

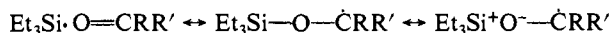
appeared to be the adduct radical.)

Discussion

The results of this work, which are summarized in Tables I and II, greatly extend and generally confirm the conclusions of Cooper, Hudson, and Jackson⁷ regarding the relative rates of reaction 1 for various types of carbonyl groups. The only significant difference to their order of reactivity is that trifluoroacetate is actually more reactive than dialkyl ketones rather than being less reactive. Our quantitative kinetic data reveal that there is an enormous spread in the reactivities of different types of carbonyl groups. Cooper et al.⁷ rationalized their results in terms of bond energy differences, stabilization of radicals formed, and polar effects. Steric factors were considered to be relatively unimportant, but our results do suggest that they play a role (vide infra). Since we do not wish merely to repeat either their arguments or those made by us with respect to the polar effect in the following paper which describes halogen atom abstractions by $\text{Et}_3\text{Si}\cdot$ radicals,⁴² only the more salient features of our results will be discussed.

Duroquinone and, presumably, other 1,4-benzoquinones react very rapidly with triethylsilyl radicals. Since the resultant adduct radicals are often persistent, the utility of this class of compounds as spin traps for silicon-centered and other group 4 metal-centered radicals^{14,17,18} can be readily understood.

The high reactivity of carbonyls bearing an adjacent phenyl group can obviously be attributed to stabilization of the adduct radical by electron delocalization into the substituent. The same is doubtless true of 1,2-diketones. The high reactivity of carbonyls bearing an adjacent perfluoroalkyl group can be attributed to polar effects. That is, if the transition state is represented by the canonical structures



it becomes clear why an electron-withdrawing perfluoroalkyl group will tend to stabilize the transition state since it will stabilize the

(42) Chatgililoglu, C.; Ingold, K. U.; Scaiano, J. C., following paper in this issue.

negative charge on the carbonyl group. A similar argument explains why anhydrides are so much more reactive than esters since an acyloxy group, $\text{RC}(\text{O})\text{O}$, is clearly much more strongly electron withdrawing than is an alkoxy group, RO . In this connection, Cooper et al.⁷ pointed out that although the relatively low reactivity of esters was probably due mainly to ground-state stabilization of their $\text{C}=\text{O}$ double bond by the (p-type) lone pair on the alkoxy group's oxygen, unfavorable polar effects might also play a role since esters accept an electron less readily than ketones.

Cyclic ketones are slightly more reactive than their acyclic counterparts. We attribute this result to the carbonyl groups being sterically less well protected in the cyclic compounds. Similarly, we suggest that the higher reactivity of aldehydes compared with ketones and of formates compared with acetates is due in some part to steric factors.

Finally, our results allow us to expand Cooper et al.'s reactivity order for carbonyl groups to 1,4-benzoquinone \approx cyclic diaryl ketones, benzaldehyde, benzil, perfluoroacid anhydride $>$ benzophenone \gg alkyl aryl ketone, alkyl aldehyde $>$ oxalate $>$ benzoate, trifluoroacetate, anhydride $>$ cyclic dialkyl ketone $>$ acyclic dialkyl ketone $>$ formate $>$ acetate. Over this series of compounds the rate constants for $\text{Et}_3\text{Si}\cdot$ radical addition vary by more than 6 orders of magnitude.

Registry No. 1, 51226-72-3; $\text{Et}_3\text{Si}\cdot$, 24669-77-0; $[\text{CF}_3\text{CF}_2\text{C}(\text{O})]_2\text{O}$, 356-42-3; $[\text{CH}_3\text{CH}_2\text{OC}(\text{O})]_2$, 95-92-1; $\text{CF}_3\text{C}(\text{O})\text{O}(\text{CH}_2)_3\text{CH}_3$, 367-64-6; $\text{C}_6\text{H}_5\text{C}(\text{O})\text{OCH}_3$, 93-58-3; $[\text{CH}_3\text{CH}_2\text{C}(\text{O})]_2\text{O}$, 123-62-6; $(\text{C}_2\text{H}_5)_2\text{CO}$, 96-22-0; $\text{HC}(\text{O})\text{OC}_2\text{H}_5$, 109-94-4; $\text{CH}_3\text{C}(\text{O})\text{OCH}_3$, 79-20-9; benzil, 134-81-6; propionaldehyde, 123-38-6; duroquinone, 527-17-3; fluorenone, 486-25-9; benzophenone, 119-61-9; benzaldehyde, 100-52-7; xanthone, 90-47-1; *p*-anisaldehyde, 123-11-5; acetophenone, 98-86-2; cyclopentanone, 120-92-3; cyclohexanone, 108-94-1; cyclobutanone, 1191-95-3; 4-(triethylsilyloxy)-2,3,5,6-tetramethylphenoxy, 82414-91-3; 9-(triethylsilyloxy)fluoren-9-yl, 82414-92-4; 9-(triethylsilyloxy)xanthen-9-yl, 82414-93-5.

