

Anchimeric Assistance in C-H Bond Homolysis. Reaction of *tert*-Butoxyl Radicals with Tetraethyl Group 4 Compounds¹

Richard A. Jackson,² Keith U. Ingold,* David Griller, and Avtar S. Nazran

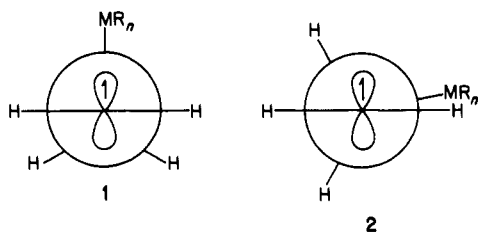
Contribution from the Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6. Received April 5, 1984

Abstract: Three complementary techniques have been used to obtain relative and absolute rate constants for the abstraction of α - and β -hydrogen atoms from $(\text{CH}_3\text{CH}_2)_n\text{M}$ ($\text{M} = \text{C}, \text{Si}, \text{Ge}, \text{Sn}$) by *tert*-butoxyl radicals. Both α and β positions of Et_4M are activated for $\text{M} = \text{Si}, \text{Ge}, \text{Sn}$, as compared with the 1- and 2-positions in *n*-pentane. The activation was greater at the β than at the α position, and followed the order $\text{Sn} > \text{Ge} > \text{Si}$. This provides unequivocal evidence for anchimeric assistance to removal of hydrogen β to a Si, Ge, or Sn atom.

The concept of "anchimeric assistance" or neighboring group participation in radical formation was propounded in 1963. Skell with his co-workers³ and Thaler⁴ independently showed that free-radical bromination of alkyl bromides by molecular bromine gave mixtures in which vicinal dibromides predominated, i.e., hydrogen abstraction by bromine atoms occurred predominantly at methylene groups adjacent to the carbon atom bearing the bromine substituent. The effect of the bromine substituent was thought to be associated with its "bridging".³⁻⁵ This implies that the β -bromoalkyl radical, formed in the abstraction reaction, was stabilized by an interaction in which the orbital containing the unpaired electron and the β -bromine atom were eclipsed. However, "bridging" was not intended to suggest that the bromine atom was symmetrically arranged between the α - and β -carbon atoms.

Systems involving bromination are complicated by the importance (or otherwise) of the elimination of bromine from β -bromoalkyl radicals and of the reversibility of hydrogen abstraction by bromine. While these complexities created experimental difficulties, the case in favor of anchimeric assistance by bromine seems to have been thoroughly proven.³ However, the question still remains as to whether other atoms or groups can induce similar effects.

Electron paramagnetic resonance (EPR) studies⁶ have shown that 2-substituted ethyl radicals, $\text{R}_n\text{MCH}_2\dot{\text{C}}\text{H}_2$, having M from rows 2, 3, and 4 of the periodic table, e.g., Si, Ge, Sn, P, As, S, and Cl, adopt a conformation in which M and the $2p_z$ orbital containing the unpaired electron are in the eclipsed conformation **1**. Similar radicals with M from row 1, e.g., C, N, O, and F,



(1) Issued as NRCC No. 23949.

(2) Visiting Fellow 1983, on sabbatical leave from the School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, U.K.

(3) Skell, P. S.; Tuleen, D. L.; Readio, P. D. *J. Am. Chem. Soc.* **1963**, *85*, 2849-2850. See also: Skell, P. S.; Shea, K. J. In "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 2, Chapter 26, p 809. Shea, K. J.; Lewis, D. C.; Skell, P. S. *J. Am. Chem. Soc.* **1973**, *95*, 7768-7776.

(4) Thaler, W. *J. Am. Chem. Soc.* **1963**, *85*, 2607-2613.

(5) See also: Skell, P. S.; Shea, K. J. *J. Am. Chem. Soc.* **1972**, *94*, 6550-6552. Traynham, J. G.; Green, E. E.; Lee, Y.-S.; Schweinsberg, F.; Low, C.-E. *J. Am. Chem. Soc.* **1972**, *94*, 6552-6553.

(6) Krusic, P. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1971**, *93*, 846-860. Cooper, J.; Hudson, A.; Jackson, R. A. *Tetrahedron Lett.* **1973**, 831-834. Lyons, A. R.; Symons, M. C. R. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 622-630. Norman, R. O. C.; Storey, P. M. *J. Chem. Soc. B* **1971**, 1009-1013. Griller, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1973**, *95*, 6459-6460; **1974**, *96*, 6715-6720.

