Kinet.*, **4**, 433 (1972); *J. Amer. Chem. Soc.*, **94**, 363 (1972).

(58) S. W. Benson and R. Shaw, *Advan. Chem. Ser.*, **No. 75**, 288 (1968).

(59) W. D. Ollis, I. O. Sutherland, and Y. Thebtaranonth, *Chem. Commun.*, 1199 (1970).