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$\delta(\Delta V)^\ddagger \cdot \rho$ that we expect an appreciable pressure effect on ρ . From our discussion, we conclude that the effect of pressure on the ρ -parameter can't be decided simply from glancing reacting substance, but it depends on reaction series, solvent, net charge change and etc. In this study we attempted to test the theoretical result with experimental data. But there are not sufficient data in the literature at high pressure. Table 2 shows for the phenol derivatives.

There are enough data at atmospheric pressure but only several substituents at high pressure. From these insufficient data we can't discuss fully but only the tendency of the pressure effect on ρ -parameter. It is clear from Table (2), in accordance with prediction. ρ values diminishes with increase in pressure inspite of low r -value. Table 3 and 4 show for the anilines and pyridines.

Pyridines have relatively enough data and $r=0.992$. In pyridines and *o*-substituted aniline, ρ -values increase with increase in pressure.

As mentioned previously, the effects of pressure on Hammett reaction parameter ρ are affected the various situation

i.e.net charge change, solvation, solvent structure, compressibility, reaction series and etc.

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Competitive Photochlorination Reactions of Silane, di-Chloro and tri-Chlorosilanes at 337.1 nm

Kyung-Hoon Jung* and Kwang Woo Jung

Department of Chemistry, Korea Advanced Institute of Science and Technology
Seoul 131. Received March 2, 1987

The hydrogen abstraction reactions of SiH_4 , SiH_2Cl_2 and SiHCl_3 by ground state chlorine atoms generated photochemically from chlorine molecules have been studied at temperatures between 15 and 100°C. The absolute rates for the reactions have been obtained by a competition technique using ethane as a competitor. The rate expressions (in $\text{cm}^3/\text{mol/s}$) are found to conform to an Arrhenius rate law: $k_{\text{SiH}_4} = (7.98 \pm 0.42) \times 10^{13} \exp[-(1250 \pm 20)/T]$, $k_{\text{SiH}_2\text{Cl}_2} = (2.25 \pm 0.12) \times 10^{15} \exp[-(1010 \pm 10)/T]$, $k_{\text{SiHCl}_3} = (9.04 \pm 0.28) \times 10^{14} \exp[-(1200 \pm 10)/T]$. The activation energies obtained from this study represent the same trend as with the carbon analogues, while this trend was not found with respect to the bond dissociation energies among silicon compound homologues. These anomalous behaviors were interpreted in terms of electronic effects and of the structural differences between these compounds.

Introduction

The reactions of the abstraction of hydrogen from

hydrocarbon molecules have been studied extensively using chlorine atoms during the last decade. However, despite the long history of these investigations, such attempts with their

silicon counterparts are relatively new and have given very little information on their kinetic behaviors.¹⁻³ These studies are of industrial importance and provide basic information on the photochlorination of silicon compounds.⁴ Some of the prototype reactions between Cl radical and SiH_{4-x}Cl_x (x = 0, 2, or 3) of these categories have now been carried out.

Since ample kinetic information on the photochlorination of C₂H₆ is available from several independent research groups⁵⁻⁸ over the relevant temperature range, the competitive photochlorinations between SiH_{4-x}Cl_x and C₂H₆ molecules in the present system were studied.

Experimental Details

The reactions was performed in a 225 cm³ borosilicate cylindrical cell, namely, 14.6 cmL. × 22 mm radius, over the temperature range of 288-383K, using 337.1 nm monochromatic light. The reaction cell, sealed both sides with optically flat borosilicate windows, was jacketed in a cylindrical aluminum block and was thermostatted by a feed-back type temperature controller. The largest temperature discrepancy was less than ±0.5°C throughout the experiment. The monochromatic light, (337.1 nm) used in this study, was obtained using a high pressure xenon arc lamp, Model XBO 150W, Oriel Co., and with a 22 cm Czerny-Turner type monochromator (Model Minimate 1670, Spex Industries Inc). The typical configuration of the monochromator was 1.5 mm outlet slit width and kinematically mounted stainless steel base 1200 grooves/mm grating with 300 nm stray light wavelength. The homogeneous and parallel light beam with beam diameter of 4.2 cm was shone perpendicularly on the window surface of the reaction cell. The light beam was obtained by passing the monochromatic light beam through a home made beam expander, made from an optical grade quartz ingot, (Toshiba Ceramics Co.) and calibrated against He-Ne laser line. The irradiation time was controlled to keep the total conversion of the reactants less than 10%. The time limit for the reaction, 15 min, was chosen on the basis of our separate study on the irradiation time effect on the reaction product ratios. In the study, the reaction was carried out for various irradiation times and showed constant reaction product ratios within 15 min of irradiation.