Supplementary Material Available: Tables giving detailed kinetic data (33 pages). Ordering information is given on any current masthead page.

Absolute Rate Constants for the Reaction of Triethylsilyl Radicals with Organic Halides¹

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Contribution from the Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6. Received December 28, 1981

Abstract: The absolute rate constants for the reactions of $\text{Et}_3\text{Si}\cdot$ radicals with a number of organic halides have been measured in solution by using laser flash photolysis techniques. The reactivities cover a wide range; e.g., the rate constants at ca. 300 K are 4.3×10^9 , 1.1×10^8 , 2.5×10^6 , and $<10^5 \text{ M}^{-1} \text{ s}^{-1}$ for $\text{CH}_3\text{CH}_2\text{I}$, $\text{C}_6\text{H}_5\text{Br}$, $(\text{CH}_3)_3\text{CCl}$, and $\text{C}_6\text{H}_5\text{CH}_2\text{F}$, respectively. Arrhenius parameters were determined for a few representative substrates. Thus, for CCl_4 , $E_a = (0.78 \pm 0.24) \text{ kcal/mol}$ and $\log(A/\text{M}^{-1} \text{ s}^{-1}) = 10.2 \pm 0.2$, data which can be combined with relative rates from the literature to yield absolute rate constants for some additional substrates. Comparison of the Arrhenius parameters for halogen abstraction from several substrates suggests the involvement of charge-transfer interactions in some of these reactions. Such rate-enhancing interactions can have a greater influence on the preexponential factor than on the activation energy. An explanation for this phenomenon is advanced. Combination of our rate constants with data from literature also allows evaluation of the rates of inversion at the silicon center in triorganosilyl radicals as being in the range $(3-12) \times 10^9 \text{ s}^{-1}$ at temperatures from 0 to 80 °C which implies that a considerable activation barrier is involved in such processes.

Many heteroatom-centered free-radicals are capable of removing a halogen atom from suitable organic halides. In some cases, this process is presumed to be a simple halogen atom ab-

straction, i.e., eq 1. In other cases an electron transfer is probably



involved, i.e., eq 2. Heteroatoms for which such processes have



been identified include, for example, boron,³ silicon,⁴⁻¹⁵ germa-

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Table I. Arrhenius Parameters and Rate Constants at ca. 300 K for Halogen Atom Abstractions by Triethylsilyl Radicals^a

substrate	temp range/K	log (A/M ⁻¹ s ⁻¹)	E/kcal mol ⁻¹	k ^b /M ⁻¹ s ⁻¹
(CH ₃) ₂ CHI				(1.4 ± 1.0) × 10 ¹⁰
CH ₃ CH ₂ I	233–319	10.4 ± 0.5	1.0 ± 0.6	(4.3 ± 0.6) × 10 ⁹
CH ₃ I				(8.1 ± 0.4) × 10 ⁹
C ₆ H ₅ I				(1.5 ± 0.4) × 10 ⁹
CH ₂ =CHCH ₂ Br				(1.5 ± 0.2) × 10 ⁹
C ₆ H ₅ CH ₂ Br	242–322	10.3 ± 0.4	1.3 ± 0.5	(2.4 ± 0.1) × 10 ⁹
(CH ₃) ₃ CBr	239–320	9.7 ± 0.1	0.85 ± 0.13	(1.1 ± 0.05) × 10 ⁹
CH ₃ (CH ₂) ₄ Br	220–303	9.3 ± 0.3	0.72 ± 0.35	(5.4 ± 0.1) × 10 ⁸
c-C ₆ H ₅ Br				(3.4 ± 0.6) × 10 ⁸
C ₆ H ₅ Br				(1.1 ± 0.8) × 10 ⁸
CCl ₄	219–307	10.2 ± 0.2	0.78 ± 0.24	(4.6 ± 0.8) × 10 ⁹
CH ₂ =CHCH ₂ Cl				(2.4 ± 0.5) × 10 ⁷
C ₆ H ₅ CH ₂ Cl	242–322	8.9 ± 0.4	2.1 ± 0.5	(2.0 ± 0.6) × 10 ⁷
(CH ₃) ₃ CCl	299–316	8.7 ± 0.5	3.2 ± 0.7	(2.5 ± 0.2) × 10 ⁶
CH ₃ (CH ₂) ₄ Cl				(3.1 ± 1.4) × 10 ⁵
C ₆ H ₅ Cl				(6.9 ± 0.2) × 10 ⁵ ^d
(CH ₃) ₃ CCl ^c	400–580	8.15	2.96	9.9 × 10 ⁵
(CH ₃) ₂ CHCl ^c	400–580	8.30	3.77	3.5 × 10 ⁵
CH ₃ (CH ₂) ₂ Cl ^c	400–580	7.90	3.46	2.4 × 10 ⁵
CH ₃ CH ₂ Cl ^c	317–399	7.99	3.81 ± 0.19	1.6 × 10 ⁵
CH ₃ Cl ^c	400–580	8.02	4.06	1.2 × 10 ⁵

