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# Liquid-Phase Reactions of CCl<sub>3</sub> Radicals with Trimethylsilane and Triethylsilane

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The  $\gamma$ -radiation-induced chain reactions in liquid solution of silane (R'<sub>3</sub>SiH) in CCl<sub>4</sub>-c-C<sub>6</sub>H<sub>12</sub>(RH) mixtures were investigated over the temperature range 303-423 K for R' = Me and 335-423 K for R' = Et. In both systems the main products are R'<sub>3</sub>SiCl, CHCl<sub>3</sub>, and RCl. By kinetic analyses of product distribution, the rate constants of hydrogen abstraction from the two silanes by CCl<sub>3</sub> radicals were competitively determined vs. hydrogen abstraction from cyclohexane. The relative rate constants combined with the known Arrhenius parameters of the reference systems gave the following Arrhenius parameters for the reaction CCl<sub>3</sub> + R'<sub>3</sub>SiH  $\rightarrow$  CHCl<sub>3</sub> + R'<sub>3</sub>Si: log A<sub>4</sub> (L mol<sup>-1</sup> s<sup>-1</sup>) = 8.49 and E<sub>4</sub> = 8.70 kcal mol<sup>-1</sup> when R' = Me, and log A<sub>4</sub> = 8.62 and E<sub>4</sub> = 8.06 when R' = Et. These results indicate that alkyl-substituted silanes are considerably more reactive than Cl<sub>3</sub>SiH in the H-atom transfer reactions with CCl<sub>3</sub> radicals. This observation is rationalized in terms of the polar effects of the alkyl substituents.

# Introduction

Kinetic studies of hydrogen-transfer reactions of SiH compounds have been carried out until now mainly in the gas phase. In these studies Arrhenius parameters for H-atom transfer reactions of silane<sup>1-6</sup> and its deuterio-,<sup>4-7</sup> methyl-,<sup>1,2,7-9</sup> fluoro-, and chloro-substituted<sup>8,10-15</sup> derivatives with different radicals have been determined. Although a considerable body of valuable kinetic information has been accumulated as a result of these studies, the reactivity patterns revealed in the hydrogen-transfer reactions of SiH compounds are far less understood than the factors that govern the reactivity trends in the analogous, and more extensively studied, reactions of CH compounds. Because of experimental difficulties encountered in trying to study liquid-phase reactions over a wide temperature range, liquid-phase Arrhenius parameters of H-atom transfer reactions of silanes have not been determined to date. The radiolytic method is particularly suited to liquid-phase kinetic studies over a wide temperature range. This method has been previously employed in this laboratory in studies in which the Arrhenius parameters of Cl-atom abstraction by Cl<sub>3</sub>Si<sup>16</sup> and Et<sub>3</sub>Si<sup>17</sup> and of various other free radical reactions<sup>18</sup> were determined. In the present work this method has been utilized for the determination of the liquid-phase Arrhenius parameters of the H-atom transfer reactions between trimethylsilane and triethylsilane and the trichloromethyl radical.

# **Experimental Section**

Materials. Cyclohexane (Fisher, Research Grade) and  $CCl_4$  (BDH, Aristar) were used without further purification.  $Et_3SiH$  (PCR) was distilled and stored under nitrogen.  $Me_3SiH$  (PCR) was purified by trap-to-trap distillation. The purity of the two silanes, as determined by gas-chromatographic analysis, was better than 99.9%.

Procedure and Analyses. The 0.5-mL samples were degassed on a greaseless vacuum line. Me<sub>3</sub>SiH was in-

le<sub>3</sub>Sin was in- chain process.

troduced from a cold finger at ice temperature, and its pressure in a calibrated volume was measured with a pressure transducer (Dynasciences, Model P7D). The samples, held in a silicon oil bath in which the temperature was controlled to  $\pm 0.3$  °C, were then irradiated in a cobalt source.

Products were analyzed by gas chromatography using an FID detector. Me<sub>3</sub>SiH-containing mixtures were analyzed by using a 12-ft 20% silicon oil DC200 column. This column was initially held at 40 °C for the separation of Me<sub>3</sub>SiH, Me<sub>3</sub>SiCl, CHCl<sub>3</sub>, and c-C<sub>6</sub>H<sub>12</sub>. Subsequently the column temperature was raised to 100 °C and c-C<sub>6</sub>H<sub>11</sub>Cl was determined. Mixtures with Et<sub>3</sub>SiH were also analyzed on the DC-200 column at 40 °C. In addition, these mixtures were analyzed on a 12-ft 20% Ucon LB 550 column at 100 °C, which was used for the separation of c-C<sub>6</sub>H<sub>11</sub>Cl from Et<sub>3</sub>SiCl.

