November, 1971] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 3113—3116 (1971) 3113

Free-Radical Chlorination of Alkylsilanes. VI.* The Hydrogen Abstraction from α-Substituted Hydrosilanes by Chlorinated Methyl Radicals

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(Received April 23, 1971)

Relative rates of hydrogen abstraction from Si-H bonds of α-substituted hydrosilanes by the trichloromethyl or the dichloromethyl radical were determined by allowing the hydrosilanes to compete in pairs for a chlorocarbon compound, carbon tetrachloride or chloroform, at 80°C in the presence of benzoyl peroxide. Results show that relative rates of the investigated hydrosilanes toward the trichloromethyl and the dichloromethyl radicals are satisfactorily correlated with the summation of Taft σ^* values for the substituent on the central silicon atom, giving ρ^* values of -0.11 and -0.08, respectively. Linear correlations are also found to exist between the relative rates and the ^{29}Si-H coupling constants.

Previously,[1-3] it has been shown that a chain reaction occurs when a hydrosilane is allowed to react with an aliphatic halide in the presence of a radical generator, *e.g.* benzoyl peroxide. The chain carrying steps[1-6] are likely to be:

$$\equiv\text{Si}\cdot + \equiv\text{CX} \longrightarrow \equiv\text{SiX} + \equiv\text{C}\cdot \qquad (1)$$

$$\equiv\text{C}\cdot + \equiv\text{SiH} \longrightarrow \equiv\text{CH} + \equiv\text{Si}\cdot \qquad (2)$$

$$(\text{X} = \text{Cl or Br})$$

The reaction makes it feasible to measure both the relative rates of halogen atom abstraction from C-Hal bonds by silyl radicals[2,5-9] and those of hydrogen abstraction from Si–H bonds by carbon radicals.

The present investigation deals with the latter reaction employing several α-substituted hydrosilanes in connection with our earlier work[10] on reactions of nuclear substituted phenylsilanes with carbon tetrachloride under free radical conditions. It was hoped that some correlation would emerge between the relative rates for reactions of the α-substituted hydrosilanes with carbon tetrachloride or with chloroform and structural variables in the substrates or in the attacking carbon radicals.

Results and Discussion

In the present study, triethylsilane, phenyldimethylsilane, diethylchlorosilane, ethyldichlorosilane and trichlorosilane were selected for the α-substituted hydrosilanes. The counter reactant was carbon tetrachloride or chloroform, so that the trichloromethyl or the dichloromethyl radical was to be generated in the system being considered. The investigated hydrosilanes were allowed to compete in pairs at 80°C toward an appropriate chlorinated methane, benzoyl peroxide being used as catalyst. The relative rates of reactions (2) were conveniently calculated by the Ingold-Shaw equation[11]

$$\frac{k_A}{k_B} = \frac{\log [A]_i/[A]_f}{\log [B]_i/[B]_f}$$

where $[A]_i$, $[B]_i$ represent the initial concentrations of two hydrosilanes, $[A]_f$, $[B]_f$ the final concentrations and k_A/k_B the ratio of rate constants for the attack of the abstracting reagent on the two species.

Table 1 summarizes the results of the analysis of the various competitive reaction mixtures. Included in the tabulation are the initial, $[A]_i$ and $[B]_i$, and final, $[A]_f$ and $[B]_f$, amounts of the hydrosilanes competing for the chlorinating reagent. The latter quantities were determined by means of vapor phase chromatography. Figure 1 indicates summaries of all the competitive experiments of Table 1 in which probable errors are included. Examination of Fig. 1 shows the results of the cross-checks on the relative rate constants for reactions of the α-substituted silanes investigated both with carbon tetrachloride and with chloroform to be satisfactory. For example, the relative rate for trichlorosilane relative to triethylsilane can be calculated *via* three possible pathways involving different compounds and the agreement between the values so calculated appears to be reasonable. The averages of the k_A/k_{Et_3SiH} values are summarized in Table 2, in which the experimental uncertainties are not included because the cross-check experiments make it difficult to estimate these quantities.

It is seen from Table 2 that the successive introduction of electron-withdrawing groups on the central silicon atom decreases the reactivity of the Si-H bonds

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* For Part V see ref. 10.