^a All of our data which are summarized in this table were obtained by using benzil as the probe in di-*tert*-butyl peroxide-triethylsilane solvent. Errors correspond to 95% confidence limits. ^b Value calculated at 300 K from Arrhenius parameters when available. Otherwise value measured at 300 ± 3 K. ^c Data from ref 9 for chlorine atom abstractions by Me₃Si· radicals in the gas phase. The data for EtCl were obtained by comparing the rate of chlorine atom abstraction with the previously measured rate for the bimolecular self-reaction of Me₃Si· radicals. Data for the other chlorides were obtained by competitive experiments with EtCl. Our own results indicate that a recent suggestion⁵⁴ that the *A* factors used for these reactions were too high by ca. 0.6 log unit is incorrect. If anything, Cadman et al.'s⁹ *A* factors are too low, not too high. ^d Reaction is probably mainly addition of Et₃Si· to the aromatic ring. Supplementary data for this and other addition reactions will be presented in a later publication.

nium,^{4,16} tin,^{4,17–23} lead,^{4,18} phosphorus,^{24,25} chromium,^{21,26} cobalt,²⁷ vanadium,²⁸ tungsten,²⁹ and some other transition metals.³⁰

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Table II. Kinetic Data for Halogen Abstraction by Et₃Si· Radicals Calculated from Competitive Studies Reported in the Literature and the Absolute Rate Data for CCl₄ Given in Table I

substrate	T/K	log (A/M ⁻¹ s ⁻¹)	E/kcal mol ⁻¹	10 ⁻⁸ k/M ⁻¹ s ⁻¹		ref
				300 K	353 K	
CCl ₄	219–293	10.2	0.78	43	52	this work
CHCl ₃	353				4.5	5
CHCl ₃	273–423	9.23	1.14	2.5	3.3	12
CH ₂ Cl ₂	303–343	9.35	2.06	0.71	1.2	12
Cl ₃ CCCl ₃	353				33	5
Cl ₃ CCCl ₃	~295–450	10.39	1.07	41	53	15
Cl ₂ CHCCl ₃	353				28	5
Cl ₂ CHCCl ₃	~295–450	9.67	0.34	26	29	15
ClCH ₂ CCl ₃	353				14	5
CH ₃ CCl ₃	353				6.4	5
Cl ₂ CHCHCl ₂	~295–450	10.01	2.30	2.2	3.8	15
N≡CCCl ₃	323–348	10.81	1.19	88	118	12
CH ₃ (CH ₂) ₅ Br	297–398	8.95	0.95	1.8	2.3	12

Frequent use is made of dehalogenation by heteroatom-centered radicals in preparative organic chemistry and also to generate specific carbon-centered radicals for examination by EPR spectroscopy or for other purposes. Qualitative and even quantitative information regarding the relative reactivities of various organic halides toward specific heteroatom-centered radicals is quite extensive. However, there are comparatively few absolute rate constants for such reactions. Specifically, absolute rate data for trialkylsilyl radicals are restricted to a single gas-phase study of chlorine atom abstraction by the Me₃Si· radical from ethyl chloride.⁹ Competitive studies were also employed to extend this "absolute" rate data to cover methyl, *n*-propyl, isopropyl, and *tert*-butyl chlorides.⁹ A preliminary account of our own work on

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halogen abstraction by Et₃Si· radicals in solution has also appeared.³¹

In the preceding paper³² absolute rate constants were reported for the reaction of Et₃Si· radicals with carbonyl-containing compounds. The most striking feature of that data was the very large range in the reactivities of different types of carbonyl group. In the present work, we find an equally broad spread of reactivities of organic halides towards the Et₃Si· radical. Future papers from this laboratory will provide absolute rate data for some of the more important reactions of other silicon-centered and of other heteroatom-centered radicals.