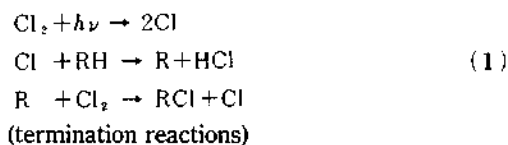
The reaction mixture was prepared in the dark to prevent any possible unnecessary reaction. The composition of the reaction mixture was chosen in such a way that each of the reaction products should be within the detection range for obtaining the optimum accuracy, e.g., 0.8 Torr Cl₂, 2.6 Torr SiH₂Cl₂ and 5.2 Torr C₂H₆ at 296°K. The dark reaction of each reaction system was checked in the temperature range. No reaction products were detected. Product analyses were carried out by GC, HP5880A single TCD, Hewlett-Packard Co., after quenching the reaction at liquid nitrogen temperature. The separation of products was achieved by a 20% OV101/80-100 mesh Chromosorb W 0.31 cm O.D. X390 cmL. s.s. column at 35°C isothermal temperature with a He flow rate of 30 cm³/min. Product identification was based on comparison of the retention times of unknown peaks with those of authentic samples. The final confirmation was provided by a GC/Mass spectrometer, (HP5985B Hewlett-Packard Co.) with the same conditions as for GC analysis.

Chlorine (>99.96% stated purity) was obtained from Matheson Co. and was degassed to eliminate its low boiling impurities. Ethane (>99.99% Matheson Co. stated purity)

was used directly without further purification. Silane (Matheson purity) was purified by repeated bulb-to-bulb distillations at liquid nitrogen temperature. Dichlorosilane, trichlorosilane and tetrachlorosilane were obtained from Chisso Minamata Co. and were purified by the same techniques as silane. The final purities of silanes were ascertained by GC.

Calculation

The general principle of the competitive chlorination technique has been described in some detail by Knox and co-workers.⁸ The basic mechanism for the competitive photochlorinations of monosilane and chloro-silanes with ethane in the gas phase is



where RH represents silane compounds or ethane. Since the termination steps for R are slow compared to the chain propagating reaction with Cl₂ and the chains are very long in laboratory experimental conditions, RCl formation becomes the rate determining step in the mechanism. The relative rate constant expression is then given by,

$$\begin{aligned} \frac{k_{\text{RH}}}{k_{\text{C}_2\text{H}_6}} &= \frac{\ln[\text{RH}]_0 - \ln[\text{RH}]_f}{\ln[\text{C}_2\text{H}_6]_0 - \ln[\text{C}_2\text{H}_6]_f} \\ &= \frac{\ln(1 - [\text{RCl}]/[\text{RH}]_0)}{\ln(1 - [\text{C}_2\text{H}_5\text{Cl}]/[\text{C}_2\text{H}_6]_0)} \end{aligned} \quad (2)$$

where the subscripts 0 and f refer, respectively, to initial and final conditions. Because of their competitive nature, [C₂H₅Cl] in Eq. (2) can be expressed as a function of [RCl] by [C₂H₅Cl] = α[RCl]. Since the reaction condition in this study has been adjusted so that the product yield is no more than 10% of the initial reactant concentration, L'Hospital's rule can be applied to Eq. (2). The reaction rate ratio between chlorination of silane to ethane then reduces to Eq. (3),¹⁰

$$\frac{k_{\text{RH}}}{k_{\text{C}_2\text{H}_6}} = \frac{1}{\alpha} \left(\beta + (\beta - \alpha) \frac{\gamma}{1 - \gamma} \right) \quad (3)$$

where α = [C₂H₅Cl]/[RCl], β = [C₂H₆]₀/[RH]₀ and γ = [RCl]/[RH]₀.

