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FREE RADICAL DICHLOROVINYLATION OF TRIETHYLSILANE BY TRICHLOROETHYLENE

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Summary

The free radical γ-radiation induced reactions in solutions of trichloroethylene in triethylsilane were investigated at 65°C. The main products, formed by a chain mechanism are *cis*- and *trans*-dichloroethylene, triethylchlorosilane, dichlorovinyltriethylsilane ($Et_3SiCH{=}CCl_2$) and hydrogen chloride. The results are interpreted in terms of a mechanism in which Et_3SiCl is formed by direct chlorine abstraction from C_2Cl_3H by the $Et_3Si^\cdot$ radical. $Et_3SiCH{=}CCl_2$ is formed via a two step mechanism addition of an $Et_3Si^\cdot$ radical to C_2Cl_3H being followed by unimolecular chlorine elimination. Product distribution in the Et_3SiH/C_2Cl_3H system and in competitive experiments in the presence of chloroform and 1-bromopentane was used for the estimation of relevant rate constants ratios.

Introduction

Free radical addition of silyl radicals to olefins was first reported by Sommer and coworkers [1]. They employed both peroxide decomposition and UV photolysis for the initiation of the chain addition of trichlorosilane to 1-octene. Subsequently, these and other methods of initiation of free radical hydrosilylation of olefinic compounds were employed, and numerous systems were investigated [2,3]. However, despite the large number of systems investigated kinetic data related to the addition of silyl radicals to olefins are still very limited. Recently Choo and Gaspar [4] determined the rate of addition of trimethylsilyl radicals to ethylene using the flash photolysis ESR combination. The rate of disilanyl radical addition to ethylene was estimated by Pollock et al. from their steady-state photolytic experiments [5]. Addition of silyl radicals to olefins is considerably faster than that of alkyl radicals. In order to explain the greater reactivity of silyl radicals, stabilization of the β adduct radicals by electronic interaction between the silicon and the radical center [6,7] and formation of bridged radicals [8] have been suggested.

In early studies of the pyrolysis of mixtures of trichlorosilane and trichloroethylene, dichlorovinyltrichlorosilane was found to be the main product [9—11]. However, further studies were not carried out, and so the controversy about the mechanism of this interesting reaction and the structure of the products has yet to be resolved. The present study of the reactions between silyl radicals and chloroolefins was initiated in an attempt to obtain further information on the mechanism and kinetics of this type of reaction, especially in view of the major importance of free radical additions of silyl hydrides to olefins in the synthesis of organosilicon compounds. The kinetics and mechanism of the analogous reaction of alkyl radicals with chloroethylenes was previously studied by Schmerling and West [12], Rust and Bell [13], Hardwick [14], Tanner et al. [15] and by us [16], and seems now to be well established. It appeared to us therefore, that a comparison of the kinetic data obtained for the silyl and alkyl radicals could be of assistance in the elucidation of the mechanism of silyl radical reactions with chloroolefins.

In the present work we report the results of the study of the liquid phase reaction between radiolytically-generated triethylsilyl radicals and trichloroethylene dissolved in triethylsilane. Radiolytic initiation of liquid phase free radical chain reactions of silanes has so far been used in very few studies [17]. This method of initiation, previously employed by us to generate Cl_3Si [18] and Et_3Si [19] radicals, offers several advantages over more conventional methods.

Experimental

Materials

Trichloroethylene (B.D.H.) contained 0.5% of an impurity that was inert under the experimental conditions, and therefore was used without further purification. Triethylsilane (P.C.R.) was vacuum distilled in a nitrogen atmosphere and found to contain 0.3% of an inert impurity. 1-Bromopentane (Fluka, purum) and chloroform (Frutarom, Analar) were used as received. Cyclohexene (Phillips, Research Grade) was used as received.