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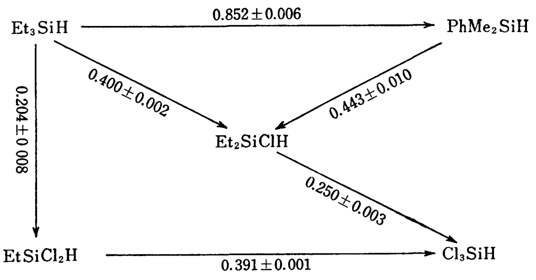
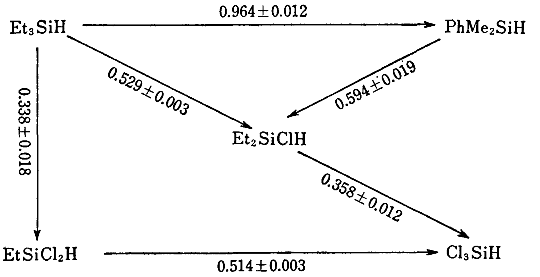
TABLE 1. COMPETITIVE CHLORINATIONS WITH CHLORINATED METHANES (80°C)

A	B	$[A]_i'$ mmol	$[A]_f'$ mmol	$[B]_i'$ mmol	$[B]_f'$ mmol	$[CCl_4]_i'$ mmol	$[CHCl_3]_i'$ mmol	k_A/k_B
Et_2SiClH	$PhMe_2SiH$	1.587	0.724	1.000	0.160	10.49	—	0.428
Et_2SiClH	$PhMe_2SiH$	1.615	0.719	1.029	0.176	11.29	—	0.458
$EtSiCl_2H$	Et_3SiH	1.648	1.283	0.826	0.225	7.50	—	0.192
$EtSiCl_2H$	Et_3SiH	1.493	1.154	0.562	0.170	8.00	—	0.215
Cl_3SiH	Et_2SiClH	1.181	0.694	1.031	0.149	6.00	—	0.275
Cl_3SiH	Et_2SiClH	1.172	0.803	1.033	0.193	6.18	—	0.225
Cl_3SiH	Et_2SiClH	1.214	1.068	1.228	0.738	7.72	—	0.251
Cl_3SiH	$EtSiCl_2H$	1.461	1.100	0.930	0.449	6.41	—	0.390
Cl_3SiH	$EtSiCl_2H$	2.490	1.850	1.000	0.469	8.54	—	0.392
$PhMe_2SiH$	Et_3SiH	1.103	0.682	1.175	0.664	8.40	—	0.843
$PhMe_2SiH$	Et_3SiH	1.367	0.599	1.387	0.532	6.33	—	0.861
Et_2SiClH	Et_3SiH	2.066	0.756	1.903	0.156	9.23	—	0.402
Et_2SiClH	Et_3SiH	2.137	1.059	1.758	0.300	9.39	—	0.397
$PhMe_2SiH$	Et_3SiH	1.198	0.994	1.050	0.862	—	6.04	0.946
$PhMe_2SiH$	Et_3SiH	1.357	1.030	1.195	0.902	—	7.45	0.981
Et_2SiClH	$PhMe_2SiH$	1.554	0.920	1.011	0.400	—	13.03	0.565
Et_2SiClH	$PhMe_2SiH$	1.846	1.310	1.027	0.592	—	12.89	0.622
Et_2SiClH	Et_3SiH	1.893	1.340	1.017	0.527	—	13.39	0.525
Et_2SiClH	Et_3SiH	2.657	1.560	1.032	0.380	—	13.27	0.533
$EtSiCl_2H$	Et_3SiH	1.728	1.144	1.026	0.273	—	10.30	0.311
$EtSiCl_2H$	Et_3SiH	2.058	1.135	1.013	0.198	—	10.46	0.365
Cl_3SiH	$EtSiCl_2H$	1.277	0.920	1.050	0.558	—	7.94	0.519
Cl_3SiH	$EtSiCl_2H$	1.502	1.096	1.046	0.563	—	7.56	0.509
Cl_3SiH	Et_2SiClH	1.351	0.694	1.189	0.201	—	8.69	0.375
Cl_3SiH	Et_2SiClH	0.996	0.401	1.016	0.070	—	9.65	0.340



(i) Relative rates toward $\cdot CCl_3$ (80°C).