# **Results and Discussion**

**Products.** The main products of the radiolysis of  $Me_3SiH-CCl_4-c-C_6H_{12}(RH)$  mixtures are  $Me_3SiCl$ , CHCl<sub>3</sub>, and  $c-C_6H_{11}Cl(RCl)$ . The rates of formation of these products at various temperatures are listed in Table I. In the Et<sub>3</sub>SiH-CCl<sub>4</sub>-RH system, Et<sub>3</sub>SiCl, CHCl<sub>3</sub>, and RCl are the main products, and their rates of formation are listed in Table II. The average values of  $(R_{RCl} + R_{Me_3SiCl})/R_{CHCl_3}$  and of  $(R_{RCl} + R_{Et_3SiCl})/R_{CHCl_3}$  derived from the results shown in Tables I and II are  $1.01 \pm 0.08(2\sigma)$  and  $0.99 \pm 0.10$ , respectively. These results indicate that the material balance relations

$$R_{\rm RCl} + R_{\rm Me_{\circ}SiCl} = R_{\rm CHCl_{\circ}} \tag{1}$$

$$R_{\rm RCl} + R_{\rm Et_3SiCl} = R_{\rm CHCl_3} \tag{2}$$

are observed. The radiolytic yields of all the three products, G values, were high and characteristic of a free radical chain process.

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TABLE I: Rates of Formation (mol  $L^{-1}$  min<sup>-1</sup>) of Main Products in the Radiolysis of Me<sub>3</sub>SiH-CCl<sub>4</sub>-c-C<sub>6</sub>H<sub>12</sub>(RH) Mixtures

		[Me_SiH].		· · · · · · · · · · · · · · · · · · ·	<u></u>			
 <i>T</i> , K	time, min	mM	$10^4 R_{\mathrm{Me}_3\mathrm{SiCl}}$	$10^4 R_{\text{CHCl}_3}$	$10^4 R_{\rm RCl}$	G(RCl)	$k_4/k_5$	
323	60	60 <sup>a</sup>	0.743	1.36	0.655	51.8	39.7	
	60	$100^a$	1.17	1.82	0.567	44.9	38.3	
	140	$100^{a}$	1.42	1.89	0.705	55.8	41.3	
	60	$100^{b}$	0.970	2.30	1.33	97.8	34.8	
	140	$100^{b}$	0.936	2,33	1.41	104	32.9	
	60	1506	1,50	2.77	1.19	87.5	40.0	
	140	$100^{c}$	0.771	2.58	1.77	155	34.1	
348	85	$32^a$	0.855	2.80	1.86	147	30.0	
	85	$60^a$	1.34	2.85	1.53	121	29.9	
	40	$100^{a}$	2.36	3.65	1.51	119	30.3	
	40	100	2.10	5.45	3.68	271	27.5	
	85	100	2.08	5.68	3.61	265	29.2	
	40	1500	3.08	6.35	3.50	257	28.3	
	40	$100^{c}$	1.98	7.25	5.00	439	30.4	
	85	$100^{c}$	1.59	6.30	4.79	420	26.3	
373	<b>26</b>	$100^{a}$	3.57	6,19	3.09	<b>244</b>	22.3	
	20	100	3.69	11.5	7.95	585	22.2	
	20	100 <sup>b</sup>	4.21	12.0	7.80	574	26.0	
	26	1006	3.33	9.96	6.58	484	24.4	
	20	$100^{c}$	3.52	14.1	10.4	912	26.1	
	20	$100^{c}$	3.45	14.0	10.6	930	24.9	
	26	$100^{c}$	2.32	9.69	7.31	841	24.2	
398	33	$60^a$	4.52	11.0	6.67	527	23.8	
	16	$100^{a}$	10.0	18.9	8.38	663	24.0	
	33	$100^{a}$	10.2	18.8	9.90	783	22.8	
	16	100 <sup>b</sup>	6.30	26.3	5.27	388	17.1	
	16	$150^{b}$	9.75	29.2	8.4	1352	17.2	
	16	$100^{c}$	6.31	31.9	24.6	2158	20.0	
	33	$100^{c}$	5.15	26.3	21.1	1851	19.8	
423	25	$60^a$	6.08	19.3	13.5	1068	15.9	
	25	$100^{a}$	13.2	32.6	18.0	1424	16.3	
	14	$100^{b}$	9.00	<b>44.6</b>	34.0	2500	13.7	
	25	$100^{b}$	8.76	47.6	36.4	2676	12.5	
	14	$150^{b}$	10.8	35.7	24.5	1801	14.3	
	14	$100^{c}$	10.1	63.3	51.8	4544	15.5	
	34	$100^{c}$	9.53	63.5	57.1	5008	14.7	