Procedure and analysis

Liquid samples were degassed in a greaseless vacuum line, and then placed in a temperature-controlled Silicone Oil bath kept at 65 ± 0.5°C and irradiated with a ^{60}Co source (γ cell 200, Atomic Energy of Canada) at a dose rate of 6.5×10^{16} eV ml^{-1} min^{-1}. A temperature programmable gas chromatograph (HP 5750) equipped with FI detector and 1/8" × 6 ft. column packed with 20% Silicone Oil DC 200 on Chromosorb W was used for product separation and analysis.

Samples frozen at liquid nitrogen temperature were opened under a layer of water, allowed to melt and shaken well. Subsequently, the aqueous layers were separated and coulometrically analyzed for hydrogen chloride with the Aminco—Cotlove chloride titrator. The organic layer was then analyzed by GLC and product yields were found to be the same as in identical samples which had not been subjected to the HCl extraction procedure. Blank experiments with Et_3SiCl solutions in Et_3SiH showed that over the time required for separation of HCl (5 min), Et_3SiCl hydrolysis is negligible.

Product identification

Commercially available materials were used for the GLC identification of all products except dichlorovinyltriethylsilane ($Et_3SiCH{=}CCl_2$). The latter was synthesized radiolytically by a 44 h irradiation of 10 ml of a 2.2 *M* solution of C_2Cl_3H in Et_3SiH. The irradiated solution was then concentrated by distillation of the reactants and 97.5% pure $Et_3SiCH{=}CCl_2$ was obtained from the residue by preparative GLC using a 1/4 in. × 6 ft. glass column filled with Silicone Oil DC-200 and kept at 110° C. A chlorine content of 31.5% was found for this product (calcd. 33% for $Et_3SiCH{=}CCl_2$ and 42.7% for $Et_3SiCHClCCl_2H$).

The assignment of the structure $Et_3SiCH{=}CCl_2$ to this product was confirmed by mass spectroscopy, NMR and IR data. The mass spectrometric analyses showed the presence of two Cl atoms and an Et_3Si group. The presence of this group was further verified by the NMR spectrum. In addition, the NMR spectrum with a singlet at δ 5.30 ppm and IR absorption at 2950 and 1575 cm^{-1} clearly pointed to the presence of a C=C group bearing a hydrogen atom.

Results

The main products of radiolysis of C_2Cl_3H solutions in Et_3SiH are *trans*- and *cis*-dichloroethylene, triethylchlorosilane, dichlorovinyltriethylsilane and hydrogen chloride. Small amounts of vinylidene chloride are also formed. An additional product that could not be isolated because of its small yield was also detected. From its retention time the structure $Et_3SiCHClCCl_2H$ was tentatively assigned to it.

The effects of irradiation time (Table 1) and trichloroethylene concentration

$$[CH_2{=}CCl_2] + [cis\text{-}CHCl{=}CHCl] + [trans\text{-}CHCl{=}CHCl] = [Et_3SiCl] \qquad (A)$$

$$[Et_3SiCH{=}CCl_2] = [HCl] \qquad (B)$$

(Table 2) were studied. The results show that the material balance relationships (A) and (B) hold. The fact that relation B is obeyed gives further support to the structure assigned to the Et_3Si-substituted chloroethylene. It can also be seen that the three dichloroethylenes are formed at constant yield ratios, although the scatter in the case of vinylidene chloride is relatively large because of its low yields. Main product yields correspond to *G* values (yield per 100 eV) as high as 800.

Competitive experiments in the presence of either chloroform or 1-bromopentane and trichloroethylene in triethylsilane were carried out and are summarized in Table 3. In these experiments difficulties in product separation were encountered. In the 1-bromopentane solutions a small amount of product which could not be separated from Et_3SiCl was observed. In the chloroform solutions methylene chloride formation did not allow determination of *cis*-$C_2Cl_2H_2$. However, in all experiments yields of a sufficient number of products could be determined to permit calculation of the yields of the other products with the help of the average product ratios determined in the experiments

TABLE 1. THE EFFECT OF IRRADIATION TIME ON THE FORMATION OF MAIN PRODUCTS IN SOLUTIONS OF C_2Cl_3H IN Et_3SiH AT 65°C [a]