Table I. Absolute Rate Constants and Relative Inter- and Intraactivities of Et_4M ($\text{M} = \text{C}, \text{Si}, \text{Ge}, \text{Sn}$) toward *tert*-Butoxyl Radicals at 25 ± 3 °C

compd	absolute rate constant ^a $10^{-6}k_1 \text{ M}^{-1} \text{ s}^{-1}$	relative interreactivity ^b $k_1/k(c\text{-C}_3\text{H}_7)$	relative intrareactivity ^{b,c} $10(k_5/\text{H})(k_4/\text{H})$
<i>n</i> -C ₅ H ₁₂		0.47 ± 0.06	1.00 ± 0.07 ^d
<i>c</i> -C ₅ H ₁₀		(1.0) ^f	
Et ₄ C	1.07 ^e	0.32 ± 0.01	2.4 ± 0.3
Et ₄ Si	1.9 ± 0.2 ^g	1.7 ± 0.05	2.5 ± 0.4
Et ₄ Ge	1.7 ± 0.6	2.1 ± 0.3	3.6 ± 0.1
Et ₄ Sn	3.4 ± 1.2	5.3 ± 0.5	6.6 ± 0.4

^a Measured by laser flash photolysis. Errors represent 95% confidence limits of reproducibility between duplicate or replicate runs. No estimate has been made for calibration errors in GC or systematic error in the laser flash experiments. ^b By GC analysis of *tert*-butyl hypochlorite chlorination products. ^c Per hydrogen atom. ^d Ratio for attack at 2-position relative to attack at 1-position. ^e Reference 23 gives $8.6 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$. ^f Assumed. ^g Reference 24 gives $(1.2 \pm 0.4) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$.

as substituents normally rotate freely about the $\text{R}_n\text{MCH}_2\text{-}\dot{\text{C}}\text{H}_2$ bond at room temperature, but show a preference for conformation **2** at low temperatures. For every unhindered radical that prefers conformation **1** there is, by implication, a bridging interaction between M and the unpaired electron. Although the concept of anchimeric assistance by 2-substituents and bridging in a 2-substituted radical are distinct, the former is not likely to occur without the latter. Hence any M from rows 2, 3, and 4 of the periodic table might be expected to show anchimeric assistance.

To test the above hypothesis, we have carried out a study of hydrogen abstraction by *tert*-butoxyl radicals from the compounds $(\text{CH}_3\text{CH}_2)_4\text{M}$ ($\text{M} = \text{C}, \text{Si}, \text{Ge}, \text{Sn}$). If anchimeric assistance is an important factor, the rate constants for hydrogen abstraction from the methyl groups in the organometallic compounds should be substantially greater than that for their carbon analogue.

Results

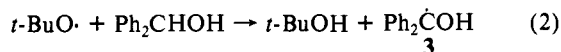
Three complementary techniques were used to investigate the kinetics of hydrogen abstraction by *tert*-butoxyl radicals from the Et_4M compounds.

Method 1. Laser Flash Photolysis. The laser flash photolysis technique was used to determine absolute rate constants, k_1 , at ambient temperatures for the overall reaction



The method used in this work has been described in considerable detail elsewhere.⁷ Briefly, flash photolysis of di-*tert*-butyl peroxide in benzene containing diphenylmethanol gives rise to $\text{Ph}_2\dot{\text{C}}\text{OH}$ (**3**) which can be readily monitored at 540 nm.

(7) Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747-7753. Paul, H.; Small R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4520-4527.

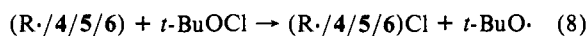
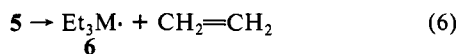
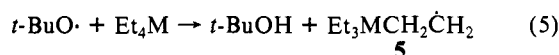
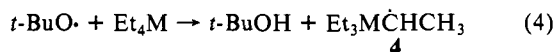


The pseudo-first-order rate constant for the growth of this signal, k_0 , corresponds to that for the decay of the *tert*-butoxyl radical. Addition of Et_4M increases the experimental pseudo-first-order rate constant for decay, k_{exptl} , which is related to k_1 by eq 3.

$$k_{\text{exptl}} = k_0 + k_1[\text{Et}_4\text{M}] \quad (3)$$

The results obtained in these experiments are reported in Table I together with the rate constant for hydrogen abstraction by *tert*-butoxyl from cyclopentane. It should be noted that cyclopentane and the four Et_4M compounds are rather unreactive in terms of the laser flash photolysis experiment. The measured rate constants are therefore less reliable than would be the case for more reactive compounds. Nevertheless, despite their imprecision they do provide a framework of absolute reactivities in which to view much more reliable relative reactivities determined by competitive chlorination (vide infra).

