*J. Am. Chem. Soc.* **1992**, *114*, 9603-9607

mW, microwave frequency, 9.37 GHz, modulation frequency, 100 KHz, modulation amplitude, 10 G. ENDOR conditions: microwave frequency, 9.44 GHz, microwave power, 5 mW, radio frequency power, 150 W, radio frequency modulation frequency, 12.5 KHz, radio frequency modulation depth, 75 KHz, scan rate, 0.125 MHz/s, number of scans, 30.

Estimates of the packing of water around the Mn$^{2+}$ ion were obtained through classical molecular dynamics simulations of a single Mn$^{2+}$ ion surrounded by 212 water molecules in a 3-dimensional periodic box of 18.621 Å (approximate density of 1.0 g/mL). The simulations were run at constant temperature and constant volume. A three-point flexible water model was used, wherein each atom possessed a partial point charge (O, −0.82 electron units (eu); H, +0.41 eu). The oxygen was a Lennard-Jones 6–12 center (distance of lowest energy interaction for homoatomic approach, $r^* = 3.553$ Å; minimum potential well depth for homoatomic approach, $\epsilon = 0.1554$ kcal/mol), and the hydrogens were a very small Lennard-Jones repulsive center ($A^{12}$ was $1 \times 10^{-8}$ for the calculation of interatomic repulsion). The geometric means combining rule was used to calculate the interatomic Lennard-Jones interaction parameters. Electrostatic interactions were computed via Coulomb's law utilizing a dielectric of 1.0. The O–H bond stretch and H–O–H angle bend were represented by harmonic potentials with equilibrium values of 0.96 Å and 104.0° and force constants of 540.6 kcal/mol/Å$^2$ and 50.0 kcal/mol/deg$^2$, respectively. This water model is available in a widely distributed biomolecular simulation package[12] and has been characterized as being comparable to other flexible water models in its duplication of structural, thermodynamic, and dynamical properties.[13] The manganese ion was represented as a Lennard-Jones 6–12 center ($\sigma = 2.45$ Å, $\epsilon = 0.1212$ kcal/mol) with charge = 2+. The cutoff used for the intermolecular interactions was 10 Å. The simulation was initiated by several hundreds steps of steepest descent minimizations followed by initial assignments of velocities from a Maxwellian distribution at 50 K. A commercially available simulation package was used which employs the leapfrog variant of the Verlet algorithm.[12,14] The system was taken to 300 K in 50 K increments of 1-ps dynamical simulation with coupling to an external temperature bath at the target temperature.[15] For the 50 K run, the temperature was gradually reduced back to 50 K in the same procedure as the heating process. The heating and cooling runs were performed in order to allow for gradual adjustment of the systems to the target temperatures. Once the target temperatures were achieved, the trajectories were allowed to evolve for several hundred picoseconds. The first 30 ps of each simulation was discarded to allow for any further equilibration process.

**Acknowledgment.** This study was supported by a postdoctoral grant from the American Cyanamid Corporation and research support from the NIH, GM39932.

**Registry No.** Mn$^{2+}$, 16397-91-4; water, 7732-18-5.

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# Kinetic EPR Studies of the Decay of *tert*-Butyl Alkoxy, Silyloxy, Germyloxy, and Stannyloxy Nitroxides

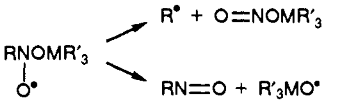
**Marco Lucarini,[†] Gian Franco Pedulli,[*,†] Angelo Alberti,[*,‡] and Massimo Benaglia[‡]**

*Contribution from the Dipartimento di Chimica Organica "A. Mangini", Via S. Donato 15, I-40127 Bologna, Italy, and I.Co.C.E.A., CNR, Via della Chimica 8, I-40064 Ozzano Emilia, Italy. Received March 9, 1992*

**Abstract:** The kinetics of decomposition of oxynitroxides Me$_3$CN(O$^\bullet$)OMR$_3$, with R$_3$M = Me$_3$C, Bu$_3$Sn, Ph$_3$Ge, and Ph$_3$Si, has been studied by EPR at different temperatures, and the activation parameters have been determined. While the first nitroxide undergoes cleavage at the nitrogen–oxygen bond more readily than at the nitrogen–carbon bond, the organometallic nitroxides essentially fragment with elimination of a *tert*-butyl radical with rates of fragmentation increasing, at ordinary temperatures, along the sequence Ph$_3$Ge < Ph$_3$Si < Ph$_3$Sn. A very large reduction of the frequency factor for the decomposition was observed on descending the periodic table. This has been explained in terms of an equilibrium between the nitroxide adduct and its dimer; experimental evidence supporting the existence of this equilibrium has been obtained.