Irradiation time (min)	$[C_2Cl_2H_2]$			$[Et_3SiX]$ [b]			[HCl] (m*M*)	$C_2Cl_2H_2$ / I	HCl / II	*cis* / *trans*	*cis* / 1.1	*G*(II)
	1.1 (m*M* × 10^2)	*trans* (m*M*)	*cis* (m*M*)	I (m*M*)	II (m*M*)	III (m*M* × 10)						
5	7.5	0.74	2.38	2.85	3.29	0.98	—	1.12	—	3.22	31.7	627
10	16.6	1.22	5.37	7.67	6.65	—	—	1.02	—	4.40	32.3	633
10	—	—	—	—	8.74	2.34	8.8		1.01	—	—	832
10	17.9	1.58	5.31	7.53	8.26	2.25	—	0.94	—	3.36	29.7	787
10	16.9	1.59	5.33	7.20	8.02	2.17	—	0.98	—	3.35	31.5	764
15	21.6	2.13	7.38	11.30	10.63	2.13	—	0.86	—	3.46	34.2	675
20	32.7	3.69	12.08	15.14	15.53	2.40	—	1.06	—	3.27	36.9	740
20	—	—	—	—	16.00	2.53	15.4		0.96	—	—	762
30	33.60	4.14	13.20	22.54	19.50	3.93	—	0.78	—	3.19	39.3	620

[a] $[C_2Cl_3H]_0$ 0.55 *M*, dose rate 6.56 × 10^{16} eV ml^{-1} min^{-1}. [b] X = Cl, C_2HCl_2 and $C_2H_2Cl_3$(?) in I, II and III, respectively.

TABLE 2. EFFECT OF SOLUTE CONCENTRATION ON THE YIELDS OF MAIN PRODUCTS IN THE RADIOLYSIS OF C_2Cl_3H SOLUTIONS IN TRIETHYLSILANE AT 65°C [a]

$[C_2Cl_3H]_0$ (m*M*)	Irradiation time (min)	$[C_2Cl_2H_2]$			$[Et_3SiX]$ [c]			[HCl] (m*M*)	$C_2Cl_2H_2$ / I	HCl / II	*cis* / *trans*	*cis* / 1.1
		1.1 (m*M* × 10^2)	*trans* (m*M*)	*cis* (m*M*)	I (m*M*)	II (m*M*)	III (m*M* × 10)					
50	7	4.00	0.55	1.93	2.69	2.76	0.60	—	0.94	—	3.51	48.2
50	7	3.70	0.56	1.95	3.05	2.93	0.66	—	0.84	—	3.48	52.7
71	7	5.81	0.69	2.19	3.23	3.11	0.66	—	0.91	—	3.17	37.7
71	7	5.41	0.60	2.13	3.04	2.97	0.71	—	0.92	—	3.55	39.4
111	10	18.30	1.50	5.33	6.92	6.53	1.41	—	1.01	—	3.55	29.1
111 [b]	10	—	—	—	—	7.03	1.20	6.83	—	0.97	—	—
111	20	22.20	2.70	9.46	14.58	12.30	2.34	—	0.85	—	3.50	42.6
111 [b]	20	—	—	—	—	10.65	2.03	12.50	—	1.17	—	—
222	10	18.00	1.43	5.34	7.22	7.07	1.58	—	0.96	—	3.73	29.7
222 [b]	10	—	—	—	—	7.01	1.94	8.23	—	1.17	—	—
222	20	21.60	2.46	9.00	12.12	12.01	2.39	—	0.96	—	3.66	41.7
222 [b]	20	—	—	—	11.00	12.19	2.29	14.60	0.96	1.19	—	—
354	7	9.10	0.95	3.04	4.55	4.51	1.01	—	0.90	—	3.20	33.4

[a] Dose rate 6.56 × 10^{16} eV ml^{-1} min^{-1}. [b] Experiments in which samples were opened under a layer of water. [c] X = Cl, C_2HCl_2 and $C_2H_2Cl_3$(?) in I, II and III, respectively.

reported in Tables 1 and 2. In order to verify the free radical mechanism of product formation cyclohexene was added as a radical scavenger. Addition of 0.1 *M* cyclohexene to a 0.2 *M* C_2Cl_3H solution in Et_3SiH reduced the total yield of dichloroethylenes by 82%. However, the presence of cyclohexene did not affect the ratio in which the three isomers of dichloroethylene were formed.