Results

The reaction products, in terms of pressure variations, and the rate constant ratios for the competitive photochlorination reaction of SiH₄, SiH₂Cl₂, and SiHCl₃ with C₂H₆ at various temperatures, are summarized in Tables 1-3. Also listed are the pressures of the reactants, i.e., silanes, C₂H₆ and Cl₂. The uncertainty factors listed in the tables represent one standard deviation. For this study, the amounts of two product chlorides were, as a precaution, brought within the same range by adjusting the reactant ratios, i.e., [silicon compounds]/[C₂H₆]. This was necessary to obtain precise measurements by the GC technique. The possible deviations of the ratios due to the changes of reactant compositions were also checked and were consistent at each combination.

Table 1. Competitive Photochlorinations of SiH₄ / C₂H₆ Systems^a

Run	Temp. (°K)	Reactants (Torr)			Products (Torr)		k _{SiH₄} / k _{C₂H₆}
		SiH ₄	C ₂ H ₆	Cl ₂	SiH ₃ Cl	C ₂ H ₅ Cl	
1	288	2.58-	1.93-	0.64-	0.002-	0.037-	0.030 ± 0.002
		6.44	5.15	1.29	0.012	0.207	
2	308	10.30	1.29	0.90	0.005-	0.016-	0.038 ± 0.001
					0.018	0.061	
3	328	10.30	1.29	0.90	0.006-	0.015-	0.049 ± 0.001
					0.015	0.039	
4	348	10.30	1.29	0.90	0.008-	0.014-	0.060 ± 0.002
					0.0026	0.054	
5	368	10.30	1.29	0.90	0.004-	0.007-	0.071 ± 0.001
					0.019	0.033	

^aError limits are one standard deviation.**Table 2. Competitive Photochlorinations of SiH₂Cl₂ / C₂H₆ Systems^a**

Run	Temp. (°K)	Reactants (Torr)			Products (Torr)		k _{SiH₂Cl₂} / k _{C₂H₆}
		SiH ₂ Cl ₂	C ₂ H ₆	Cl ₂	SiHCl ₃	C ₂ H ₅ Cl	
1	296	2.58	5.15	0.77-	0.014-	0.013-	2.179 ± 0.086
				1.29	0.293	0.291	
2	313	2.58-	5.15	0.77	0.026-	0.019-	2.596 ± 0.057
		2.70			0.307	0.259	
3	328	2.58	5.15-	0.77	0.013-	0.013-	2.993 ± 0.163
			7.73		0.291	0.193	
4	343	2.58	5.15	0.77	0.008-	0.005-	3.318 ± 0.112
					0.043	0.026	
5	358	2.58	7.73	0.77	0.010-	0.008-	3.742 ± 0.117
					0.284	0.244	

^aError limits are one standard deviation.**Table 3. Competitive Photochlorinations of SiHCl₃ / C₂H₆ Systems^a**

Run	Temp. (°K)	Reactants (Torr)			Products (Torr)		k _{SiHCl₃} / k _{C₂H₆}
		SiHCl ₃	C ₂ H ₆	Cl ₂	SiCl ₄	C ₂ H ₅ Cl	
1	299	10.04-	2.49-	1.93-	0.197-	0.097-	0.471 ± 0.011
		21.50	5.02	2.51	1.006	0.501	
2	323	10.04-	2.45-	1.29-	0.157-	0.062-	0.627 ± 0.017
		10.11	2.51	2.06	0.286	0.112	
3	343	10.04-	2.51-	1.29-	0.085-	0.034-	0.760 ± 0.022
		10.11	3.03	2.00	0.334	0.106	
4	363	10.04	2.51	2.00	0.309-	0.085-	0.903 ± 0.017
					0.502	0.141	
5	383	10.04	2.51	2.00	0.334-	0.075-	1.070 ± 0.035
					0.470	0.107	

^aError limits are one standard deviation.