<sup>a</sup>  $[c-C_6H_{12}] = 1.85 \text{ M}, [CCl_4] = 8.29 \text{ M}.$  <sup>b</sup>  $[c-C_6H_{12}] = 4.63 \text{ M}, [CCl_4] = 5.18 \text{ M}.$  <sup>c</sup>  $[c-C_6H_{12}] = 7.40 \text{ M}, [CCl_4] = 2.07 \text{ M}.$ 

TABLE II:	Rates of Formation (	mol L <sup>-1</sup> min <sup>-1</sup>	) of Main Products in the	Radiolysis of Et₃SiH·	-CCl <sub>4</sub> -c-C <sub>6</sub> H <sub>12</sub> (RH) Mixtures
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<i>T</i> , K	time, min	[Et <sub>3</sub> SiH], mM	$10^4 R_{\mathrm{Et}_3\mathrm{SiCl}}$	R <sub>CHCl<sub>3</sub></sub>	R <sub>RCl</sub>	$G(\mathbf{RCl})$	$k_4/k_5$
335	95	$62.8^{a}$	1.85	2.77	1.05	83	60.7
		$94.2^{b}$	2.61	4.78	2.57	189	57.3
		$62.8^{b}$	1.87	4.87	2.77	<b>204</b>	58.0
		$62.8^{c}$	1.27	4.29	2.79	245	59.2
348	45	$62.8^{a}$	2.84	4.88	1.69	134	55.6
		$94.2^{b}$	3.73	7.87	3.69	271	54.4
	,	$62.8^{b}$	2.56	6.56	3.76	276	55.2
		$62.8^{c}$	1.86	6.60	4.73	415	49.4
373	35	$62.8^{a}$	4.77	8.11	3.80	300	42.5
		$94.2^{b}$	4.20	9.11	5.00	368	44.8
		$62.8^{b}$	4,60	14.6	9.34	687	41.6
		$62.8^{c}$	4.02	17.0	12.7	1114	44.2
388	33	$62.8^{a}$	6,61	12.0	6.61	523	35.6
		$94.2^{b}$	9.52	27.9	16.1	1184	34.9
		$62.8^{b}$	6.61	24.9	18.1	1330	32.5
		$62.8^{c}$	5.70	27.5	21.1	1851	37.6
413	18	$62.8^{a}$	11.9	25.4	15.4	1218	27.4
		$94.2^{b}$	16.8	53.7	34.5	2537	28.5
		62.8 <sup>b</sup>	12.6	53.5	43.2	3176	26.3
		$62.8^{c}$	8.78	57.7	45.7	4008	26.2
423	12	$62.8^{a}$	15.4	39.5	23.9	1890	22.2
		$94.2^{o}_{h}$	22.3	78.8	55.0	4044	23.1
		62.8°	18.0	86.7	73.2	5382	21.9
		$62.8^{c}$	12.3	87.1	74.2	6508	22.0

<sup>a</sup>  $[c-C_6H_{12}] = 1.85 \text{ M}, [CCl_4] = 8.29 \text{ M}.$  <sup>b</sup>  $[c-C_6H_{12}] = 4.63 \text{ M}, [CCl_4] = 5.18 \text{ M}.$  <sup>c</sup>  $[c-C_6H_{12}] = 7.40 \text{ M}, [CCl_4] = 2.07 \text{ M}.$ 