Discussion

General aspects

The high radiolytic yields (*G* values) of the main products and the inhibiting effect of cyclohexene indicate that these products are formed by a free radical chain mechanism. Initiation of the chain can be schematically described by reaction 1:

$$2\ Et_3SiH \rightarrow 2\ Et_3Si^{\cdot} + H_2 \tag{1}$$

Radicals other than the triethylsilyl radical can be formed at the initial stage of radiolysis from the solvent triethylsilane as well as from the solute trichloroethylene. However all these radicals will eventually react with the Et_3SiH present in large excess and will be converted into $Et_3Si^{\cdot}$ radicals. Thus the details of the radiolytic initiation are of little importance, insofar as the formation of main products is concerned.

The overall chemical change in the γ irradiated solutions of trichloroethylene in triethylsilane is described by reaction 2.

$$Et_3SiH + C_2Cl_3H \rightarrow$$
$$Et_3SiCl + Et_3SiCH{=}CCl_2 + CH_2{=}CCl_2 + CHCl{=}CHCl + HCl \tag{2}$$

The purpose of the present discussion is to establish the mechanism of the individual reactions through which this overall change occurs. In all previous studies of chlorovinylation of alkanes by a free radical reaction of alkyl radicals with chloroethylene, no products formed by replacement of a chlorine atom by a hydrogen atom were observed [12—16]. Therefore, even if the formation of $Et_3SiCH{=}CCl_2$ proceeds via a reaction path suggested for chlorovinylation of alkenes, additional reactions must be postulated in order to account for the formation of the isomers of dichloroethylene in the silane matrix.

Formation of dichlorovinyltriethylsilane

In analogy with the mechanism suggested for the chlorovinylation of alkanes [12,15,16], formation of dichlorovinyltriethylsilane ($Et_3SiCH{=}CCl_2$) can be described in terms of the "free radical addition elimination mechanism" given by reactions 3—6:

$$Et_3Si^{\cdot} + CHCl{=}CCl_2 \rightarrow Et_3SiCHClCCl_2^{\cdot} \tag{3}$$

$$Et_3SiCHClCCl_2^{\cdot} \rightarrow Et_3SiCH{=}CCl_2 + Cl^{\cdot} \tag{4}$$

$$Et_3SiCHClCCl_2^{\cdot} + Et_3SiH \rightarrow Et_3SiCHClCCl_2H + Et_3Si^{\cdot} \tag{5}$$

$$Cl^{\cdot} + Et_3SiH \rightarrow HCl + Et_3Si^{\cdot} \tag{6}$$

An alternative mechanism of $Et_3SiCH{=}CCl_2$ formation, namely the "free

TABLE 3

YIELD OF MAIN PRODUCTS IN COMPETITIVE EXPERIMENTS IN 0.554 *M* SOLUTION OF C_2Cl_3H IN Et_3SiH IRRADIATED AT 65°C [a,b]

Irradiation time (min)	$[C_5H_{11}Br]_0$ (m*M*)	$[CHCl_3]_0$ (m*M*)	$[C_5H_{12}]$ (m*M*)	$[CH_2Cl_2]$ (m*M*)	[*cis*-$C_2Cl_2H_2$] (m*M*)	[*trans*-$C_2Cl_2H_2$] (m*M*)	$[Et_3SiCl]$ (m*M*)	$[Et_3SiCH{=}CCl_2]$ (m*M*)
10	74	—	15.03	—	3.24	1.24	4.98	4.81
10	74	—	10.77	—	2.63	0.88	4.68	5.28
7	—	125	—	5.49	(0.93)	0.27	6.62	0.78
7	—	125	—	6.94	(0.80)	0.24	7.51	0.85
7	—	125	—	6.61	(0.83)	0.24	5.59	0.69

[a] Dose rate 6.56×10^{16} eV ml^{-1} min^{-1}. [b] Yields in parentheses were computed as described in the text.