The reduction of tertiary aliphatic nitro compounds to the corresponding alkanes using tributyltin hydride in the presence of radical initiators has been extensively used for synthetic purposes during the last decade.[1-4] Mechanistic studies are consistent with a free radical chain reaction where the key propagation steps are the addition of Bu$_3$Sn$^\bullet$ radicals to the nitro group and the cleavage of the resulting oxynitroxides, RN(O$^\bullet$)OSnBu$_3$, into R$^\bullet$ radicals and nitrites.[5,6] As an alternative pathway, it has been proposed that electron transfer takes place between the tin radical and the nitro compound followed by fragmentation of the resulting radical anion.[7-9] This latter mechanism, although not yet universally rejected,[10,11] appears to be unlikely on the basis of a recent report where it was shown by combining oxidation potentials and thermochemical data that the electron-transfer reaction is not a feasible process.[6]

From the synthetic point of view the value of this reaction is a consequence of the fact that the decomposition of the intermediate takes place by cleavage of the carbon–nitrogen (route 1a) bond rather than the nitrogen–oxygen (route 1b) bond.



(1a)

(1b)

Actually, tris(trimethylsilyl)silane, which is a good substitute for

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tributyltin hydride in many reduction processes,[12] is not able to reduce nitroalkanes because, in this case, the nitroxide adducts fragment via route 1b.[13]

In order to have a more general picture of the fragmentation reaction of oxynitroxides, we have undertaken a kinetic EPR investigation of the decay of $Me_3CN(O^•)OX$ radicals, where X is a $Me_3C$, $Ph_3Si$, $Ph_3Ge$, or $Bu_3Sn$ group.

## Results and Discussion

***tert*-Butyl *tert*-Butoxy Nitroxide ($Me_3CN(O^•)OCMe_3$ 1).** The decomposition of **1** obtained by reaction of *tert*-butoxy radicals with 2-methyl-2-nitrosopropane was studied by Perkins and Roberts several years ago.[14] In the presence of significant amounts of $Me_3CN{=}O$, this nitroxide, owing to the reversibility of reaction 2, decays essentially by route 3, i.e., by elimination of $Me_3C^•$

$$Me_3CN(O^•)OCMe_3 \rightleftarrows Me_3CN{=}O + Me_3CO^• \quad (2)$$

$$Me_3CN(O^•)OCMe_3 \rightarrow Me_3C^• + Me_3CON{=}O \quad (3)$$

radicals. The Arrhenius parameters for the latter reaction were determined as $\log (A/s^{-1}) = 16$ and $E_a = 27.3$ kcal mol$^{-1}$, from which $k_3^{298}$ can be calculated as $1 \times 10^{-4}$ s$^{-1}$. In the same investigation these authors tried also to measure the rate constant for the other fragmentation process by carrying out the experiments at low nitrosobutane concentration and in the presence of cumene as a scavenger of $Me_3CO^•$ radicals. At 40 °C, $k_2$ was estimated to be 0.14 s$^{-1}$, indicating that cleavage at the N–O bond is about 3 orders of magnitude faster than at the N–C bond.

We have reinvestigated this fragmentation in experimental conditions where the reversibility of reaction 2 is not important, i.e., by generating the same nitroxide from 2-methyl-2-nitropropane rather than from $Me_3CN{=}O$. Nitroxide **1** was first produced by reacting $Me_3C{-}NO_2$ with $Me_3C^•$ radicals obtained, via eqs 4 and 5, from triethyl phosphite and photolytically produced *tert*-butoxyl radicals in deoxygenated benzene solutions. These conditions are very convenient for measuring the rate constant of addition of $Me_3C^•$ radicals to the nitro compound. When using 0.5–1 M $Me_3CNO_2$, in fact, the EPR spectra of both $Me_3C^•$ and $Me_3CN(O^•)OCMe_3$ radicals present in ca. $10^{-6}$–$10^{-7}$ M concentrations can be simultaneously detected.

The formation of **1** ($a_N$ 27.12 G, $g$ 2.0055) is described by reactions 4–6, while its decay is due to the occurrence of reactions

$$Me_3CO{-}OCMe_3 \xrightarrow{R_i} 2Me_3CO^• \quad (4)$$

$$Me_3CO^• + P(OEt)_3 \rightarrow Me_3C^• + OP(OEt)_3 \quad (5)$$

$$Me_3C^• + Me_3CNO_2 \rightarrow Me_3CN(O^•)OCMe_3(\mathbf{1}) \quad (6)$$

2 and 3 as well as to the combination (eq 7) with $Me_3C^•$ radicals which in turn may also decay by self-reaction (eq 8).

$$Me_3C^• + Me_3N(O^•)OCMe_3 \rightarrow \text{products} \quad (7)$$

$$2Me_3C^• \rightarrow \text{products} \quad (8)$$

Since the phosphite is present in a large amount (ca. 0.5 M) and reaction 5 is very fast ($k_5^{301} = 1.7 \times 10^9$ M$^{-1}$ s$^{-1}$),[15] other reactions of $Me_3CO^•$ radicals, such as the combination with $Me_3C^•$ or with nitroxide radicals, can be safely neglected. Under continuous photolysis the steady-state approximation for the rate of formation of the various radical species can be applied. Thus, eq 9 for the rate of addition of $Me_3C^•$ radicals to 2-methyl-2-nitropropane can be worked out.