Experimental Section

The experimental procedures were identical with those employed to study the addition of Et₃Si· radicals to carbonyl groups.³² The triethylsilyl radicals were again generated by laser flash photolysis of di-*tert*-butyl peroxide in the presence of triethylsilane. Rate constants for the reactions of Et₃Si· radicals with the organic halides were determined in di-*tert*-butyl peroxide-triethylsilane solvent by using benzil as the probe.³² The growth of the triethylsilyl-benzil adduct radical was monitored at its absorption maximum (380 nm). The reliability of this procedure was confirmed by monitoring the growth of the benzyl radical's absorption at 316 nm with benzyl bromide and benzyl chloride as substrates (*vide infra*). All error limits reported correspond to 95% confidence level and include only random errors.

Results

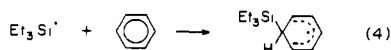
Rate constants at 300 K for the generalized reaction (3) are given in Table I for a wide variety of organic halides. Arrhenius



parameters are also given for a number of substrates. Full kinetic data are available as supplementary material. The measurements for 2-iodopropane were particularly difficult, apparently because of extensive substrate consumption upon laser excitation. The value given is based on only two measurements; no supplementary material is provided for this substrate. The gas-phase results of Cadman et al.⁹ on the reaction of Me₃Si· radicals with simple alkyl chlorides have been included in Table I both for comparative purposes and to provide a comprehensive listing of the rate data available for this class of reactions. Absolute rate data which can be derived by combining our results with the results of competitive experiments by others^{5,12,15} are listed in Table II.

The validity of the benzil probe method for measuring rate constants for halogen atom abstraction by Et₃Si· radicals was tested with benzyl bromide and chloride. Direct monitoring of the growth of the benzyl radical absorption after the laser flash gave, at 300 K, $k = (1.4 \pm 0.4) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $(1.0 \pm 0.4) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for the bromide and chloride, respectively. These values are in satisfactory agreement with the rate constants given in Table I, as are the Arrhenius parameters obtained by monitoring the formation of the PhCH₂ radical, i.e., activation energies of (2.1 ± 0.5) and (2.3 ± 0.4) kcal/mol and $\log(A/\text{M}^{-1} \text{ s}^{-1})$ values of (10.6 ± 0.4) and (8.7 ± 0.3) for benzyl bromide and chloride, respectively. A small systematic difference, leading to somewhat smaller rate constants in the direct measurements, is apparent. It seems likely that this difference reflects errors in the direct measurements, since it is necessary to monitor absorptions at wavelengths (316 nm) shorter than that used for excitation (337 nm), and at the shorter wavelength the samples are strongly absorbing.

EPR spectroscopic studies have shown that trialkylsilyl radicals readily add to aromatic compounds in solution to form cyclohexadienyl radicals,^{33,34} e.g., eq 4 For this particular reaction



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a rate constant of $\geq 10^5 \text{ M}^{-1} \text{ s}^{-1}$ at 298 K has been estimated from an EPR spectroscopic experiment.³⁵ Laser flash photolysis gave $k_4 = 4.6 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ at the same temperature.³⁶ For chlorobenzene the measured rate constant probably refers mainly to the addition rather than to the abstraction reaction.

Discussion

The trends in reactivity for halogen atom abstraction from RX by Et₃Si· radicals are, by and large, those which would be expected. That is, for a particular R group the rate constants decrease along the series X = I > Br > Cl > F, while for a particular X the rate constants decrease along the series R = allyl > benzyl > *tert*-alkyl (>*sec*-alkyl) > primary alkyl > cyclopropyl > phenyl. It should be noted that for iodides, for some bromides, and for some polychlorinated materials, the halogen abstraction occurs at a rate equal or close to the diffusion-controlled limit. This does not mean that the small differences observed in the rate constants and Arrhenius parameters for these substrates are without significance (*vide infra*). However, such differences must be interpreted with care—a fact that is all too often ignored by those who carry out competitive experiments without knowledge as to whether the absolute rates are, or are not, close to the diffusion-controlled limit.