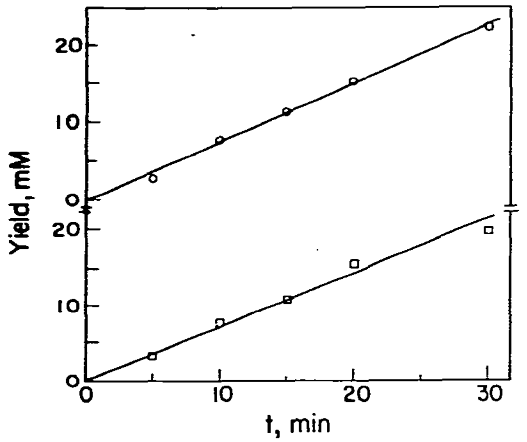

Fig. 1. The effect of irradiation time on the formation of Et_3SiCl (○) and $Et_3SiCH{=}CCl_2$ (□).

radical addition—abstraction molecular elimination mechanism", must also be considered. In this mechanism, reactions 3 and 5 would be followed by reaction 7. A similar mechanism has been suggested by Rust and Bell [13] for the

$$Et_3SiCHClCCl_2H \rightarrow Et_3SiCH{=}CCl_2 + HCl \tag{7}$$

trichlorovinylation of n-hexane, and by Park and Pearson [20] for substitution of the Cl atom in 1,2-chloro-substituted polyfluorobutene and polyfluorocyclopentene. However, pyrolytic decomposition of MCH_2CH_2Cl compounds, where M = Cl_3Si, Cl_2HSi, Et_2HSi and R_3Si, has activation energies ranging from 37.5 to 45 kcal mol^{-1} [21—24]. Therefore thermal decomposition of the related compound $Et_3SiCHClCCl_2H$ can be expected to be negligible at 65°C. The observed thermal stability of Cl_3SiCF_2CHFCl [25] further supports this conclusion.

Finally, the results given in Tables 1 and 2 and Fig. 1 show that the product ratios $C_2H_2Cl_2/Et_3SiCl$ and $Et_3SiCH{=}CCl_2/Et_3SiCl$ are independent of irradiation time and HCl concentration. Apparently, under our experimental conditions the secondary reaction 8 does not take place.

$$Et_3Si^{\cdot} + HCl \rightarrow Et_3SiCl + H^{\cdot} \tag{8}$$

Formation of dichloroethylenes

cis- and *trans-*1,2-dichloroethylenes and vinylidene chloride can be formed by reactions 9—12, i.e.:

$$Et_3Si^{\cdot} + CHCl{=}CCl_2 \rightarrow Et_3SiCl + CHCl{=}CCl^{\cdot} \tag{9}$$

$$Et_3Si^{\cdot} + CHCl{=}CCl_2 \rightarrow Et_3SiCl + {}^{\cdot}CH{=}CCl_2 \tag{10}$$

$$CHCl{=}CCl^{\cdot} + Et_3SiH \rightarrow \textit{cis}\text{-}CHCl{=}CHCl + \textit{trans}\text{-}CHCl{=}CHCl + Et_3Si^{\cdot} \tag{11}$$

$${}^{\cdot}CH{=}CCl_2 + Et_3SiH \rightarrow CH_2{=}CCl_2 + Et_3Si^{\cdot} \tag{12}$$

It should be noted that reaction 9, i.e. bimolecular chlorine transfer, represents an unreported method of vinyl radical generation. Vinyl radicals are mostly formed by addition to triple bonds. Several studied of hydrosilylation via vinylic radicals have been reported [26,27]. Most evidence seems to support the contention that when both *cis* and *trans* isomeric products are formed in the liquid phase from vinyl radicals, the relative yields of the isomers are controlled by the stability of the products. This in turn would mean that the vinyl radical can undergo a reversible structural rearrangement. ESR studies of the $CH_2{=}CH$ radical have confirmed the occurrence of this type of rearrangement [28]. Retention of configuration in vinylic radicals occurs only at very low temperatures, although in one case it is reported to take place in solution at room temperature [29].