$$k_6 = \frac{(k_7[Me_3C^•] + k_2 + k_3)[\mathbf{1}]}{[Me_3C^•][Me_3CNO_2]} \quad (9)$$

The value of $k_7$ has been assumed to be the same (ca. $8 \times 10^8$ M$^{-1}$ s$^{-1}$) as that determined by Ingold and co-workers[16] for the reaction of $Me_3C^•$ radicals with other nitroxides, i.e., with 2,2,6,6-tetramethylpiperidine-*N*-oxyl ($7.6 \times 10^8$ M$^{-1}$ s$^{-1}$) and 1,1,3,3-tetramethylisoindoline-*N*-oxyl ($8.8 \times 10^8$ M$^{-1}$ s$^{-1}$). This implies that in eq 9 $k_2$ (ca. $10^{-1}$ s$^{-1}$) and $k_3$ (ca. $10^{-4}$ s$^{-1}$)[14] can be neglected with respect to $k_7[Me_3C^•] \geq 10^2$ s$^{-1}$. Thus, eq 9 simplifies to eq 10.

$$k_6 = \frac{k_7[\mathbf{1}]}{[Me_3CNO_2]} \quad (10)$$

By measuring, under continuous photolysis, the amount of the nitroxide at different concentrations of the nitro compound, an average value of $k_6^{298} = (1.25 \pm 0.20) \times 10^3$ M$^{-1}$ s$^{-1}$ was obtained.

The system consisting of $Me_3COOCMe_3$ and triethyl phosphite is not suitable for studying the kinetics of the decay of nitroxide **1** upon shuttering the UV irradiation, because the $Me_3CO^•$ radicals formed in reaction 2 will readily react with the phosphite to produce new $Me_3C^•$ radicals, which may either regenerate the nitroxide by reacting with $Me_3CNO_2$ or scavenge **1** itself, giving diamagnetic products. Since the relative importance of these reactions varies with the concentration of the nitroxide, mixed-order kinetic curves are expected.

A more convenient source of $Me_3C^•$ radicals is the photodecomposition of 2,2,4,4-tetramethyl-3-pentanone, $(Me_3C)_2C{=}O$, in a hydrogen-donating solvent, such as toluene, capable of intercepting the $Me_3CO^•$ radicals formed in reaction 2. When interrupting the irradiation, only reactions 2, 11, and 12 need be taken into account.

$$Me_3CO^• + PhCH_3 \rightarrow Me_3COH + Ph\dot{C}H_2 \quad (11)$$

$$Ph\dot{C}H_2 + Me_3CN(O^•)OCMe_3 \rightarrow \text{products} \quad (12)$$

The reaction of $Me_3CO^•$ with $Me_3CN(O^•)OCMe_3$ radicals can be neglected because in toluene solutions it cannot compete with reaction 11 ($k_{11}^{295} = 2.3 \times 10^5$ M$^{-1}$ s$^{-1}$).[17] Addition of benzyl radicals to 2-methyl-2-nitropropane can also be neglected since the rate constant for this reaction seems very low, as implied by the failure of detecting the corresponding nitroxide adduct when photolyzing 1 M $Me_3CNO_2$ solutions in toluene containing di-*tert*-butyl peroxide.

We can therefore write eq 13 for the decay of **1**. Assuming that every $Me_3CO^•$ radical formed in reaction 2 reacts with the solvent to give benzyl radicals which in turn react with **1**, the two

$$-d[\mathbf{1}]/dt = k_2[\mathbf{1}] + k_{12}[PhCH_2^•][\mathbf{1}] \quad (13)$$

terms on the right-hand side of eq 13 must be equal. Thus eq 13 reduces to

$$-d[\mathbf{1}]/dt = 2k_2[\mathbf{1}] \quad (14)$$

The experimental rate constant observed for the decay of the nitroxide is therefore twice the true rate constant for fragmentation, $k_2$. From a detailed study of this reaction at different temperatures (303–360 K), the Arrhenius plot shown in Figure 1 and the activation parameters $\log (A/s^{-1}) = 13.22 \pm 0.56$ and $E_a = 19.98 \pm 0.80$ kcal mol$^{-1}$ were obtained. From these data $k_2^{313}$ can be calculated as 0.18 s$^{-1}$, which is very close to the value (0.14 s$^{-1}$) estimated by Perkins and Roberts.[14]

We have also investigated the decomposition of the 1-adamantyl adduct to 2-methyl-2-nitropropane. This radical ($a_N$ 27.10 G, $g$ 2.0055), formed by photolyzing a toluene solution of adamantane (ca. 1 M) and the nitro compound, containing di-*tert*-butyl peroxide, also decayed by clean first-order kinetics when freshly

