Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. V. Self-Reactions of Some Group IV Radicals[1]

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Abstract: The bimolecular rate constants, $2k_t$, for the self-reactions of methyl radicals and of radicals with the structures $(CH_3)_3M\cdot$, $(CH_3)_3M\dot{C}H_2$, $(CH_3)_3M\dot{M}(CH_3)_2$, and $(CH_3)_3MM(CH_3)_2\dot{C}H_2$, where M is carbon, silicon, germanium, or tin, have been measured at room temperature in di-*tert*-butyl peroxide as solvent. Values of $2k_t$ range from $1.1 \times 10^{10}\ M^{-1}\ \text{sec}^{-1}$ for methyl to $1.6 \times 10^9\ M^{-1}\ \text{sec}^{-1}$ for $(CH_3)_3GeGe(CH_3)_2\dot{C}H_2$. The logarithms of the rate constants exhibit a surprisingly good linear correlation with the molecular weight of the radical. This is attributed to the fact that the radius for diffusion increases with increasing size of the radical while the radius for reaction remains almost unchanged. For the trichloromethyl radical in the temperature range −75 to −15°, $2k_t = 1.2 \times 10^8\ M^{-1}\ \text{sec}^{-1}$, which is significantly below the diffusion-controlled limit. The slow decay of this radical is attributed to polar effects.

Classical methods for measuring the rate constants of radical–radical reactions in solution are laborious and are not always very accurate. In 1968 some reasonably reliable rate constants for the bimolecular self-reactions of a few low molecular weight alkyl radicals were obtained by the rotating sector technique.[3,4] However, in that same year, Weiner and Hammond[5] made an important advance in electron paramagnetic resonance (epr) techniques that eliminated the necessity for the time-consuming classical procedures. Alkyl radicals were generated in measurable concentration in an epr spectrometer by the photolysis of azo compounds. The epr signal was passed into a CAT (computer of average transients) and, by synchronizing light chopping with signal collection, a large number of identical radical decays could be accumulated. The bimolecular rate constants for the radical–radical reactions could then be easily and accurately calculated.[6] In subsequent papers, Hammond's group has utilized the same experimental technique to obtain rate constants for the self-reactions of a variety of alkyl,[9] ketyl,[10,11] and semidione radicals.[12]

Our interest in absolute rate constants for alkyl and other group IV radicals[4,13–16] prompted us to set up a similar experimental arrangement to that of Weiner and Hammond. The present paper reports bimolecular rate constants for the self-reactions of radicals with structures $(CH_3)_3M\cdot$, $(CH_3)_3M\dot{C}H_2$, $(CH_3)_3M\dot{M}(CH_3)_2$, and $(CH_3)_3MM(CH_3)_2\dot{C}H_2$, where M is carbon, silicon, germanium, or tin. The methyl, 3-ethylpent-3-yl, and trichloromethyl radicals were also examined. With the exception of methyl, all the radicals were generated by a two-step process in which the hydrogen-containing precursor reacted with *tert*-butoxy radicals (BO·) generated photochemically from di-*tert*-butyl peroxide (BOOB).[17] The rate constant for radical decay, $2k_t$, is

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

$$\text{BO}\cdot + \text{RH} \longrightarrow \text{BOH} + \text{R}\cdot$$

$$\text{R}\cdot + \text{R}\cdot \xrightarrow{2k_t} \text{molecular products}$$

defined by the relation

$$\frac{-\text{d}[\text{R}\cdot]}{\text{d}t} = 2k_t[\text{R}\cdot]^2$$

Experimental Section

Materials. Most of the substrates used in this work were commercial compounds which were further purified by conventional methods. Trimethylgermanium hydride and trimethyltin hydride were prepared by reaction of the bromide and chloride, respectively, with tri-*n*-butyltin hydride. Hexamethyldigermane was prepared from trimethylgermyl bromide by reaction with metallic potassium.[18] Pentamethyldisilane was prepared by lithium aluminum hydride reduction of pentamethylchlorosilane.[19]

Procedure. The solvent employed throughout this work was di-*tert*-butyl peroxide. It was passed through alumina immediately prior to use in order to remove any traces of hydroperoxide (which would give rise to peroxy radicals[20]). For all the radicals except

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Table I. Epr Data for Some Group IV Radicals in Solution