Method 2. Reaction of Et_4M with *tert*-Butyl Hypochlorite. Product studies of the reaction between *tert*-butyl hypochlorite and Et_4M were carried out by using pentane or cyclopentane as standards. These experiments were used to determine the relative reactivities of Et_4M toward *tert*-butoxyl radicals and ratios of k_5/k_4 , eq 4–8.



Reactions with *tert*-butyl hypochlorite were carried out at room temperature by using mixtures containing an Et_4M compound and the hydrocarbon standard. They were photoinitiated by using a tungsten lamp. Trichloroethylene (5% v/v) was added to the mixture so as to suppress any chain reactions carried by chlorine atoms.⁸ The reactions were always carried out under oxygen-free conditions and with small quantities of *tert*-butyl hypochlorite so that the extent of conversion of starting materials was very small (ca. 5%).

The reaction products were analyzed qualitatively on a GC/MS and quantitatively on an analytical GC. The only products from Et_4M , where $\text{M} = \text{C}$ or Si , were chlorides derived from **4** and **5**. However, for $\text{M} = \text{Ge}$ reaction **6** was important and significant amounts of Et_3GeCl were detected. For $\text{M} = \text{Sn}$ this route became the dominant pathway for the loss of **5** and Et_3SnCl was a major product. The chlorides derived from **4** and **5** were identified from their relative GC retention times and their mass spectral fragmentation patterns. The correctness of these assignments was later confirmed in a series of EPR spectroscopic experiments (vide infra). The relative reactivities of the Et_4M compounds measured in these competition studies are in reasonable agreement with those calculated from the laser flash photolysis results.⁹ Values are given in Table I together with the ratios k_5/k_4 for each Et_4M that

(8) Walling, C.; McGuiness, J. A. *J. Am. Chem. Soc.* **1969**, *91*, 2053–2058. Zavitsas, A. A.; Blank, J. D. *Ibid.* **1972**, *92*, 4603–4608. Walling, C.; Clark, R. T. *Ibid.* **1974**, *96*, 4530–4534. Sutcliffe, R.; Anpo, M.; Stolow, A.; Ingold, K. U. *Ibid.* **1982**, *104*, 6064–6070.

(9) The agreement for Et_4Sn is rather poor. A previous competitive EPR study (see method 3 and ref 10) involving Et_4Sn and cyclopentane was carried out at -84°C . After correction to 25°C , on the assumption that the differences in reactivity are due entirely to enthalpy differences for H abstraction from the two compounds, the $\text{Et}_4\text{Sn}/\text{c-C}_5\text{H}_{10}$ relative reactivity was found to be 6.0 in satisfactory agreement with the relative reactivities determined by the hypochlorite method. For this reason the relative reactivities given in Figure 1 are derived from the *tert*-butyl hypochlorite reactivity data only.

(10) Davies, A. G.; Roberts, B. P.; Tse, M.-W. *J. Chem. Soc., Perkin Trans. 2* **1978**, 145–150.

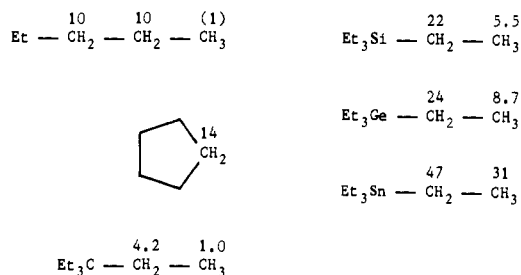
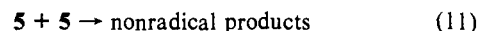
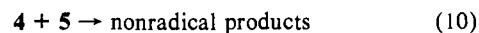
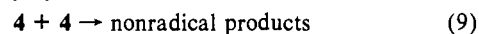


Figure 1. Relative reactivities toward the *tert*-butoxyl radical of individual positions (per hydrogen atom) relative to a hydrogen atom in a methyl group in pentane.

have been statistically corrected for the number of available hydrogen atoms.