Our results with tertiary and primary alkyl chlorides are in gratifyingly close agreement with the gas-phase data of Cadman et al.⁹ (see Table I). On the basis of our absolute rate data for CCl₄, the competitive experiments of Aloni et al.¹² involving CCl₄ and 1-bromopentane yield a result for the latter compound in reasonable agreement with that we obtain by direct measurement (*cf.* Tables I and II). With our CCl₄ results as a base, the rate constants calculated for the reactions of Et₃Si· radicals with CHCl₃, C₂Cl₆, and Cl₂HCCCl₃ at 353 K from the data of Nagai et al.⁵ are in satisfactory or excellent agreement with the rate constants that can be calculated on the same basis from the data of Aloni et al.^{12,15} (see Table II). The other results given in this Table are, therefore, probably fairly reliable.

The high reactivity of CCl₄ and other polychlorinated alkanes relative to the monochlorinated substrates (including benzyl chloride) cannot be entirely attributed to more favorable thermodynamic factors. That is, the very high silicon-chlorine bond strength, $D[\text{Me}_3\text{Si}-\text{Cl}] \approx 114 \text{ kcal/mol}$,³⁷ means that chlorine atom abstraction is highly exothermic not only for CCl₄, $D[\text{Cl}_3\text{C}-\text{Cl}] \approx 70 \text{ kcal/mol}$,³⁸⁻⁴¹ but also for the various monochlorinated compounds, e.g., $D[\text{Me}_3\text{C}-\text{Cl}] \approx 81 \text{ kcal/mol}$ ^{38,41} and $D[\text{C}_6\text{H}_5\text{CH}_2-\text{Cl}] \approx 69 \text{ kcal/mol}$.^{38,41} Thus, although the difference in the reactivities of *tert*-butyl chloride and benzyl chloride are due mainly to the difference in their activation energies (which arise from the different enthalpies of reaction), this is not the case for the difference in the reactivities of benzyl chloride and carbon tetrachloride. In fact, the rate constant for the Et₃Si· + CCl₄ reaction at 300 K is about 6 times greater than the preexponential factor for the Et₃Si· + C₆H₅CH₂Cl reaction. The high reactivity of CCl₄ is a consequence of its large Arrhenius preexponential factor, viz., $10^{10.2} \text{ M}^{-1} \text{ s}^{-1}$ vs. $10^{7.9-8.9} \text{ M}^{-1} \text{ s}^{-1}$ for the monochlorinated substrates (see Table I). Since the statistical effects which would operate if a simple atom-transfer mechanism is assumed can enhance the preexponential factor for CCl₄ relative to that for a monochlorinated substrate by no more than a factor of 4 ($\sim 10^{0.6}$), we are forced to conclude that other, nonstatistical, effects are considerably more important. Specifically, we attribute

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(40) A value of 73 kcal/mol has also been estimated for this bond strength.⁴¹

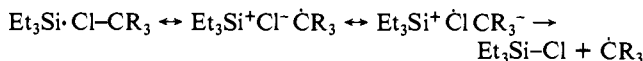
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Table III. Absolute Rate Constants for Some Halogen Atom Abstraction by Some Organometallic Radicals at ca. 300 K

substrate	Et ₃ Si ^a	<i>n</i> -Bu ₃ Sn ^b	Co ^{II} ^c	Cr ^{II} ^d	Rh ^{II} ^e
CH ₃ I	8.1 × 10 ⁹	2.5 × 10 ⁹	9.5 × 10 ⁻³	17 ^f	
C ₆ H ₅ CH ₂ Br	2.4 × 10 ⁹		2.3		2.5 × 10 ⁵
(CH ₃) ₃ CBr	1.1 × 10 ⁹	8.5 × 10 ⁷		9.6	5.0 × 10 ³ ^g
(CH ₃) ₃ CCl	2.5 × 10 ⁶	1.6 × 10 ⁴		4.8 × 10 ⁻²	
CH ₃ (CH ₂) _n Cl	3.1 × 10 ⁵	8.5 × 10 ²		1.7 × 10 ⁻³	