Radical	Coupling constant[a] α-H	β-H	γ-H	*g* value	Ref
$(CH_3)_3C\cdot$		22.7		2.0029	*e, f*
$(CH_3)_3Si\cdot$		6.3		2.0031	*g–i*
$(CH_3)_3Ge\cdot$		5.5		2.0104	*h*
$(CH_3)_3Sn\cdot$		2.75		2.017[b]	This work
$(CH_3)_3C\dot{C}(CH_3)_2$		22.0	*c*	2.0029	This work
$(CH_3)_3Si\dot{S}i(CH_3)_2$		8.2	0.47	2.0036	*h, i*
$(CH_3)_3CC(CH_3)_2\dot{C}H_2$	20.8		0.83	2.0021	This work
$(CH_3)_3SiSi(CH_3)_2\dot{C}H_2$	20.15		0.24	*d*	*j*
$(CH_3)_3GeGe(CH_3)_2\dot{C}H_2$	19.8		*c*	2.0027	This work
$(CH_3CH_2)_3C\cdot$		16.5	*c*	2.0030	This work

[a] The field sweep of the spectrometer was calibrated with an ethylene glycol solution of 2,2,6,6-tetramethylpiperidone nitroxide, $a_N = 15.15$ G (R. Briere, H. Lemaire, and A. Rassat, *Bull. Soc. Chim. Fr.*, 3273 (1965)). [b] In matrices: triisobutyltin $g_{\parallel} \sim 2.034$, $g_{\perp} \sim 2.002$ (ref 25a); $H_3Sn\cdot$, $g_{\parallel} = 2.003$; $g_{\perp} = 2.025$, $g_{av} = 2.017 \pm 0.040$, $a_H = 26 \pm 4$ G (ref 25b); $(CH_3)_3Sn\cdot$, $g_{av} = 2.0163$, $a_H = 2.8$ G (ref 25c). [c] Not resolved. [d] Not given. [e] Reference 7. [f] Reference 17f. [g] Reference 17b. [h] Reference 17e. [i] Reference 17g. [j] Reference 17c.

methyl the peroxide also served as a reactant. Equimolar (or saturated) solutions of the radical precursor, RH, and peroxide were degassed and sealed in quartz epr tubes under vacuum. The tubes were photolyzed in the cavity of a Varian E-3 epr spectrometer with the focused but unfiltered light from a 200-W Osram super-pressure mercury lamp (HBO-200W). The light beam was chopped by a rapidly rotating sectored disk (light:dark, 1:9). At the appropriate rotation speed a large number of identical radical decays were collected by a Fabri-Tek 1072 signal averager. The sample temperature was controlled using the V-4557 variable-temperature accessory of the spectrometer.

Radical concentrations were measured relative to DPPH by the usual procedures.[21] In these measurements and in the decay measurements the epr modulation amplitude was adjusted to yield the maximum signal to noise ratio. Rates of radical decay were, where possible, measured at 25°. However, it was necessary to lower the temperature in a few cases in order to obtain an acceptable signal to noise ratio. That the radical decays were accurately second order was checked both from the individual decay curves and by measuring the change in radical concentration under steady illumination when screens of known transmittance were inserted in the light beam.[16]

Methyl radicals were prepared by the photolysis of acetyl peroxide.[22] Di-*tert*-butyl peroxide was used as the solvent and proved to have unexpected advantages since the methyl radicals decayed with second-order kinetics in this solvent, whereas in benzene and in $CFCl_3$ they decayed with first-order kinetics.

Results

Epr Spectra of Radicals. The spectra of most of the radicals prepared in the present work have been reported previously. Our own spectra for these radicals agreed with data in the literature. However, it is interesting to note that the neopentyl radical has not previously been prepared by the BO· + RH route, apparently because the photolyses were carried out at low temperatures.[17c,17f] An excellent signal due to this radical can be obtained at room temperature by this technique. The trichloromethyl radical has been obtained previously by photolysis of BOOB and a trialkylsilane in carbon tetrachloride at low temperatures.[23] Just as good a signal can be obtained by photolyzing BOOB in chloroform at the same temperatures.[23] We failed to detect any signal when BOOB was photolyzed in cumene, a result which is consistent with the very high value of $2k_t$ (1.6×10^{10} M^{-1} sec^{-1}) that has been reported for the cumyl radical.[9]

The coupling constants and *g* values of radicals which have not previously been reported are listed in Table I together with data from the literature for radicals of comparable structure. There are consistent trends in these quantities for the various types of group IV radical. These trends have been discussed in some detail by others[17,24] and so will not be discussed here. Radicals with the unpaired electron centered on tin have been previously prepared and detected in low-temperature matrices,[25] but not in solution. Our spectrum was not sufficiently intense for us to detect the lines due to the 117 and 119 tin isotopes.