Method 3. EPR Spectroscopy. Photolysis of mixtures containing di-*tert*-butyl peroxide and Et_4M (4:1 v/v; $\text{M} = \text{Si}, \text{Ge}$) in the cavity of an EPR spectrometer gave the spectra of **4** and **5**. The formation of the radicals is described by reactions 4 and 5 and their decay by reactions 9–11.



Reactions between small, unhindered alkyl radicals normally proceed at the diffusion controlled limit.¹¹ Since **4** and **5** have the same molecular weight, and hence similar diffusion coefficients, it is safe to assume that $2k_9 = k_{10} = 2k_{11}$. Under such conditions the ratio $[\mathbf{5}]/[\mathbf{4}]$ will be equal to k_5/k_4 . The values obtained for this ratio were 0.2 and 0.25 for $\text{M} = \text{Si}$ at 30 and -30°C , respectively, and 0.5 for $\text{M} = \text{Ge}$ at -30°C . Rather poor signal-to-noise levels precluded a detailed study of the relative temperature dependence of reactions 4 and 5. However, the limited data obtained were quite sufficient to confirm the assignments of the mass spectra of the isomeric chlorides that had been made in the quantitative hypochlorite study.

Discussion

The data in Table I were used to calculate the relative reactivities of all of the hydrogens in the molecules studied. These are shown in Figure 1.

As would be expected, the 2- and 3-positions in pentane have the same reactivity within experimental error and the relative reactivities of its methylene and methyl groups are in fair agreement with data reported from a similar experiment with hexane.¹² The methylene groups in cyclopentane are 1.4 times more reactive than those of pentane, as has been noted previously.¹² This enhanced reactivity presumably reflects the fact that conversion of cyclopentane to the cyclopentyl radical leads to a reduction of the strain between eclipsing methylene groups.

The methyl hydrogens of Et_4C have the same reactivity as those in pentane. However, the methylene hydrogens in Et_4C have less than half the reactivity of those in pentane. In the compact Et_4C molecule, the methylene groups must be sterically protected from attack by *tert*-butoxyl whereas the methyl groups on its periphery can be approached without hindrance.

The activating influence of the Et_3M ($\text{M} = \text{Si}, \text{Ge}, \text{Sn}$) is clear-cut and unequivocal: in each case and in both the α (product from **4**) and the β (product from **5**) positions there is a pronounced increase in reactivity compared with either Et_4C or pentane, and there is a monotonic increase from silicon to tin, although the differences between silicon and germanium are relatively small.

It is particularly interesting to compare our relative reactivities for H-atom abstraction by *tert*-butoxyl with the results recently reported by Wilt and co-workers¹³ for chlorine and bromine atom

(11) Griller, D. "Landolt-Börnstein"; Springer-Verlag, New York, 1984; New Series Vol. II/13, Subvolume a, Chapter 1.

(12) Bunch, N. J.; Hadley, M. *J. Org. Chem.* **1974**, *39*, 2271–2276.

(13) Wilt, J. W.; Belmonte, F. G.; Zieske, P. A. *J. Am. Chem. Soc.* **1983**, *105*, 5665–5675.

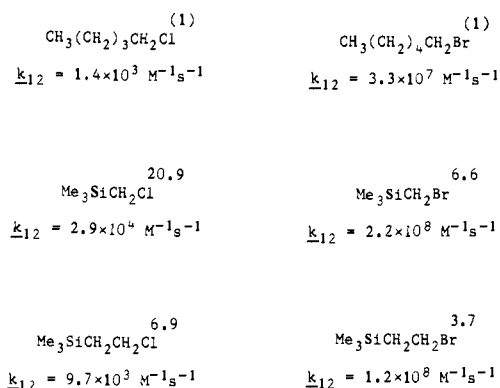
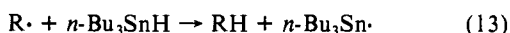
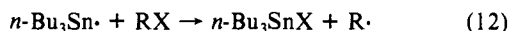


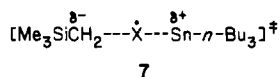
Figure 2. Relative reactivities and absolute rate constants at 25 °C for halogen atom abstraction by the tri-*n*-butyltin radical.

abstractions from some halosilanes by tri-*n*-butyltin radicals. Reactions of the halosilanes (or 1-halopentane) with tri-*n*-butyltin hydride can be represented by reactions 12 and 13.