Similarly, the variation of the [reactant]_{total} / [Cl₂] likewise had also shown no effect on the rate constant ratios as long as the secondary chlorination of the products was avoided. Thus the ratios of rate constants for a given temperature were from the possible deviations that could arise from the varia-

tion of the reactant mixture composition within the error limits. The rate constant ratios are displayed as a function of temperature in Figure 1. From the plot, the activation energy differences, ΔE_a, and pre-exponential factor ratios were obtained by linear least square analysis and are given in Table

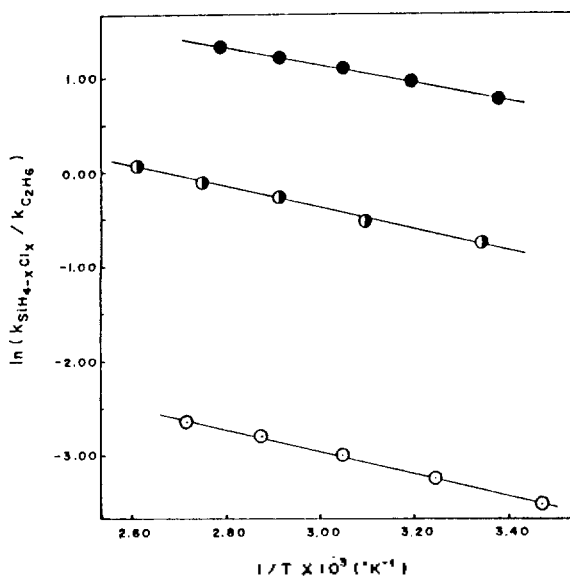


Figure 1. The photochlorination rate constant ratios between chlorosilanes and ethane as a function of reaction temperature at 337.1 nm: (○) SiH₄; (◐) SiHCl₃; (●) SiH₂Cl₂.

4. Each point in this figure represents the mean of all experimental values obtained at that temperature.

Among several values for $k_{C_2H_6}$ available in literature, we have adopted the value listed in JPL Publication Note¹¹ to calculate the absolute rate parameters of silanes. The rate expression in the JPL report is given by,

$$k_{C_2H_6} = 4.64 \times 10^{13} \exp[-90/T] \text{ cm}^3/\text{mol/s} \quad (4)$$

where the temperature range of the data covered was from 220 to 350°K. Combining Arrhenius parameters, from the absolute rate measurement for photochlorination of ethane, with our relative results, the absolute rate expressions for the photochlorinations of SiH₄, SiH₂Cl₂, and SiHCl₃ can be described by,

$$k_{SiH_4} = (7.98 \pm 0.42) \times 10^{11} \exp[-(1250 \pm 20)/T] \text{ cm}^3/\text{mol/s} \quad (5)$$

$$k_{SiH_2Cl_2} = (2.25 \pm 0.12) \times 10^{15} \exp[-(1010 \pm 10)/T] \text{ cm}^3/\text{mol/s} \quad (6)$$

$$k_{SiHCl_3} = (9.04 \pm 0.28) \times 10^{14} \exp[-(1200 \pm 10)/T] \text{ cm}^3/\text{mol/s} \quad (7)$$

Discussion

The absolute kinetic parameters derived from the relative values in Table 4 are given in Table 5, together for comparison, with those of their hydrocarbon counterparts.¹² The rate constants for the abstraction reaction exhibit strikingly little variation in the pre-exponential factors and in the activation energies for different alkyl radicals on the same silicon-hydrogen bond.¹³ Since very little kinetic information is available for the reactions of chlorine atoms with silicon compounds, direct comparison between silicon compounds of kinetic behavior is not possible. Nevertheless, in this study, the reactions of chlorosilanes were characterized by larger pre-exponential factors and lower activation energies in comparison with the corresponding carbon compounds, which may be considered as an indication of the weak Si-H bond

Table 4. Relative Arrhenius Parameters for the Competing Reactions^a

$$R_aH + Cl = R_a + HCl$$

$$R_bH + Cl = R_b + HCl$$

Mixture	A_{R_aH}/A_{R_bH}	$(E_{R_aH} - E_{R_bH})/R$	Temperature range (°K)
R _a H/C ₂ H ₆			
SiH ₄ /C ₂ H ₆	1.72 ± 0.09	1160 ± 20	288-368
SiH ₂ Cl ₂ /C ₂ H ₆	48.42 ± 2.49	920 ± 10	296-358
SiHCl ₃ /C ₂ H ₆	19.49 ± 0.60	1110 ± 10	299-383

^aR_a and R_b represent the silanes and C₂H₆, respectively.