The photolysis of neat hexamethyldisilane yielded a weak signal attributable to the $(CH_3)_3SiSi(CH_3)_2\dot{C}H_2$ radical. While this raises some intriguing possibilities we were unable to rule out a possible contamination of the reactant by traces of peroxide. No signal could be detected when neat hexamethylditin was photolyzed. In the presence of BOOB, photolysis yielded a weak signal due to $(CH_3)_3Sn\cdot$ rather than the expected strong signal due to $(CH_3)_3SnSn(CH_3)_2\dot{C}H_2$. Apparently with this molecule *tert*-butoxy radicals enter into SH2 reactions at tin more readily than at hydrogen.

$$BO\cdot + (CH_3)_3SnSn(CH_3)_3 \longrightarrow (CH_3)_3SnOB + (CH_3)_3Sn\cdot$$

Neumann, *et al.*,[26] have shown previously that tri-*n*-butyl-*tert*-butoxytin is formed in a similar reaction when BOOB is thermally decomposed at 130° in the presence of hexabutylditin.

The photolysis of bis(trimethylsilyl)mercury[27] was examined briefly as a possible alternative source of trimethylsilyl radicals. However, *no* epr signal could be detected although photolysis in benzene was extremely rapid as evidenced by the formation of a cloud of mercury after a few seconds under full illumination. We are at a loss to explain this result unless radical formation is not a major pathway in the photolytic decomposition of this compound. In this connection, it is worth noting that recent work by others has in-

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Table II. Rate Constants for the Bimolecular Self-Reactions of Some Group IV Radicals

No.	Radical	Range in initial concn × 10^8, M	$2k_t \times 10^{-9}$, M^{-1} sec^{-1} [a]		
				Lit.	
			This work[b]	Liquid phase[c] (ref)	Gas phase (ref)
1	$H_3C\cdot$	4–15	11 ± 1.0 (−18°)	8.9 (*l*); 1.3 (*m*)[d]	22 (*t*)[e]
2	$(CH_3)_3C\cdot$	5–20	8.1 ± 0.3	2.1 (*l*); 4.4 (*n*)	15 (*u*)[f]
3	$(CH_3)_3C\dot{C}H_2$	3–40	4.0 ± 0.2		
4	$(CH_3)_3C\dot{C}(CH_3)_2$	10–40	3.1 ± 0.1		
5	$(CH_3)_3CC(CH_3)_2\dot{C}H_2$	10–40	2.6 ± 0.1		
6	$(CH_3CH_2)_3C\cdot$	6–30	1.5 ± 0.2 (−65°)		
7	$(CH_3)_3Si\cdot$	40–50	5.5 ± 0.2	2.2 (*o*)[g]	180 (*v*)[h]
8	$(CH_3)_3Ge\cdot$	4–15	3.6 ± 0.2 (−65°)		
9	$(CH_3)_3Sn\cdot$	4–20	2.8 ± 0.3 (−65°)	3.1 (*l*)	
10	$(CH_3)_3Si\dot{C}H_2$	4–50	4.6 ± 0.2		
11	$(CH_3)_3Ge\dot{C}H_2$	10–50	2.5 ± 0.2		
12	$(CH_3)_3Sn\dot{C}H_2$	7–30	1.9 ± 0.2 (−40°)		
13	$(CH_3)_3Si\dot{S}i(CH_3)_2$	7–30	1.4 ± 0.4 (−65°)		
14	$(CH_3)_3SiSi(CH_3)_2\dot{C}H_2$	2–30	3.1 ± 0.1		
15	$(CH_3)_3GeGe(CH_3)_2\dot{C}H_2$	10–50	1.6 ± 0.1		
16	$Cl_3C\cdot$	75–300	0.12 ± 0.02 (−75 to −15°)	~0.1 (*p–s*);[i] 1.2 (*m*)[d]	4.6 (*w*);[j] 3.9 (*x*)[k]