*Kinetics and Mechanism.* When a long free radical chain reaction is initiated by ionizing radiation, various reactive species, ions, "hot" fragments and atoms and excited molecules are formed. It is not important to know the exact nature of the initiation process, since the fate of these reactive species is to end up as neutral ground-

state molecules or as atoms and free radicals. These atoms and radicals propagate the chain process by reacting with the solvent. Accordingly, in  $CCl_4$ -RH mixtures the initiation can be schematically described by eq 3. The

$$CCl_4 + RH \rightarrow CCl_3 + R + products$$
 (3)



Figure 1. Variation of  $R_{\text{Me}_3\text{SiCl}}/R_{\text{c-C}_8\text{H}_1,\text{Cl}}$  with  $[\text{Me}_3\text{SiH}]_{\text{av}}/[\text{c-C}_8\text{H}_{12}]$ .

propagation step of the  $\gamma$ -radiation-induced radical chain process in Me<sub>3</sub>SiH and Et<sub>3</sub>SiH (R'<sub>3</sub>SiH) solutions can be described in terms of the following reaction scheme:

 $CCl_3 + R'_3SiH \rightarrow CHCl_3 + R'_3Si$  (4)

$$CCl_3 + RH \rightarrow CHCl_3 + R \tag{5}$$

$$\mathbf{R'}_{3}\mathbf{Si} + \mathbf{CCl}_{4} \to \mathbf{R'}_{3}\mathbf{SiCl} + \mathbf{CCl}_{3} \tag{6}$$

$$R + CCl_4 \rightarrow RCl + CCl_3 \tag{7}$$

Implied in this mechanism is the assumption that under our experimental conditions, where  $[CCl_4] \gg [R'_3SiH]$ , cyclohexyl radicals react only with  $CCl_4$ , and the hydrogen-transfer reaction

$$R + R'_{3}SiH \rightarrow RH + R'_{3}Si \qquad (8)$$

does not occur. This assumption is based on the fact that at 423 K reaction 7 is faster than hydrogen abstraction from Me<sub>3</sub>SiH by methyl radicals. The data of Katz et al.<sup>19</sup> yield a value of  $2.3 \times 10^6$  for  $k_7$ , whereas the rate constant for hydrogen abstraction by methyl radicals obtained from the Arrhenium parameters determined by Berkley and co-workers<sup>7</sup> is  $2.49 \times 10^4$  L mol<sup>-1</sup> s<sup>-1</sup> at this temperature. Hydrogen abstraction by methyl radicals is considerably more exothermic than the abstraction by cyclohexyl radicals since  $D(CH_3-H)^{20} = 104$  kcal mol<sup>-1</sup> while  $D(c-C_6H_{11}-H)$  has been recently estimated as being  $94.9^{21}$  and  $95.5^{22}$  kcal mol<sup>-1</sup>. Therefore, when  $R = c-C_6H_{11}$ , reaction 8 can be expected to be slower than when R = Me. Furthermore, in terms of the previously outlined mechanism, and provided that reaction 8 does not take place, the following relation should be obeyed:

$$R_{\text{R'}_{3}\text{SiCl}}/R_{\text{RCl}} = k_{5}[\text{R'}_{3}\text{SiH}]_{\text{av}}/k_{4}[\text{RH}]$$
(9)

The experimental results fit this equation as can be seen from Figures 1 and 2, in which plots of  $R_{\text{MegSiCl}}/R_{\text{RCl}}$  vs. [Me<sub>3</sub>SiH]/[RH] and of  $R_{\text{Et_SiCl}}/R_{\text{RCl}}$  vs. [Et<sub>3</sub>SiH]/[RH] are respectively shown. The good linear plots, which in most cases pass through the origin, lend further support to the assumption that reaction 8 can be neglected in the two systems.

Arrhenius Parameters. Expression 9 can be used to derive the rate constant ratio  $k_4/k_5$  from the experimentally determined rates of formation,  $R_{\rm R'_3SiCl}$  and  $R_{\rm RCl}$ . The  $k_4/k_5$  values thus obtained are summarized in Tables I and



Figure 2. Plot of  $R_{\text{Et_3SICI}}/R_{\text{c-C_6H_{11}CI}}$  vs.  $[\text{Et_3SIH}]_{av}/[\text{c-C_6H_{12}}]$ .



Figure 3. Arrhenius plots of  $k_4/k_5$ .