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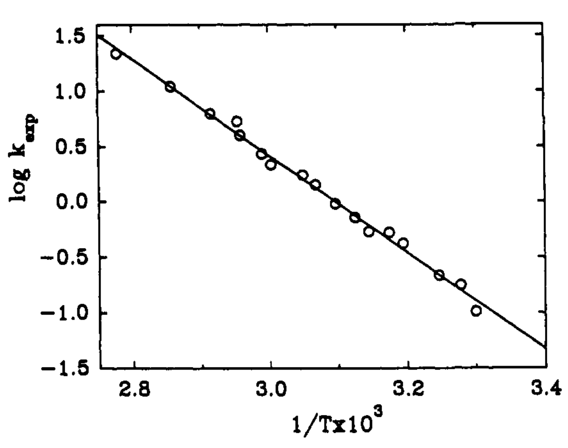

**Figure 1.** Arrhenius plot for the decay of $\mathrm{Me_3CN(O^\bullet)OCMe_3}$ (**1**) in toluene solution.

prepared samples were used in order to keep the concentration of $\mathrm{Me_3CN{=}O}$ negligibly small. The measured rate constants for reaction 15 were 3–4 times larger than those observed for the decay

$$\mathrm{Me_3CN(O^\bullet)OAd \rightarrow Me_3CN{=}O + AdO^\bullet} \qquad (15)$$

of **1** at the same temperatures and are expressed by the activation parameters log $(A/\mathrm{s^{-1}}) = 14.1 \pm 0.3$ and $E_a = 20.5 \pm 0.5$ kcal mol$^{-1}$.

Perkins and Roberts[14] also estimated the rate constant $k_{-2}$ for the addition of $\mathrm{Me_3CO^\bullet}$ radicals to 2-methyl-2-nitrosopropane at 40 °C as $8 \times 10^6$ M$^{-1}$ s$^{-1}$ by competition with the hydrogen abstraction by $\mathrm{Me_3CO^\bullet}$ from cumene. The latter rate constant, which in the lack of experimental data was assumed to be ca. $10^5$ s$^{-1}$, has been measured by Scaiano et al.[18] as $8.7 \times 10^5$ M$^{-1}$ s$^{-1}$ at 295 K; thus $k_{-2}$ can be recalculated as $9.8 \times 10^7$ M$^{-1}$ s$^{-1}$. This value seems too large when compared to that of $1.5 \times 10^6$ M$^{-1}$ s$^{-1}$ reported by Janzen and co-workers[19] from competitive studies with the hydrogen abstraction of $\mathrm{Me_3CO^\bullet}$ from cyclohexane for which a rate constant of $1 \times 10^5$ M$^{-1}$ s$^{-1}$ was assumed. Since this was more recently measured[20] as $1.6 \times 10^6$ M$^{-1}$ s$^{-1}$, a value of $2.1 \times 10^7$ M$^{-1}$ s$^{-1}$ could be calculated for $k_{-2}$.

***tert*-Butyl (tri-*n*-Butylstannyl)oxy Nitroxide ($\mathrm{Me_3CN(O^\bullet)OSnBu_3}$, 2).** The EPR spectrum observed when 2-methyl-2-nitropropane was photoreacted with hexabutylditin, $\mathrm{Bu_6Sn_2}$, in *tert*-butylbenzene solution consisted of three lines ($a_N$ 28.80 G, $g$ 2.0051) further split into a 0.20-G decet, with satellites due to $^{117}$Sn and $^{119}$Sn ($I = {}^1/_2$, natural abundance 7.61 and 8.58, respectively) appearing on both sides of the main lines and separated by 4.66 G. We believe these values to be characteristic of the nitroxide adduct **2** rather than of the radical anion $\mathrm{Me_3CNO_2^{\bullet -}}$ for the following reasons. The detection of radical ion pairs involving a tin cation, especially in hydrocarbon solutions, would be unprecedented, to the best of our knowledge. Moreover, the nitrogen splitting is very close to those exhibited by the silyl and germyl adducts, while a lower value would be expected for a radical anion. Actually, we generated $\mathrm{Me_3CNO_2^{\bullet -}}$ by photolytically reducing 2-methyl-2-nitropropane in a 1:3:4 mixture of sodium methoxide, methanol, and dimethoxyethane (DME) and found spectral parameters ($a_N$ 26.95 G, $g$ 2.0054) markedly different from those obtained when $\mathrm{Me_3CNO_2}$ was reacted with tin-centered radicals. It should also be emphasized that, owing to the hydrogen bonding ability of the alcoholic medium, the measured nitrogen splitting represents an upper limit for the anion. For instance, the radical anion of nitrobenzene shows $a_N$ values of 9.50 G in DME[21] and 13.60 G in methanol.[22]