(ii) Relative rates toward $\cdot CCl_2H$ (80°C).

Fig. 1. Summary of competitive chlorinations.[a]

[a] Arrows indicate direct competitions and numbers stand for the rate of the compound at the head of an arrow relative to that at the tail.

toward either the trichloromethyl or the dichloromethyl radical. This trend is in keeping with electron-seeking character of the presumed attacking radical, the trichloromethyl or the dichloromethyl radical, serving as an electron acceptor from the hydride hydrogen atom.

TABLE 2. RELATIVE RATES FOR REACTIONS OF α-SUBSTITUTED HYDROSILANES (80°C)

Silane	k_{rel} (with CCl_4)	k_{rel} (with $CHCl_3$)	$\sum\sigma^{*a)}$
Et_3SiH	1.0	1.0	−0.30
$PhMe_2SiH$	0.84	0.89	+0.60
Et_2ClSiH	0.37	0.53	+2.7
$EtSiCl_2H$	0.24	0.37	+5.8
Cl_3SiH	0.093	0.19	+8.8

a) The summation of Taft σ^* values for three substituents on silicon. The value for Cl is calculated from multiplying the value for CH_2Cl by 2.8.

$$[\equiv Si{:}H\cdot C\equiv] \longleftrightarrow [\equiv Si^+\ H{:}C^-\equiv] \longleftrightarrow [\equiv Si\cdot H{:}C\equiv]$$

Kinetic data listed in Table 2 are plotted in Fig. 2 against the summation of Taft σ^* values[12] for three substituents on silicon. As will be shown in Fig. 2, the plots for reactions with carbon tetrachloride afford an excellent correlation with a slope of −0.11 and a correlation coefficient of 0.992. A linear correlation is also found to exist for reactions with chloroform with a slope of −0.08 and a correlation coefficient of 0.995. The observed linear correlations may imply that, within this class of substrates, polar factor is of primary importance in determining the rate for the Si-H hydrogen abstraction and that steric or other contributions for a set of the intermediate silyl radicals are nearly constant or vary linearly with changes in electronic effects of the substituents. The reaction constant (in

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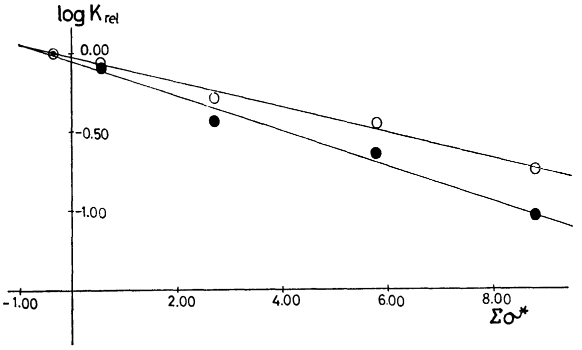

Fig. 2. Plots of relative rates *versus* $\sum\sigma^*$. Open circles represent reactions of carbon tetrachloride and solid circles those of chloroform.

absolute magnitude) is slightly larger for reactions with the trichloromethyl radical than for those with the dichloromethyl radical. Although such a comparison of the ρ^* values may be valid only if allowance is made as to the different solvents in which results have been obtained, the trend found in this study is expected from the polarity of the attacking radicals.

Importance of polar effects in the reaction of hydrosilanes with radicals can be seen in other instances.[13,14] For example, Morris and Thynne[14] reported that trimethylsilane is more reactive toward attack of the trifluoromethyl radical than is trichlorosilane by a factor of about 5 (at 164°C).

It is noteworthy that points for phenyldimethylsilane fall on the straight lines and from this fact the conjugation between the reaction site and phenyl substituent in the transition state is considered to be of only minor importance. This conclusion is reasonable since $3p_\pi$ (Si)—$2p_\pi$(C) orbital overlap seems to be ineffective.[15]

It has recently been quoted that linear correlations emerge between the ^{13}C–H coupling constants and CH reactivities toward the abstracting reagents such as the chlorine atom[16,17] or the methyl radical.[18] By analogy, it might be expected that similar correlations would exist between the ^{29}Si-H coupling constants and SiH reactivities toward the attacking radicals employed in the present investigation (See Fig. 3). Although the factors governing the magnitude of J(^{29}Si-H) values are not yet fully understood,[19] the observed correlations are of interest and may imply correlations between change in the fraction of s character employed by silicon in a Si-H bond reflecting change in the electron density around the hydrogen and the ease of removal of the hydrogen by the abstracting radical.