^a This work. ^b Reference 17. ^c Reference 27, reaction of pentacyanocobalt(II) in 1:4 (v/v) water:methanol. ^d Reference 26, reaction of ethylenediaminechromium(II) reagent (ethylenediamine/Cr(II) = 3) in aqueous dimethylformamide. ^e Reference 55, reaction of a mononuclear Rh^{II} rhodoxime, Rh(dmgh)₂PPh₃, in ethanol. ^f Value for *n*-butyl iodide. ^g Value for isopropyl bromide.

the high preexponential factor for CCl₄ to the greater importance of polar contributions to the transition state for this chlorine atom abstraction relative to chlorine abstractions from monochlorinated alkanes.^{42,43}



That is, the greater the electron affinity of the halogen atom donor, the greater will be the contribution that canonical structures with charge separation make to the transition state. It has long been recognized⁴² that polar contributions to the transition state enhance the reaction rate by reducing the activation energy. However, to our knowledge it has not heretofore been recognized that *polar* contributions to the transition state can also enhance the reaction rate by increasing the Arrhenius preexponential factor.⁴⁴ That is, the greater the polar contribution, the smaller will be the restriction on the orientation of the Et₃Si· radical with respect to the carbon-halogen bond being broken. Thus, if there was little or no polar contribution to the transition state, the reaction would probably occur only when the Si, Cl, and C atoms were colinear, or nearly so. A strong polar contribution to the transition state will relax this restriction. In the limiting case of complete electron transfer⁴³ the resultant ion pair would not be subject to any restriction in their relative rotational motion. This gain of two rotational degrees of freedom in the transition state would enhance the preexponential factor by ca. 10². The fact that the *A* factor for CCl₄ is about 2 orders of magnitude greater than that for monochlorinated alkanes means (even if there is some contribution from statistical factors) that electron transfer is extensive in the Et₃Si·/CCl₄ transition state.

In a similar way, the increase in reactivity for monohalogenated compounds along the series Cl < Br < I is due in large part to an increase in the preexponential factors⁴⁵ (see Table I), which we attribute to the increased importance of polar effects along this series. For some of the iodides the reaction may occur entirely by dissociative electron capture, the rate being limited only by diffusion.⁴⁶ Electron transfer is also known to play an important role in the reaction of triorganotin radicals with organic iodides.^{21,23} Nevertheless, all organic halides, including iodides, react more rapidly with triethylsilyl radicals than with trialkyltin radicals or any other organometallic radicals for which the rate constants have been measured (see Table III).

A series of reports during the last decade has shown that radicals generated from an optically active triorganosilane or -germane can yield products that are optically active and have retained the configuration of the starting compound.⁴⁷ Particularly relevant

(42) For general discussions of polar effects in radical reactions see: Russell, G. A. *Free Radicals* 1973, 1, 275-331. Minisci, F.; Citterio, A. *Adv. Free-Radical Chem.* 1980, 6, 65-153. See also ref 21 and 23.

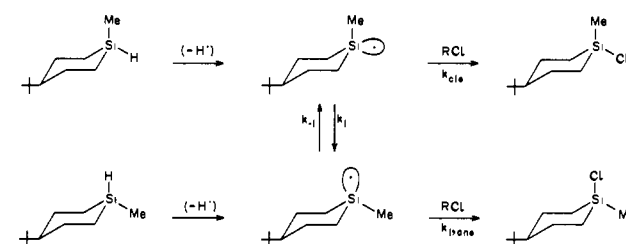
(43) For a review of the role of electron and charge transfer in organometallic chemistry see: Kochl, J. K. *Pure Appl. Chem.* 1980, 52, 571-605.

(44) Aloni et al.^{12,15} have pointed out that the reactivity trends in the chlorine-transfer reactions of Et₃Si· radicals with polychlorinated compounds (see Table II) appear to primarily reflect the variation in entropy of activation rather than in activation energies. However, the origin of this phenomenon was not commented upon.

(45) This may not, however, be true for the differences in the reactivities of monohalogenated compounds towards the tri-*n*-butyltin radical; see ref 18.

(46) A recent study indicates that the preexponential factors for electron-transfer reactions should be expected to be substantially higher than generally anticipated: Marcus, R. A. *Int. J. Chem. Kinet.* 1981, 13, 865-872.