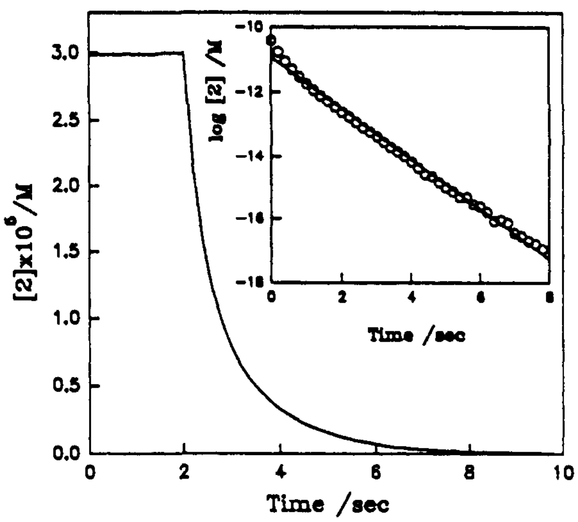

**Figure 2.** Decay of radical **2** produced by the reaction of $\mathrm{Me_3CNO_2}$ (0.0118 M) with $\mathrm{Bu_3SnSnBu_3}$ (0.247 M) under irradiation at 295 K. Insert: plot of log [**2**] vs time.

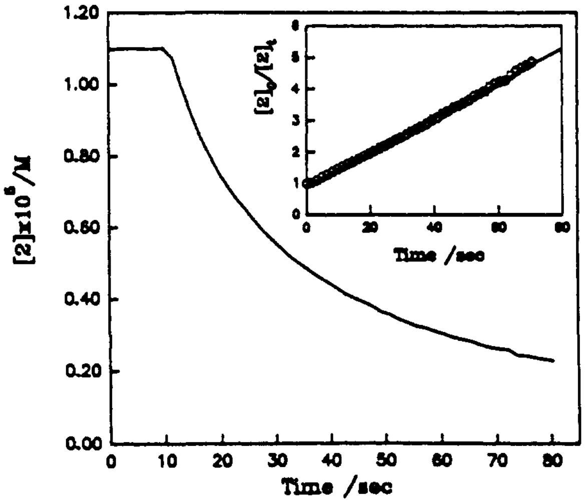

**Figure 3.** Decay of radical **2** produced by the reaction of $\mathrm{Me_3CNO_2}$ (0.110 M) with $\mathrm{Bu_3SnH}$ (0.247 M) and di-*tert*-butyl peroxide under irradiation at 295 K. Insert: plot of $[\mathbf{2}]_0/[\mathbf{2}]_t$ vs time.

The kinetics of the decay of radical **2** has been investigated by time-resolved EPR spectroscopy by Korth et al.[5] In the temperature range of 248–326 K the process was found to follow first-order kinetics with $E_a = 8.3 \pm 0.1$ kcal mol$^{-1}$ and log $(A/\mathrm{s^{-1}}) = 5.7 \pm 0.1$. In the present study we have repeated the kinetic investigation over a wider and higher temperature range (298 to 399 K) by monitoring the decay of the signal of **2** in the absence of UV irradiation.

The photolysis was carried out with the light from an unfiltered mercury lamp, using freshly prepared solutions to reduce the amount of di-*tert*-butyl nitroxide, presumably formed by photocleavage of the stannyloxy nitroxide via route 1b and subsequent interception of *tert*-butyl radicals by the resulting nitroso compound. The absence of signals due to this very long lived nitroxide ensures that the decay of **2** occurs by cleavage at the carbon–nitrogen bond (route 1a). The decay process can therefore be described by reactions 16 and 17, with $\mathrm{MR_3 = SnBu_3}$. Accordingly, first-order kinetics should be expected, with $k_{exp} = 2k_{16}$;

$$\mathrm{Me_3CN(O^\bullet)OMR_3 \rightarrow Me_3C^\bullet + O{=}NOMR_3} \qquad (16)$$

$$\mathrm{Me_3C^\bullet + Me_3CN(O^\bullet)OMR_3 \rightarrow Me_3CN(OCMe_3)OMR_3} \qquad (17)$$

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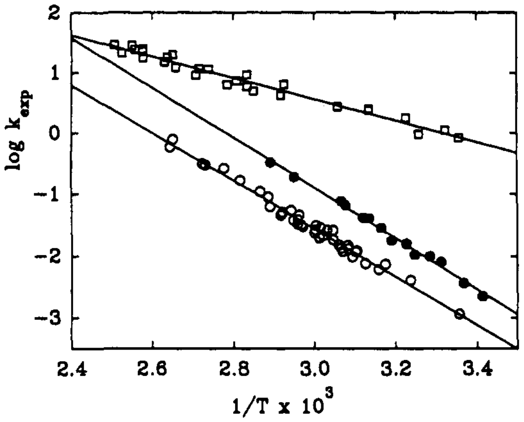

**Figure 4.** Arrhenius plot for the decay of radicals **2** (□), **3** (○), and **4** (●) in *tert*-butylbenzene.

the experimental decays were actually first order but exhibited an initial deviation whose extent decreased with increasing temperature (see Figure 2). From the Arrhenius plot of the $k_{16}$ values so obtained (Figure 4), we determined activation parameters similar to those already reported, i.e., $E_a = 8.11 \pm 0.56$ kcal mol$^{-1}$ and log ($A$/s$^{-1}$) = 5.58 ± 0.36, the most striking feature of our results and those of Korth et al. being the very small log $A$ value found for the decay of the stannyloxy nitroxide.