[a] At or near 25° unless otherwise noted. [b] Error limits are standard deviations calculated from not less than seven separate experiments. [c] In cyclohexane unless otherwise noted. [d] Termination rate constant obtained by the rotating sector method for the chain reaction of tributylgermanium hydride with CH_3I or CCl_4. We cannot explain why these values are so different from values found in analogous experiments in the same experimental system (*e.g.*, $2k_t$ for $\cdot CH_3$ from the tributyltin hydride, CH_3I reaction (ref 4), and $2k_t$ for $\cdot CCl_3$ from the *tert*-butyl hypochlorite, $CHCl_3$ reaction (D. J. Carlsson and K. U. Ingold *J. Amer. Chem. Soc.*, **89**, 4885, 4891 (1967)); [e] 125–175°. [f] 115°. There is a possibility that this value is too high (S. W. Benson, private communication). [g] In BOOB. [h] 44–126°. [i] In various olefins and chloroform. [j] 30–150°. [k] 112–183°. [l] Reference 4. [m] Reference 13. [n] Reference 9. [o] Reference 16. [p] H. W. Melville, J. C. Robb, and R. C. Tutton, *Discuss. Faraday Soc.*, **10**, 154 (1951); **14**, 150 (1953). [q] W. I. Bengough and R. A. M. Thomson, *Trans. Faraday Soc.*, **57**, 1928 (1961). [r] Kh'.S. Bagdasar'yan and A. F. Revzin, *Kinet. Katal.*, **4**, 844 (1963). [s] See Carlsson and Ingold, footnote *d*. [t] A. Shepp, *J. Chem. Phys.*, **24**, 939 (1956). [u] E. L. Metcalfe, *J. Chem. Soc.*, 3560 (1963). [v] P. Cadman, G. M. Tilsley, and A. F. Trotman-Dickenson, *Chem. Commun.*, 1721 (1970). [w] G. R. De Maré and G. Huybrechts, *Trans. Faraday Soc.*, **64**, 1311 (1968). [x] M. L. White and R. R. Kuntz, *Int. J. Chem. Kinet.*, **3**, 127 (1971).

dicated that the photolysis in anisole is not wholly a radical process.[28]

Decay of Radicals. The bimolecular decay rate constants, $2k_t$, measured in this work are listed in Table II together with the range in initial radical concentrations over which the rate measurements were made. Most decays were measured only at 25° but the temperature was lowered when necessary in order to obtain a reasonable signal to noise ratio. The temperature also had to be lowered with 3-ethylpentane in order to obtain a clean spectrum of the $(CH_3CH_2)_3C\cdot$ radical uncontaminated by the $(CH_3CH_2)_2CH\dot{C}HCH_3$ radical. Low temperatures were also necessary with tetramethyltin since the $(CH_3)_3Sn\dot{C}H_2$ radical decayed with first-order kinetics at room temperature. Rate constants were only measured over a range of temperature for the trichloromethyl radical since this was the only radical that decayed at a rate significantly below the diffusion-controlled limit. In the range −75 to −15° the $\cdot CCl_3$ decay rate constant was found to be independent of the temperature.

On a relative basis the rate constants obtained in the present work are probably accurate to about ±40% since the experimental procedure was exactly the same for all radicals. However, the absolute values of the rate constants may be less accurate because of systematic errors in determining radical concentrations. (This is the cause of the discrepancy between the $2k_t$ value found for $(CH_3)_3Si\cdot$ in the present work and that previously reported[16].) Table II also includes the rather limited data available on $2k_t$ values in solution and in the gas phase for radicals common to previous studies and the present work.

Discussion

The bimolecular rate constants for the self-reactions of the group IV radicals listed in Table II cover a disappointingly small range. That is, if the trichloromethyl radical is excepted, the $2k_t$ values for a wide variety of primary and tertiary alkyl radicals and for the trimethylsilicon, -germanium, and -tin radicals all lie in the range 1.4×10^9–11×10^9 M^{-1} sec^{-1}. Models suggested that steric effects might have been quite important in some of these reactions yet this is not reflected by an exceptionally low $2k_t$ value for any of these radicals.[29] The only obvious trend in the data is that $2k_t$ decreases as the molecular weight of the radical increases. A similar phenomenon has been previously reported by Bertrand, *et al.*,[30] for the self-reactions of a number of alkyl and halogenated alkyl radicals in the gas phase. Following their example, we have plotted log $2k_t$ against the molecular weight of the radical in Figure 1. As in the gas phase (for which the appropriate line[30] has also been drawn) the correlation is surprisingly good.