II. A least-squares treatment of these values yields the following Arrhenius expressions

$$Me_{3}SiH: log k_{4}/k_{5} = [(-0.304 \pm 0.150) + (2.38 \pm 0.27)]/\theta$$
(10)

Et<sub>3</sub>SiH:  
log 
$$k_4/k_5 = [(-0.170 \pm 0.250) + (3.02 \pm 0.25)]/\theta$$
 (11)

where the error limits are two standard deviations and  $\theta$  = 2.303*RT* in kcal mol<sup>-1</sup>. The corresponding Arrhenius plots of average values of  $k_4/k_5$  are shown in Figure 3. The Arrhenius parameters of H-atom transfer from liquid cyclohexane to the trichloromethyl radical determined by Katz and co-workers<sup>23</sup> are log  $A_4$  (L mol<sup>-1</sup> s<sup>-1</sup>) = 8.79 and  $E_4 = 11.08$  kcal mol<sup>-1</sup>. Upon substitution of these Arrhenius parameters into expressions 10 and 11, the absolute Arrhenius parameters for hydrogen abstraction from Me<sub>3</sub>SiH and Et<sub>3</sub>SiH listed in Table III are obtained.

Reactivity Patterns. The factors governing the reactivity of SiH compounds in their free radical hydrogen-transfer reactions can best be seen by comparing the results obtained in studies in which the effect of the attacking radical and the structure of the substrate on reactivity have been determined. This comparison can be carried out by using the data of Table III in which are summarized the results of this work together with relevant data available in the literature. It should be emphasized

TABLE III: Arrhenius Parameters and Rate Constants for H-Transfer Reactions of SiH Compounds

				log	
				k(400	
radical	substrate	$\log A^e$	$E^{f}$	K) <sup>g</sup>	ref
CCl <sub>3</sub>	Cl <sub>3</sub> SiH	8.21	9.02	3.28	14
	Me SiH	8.49	8.70	3.74	а
	Et <sub>3</sub> SiH	8.62	8.06	4.22	a
CF,CCl,	Cl <sub>3</sub> SiH	7.84	8.35	3.28	14
CH <sub>3</sub>	SiH₄	8.89	6.98	5.08	b
-	SiH	8.90	7.00	5.08	с
	Me <sub>3</sub> SiH	8.10	7.21	4.16	b
	Me SiH	8.31	7.80	4.05	с
	Cl <sub>3</sub> SiH	10.41	8.48	5.78	8
	Cl <sub>3</sub> SiH	7.84	4.32	5.48	11
	F <sub>3</sub> SiH	9.21	8.43	4.60	9
$CF_3$	SiH₄	8.97	5.11	6.18	b
	Me <sub>3</sub> SiH	9,28	5.58	6.23	2
	Cl <sub>3</sub> SiH	8.81	6,20	5.42	b

<sup>a</sup> This work. <sup>b</sup> Best value from ref 24. <sup>c</sup> Best value from ref 25. d Notice the difference between the "best values" taken from the two compilations<sup>24,25</sup> which are based on slightly different treatment of the same experimental data.  ${}^{e}A$  is in units of L mol<sup>-1</sup> s<sup>-1</sup>. of kcal mol<sup>-1</sup>.  ${}^{g}k$  is in units of L mol<sup>-1</sup> s<sup>-1</sup>. f E is in units

here that it is generally not legitimate to compare liquidphase and gas-phase kinetic data which do not take into consideration phase effects. However, as has been shown by Patrick,<sup>26</sup> this approach is completely justified for bimolecular reactions that do not involve a change in the number of molecules and that take place in nonpolar liquids. The Arrhenius parameters derived in the present study were determined in nonpolar liquid systems. Therefore their values can be assumed to be equal to the values expected for identical gas-phase reactions.

Previous interpretations of reactivity trends in Htransfer reactions of silanes in terms of enthalpy and polar effects were seriously hindered by the absence of reliable bond dissociation data. The uncertainties in bond dissociation energies of silanes have been removed by the recent determination of Potzinger, Ritter, and Krause<sup>27</sup> and of Walsh and co-workers.<sup>28-31</sup> The appearance potential measurements of Potzinger et al.<sup>27</sup> yield the following BDE values:  $D(Me_3Si-H) = 89$ ,  $D(Cl_3Si-H) = 91.7$ , and  $D-(H_3Si-H) = 91$  kcal mol<sup>-1</sup>. Walsh and co-workers, using the kinetic iodination technique of BDE determination, devised by Benson,<sup>32</sup> have obtained for Me<sub>3</sub>SiH,<sup>26</sup> Cl<sub>3</sub>SiH<sup>29</sup> and  $F_3$ SiH,<sup>30</sup> and  $H_3$ Si-H<sup>31</sup> D(Si-H) values of 90, 91.2, and 100<sup>30</sup> kcal mol<sup>-1</sup>, respectively. This new set of bond dissociation data brings together the bond dissociation energies in Me<sub>3</sub>SiH, Cl<sub>3</sub>SiH, and SiH<sub>4</sub> and seems to indicate that the reactivity trends in H-atom transfer reactions of silanes cannot be rationalized solely in terms of the overall enthalpy changes.