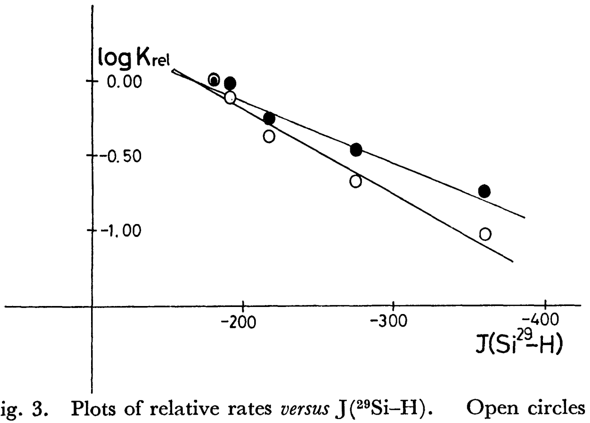

Fig. 3. Plots of relative rates *versus* J(^{29}Si–H). Open circles represent reactions of carbon tetrachloride and solid circles those of chloroform.

Experimental

Starting Materials. Triethylsilane (bp 106.0—106.5°C, lit.[20] 107°C/733 mm.), phenyldimethylsilane (bp 155.0—155.3°C, lit.[21] 158°C), diethylchlorosilane (bp 96—98°C, lit.[22] 99.2°C), ethyldichlorosilane (bp 73.5—74.0°C, lit.[22] 74.2°C) and trichlorosilane (bp 30.5°C, lit.[20] 31.5—32.0°C/729 mmHg) were prepared as described in the literature. Carbon tetrachloride and chloroform were purified according to the standard procedures.[23] VPC analysis of these materials showed negligible impurities. Benzoyl peroxide was commercially obtained as a special grade.

Products. Among the samples necessary for identification of the reaction products, triethylchlorosilane (bp 147°C, lit.[20] 147°C/729 mmHg), phenyldimethylchlorosilane (bp 190—191°C, lit.[21] 192—194°C), diethyldichlorosilane (bp 130°C, lit.[24] 131°C/740 mmHg) and ethyltrichlorosilane (bp 96.5—97.0°C, lit.[25] 97.9°C) were prepared according to the literature. Silicon tetrachloride and dichloromethane were commercially available.

Structures of reaction products were confirmed by comparing infrared spectrum of the respective sample which had been collected by preparative VPC from a reaction mixture with that of the corresponding authentic sample.

Procedure for Kinetic Runs. A solution of two different hydrosilanes was mixed in approximately 3—5 fold excess of an appropriate chloromethane with a catalytic amount of benzoyl peroxide and the resulting solution introduced into a tube which was sealed after the mixture was degassed several times. Then, the reaction tube was maintained at 80°C in a constant temperature bath for 3—5 h. It was found that about 15—90% of the hydrosilanes had reacted during the period of time. The reaction mixtures were subjected to VPC analysis, using column materials such as Silicone DC 550, 710 and so on. It was found by VPC analysis that with all the competitive experiments polydechlorination of carbon tetrachloride or of chloroform had occurred to

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negligible extent. Corrections were made for the thermal conductivity of the various components. The relative rates were calculated from original data with equation (3).

NMR Spectra. $J(^{29}Si\text{-}H)$ data were determined from spectra obtained on a Varian Model A-60D high resolution nuclear magnetic resonance spectrometer. NMR spectra were studied in the pure liquid phase. The coupling constants were evaluated from the satelite bands produced by the ^{29}Si in natural abundance which are symmetrically disposed about the main Si-H proton signals. The numerical values obtained are shown in Table 3.

TABLE 3. THE ^{29}Si-H COUPLING CONSTANTS

Compound	Et_3SiH	$PhMe_2SiH$	Et_2SiClH	$EtSiCl_2H$	Cl_3SiH
$J(^{29}Si\text{-}H)$, Hz	−179	−188	−216	−275	−363
Ref.	26)	26)	a	a	27)

a) Present work

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