Since in the reduction of tertiary nitro compounds on a preparative scale $Bu_3SnH$ is used instead of $Bu_6Sn_2$, we have also investigated the kinetics of the decay of **2** in the presence of tri-*n*-butyltin hydride at room temperature. Under these conditions, besides eqs 16 and 17 ($MR_3 = SnBu_3$) we should also take into account the hydrogen abstraction from the tin hydride by $Me_3C^\bullet$ radicals and the addition of the resulting stannyl radicals to the nitro compound to regenerate the nitroxide (eqs 18 and 19, $MR_3 = SnBu_3$).

$$Me_3C^\bullet + R_3MH \rightarrow Me_3CH + R_3M^\bullet \qquad (18)$$

$$R_3M^\bullet + Me_3CNO_2 \rightarrow Me_3CN(O^\bullet)OMR_3 \qquad (19)$$

By solving the kinetic equations under the steady-state approximation for the transient species $Me_3C^\bullet$ and $Bu_3Sn^\bullet$, the rate of decay of **2** is expressed by eq 20. Since $k_{18}{}^{298}$ is[23] 1.7 × 10$^6$

$$\frac{-d[Me_3CN(O^\bullet)OMR_3]}{dt} = \frac{2k_{17}k_{16}[Me_3CN(O^\bullet)OMR_3]^2}{k_{18}[R_3MH] + k_{17}[Me_3CN(O^\bullet)OMR_3]} \qquad (20)$$

M$^{-1}$ s$^{-1}$ and assuming $k_{17}{}^{298}$ is ca. 8 × 10$^8$ M$^{-1}$ s$^{-1}$ (vide supra), under the present experimental conditions, i.e., [$Bu_3SnH$] ca. 0.5 M and [**2**] ca. 1 × 10$^{-5}$ M, the term $k_{17}$[**2**] can be neglected with respect to $k_{18}[Bu_3SnH]$ and eq 20 reduces to eq 21. Second-order

$$\frac{-d[\mathbf{2}]}{dt} = \frac{2k_{17}k_{16}[\mathbf{2}]^2}{k_{18}[Bu_3SnH]} \qquad (21)$$

decay of the nitroxide signal is therefore expected with an apparent rate constant given by $k_{exp} = 2k_{17}k_{16}/(k_{18}[Bu_3SnH])$.

Actually, very good second-order kinetics was experimentally observed (see Figure 3) with rate constants varying linearly with the reciprocal of the tin hydride concentration in the range of 0.05–1 M. From these measurements $k_{16}{}^{298}$ could be determined as 0.36 ± 0.20 s$^{-1}$, which compares favorably with the value of 0.42 s$^{-1}$ determined at the same temperature when $Bu_6Sn_2$ was used.

As pointed out before, the measured frequency factor is unusually small for a unimolecular decomposition, and similar values have been found when the apparent rate constant for decay contains the monomer–dimer equilibrium constant. This possibility was checked by carrying out temperature jump experiments during the decay of nitroxide **2**; no such effect could be observed at or above room temperature.

We therefore repeated the experiments by monitoring the decay at lower temperatures in order to shift a possible monomer–dimer equilibrium toward the dimer. A positive effect was observed when the temperature jumped from 203 to 243 K; this effect decreased quickly with increasing temperature and could not be observed when we started from temperatures higher than 240 K.

***tert*-Butyl (Triphenylgermyl)oxy Nitroxide ($Me_3CN(O^\bullet)OGePh_3$, 3).** This radical was produced by reacting $Me_3CNO_2$ with $Ph_3GeH$ and di-*tert*-butyl peroxide under irradiation with filtered light (366 nm). The observed spectrum shows strong signals due to **3** ($a_N$ 29.00 G, $g$ 2.0053) along with very weak signals due to $(Me_3C)_2NO^\bullet$, indicating that **3** also essentially undergoes fragmentation via route 1a.

The decay of the germyloxy nitroxide was found to depend markedly on the initial amount of germanium hydride, being very slow and following approximately second-order kinetics with high concentrations of $Ph_3GeH$. When the amount of the germanium hydride was reduced, **3** decayed faster following mixed first- and second-order kinetics and eventually clean first-order kinetics. The kinetic treatment is similar to that given before for the decay of **2** in the presene of tin hydride, and therefore eq 20 ($MR_3 = GePh_3$) still holds. In the present case $k_{18}$ is not available, but we may approximate it to be that determined for the hydrogen abstraction from $Bu_3GeH$ by the tertiary alkyl radical 6-methylhepten-6-yl in competition with its cyclization.[24] The calibration of this radical clock has been recently reported,[25] and when the competitive rate constant of abstraction is combined with that of cyclization, $k_{18}{}^{298}$ ($R_3M = Bu_3Ge$) is calculated as 1.99 × 10$^4$ M$^{-1}$ s$^{-1}$. From eq 20 it turns out that for nitroxide concentrations of the order of 10$^{-5}$ M, the term $k_{18}[Ph_3GeH]$ is negligible with respect to $k_{17}$[**3**], provided that the hydride concentration is lower than 0.01 M. Thus, eq 20 reduces to eq 22 and first-order decay is expected as experimentally observed.