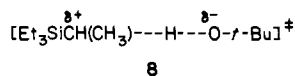


Reactivities of the chlorides and bromides of interest are given relative to the reactivity of the corresponding 1-halopentane in Figure 2. It can be seen that the positions α and β to silicon are strongly activated relative to the 1-position of pentane. The activating effect for the α -position of the Me_3Si group is larger for halogen abstraction by the tributyltin radical than that of the Et_3Si group for hydrogen abstractions by *tert*-butoxyl radical, viz., 20.9 for Cl and 6.6 for Br vs. 2.2 for H (the last value being obtained by comparison of a CH_2 in Et_4Si with a CH_2 in pentane rather than with one in Et_4C so as to reduce the importance of steric hindrance). It should be noted that the enhanced activating effect of silicon for halogen abstraction from the α -position is not a consequence of these reactions being slower than the H-atom abstractions. Absolute rate constants for these halogen atom abstractions can be calculated by combining Wilt et al.'s¹³ results with published data.¹⁴⁻¹⁶ Values are given in Figure 2. Comparison with the absolute (molecular) rate constants for H-atom abstraction and the positional selectivities given in Table I shows that for each position Cl-atom abstraction is slower and Br-atom abstraction is faster than the corresponding H-atom abstraction.

Wilt and co-workers¹³ attributed the enhanced reactivity of the $\text{Me}_3\text{SiCH}_2\text{X}$ compounds (relative to $n\text{-C}_5\text{H}_{11}\text{X}$) to stabilization of the transition state for halogen abstraction by a polar contribution in which the silicon atom stabilized an adjacent electron rich center, i.e., to a contribution to the transition state of the dipolar canonical structure 7. For our H-atom abstractions, any polar



contribution to the transition state is likely to be in the opposite sense, i.e., 8. Since the rate enhancement at the α -position for



the halogen abstractions are appreciably greater than that found for the hydrogen abstraction we must agree that polar factors of

(14) Carlsson, D. J.; Ingold, K. U. *J. Am. Chem. Soc.* **1968**, *90*, 7047-7055.

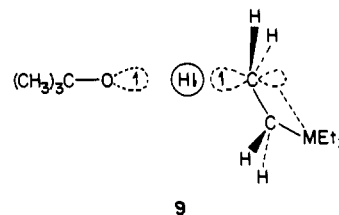
(15) Ingold, K. U.; Luszyk, J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *105*, 343-348.

(16) Absolute rate constants reported¹⁴ for 1-haloalkanes have been multiplied by a factor of 1.7 as recommended.¹⁵ Values for chlorides were obtained by combining a relative reactivity of 0.9 for the *t*-BuCl/ $\text{Me}_3\text{SiCH}_2\text{Cl}$ couple¹³ with absolute rate constants for $n\text{-C}_5\text{H}_{11}\text{Cl}$ and *t*-BuCl.¹⁴ Values for bromides were obtained by combining a relative reactivity of 6.6 for the $\text{Me}_3\text{SiCH}_2\text{Br}/n\text{-C}_5\text{H}_{11}\text{Br}$ couple¹³ with the absolute rate constant for $n\text{-C}_6\text{H}_{13}\text{Br}$.¹⁴

the type indicated in 7 play a role in the former reactions. We therefore attribute the small but significant activating effect of silicon on the α -H abstraction to a small degree of stabilization of α -silylalkyl radicals relative to similar, but unsubstituted, alkyl radicals. Such stabilization¹⁷ of α -silylalkyl radicals by odd-electron delocalization¹⁸ has been suggested previously¹⁹ and kinetic studies by Doncaster and Walsh²¹ have shown that the C-H bond in neopentane is 1.8 ± 0.7 kJ/mol (~ 0.4 kcal/mol) stronger than that in tetramethylsilane. Our results would be consistent with this small difference in C-H bond strengths.

We attribute the slight increase in activation at the α -position for H-atom abstraction on going from Si to Ge and the larger increase on going from Ge to Sn to increasing stabilization of $\text{Et}_3\text{MCHCH}_3$ radicals by the heavier atoms. However, it is possible that part of the effect is due to lessening of steric hindrance along the series Si, Ge, Sn.