Turning now to hydrogen-abstraction reactions of CCl<sub>3</sub> radicals with Cl<sub>3</sub>SiH and Me<sub>3</sub>SiH, it can be seen that these reactions proceed less readily than the reactions of both  $CH_3$  and  $CF_3$  radicals with these substrates. The order of reactivity parallels the C-H bond dissociation energies in  $CF_3H$ ,  $CH_4$ , and  $CHCl_3$  that are equal to 106, 104, and 96 kcal mol<sup>-1</sup>, respectively.<sup>33</sup> However the observation that  $E_{abs}(Me_3SiH) < E_{abs}(Cl_3SiH)$  when attacked by  $CCl_3$  and  $CF_3$  radicals cannot be explained by a difference in SiH bond dissociation energies in the two silanes since, as we have seen before, they are almost equal.

The higher reactivity of  $Me_3SiH$  can be rationalized in terms of polar effects. The attack of the electrophilic CCl<sub>3</sub> radical on the Si-H bond can be expected to be affected by the electron density on the hydrogen atom which is in turn influenced by the polar properties of the other substituents. Thus the electron-withdrawing Cl atoms in Cl<sub>3</sub>SiH reduce this electron density and increase the activation energy for hydrogen abstraction. According to Bell and Zucker<sup>34</sup> this effect is less pronounced than expected because of  $d\pi \leftarrow p\pi$  bonding which to some extent offsets the inductive effect of the Cl atoms. On the other hand alkyl radicals exert an opposite effect on the electron density of the Si-H bond. In the case of alkyl substitution, the inductive effect increases the electron density at the Si-H bond and at the same time increases the reactivity of this bond to an attack by electrophilic radicals. Further support for this conclusion is provided by the observation that Et<sub>3</sub>SiH is more reactive than Me<sub>3</sub>SiH toward attack by CCl<sub>3</sub> radicals. This order of reactivity is in line with the  $\sigma_{\rm I}$  Taft values of Et and Me radicals of -0.055 and -0.046, respectively.<sup>35</sup>

It should be stressed that in most cases a clear-cut separation between enthalpic and polar factors is not possible. A typical example of this situation is provided by the reactions of  $CH_3$  with  $F_3SiH$  and  $Cl_3SiH$ . The lower reactivity of F<sub>3</sub>SiH (see Table III) can be attributed to a lesser degree of  $d\pi \leftarrow p\pi$  bonding. A recent determination by Doncaster and Walsh<sup>33</sup> gives a  $D(F_3Si-H)$  value of 100 kcal mol<sup>-1</sup>, which is higher by 9 kcal than  $D(Cl_3Si-H)$ . One could therefore argue that, as expected, the more exothermic reaction with Cl<sub>3</sub>SiH requires a lower activation energy than the reaction with  $F_3SiH$ . In other words, the lower reactivity of F<sub>3</sub>SiH can be explained equally well in terms of the overall enthalpy change or the polar effects.

In conclusion, it appears that both polar and enthalpic effects are important in hydrogen-transfer reactions of SiH compounds. However, considerably more kinetic and thermochemical information is required in order to discern a pattern in the results. Particularly important in this respect is the need to ascertain the effect of various substituents on the strength of the Si-H bond and on the electron density in this bond.

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# Kinetics of Solute Excited-State Formation in the Pulse Radiolysis of Liquid Alkanes. Comparison between Theory and Experiment<sup>1</sup>

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The theoretical treatment of Rzad for calculating the kinetics of excited-state production is modified to allow for a change in mobility of the positive ion upon scavenging by the solute. Calculated and experimental results in the case of cyclohexane containing various concentrations of 9,10-diphenylanthracene (DPA) or p-terphenyl (PT) are compared, and significant discrepancies are found. Although no conclusions are reached, possible reasons for the disagreement are examined.