$$\frac{-d[\mathbf{3}]}{dt} = 2k_{16}[\mathbf{3}] \qquad (22)$$

The kinetic measurements were carried out in *tert*-butylbenzene solution in the temperature range of 298–377 K, and the results are shown in Figure 2, which provides the activation parameters log ($A$/s$^{-1}$) = 9.86 ± 0.48 and $E_a = 17.86 \pm 0.72$ kcal mol$^{-1}$.

***tert*-Butyl (Triphenylsilyl)oxy Nitroxide ($Me_3CN(O^\bullet)OSiPh_3$, 4).** Radical **4** ($a_N$ 29.36 G, $g$ 2.0054) was obtained by the photolysis of *tert*-butylbenzene solutions of $Me_3CNO_2$, $Ph_3SiH$, and di-*tert*-butyl peroxide. Since only weak signals of both $(Me_3C)_2NO^\bullet$ and $Me_3CN(O^\bullet)OCMe_3$ were detected, along with the dominating spectrum of **4**, upon photolysis with filtered light, it is also concluded that the silyloxy nitroxide fragments preferentially at the nitrogen–carbon bond.

The first-order decay of the signals from **4** observed at low silane concentration (≤0.1 M) indicates that in eq 20 ($R_3M = Ph_3Si$) the term $k_{18}[Ph_3SiH]$ is much smaller than $k_{17}[Me_3CN(O^\bullet)OSiPh_3]$. Although the rate of hydrogen abstraction from silanes by tertiary alkyl radicals is unknown, the reported values for the analogous abstraction by primary radicals fall in the range of 2 × 10$^4$ (50 °C)[26]–3 × 10$^4$ M$^{-1}$ s$^{-1}$ (90 °C).[27] It is reasonable to expect that $k_{18}$($R_3M = Ph_3Si$) is at least 1 order of magnitude smaller, i.e., ca. 10$^3$ M$^{-1}$ s$^{-1}$. The decay process may then be described by eq 23, and the measured rate constants afford the

$$\frac{-d[\mathbf{4}]}{dt} = 2k_{16}[\mathbf{4}] \qquad (23)$$

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**Table I.** Conversions for the Reductions of $Me_3CCH_2CMe_2NO_2$ (ca. 0.15 M) by Organometallic Hydrides (ca. 0.2 M) and Yields of the Corresponding Hydrocarbon and Nitroso Compounds in *tert*-Butylbenzene at 40 °C

| $R_3MH$ | conv/% | time/h | alkane/% | nitrosoalkane/% |
|---|---|---|---|---|
| $Bu_3SnH$ | 66 | 1 | 76 | 6 |
| $Ph_3GeH$ | 33 | 2.5 | 49 | 6 |
| $Ph_3SiH$ | 21 | 3.5 | 31 | 7 |

**Table II.** Activation Parameters and First-Order Rate Constants ($k = k_{exp}/2$) at 298 K for the Cleavage of the Oxynitroxides **1–4**[a]

| $R_3M$ | route | $k/s^{-1}$ | $\log (A/s^{-1})$ | $E_a$/kcal mol$^{-1}$ | ref |
|---|---|---|---|---|---|
| $Me_3C$[b] | 1a | $1.0 \times 10^{-4}$ | 16 | 27.3 | 14 |
| $Me_3C$ | 1b | $3.7 \times 10^{-2}$ | 13.22 ± 0.56 | 19.98 ± 0.80 | this work |
| $Ph_3Si$ | 1a | $2.2 \times 10^{-3}$ | 11.13 ± 0.64 | 18.80 ± 0.92 | this work |
| $Ph_3Ge$ | 1a | $5.8 \times 10^{-4}$ | 9.86 ± 0.48 | 17.86 ± 0.72 | this work |
| $Bu_3Sn$ | 1a | $4.3 \times 10^{-1}$ | 5.58 ± 0.36 | 8.11 ± 0.56 | this work |

[a] Errors correspond to a 95% confidence interval ($2\sigma$). [b] The rate constant at 298 K for the formation of **1** is $1.25 \times 10^{-3}$ M$^{-1}$ s$^{-1}$ via the reaction of $Me_3C^{\bullet}$ radicals with $Me_3CNO_2$ and $2.1 \times 10^{7}$ M$^{-1}$ s$^{-1}$ via the reaction of $Me_3CO^{\bullet}$ radicals with $Me_3CN{=}O$ (see text).

activation parameters $\log (A/s^{-1}) = 11.13 \pm 0.64$ and $E_a = 18.80 \pm 0.92$ kcal mol$^{-1}$.