The enhancement in the reactivity at the β -position for halogen atom abstraction from $\text{Me}_3\text{SiCH}_2\text{CH}_2\text{X}$ relative to $n\text{-C}_5\text{H}_{11}\text{X}$ is similar, both for Cl (viz., 6.9) and for Br (viz., 3.7), to the enhancement for β -H-atom abstraction from Et_4Si relative to a methyl hydrogen in pentane (viz., 5.5). This fact, plus the expected large attenuation of a polar effect by the intermediate CH_2 group, leads us to suggest that polar factors are relatively unimportant in halogen abstraction from $\text{Et}_3\text{SiCH}_2\text{CH}_2\text{X}$. Wilt et al.'s¹³ results for these β -halogen atom abstractions together with our own results for β -H atom abstractions (for which the activating effect for Si, Ge, and Sn is greater than at the α -position, see Figure 1), provide, in our view, unequivocal evidence for anchimeric assistance by the Et_3M group ($\text{M} = \text{Si, Ge, Sn}$) to the formation of the $\text{Et}_3\text{MCH}_2\text{CH}_2$ radical.²² We presume that the $\text{Et}_3\text{MCH}_2\text{CH}_2$ radical will be formed in its preferred eclipsed conformation, 1, since some of the stabilization energy of the incipient radical should be available in the transition state if attack takes place *anti* to the MEt_3 group, i.e., 9. Thus the heavy atom provides anchimeric



assistance to the hydrogen (and halogen) atom transfer. The larger size and the greater availability of low-lying unfilled orbitals in tin compared with germanium or silicon is no doubt responsible for the larger effect noted for tin.

Conclusion

Anchimeric assistance in the formation of β -substituted alkyl radicals by heavy atoms is a general phenomenon that appears to be associated with bridging.

Experimental Section

Materials. *tert*-Butyl hypochlorite was prepared by the method of Mintz and Walling.²⁵ Di-*tert*-butyl peroxide was washed with aqueous

(17) Cf.: Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1976**, *9*, 13-19.

(18) Possibilities include (d-p) π -type stabilization^{13,19,20} or involvement with the Si-C σ^* orbital.^{13,20}

(19) Wilt, J. W.; Kolewe, O.; Kraemer, J. K. *J. Am. Chem. Soc.* **1969**, *91*, 2624-2631.

(20) Pitt, C. G. *J. Organomet. Chem.* **1973**, *61*, 49-70.

(21) Doncaster, A. M.; Walsh, R. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 2908-2916.

(22) Wilt (private communication) has suggested that the rate of β -H atom abstraction from Et_3M ($\text{M} = \text{Si, Ge, Sn}$) may be enhanced by polar factors (of the type $\text{R}_3\text{MCH}_2\text{CH}_2^{\delta+}\text{---}\text{H}\text{---}\text{OBu-}t^{\delta-}$) since metalloids are known to stabilize positive charge on β -carbons. The stabilizing influence of R_3M on the product radical $\text{R}_3\text{MCH}_2\text{CH}_2\cdot$ may therefore be "diluted" in our H-atom abstractions by the influence of the R_3M group on the transition state.

(23) Wong, P. C.; Griller, D.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5106-5108.

(24) Chatgililoglu, C.; Scaiano, J. C.; Ingold, K. U. *Organometallics* **1982**, *1*, 466-469.

silver nitrate solution to remove olefinic impurities. It was then washed with water, dried over magnesium sulfate, and finally passed through a column of alumina to remove hydroperoxide impurities. All other materials were commercially available in >98% purity (GC analysis) and were used without further purification.

Instruments. The apparatus used in this work has been described in detail elsewhere. Briefly, the laser flash photolysis system employed pulses from a nitrogen laser (10 mJ, 10 ns, 337 nm) for sample photolysis. Transient absorptions were detected with a monochromator and photomultiplier tube, and signals from the latter were fed to a transient digitizer-computer system for storage and kinetic analysis.

Qualitative analyses of reaction mixtures were carried out on a Hewlett-Packard 5995 GC/MS. Quantitative analyses were made on a Varian 3500 gas chromatograph. Both instruments were fitted with capillary columns.

Response factors for unavailable halides were calculated on the basis of an assumed zero mass response for chloride (correct to within a few percent for the alkyl chlorides measured) with the assumption that a similar correction factor can be applied to chlorinated organometallics to obtain a response factor from the (measured) Et_4M response factors.