Reaction 9 results in the formation of the two isomeric 1,2-dichlorovinyl radicals which then give the *cis* and *trans* isomers of dichloroethylene. The relative yields of these two isomers permit further examination of the factors which control this type of vinyl radical reaction.

The results given in Tables 1 and 2 show a value of 3.48 ± 0.59 (95% confidence limits) for the ratio of the *cis* to *trans* isomers of dichloroethylene, indicating that formation of the more stable [30] *cis* isomer is preferred. Our result is slightly higher than the *cis/trans* ratio of 2 determined by Beadle and Knox [31] and Wai and Rowlands [32] from the gas phase photochlorination studies in which the chlorine sensitized isomerization of *cis*- and *trans*-$C_2Cl_2H_2$ was investigated. A photostationary *cis/trans* ratio of 1.8 was recently also determined by Bottenheim and Wampler [33] in their study of the $^3SO_2$-sensitized isomerization of 1,2-$C_2Cl_2H_2$ at 22°C. In liquid cyclohexane at 150°C, unimolecular chlorine elimination from 1,1,2-trichloroethyl radicals formed in reaction 13 leads to the formation of *cis*- and *trans*-$C_2Cl_2H_2$ in a 3.9 ± 1.0 ratio calculated from the results in ref. 34 and corrected for the occurrence of a secondary reaction by using the relative rate constants of cyclo-C_6H_{11} radical addition to dichloroethylenes. Reaction 14 is endothermic by 18 kcal mol^{-1} [35], while

$$\text{cyclo-}C_6H_{11} + CHCl_2CHCl_2 \rightarrow \text{cyclo-}C_6H_{11}Cl + CHCl_2CHCl \tag{13}$$

$$CHCl_2CHCl \rightarrow cis\text{-}C_2Cl_2H_2 + trans\text{-}C_2Cl_2H_2 + Cl \tag{14}$$

reaction 11 is exothermic by about 15—20 kcal mol^{-1} [2]. However, irrespective of the large enthalpy difference the ratio of the two dichloroethylene isomers formed in these two reactions is the same. This further supports the view that formation of the *cis* and *trans* isomers from the same precursor is mostly controlled by their stability. The difference between the gas and liquid phase isomer distribution probably reflects an increase in the difference between the heats of formation of the two isomers upon transfer to solution.

Rate constants

In the mechanism outlined above the formation of products in the Et_3SiH/C_2Cl_3H system is described by reactions 3—6 and 9—12. Therefore $k_3/k_9 \equiv k_{ad}/k_{Cl}$ and $k_9/k_{10} \equiv k_{Cl}/k'_{Cl}$ are given by expressions C and D. Also if the product

$$\frac{k_{ad}}{k_{Cl}} = \frac{k_3}{k_9} = \frac{[Et_3SiCH{=}CCl_2]}{[1,2\text{-}C_2Cl_2F_2]} = \frac{[Et_3SiCH{=}CCl_2]}{[Et_3SiCl] - [1,1\text{-}C_2Cl_2H_2]} \tag{C}$$

$$\frac{k_{Cl}}{k'_{Cl}} = \frac{k_9}{k_{10}} = \frac{[cis\text{-}C_2Cl_2H_2] + [trans\text{-}C_2Cl_2H_2]}{[1,1\text{-}C_2Cl_2H_2]} \tag{D}$$

TABLE 4

RATE CONSTANTS FOR THE REACTIONS IN SOLUTIONS OF TRICHLOROETHYLENE IN TRIETHYSILANE AND IN CYCLOHEXANE AT 65°C

Solvent	k_{ad}/k_{Cl}	k_{Cl}/k'_{Cl}	k_{ad}/k_{17}	k_{el}/k_{abs}	k_{ad}/k_{19}
Et_3SiH	1.09 ± 0.11	37 ± 14	0.0285 [a]	290 ± 100	0.0019 [c]
cyclo-C_6H_{12}	$>10^3$	—	70. [b]	25 ± 0.5	0.114