# Introduction

The investigation of fluorescence from excited states of scintillators dissolved in liquid alkanes, using pulseradiolysis techniques, should provide an excellent method of testing theories of recombination of geminate ion pairs. A theoretical treatment by Rzad<sup>2</sup> did not allow for the fact that some solvents (e.g., cyclohexane) exhibit high-mobility positive ions,<sup>3</sup> but reasonably good agreement with experimental observation of excited-state fluorescence as a function of time was obtained for nanosecond (ca. 5-ns pulses) pulse radiolysis of biphenyl, naphthalene, or anthracene in cyclohexane. A subsequent treatment in which the concentration vs. time profiles for solute positive and negative ions were calculated by Infelta and Rzad<sup>4</sup> took into account the possibility of a high mobility of the solvent positive ion (hole), which was found to be necessary to unify the description of steady-state and pulse-radiolysis experiments, and general agreement was obtained with the experimental observations of Beck and Thomas<sup>5</sup> on the kinetics of the negative ion of biphenyl (in cyclohexane) following a 45-ps (fwhm) pulse.

Comparison of theory with experiment has until now not been attempted in the case of experimental studies of solute fluorescence following picosecond pulse radiolysis with time resolution in the range of 100 ps or better.<sup>5–8</sup> The interpretation of experimental data on solute fluorescence vs. time in terms of production of excited states by geminate recombination reactions, i.e.

$$e^- + S^+ \to S^* \tag{1}$$

$$S^- + RH^+ \rightarrow S^*$$
 (2)

$$S^- + S^+ \to S^* \tag{3}$$

where S represents the solute molecule, e<sup>-</sup> the electron,  $\mathbf{R}\mathbf{H}^{+}$  the positive ion of the alkane solvent, and  $\mathbf{S}^{*}$  the singlet and triplet excited scintillator molecules, must take into account the possibility that the fluorescing state of the solute may also be produced via excited solvent molecules. The importance of such an energy-transfer process should, however, be discernible on the basis of the dependence of fluorescence kinetics on [S]. However, agreement on the interpretation of results related to this point is lacking.<sup>5,7,8</sup>

# **Theoretical Treatment and Method of Calculation**

The treatment following is an extension of the work of Rzad<sup>2</sup> and includes the possibility that the mobility of the positive ion changes upon scavenging by the solute. The treatment presented here also allows the effects of additional electron or positive ion scavengers to be included.

A basic premise of the theoretical treatment<sup>2</sup> is that the lifetime distribution function for the e<sup>-</sup>···RH<sup>+</sup> geminate ion pairs is given by eq I, in which  $\lambda$  is a constant (di-

$$\mathbf{f}(t) = \lambda \{ (\pi \lambda t)^{-1/2} - \exp(\lambda t) \operatorname{erfc}[(\lambda t)^{1/2}] \}$$
(I)

mension  $s^{-1}$ ). f(t) is the fraction of ions which recombine between t and t + dt. (The error function complement of x, erfc(x), is 1 - erf(x), where  $erf(x) = 2(\pi)^{-1/2} \int_0^x exp$ .  $(-u^2)$  du.) Equation I is based on experimental studies of the effects of charge scavengers on product formation. Scavenging of e<sup>-</sup> or RH<sup>+</sup> is assumed to lengthen the recombination time in proportion to the ratio of the mutual mobility of an ion pair before scavenging to that after scavenging (specified by  $r_{\rm D}$ ); i.e., if the lifetime of the e<sup>-</sup> -  $RH^+$  pair is t, and the scavenging reaction occurs at t', the new lifetime of the ion pair is  $t'' = t' + (t - t')r_{\rm D}$ .

It is clear that if both e<sup>-</sup> and RH<sup>+</sup> have different mobilities than  $S^-$  and  $S^+$ , respectively, the lifetime of the geminate pair can change twice, i.e., once upon scavenging of each ion, and that four different values of  $r_{\rm D}$  must be considered.

In addition to reactions 1–3, we allow for the possibility of formation of excited S through

$$S^- + B^+ \to S^* \tag{4}$$

$$S^+ + A^- \to S^* \tag{5}$$

where  $A^{-}$  and  $B^{+}$  represent the ions of scavengers present in addition to S. The probabilities for reactions 1-5 of