Assignment of Structure of Chlorinated Organometallics. Mass spectral analysis distinguished between the isomers of the chlorinated organometallic compounds on the basis of the fragmentation products (more Et_3M^+ and Et_2MH^+ from the α -compound, more Et_2MCl^+ from the β -compound). These assignments indicate that the β -isomer should

(25) Mintz, M. J.; Walling, C. "Organic Syntheses"; Wiley: New York, 1975; Collect. Vol. V, p 184.

have the longer retention time and accord with the EPR results. Individual mass spectral results follow in the order m/e (relative abundance) assignment. For Ge and Sn compounds, only the ^{74}Ge and ^{120}Sn peaks in the pattern are listed.

$\text{Et}_3\text{SiCHClCH}_3$: 87 (100) Et_2SiH , 121 (84) $\text{Et}_2\text{Si}^{35}\text{Cl}$, 115 (76) Et_3Si , 93 (67) $\text{EtSiH}^{35}\text{Cl}$, 59 (40) SiEtH_2 , 123 (30) $\text{Et}_2\text{Si}^{37}\text{Cl}$.

$\text{Et}_3\text{SiCH}_2\text{CH}_2\text{Cl}$: 121 (100) $\text{Et}_2\text{Si}^{35}\text{Cl}$, 93 (67) $\text{EtSiH}^{35}\text{Cl}$, 123 (36) $\text{Et}_2\text{Si}^{37}\text{Cl}$, 95 (25) $\text{EtSiH}^{37}\text{Cl}$, 65 (17) $\text{Si}^{35}\text{ClH}_2$, 87 (11) Et_2SiH .

$\text{Et}_3\text{GeCHClCH}_3$: 133 (100) Et_2GeH , 161 (71) Et_3Ge , 103 (61) EtGe , 167 (45) $\text{Et}_2\text{Ge}^{35}\text{Cl}$, 139 (41) $\text{EtGe}^{35}\text{ClH}$, 109 (29) Ge^{35}Cl .

$\text{Et}_3\text{GeCH}_2\text{CH}_2\text{Cl}$: 167 (100) $\text{Et}_2\text{Ge}^{35}\text{Cl}$, 139 (80) $\text{EtGe}^{35}\text{ClH}$, 109 (37) Ge^{35}Cl , 103 (28) EtGe , 133 (18) Et_2GeH , 75 (18) GeH .

$\text{Et}_3\text{SnCHClCH}_3$: 149 (100) EtSn , 151 (80) EtSnH_2 , 179 (70) Et_2SnH , 155 (67) Sn^{35}Cl , 207 (65) Et_3Sn , 121 (61) SnH , 213 (52) $\text{Et}_2\text{Sn}^{35}\text{Cl}$.

$\text{Et}_3\text{SnCH}_2\text{CH}_2\text{Cl}$: 155 (100) Sn^{35}Cl , 149 (97) EtSn , 151 (97) EtSnH_2 , 207 (81) Et_2Sn , 179 (68) Et_2SnH , 213 (64) $\text{Et}_2\text{Sn}^{35}\text{Cl}$, 121 (47) SnH [EtSn , EtSnH_2 , and SnCl have overlapping isotope patterns].

Acknowledgment. We thank D. A. Lindsay for his technical help and advice with these experiments.

Registry No. $n\text{-C}_5\text{H}_{12}$, 109-66-0; $c\text{-C}_3\text{H}_8$, 287-92-3; Et_4C , 1067-20-5; Et_4Si , 631-36-7; Et_4Ge , 597-63-7; Et_4Sn , 597-64-8; $t\text{-BuO}$, 3141-58-0; $\text{CH}_3(\text{CH}_2)_3\text{CH}_2\text{Cl}$, 543-59-9; $\text{Me}_3\text{SiCH}_2\text{Cl}$, 2344-80-1; $\text{Me}_3\text{SiCH}_2\text{CH}_2\text{Cl}$, 17336-78-6; $\text{CH}_3(\text{CH}_2)_4\text{CH}_2\text{Br}$, 111-25-1; $\text{Me}_3\text{SiCH}_2\text{Br}$, 18243-41-9; $\text{Me}_3\text{SiCH}_2\text{CH}_2\text{Br}$, 18156-67-7; $n\text{-Bu}_3\text{Sn}$, 20763-88-6; $t\text{-BuOCl}$, 507-40-4; H_2 , 1333-74-0; $\text{Et}_3\text{SiCHClCH}_3$, 18279-74-8; $\text{Et}_3\text{GeCHClCH}_3$, 90225-46-0; $\text{Et}_3\text{GeCH}_2\text{CH}_2\text{Cl}$, 93304-70-2; $\text{Et}_3\text{SnCH}_2\text{CH}_2\text{Cl}$, 93304-71-3; di-*tert*-butyl peroxide, 110-05-4.