[a] Computed using the average of all data of Table 3. [b] Reaction 17 $\equiv$ cyclo-C_6H_{11} + $CHCl_3 \rightarrow$ cyclo-$C_6H_{11}Cl + {}^{\cdot}CHCl_2^{\cdot}$ the ratio calculated from Arrhenius parameters of refs. 16 and 37. [c] Reaction 19 $\equiv R + CCl_4 \rightarrow RCl + CCl_3^{\cdot}$ where R = Et_3Si and cyclo-C_6H_{11} in Et_3SiH and cyclo-C_6H_{12}, respectively, see refs. 19 and 37.

we considered to be $Et_3SiCHClCCl_2H$ was correctly identified, then $k_4/k_5 \equiv k_{el}/k_{abs}$ can be computed using relationship E. The rate constant ratios thus obtained are summarized in Table 4.

$$\frac{k_{el}}{k_{abs}[Et_3SiH]} = \frac{k_4}{k_5[Et_3SiH]} = \frac{[Et_3SiCH{=}CCl_2]}{[Et_3SiCHClCHCl_2]} \tag{E}$$

In the competitive experiment carried out in solutions of 1-bromopentane and C_2Cl_3H in Et_3SiH, reactions 15 and 16 occur in addition to the reactions in systems deserved in absence of added 1-bromopentane, while in the experiments with added chloroform the additional reactions are 17 and 18:

$$Et_3Si^{\cdot} + C_5H_{11}Br \rightarrow Et_3SiBr + C_5H_{11}^{\cdot} \tag{15}$$

$$C_5H_{11}^{\cdot} + Et_3SiH \rightarrow C_5H_{12} + Et_3Si^{\cdot} \tag{16}$$

$$Et_3Si^{\cdot} + CHCl_3 \rightarrow Et_3SiCl + CHCl_2^{\cdot} \tag{17}$$

$$CHCl_2^{\cdot} + Et_3SiH \rightarrow CH_2Cl_2 + Et_3Si^{\cdot} \tag{18}$$

The rate constant ratios $k_{ad}/k_{15} = 4.54$ and $k_{ad}/k_{17} = 2.78$ were computed by substituting the results reported in Table 3 into expressions F and G. These

$$\frac{k_{ad}}{k_{15}} = \frac{[Et_3SiCH{=}CCl_2][C_5H_{11}Br]_{av.}}{[C_5H_{12}][C_2Cl_3H]_{av}} \tag{F}$$

$$\frac{k_{ad}}{k_{17}} = \frac{[Et_3SiCH{=}CCl_2][CHCl_3]_{av.}}{[CH_2Cl_2][C_2Cl_3H]_{av}} \tag{G}$$

results are in good agreement as they give a value of 1.64 for k_{17}/k_{15}, which compares well with 1.55 computed from the directly determined relative Arrhenius parameters of these two reactions [19].

Comparison with cyclohexane/C_2Cl_3H solutions

The characteristic features of the free radical reactions in the Et_3SiH/C_2Cl_3H system can best be seen by comparing it with the analogous cyclohexane/C_2Cl_3H system [36]. The rate constants of the various reactions in the two systems are given in Table 4. Cyclohexyl radicals only add to C_2Cl_3H, while the triethylsilyl radicals abstract Cl atoms from C_2Cl_3H and add to it at about equal rates. The ability of the $Et_3Si^{\cdot}$ radical to remove the strongly bound vinylic

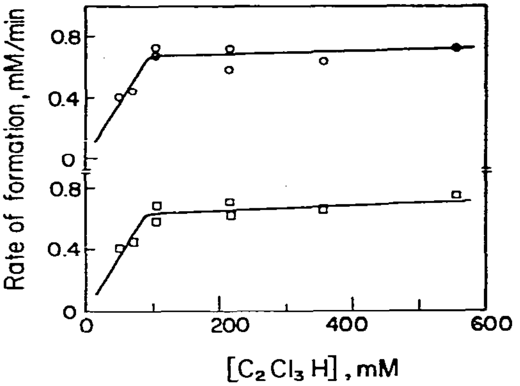

Fig. 2. The effect of trichloroethylene concentration on the rates of formation of Et_3SiCl (○) and Et_3Si-$CH{=}CCl_2$ (□).