**Product Studies.** Product studies were carried out using a tertiary nitroalkane, 2-nitro-2,4,4-trimethylpentane, which upon reduction affords a hydrocarbon less volatile than 2-methylpropane and hence more readily detectable by GC. The reduction were performed at 40 °C with tributyltin hydride, triphenylgermane, or triphenylsilane. Di-*tert*-butyl hyponitrite was the radical initiator of choice because the more popular AIBN leads, by thermal decomposition, to resonance-stabilized alkyl radicals which are not able to abstract hydrogen from the silane. Conversions and yields measured with respect to *n*-dodecane, used as an internal standard for GC experiments, are reported in Table I.

From the data it appears that conversion decreases along the series tin, germanium, and silicon hydrides, despite the increasing reaction time. This trend, indicating a shortening of the radical chain length, is entirely expected in view of the known bond dissociation energies of the metal–hydrogen bond, which increase on passing from $Me_3Sn–H$ (74 kcal/mol)[28] to $Ph_3Ge–H$ (80.2 kcal/mol)[27] and $Ph_3Si–H$ (84 kcal/mol).[29]

Although the yield of the hydrocarbon decreases in the same order, that of nitrosoalkane remains low; this may be taken as an indication that the dominant fragmentation process of the organometallic oxynitroxides is in all cases the cleavage of the carbon–nitrogen bond, in agreement with the EPR experiments.

## Conclusions

The kinetic constants measured at 298 K and the Arrhenius parameters for the fragmentation of nitroxides **1–4** are summarized in Table II. For radical **1** the rate constants for the cleavage of both the carbon–nitrogen (route 1a) and the nitrogen–oxygen bond (route 1b) are available, while for the organometallic derivatives **2–4** only values for the former process could be determined. The spectroscopic results, i.e., the observation of only weak signals from the very persistent $(Me_3C)_2N–O^{\bullet}$ radical which should be formed if route 1b were followed, and product studies indicating the formation of minor amounts of $Me_3CN{=}O$ suggest that the prevailing fragmentation path of these nitroxides is path 1a. Since the rate constants for the decay of **3** and **4** are smaller than that for the cleavage of the nitrogen–oxygen bond in **1**, it appears that substitution of carbon with silicon or germanium induces a strengthening of the adjacent nitrogen–oxygen bond. This may be due to a weakening of the repulsive interaction between the electron lone pairs on nitrogen and oxygen caused by the attraction of the electron cloud on oxygen toward the metal atom.

As far as the Arrhenius parameters for the cleavage of the carbon–nitrogen bond are concerned, both the log *A* and the activation energy experience a marked decrease on descending the periodic table. Of particular interest is the dramatic reduction of log *A* from 16 for **1** to 5.6 for **4**; the former value is in line with the fact that the fission of a molecule is expected to give rise to a substantial increase in entropy in the transition state and hence to a very large *A* factor.[30] On the other hand, the unusually low value of log *A* found for **2** and, to a smaller extent, for **3** and **4** indicates either that the organometallic oxynitroxides are in equilibrium with their dimers or that a highly ordered transition state is involved in the fragmentation. In the latter case, however, a frequency factor not lower than $10^{11}$ can be justified.[30]

As pointed out in the previous section, the low *A* factor seems to arise from the existence of a monomer–dimer equilibrium. At or above room temperature the relative amount of dimer is too small to allow the observation of a temperature jump effect; on the other hand, it may be held responsible for the initial deviations from first-order kinetics observed at the lower temperatures. The amount of dimer is also sufficient to affect the decay rate constant and its temperature dependence, thus leading to the anomalously small value of log *A* observed.

## Experimental Section

**EPR Measurements.** EPR spectra were recorded on a Bruker ESP300 spectrometer equipped with a Hewlett-Packard 5350B frequency counter for the determination of the *g* factors, which were corrected with respect to that of the perylene radical cation (2.002 58). Photolysis was carried out with the light from a 500-W high pressure mercury lamp filtered with an AEO interference filter (maximum transmittance 366.3 nm). The temperature was controlled with a standard variable temperature accessory and was monitored before and after each run with a copper–constantan thermocouple. Radical concentrations were measured by comparing the double integral of the EPR spectrum of the nitroxide with that given by a DPPH solution of known concentration and by using an artificial ruby crystal as internal standard.

**Materials.** 2-Nitro-2,4,4-trimethylpentane[32] and 2-nitroso-2,4,4-trimethylpentane[33] were prepared according to literature procedures. All other chemicals were commercially available and were used as received.

**General Procedure for the Product Studies.** A solution containing the nitro compound (ca. 0.15 M), the organometallic hydride (0.2 M), and di-*tert*-butyl hyponitrite (3–5%) as radical initiator in *tert*-butylbenzene was heated at 40 °C and then analyzed by GC. Yield and consumption were quantified using *n*-dodecane as internal standard and authentic samples to calibrate the response of the detector.

**Acknowledgment.** Financial support from Progetto Finalizzato del CNR: Chimica Fine II and from MURST is gratefully acknowledged.

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