Scheme I



to us is Sommer and Ulland's⁴⁸ study of the (1-naphthyl)-phenylmethylsilyl radical which, when generated from an optically active precursor, gave variable degrees of optical purity in the products, depending upon the concentration of CCl₄, the compound used as the silyl radical scavenger. Their experimental results have been presented in sufficient detail for us to recalculate the data from their Table II by using a Stern-Volmer type of approach, i.e., eq 5, where *k*_{inv} is the rate constant for inversion at

$$\frac{1}{\text{optical purity}} = \alpha + \alpha \frac{k_{\text{inv}}}{k_{\text{trap}}} \frac{1}{[\text{CCl}_4]} \quad (5)$$

the silicon center, *k*_{trap} is the trapping rate constant (corresponding to the reaction with CCl₄), and α is an arbitrary constant. The ratio of slope-to-intercept of a plot of (optical purity)⁻¹ vs. [CCl₄]⁻¹ yields *k*_{inv}/*k*_{trap} = (1.30 ± 0.13) M at the temperature of their experiment, viz, ca. 80 °C. If it can be assumed that the rate of reaction of triorganosilyl radicals with CCl₄ is insensitive to the detailed substitution at the silicon atom,⁴⁹ then combination of this data with our rate constant for CCl₄ at 80 °C yields *k*_{inv} = 6.8 × 10⁹ s⁻¹ at this temperature, corresponding to a half life for inversion of ca. 104 ps. To the best of our knowledge, this is the first rate constant ever reported for a radical rearrangement of this type. If one assumes that inversion at the silicon center will have a "normal" preexponential factor (i.e., ~10^{13.3} s⁻¹), then it is possible to estimate the activation barrier for the inversion process as ca. 5.6 kcal/mol, a surprisingly high value, that can be taken as an illustration of the strong preference of silicon for a pyramidal structure.

Some confirmation of the foregoing calculation of the rate of inversion of triorganosilyl radicals can be obtained from Sakurai and Murakami's⁵³ study of the free radical chlorination of isom-

(47) For a review on this problem see: Beckwith, A. L. J.; Ingold, K. U. "Rearrangements in Ground and Excited States"; deMayo, P., ed.; Academic Press: New York, 1980; Vol. 1, Essay #4.

(48) Sommer, L. H.; Ulland, L. A. *J. Org. Chem.* 1972, 37, 3878-3881.

(49) Since this reaction is close to diffusion controlled, it seems reasonable to expect it to be rather insensitive to substitution at the radical center. Further, aryl substitution is known not to introduce significant stabilization of silyl radicals⁵⁰ and has little or no effect on the rates of reaction of triorganosilanes with CCl₃ radicals,⁵¹ with *tert*-butoxy radicals,⁵² or with triplet ketones.⁵²

(50) Walsh, R. *Acc. Chem. Res.* 1981, 14, 246-252.

(51) Sommer, L. H.; Ulland, L. A. *J. Am. Chem. Soc.* 1972, 94, 3803-3806.

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

(53) Sakurai, H.; Murakami, M. *Bull. Chem. Soc. Jpn.* 1977, 50, 3384-3387.

(54) Davidson, I. M. T.; Matthews, J. I. *J. Chem. Soc., Faraday Trans. 1* 1981, 77, 2277-2280.

erically pure *cis*- and *trans*-1-methyl-4-*tert*-butyl-1-silacyclohexane (see Scheme I). Their experiments were carried out at 0 °C, and their product yields in CCl₄ and in CHCl₃ can be used to calculate the inversion rate constants k_1 and k_{-1} at this temperature with the assumption that the *cis*- and *trans*-silyl radicals react with the chlorinating agent at the same rate. That is, $k_{cis} = k_{trans} = 3.78 \times 10^9 \text{ M}^{-1}$ and $2.07 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for CCl₄ (see Table I) and CHCl₃ (see Table II), respectively, at 0 °C. The data tabulated by Sakurai and Murakami⁵³ yield $k_1 = 6.4 \times 10^9 \text{ s}^{-1}$ (CCl₄) and $11.5 \times 10^9 \text{ s}^{-1}$ (CHCl₃) and $k_{-1} = 2.9 \times 10^9 \text{ s}^{-1}$ (CCl₄) and $4.3 \times 10^9 \text{ s}^{-1}$ (CHCl₃). The two chlorinating solvents yield individual inversion rate constants k_1 and k_{-1} which are in good agreement. More importantly, these rate constants are in the same range as that calculated for the inversion of Sommer and Ulland's⁴⁸

(1-naphthyl)phenylmethylsilyl radical.