In solution a decrease in $2k_t$ with increasing molecular weight of the radical is a perfectly reasonable phenomenon. Theory[31] gives the observed bimolecular rate constant for a diffusion-controlled reaction as k_{diff} =

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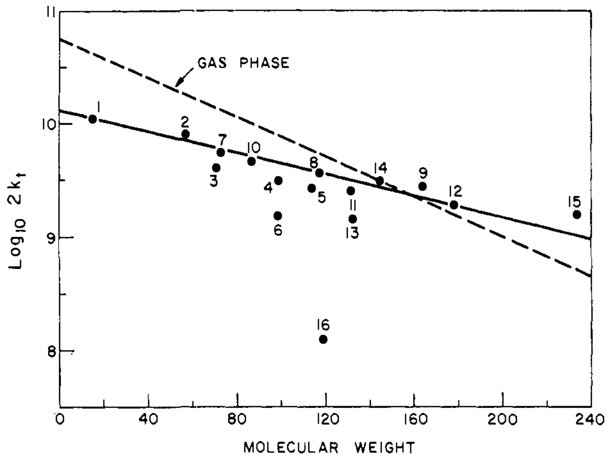

Figure 1. Plot of log $2k_t$ against molecular weight. Dashed line is gas-phase line from ref 30.

$(4\pi N/1000)(\sigma_A + \sigma_B)(D_A + D_B)$, where D_A and D_B are the diffusion coefficients of the reactants A and B in the solvent medium and σ_A and σ_B are the molecular radii defined in terms of the distance across which reaction can take place between A and B. In the absence of diffusion coefficient data, it is common to use the Stokes-Einstein equation in the form $D = kT/6\pi\eta r$ (or $D = kT/4\pi\eta r$)[32] and to identify the diffusion radius r with the radius for reaction in which case $k_{\text{diff}} = 8RT/(3 \times 10^3\eta)\ M^{-1}\ \text{sec}^{-1}$. This equation implies that the diffusion-controlled rate constant for a bimolecular reaction is independent of the size of the reactants. While this may be true of radicals in which the electron is completely delocalized so that reaction is equally probable at any location (*e.g.*, certain aromatic π radicals) it cannot be true of saturated alkyl radicals and σ-type radicals. For these species the unpaired electron is localized and reaction can, therefore, only occur at a particular site on the radical. That is, as the size of these radicals increases, their diffusion radii continue to grow but their radii for reaction do not change appreciably. In consequence, $2k_t$ decreases as the molecular weight (or any other measure of the size of the radical[33]) increases.

Only the trichloromethyl radical lies further from the line in Figure 1 than can be accounted for by experimental error or by minor steric effects. The divergence of this radical is surprising since the gas-phase correlation of $2k_t$ with molecular weight fits alkyl and halogenated alkyl radicals, including $\cdot CCl_3$, equally well. The small value of $2k_t$ for $\cdot CCl_3$ radicals in solution is not due to steric factors since this radical is less hindered than the *tert*-butyl radical. The radical is not resonance stabilized to any great extent and so the low value of $2k_t$ must be ascribed to polar factors. That is, to form C_2Cl_6 requires that the positive ends of two dipoles, $Cl_3^{\delta-}C\cdot^{\delta+}$, be forced together and this must introduce some barrier that hinders the combination. It is not clear why such an effect does not appear to be operative in the gas phase.

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(32) E. McLaughlin, *Trans. Faraday Soc.*, **55**, 28 (1959).

(33) The correlation can be improved by plotting log $2k_t$ against (molecular weight)$^{1/3}$ presumably because this function better represents the change in the size of the radicals.

Absolute Asymmetric Synthesis. I. On the Mechanism of the Photochemical Synthesis of Nonracemic Helicenes with Circularly Polarized Light. Wavelength Dependence of the Optical Yield of Octahelicene

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Abstract: The synthesis of nonracemic yields of hexa-, hepta-, octa-, and nonahelicene with circularly polarized light was observed, and the structural and wavelength dependence of the induced optical yields was examined. The results obtained, together with a detailed consideration of the mechanism of helicene synthesis from the parent diarylolefins, indicate that the induced optical activity is due to selective reaction of enantiomeric conformations of the parent *cis*-diarylolefins by circularly polarized light.

Numerous attempts have been made to induce asymmetric synthesis in photochemical reactions by employing circularly polarized light.[1-3] Until recently, however, the rotations found were marginal, and in no case was the source of the rotation positively

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