chlorine can be attributed to the difference between the Si—Cl and C—Cl bond dissociation energies (*BDE*). The fact that abstraction from the site with two chlorine atoms is 37 times faster than the chlorine abstraction from the other site seems to indicate that there is a significant difference between the two C—Cl *BDE* in trichloroethylene. The rate constants of the addition and chlorine abstraction reactions of the Et_3Si radical with trichloroethylene are markedly lower than the rate constants for chlorine transfer from chloromethanes, see Table 4. Cyclohexyl radicals on the other hand add to the trichloroethylene faster than they abstract chlorine from chloroform. A similar order of reactivity is observed for the reaction with carbon tetrachloride.

For the gas [38] and liquid phase reactions [18] of CCl_3Si radicals with chloromethanes variations of an order of magnitude were found in the preexponential Arrhenius coefficients (*A*) for chlorine transfer. Similar variations in *A* factors were observed in the liquid phase reaction of Et_3Si radicals [19] with chloromethanes. Thus it is conceivable that the "slowness" of the chlorine transfer and addition reactions of the $Et_3Si^\cdot$ radical with trichloroethylene as compared to its chlorine transfer reaction with chloromethanes reflects a simultaneous increase in activation energy and decrease in *A* factors.

Because of the relative weakness of the Si—H bond, hydrogen abstraction from silanes should occur readily. Indeed the expected effect can be seen by comparison of the rates of chlorine elimination and hydrogen abstraction of the C_2Cl_5 radical in triethylsilane [39] with those obtained in cyclohexane [40]. However the present results show (Table 4) that k_{el}/k_{ab} for the Et_3SiCH-$ClCCl_2$ radical is larger by about an order of magnitude than the analogous rate constant ratio for the cyclo-C_6H_{11} radical. This unexpected result can be attributed either to a decrease in the chlorine elimination activation energy, equal to *D*(C—Cl) in the $Et_3SiCHClCl_2$ radical, or to an increase in the activation energy for hydrogen abstraction. Possibly the two effects occur simultaneously. Now, if a β-silicon substituent stabilizes a carbon centered radical by about 5 kcal, as has been suggested by Kawamura and Kochi [41], then a similar effect in the $Et_3SiCHClCCl_2$ radical could, indeed, bring about an increase in the activation energy for hydrogen abstraction. A decrease in *D*(C—Cl) as a result of substitution by an Et_3Si group would require the stabilization energy of the unsaturated product $Et_3SiCH{=}CCl_2$ to be even larger than that of the $Et_3SiCHClCCl_2^{\cdot}$ radical.

Finally, it can be seen from Fig. 2 that, except from the lowest C_2Cl_3H concentrations, the rates of product formation are practically constant. In terms of our mechanism these observations suggest that the concentration of $Et_3Si^{\cdot}$ radicals in the system is small in comparison with the concentration of $Et_3SiCHCl$-$CCl_2^{\cdot}$ and $CHClCCl^{\cdot}$ radicals. In turn this means that in our system the reactions of these two radicals are slower than the reactions of the $Et_3Si^{\cdot}$ radical. It is of interest to note that in the C_2Cl_4/cyclohexane system [16], for which the yield of cyclo-$C_6H_{11}C_2Cl_3$ was studied at 55°C as a function of solute concentration, the kinetic evidence did not point out the predominance of the adduct radicals. However, since the addition of cyclohexyl radicals to C_2Cl_3H proceeds about five times faster than to C_2Cl_4 [16] it appears reasonable to assume that at comparable temperatures and solute concentrations the percentage of solvent radicals in the total radical population in the C_2Cl_3H/cyclohexane system does not differ significantly from that in the Et_3SiH/C_2Cl_3H system.

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