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Registry No. Et₃Si, 24669-77-0; (CH₃)₂CHI, 75-30-9; CH₃CH₂I, 75-03-6; CH₃I, 74-88-4; C₆H₅I, 591-50-4; CH₂=CHCH₂Br, 106-95-6; C₆H₅CH₂Br, 100-39-0; (CH₃)₃CBr, 507-19-7; CH₃(CH₂)₄Br, 110-53-2; *c*-C₃H₅Br, 4333-56-6; C₆H₅Br, 108-86-1; CCl₄, 56-23-5; CH₂=CHC-H₂Cl, 107-05-1; C₆H₅CH₂Cl, 100-44-7; (CH₃)₃CCl, 507-20-0; CH₃(C-H₂)₄Cl, 543-59-9; C₆H₅Cl, 108-90-7; C₆H₅CH₂F, 350-50-5; CHCl₃, 67-66-3; CH₂Cl₂, 75-09-2; Cl₃CCl₃, 67-72-1; Cl₂CHCCl₃, 76-01-7; ClC-H₂CCl₃, 630-20-6; CH₃CCl₃, 71-55-6; Cl₂CHCHCl₂, 79-34-5; N≡CC-Cl₃, 545-06-2.

Supplementary Material Available: Tables of absolute rate constants for reactions of triethylsilyl radical with alkyl and aryl halides (31 pages). Ordering information is given on any current masthead page.

(55) Espenson, J. H.; Tinner, U. *J. Organomet. Chem.* **1981**, *212*, C43-C46.

Intramolecular Charge-Transfer Absorption and Emission Resulting from Through-Bond Interaction in Bichromophoric Molecules

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Abstract: A series of molecules is studied (1-9 in Scheme I) that incorporate an electron-donor (D) and an electron-acceptor (A) chromophore connected by various alicyclic frameworks. The conformation of the latter prevents close approach of D and A. Nevertheless, intramolecular charge-transfer (CT) interaction between D and A is evident from the absorption and emission spectra for many of the molecules studied. It is concluded that the mode of interaction must be mainly of the through-bond type (TBI). The results indicate that under favorable circumstances such TBI leads to discrete intramolecular CT absorption and emission even if D and A are separated by as many as five σ bonds. It is proposed that TBI may be of significance in many bichromophoric molecules, the photophysical properties of which have heretofore only been discussed within the framework of through-space interactions (TSI). Finally the present results allow formulation of a tentative set of conditions that govern the appearance of a discrete optical transition due to TBI in bichromophoric molecules.

The photophysical properties of bichromophoric molecules containing two chromophores (M, M') connected by a saturated paraffinic moiety (e.g., M-(CH₂)_n-M') have been studied extensively.¹ In many cases the occurrence of intramolecular exciplex type emission^{1,2} or intramolecular charge-transfer (CT) absorption^{3,4} was reported. The mode of interaction between the chromophores responsible for these phenomena has largely, although not exclusively,^{5,6} been considered to be through-space interaction (TSI) and thus to be limited to molecules that adopt a "folded" conformation, which allows direct overlap between the chromophores in the ground or excited state.

In other fields of spectroscopy (e.g., photoelectron spectroscopy⁷), however, ubiquitous data have been collected to show the

possibility of interaction between two functional groups via limited⁸ arrays of σ bonds (i.e., through-bond interaction TBI) as theoretically predicted by Hoffmann et al.¹⁴ Although both TSI and TBI are expected^{14,15} to be conformation dependent, the latter is certainly not limited to "folded" conformations and thus provides a mode of intramolecular interaction in bichromophoric molecules adopting various "stretched" conformations as well as one that may add considerably to the overall interaction¹⁶ (i.e., TSI + TBI)

(8) TBI over three σ bonds has been studied most extensively.^{7,9} Significant interaction over four,^{10,11,12} five,¹² and even six σ bonds¹³ has, however, recently been detected by photoelectron spectroscopy.

(9) For a recent example of remarkably effective TBI over three bonds, see: Greenberg, A.; Liebman, J. F. *J. Am. Chem. Soc.* **1981**, *103*, 44-48.

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(12) Dougherty, D.; Brint, P.; McGlynn, S. P. *J. Am. Chem. Soc.* **1978**, *100*, 5597-5603.

(13) M. N. Paddon-Row, private communication.

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(15) Schoeller, W. W. *J. Chem. Soc., Perkin Trans. 2* **1979**, 366-368.

(16) Simultaneous operation of TSI and TBI in the enforced folded conformation of [*n,n*]paracyclophanes (*n* = 2, 3) was convincingly shown by Heilbronner et al.^{17,18}

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