Nitrosation of Organic Hydroperoxides by Nitrogen Dioxide/Dinitrogen Tetraoxide

William A. Pryor,* Laurence Castle, and Daniel F. Church*

Contribution from the Departments of Chemistry and Biochemistry, Louisiana State University, Baton Rouge, Louisiana 70803. Received June 28, 1984

Abstract: Cumyl and *tert*-butyl hydroperoxides react rapidly with $\text{NO}_2/\text{N}_2\text{O}_4$ in organic solvents in the presence of a base to form the organic nitrate (RONO_2) as the major product, together with smaller amounts of the corresponding nitrite (RONO), alcohol, and carbonyl compound (acetophenone or acetone from cumyl and *tert*-butyl hydroperoxide, respectively). The products from *tert*-butyl hydroperoxide are similar whether a base is present or not but those from cumyl hydroperoxide are more complex. We have formulated the initial reaction as a nitrosation of the hydroperoxide by N_2O_4 to give the pernitrite ester. This latter species is unstable and either rearranges to give the nitrate or dissociates to form alkoxy radicals and nitrogen dioxide that ultimately give the other observed products. The kinetics of the reaction were studied by stopped flow and are complex, but we conclude the kinetics are consistent with the nitrosation mechanism. The rate constants at 30 °C are 2.4×10^6 and $8.1 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ for *tert*-butyl and cumyl hydroperoxides, respectively. We suggest that this facile reaction of $\text{NO}_2/\text{N}_2\text{O}_4$ with hydroperoxides may have important consequences with respect to the pulmonary toxicity of NO_2 in smoggy air.

Nitrogen dioxide (NO_2) is one of the most important toxic components of photochemical smog,¹ and understanding the reactions that NO_2 undergoes in the lungs of persons exposed to smoggy air is, therefore, of considerable importance. Previous work has shown that NO_2 initiates the autoxidation of polyunsaturated fatty acids² and oxidizes thiols to disulfides.³ At the higher levels present in cigarette smoke, NO_2 reacts with simple olefins in the gas phase to give scavengeable oxygen-centered radicals.^{4,5,6}

The gas-phase reactions of NO_2 and nitric oxide (NO) with hydrogen peroxide have been studied by atmospheric chemists^{7,8} and are believed to produce hydroxyl radicals by a homolytic displacement reaction at the O-O bond by NO_x . There is one brief report of the reaction of NO with an organic hydroperoxide in solution;⁹ a radical mechanism was proposed that also involves

(1) Pryor, W. A. In "Environmental Health Chemistry"; McKinney, J. D., Ed.; Ann Arbor Science Publishers: Ann Arbor, MI, 1980; pp 445-467.

(2) Pryor, W. A. In "Lipid Peroxides in Biology and Medicine"; Yagi, K., Ed.; Academic Press: New York, 1982; p 1-22.

(3) Pryor, W. A.; Church, D. F.; Govindan, C. K.; Crank, G. J. *Org. Chem.* **1982**, *47*, 156.

(4) Pryor, W. A. In "Molecular Basis of Environmental Toxicity"; Bhatnagar, R. S. Ed.; Ann Arbor Science Publishers: Ann Arbor, MI, 1980; pp 3-36.

(5) Pryor, W. A.; Lightsey, J. W. *Science (Washington, D.C.)* **1981**, *214*, 435.

(6) Pryor, W. A.; Lightsey, J. W.; Church, D. F. *J. Am. Chem. Soc.* **1982**, *104*, 6685.

(7) Audley, G. J.; Baulch, D. L.; Campbell, I. M. *J. Chem. Soc. Chem. Commun.* **1982**, 1053.

(8) Gray, D.; Lissi, E.; Heicklen, J. *J. Chem. Phys.* **1972**, *76*, 1919.