Table 5. Arrhenius Parameters^a for Hydrogen Abstraction from Monosilane, di- and tri-Chlorosilanes, and Their Corresponding Carbon Compounds

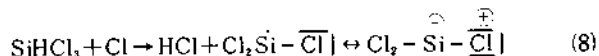
Reaction	log A	E	log k at 300°K	Reference
Cl + SiH ₄	13.90	2.48	12.09	this work
Cl + SiH ₂ Cl ₂	15.35	2.01	13.89	this work
Cl + SiHCl ₃	14.96	2.38	13.22	this work
Cl + CH ₄	13.38	3.85	10.58	12
Cl + CH ₂ Cl ₂	13.48	3.00	11.29	12
Cl + CHCl ₃	12.84	3.34	10.40	12

^a Units are A in cm³/mol/s, k in cm³/mol/s, and E in kcal/mol.

strength. The bond dissociation energies of monosilane¹⁴ and chloro-silanes,^{15,16} however, show much higher values than those expected considering the reactivities. This behavior of silane and chlorosilanes towards chlorine radical may be attributed to their large pre-exponential factors and low activation energies.

The large pre-exponential factors for silicon compounds, compared with those of carbon counterparts, may be attributed to the silicon d-orbitals.¹⁷ In the transition state, the unpaired electron of silyl radicals may be accommodated by the d-orbital of silicon. An alternative interpretation may also be possible as Pritchard suggested¹⁸ for high A-factors. Contributions of the internal degrees of freedom to the activation process may give rise to high A-factors in bimolecular reactions. Therefore, it seems possible that the low vibrational frequencies of Si-Cl bond stretching in chlorosilanes may result from "loose" transition state.

The stabilization of the incipient free radical by the mesomeric donating effect¹⁹ of the halogen substituent and the empty d-orbital of silicon may be attributed to the lower activation energies of monosilane and chloro-silanes than their corresponding carbon analogues,



However, the activation and bond energy relationships²⁰ suggested by Polanyi-Evans did not apply in the present system. This may be interpreted in two ways. Firstly, the disagreement can be tentatively ascribed to dynamic effect of attractive dispersion forces between the attacking chlorine atom and the chlorine atoms already bound to the molecule. As suggested by Johnston and Goldfinger,²¹ the preferential attraction of the chlorine atoms by the bound chlorine results in the form HCl₂Si-Cl...Cl in collision complexes. Thus the activated complex or hydrogenatom transfer complex has no

chance of being formed unless the approaching atom has a relatively large kinetic energy. This effect may play a more dominant role in SiHCl_3 than in SiH_2Cl_2 , and is directly related to the polarizabilities of the bound atoms, e.g., polarizability of H = 0.42×10^{-24} and of Cl = 2.28×10^{-24} cm³. Secondly, the variation in activation energy may be linked to the changes of electron density on the hydrogen atom, where the lower activation energy is associated with the H having the higher electron density. The polar effect may therefore be expected in the chloro-silanes involving the attack by the electrophilic Cl radical, where the inductive effect of Cl atoms should decrease the H electron density on the silanes with higher numbers of chlorine atoms. On the other hand, the inductive effect is offset to some extent by $d\pi\text{-}P\pi$ bonding which plays an important role in the case of the chlorine atom. This back-coordination reaches a maximum when three chlorine atoms are attached to silicon.²² From the foregoing discussion, we suggest that the inductive effect gives a small contribution to di- and tri-chloro substitutions, leading to a similar electron density on the hydrogen atoms and thus to a slight difference in activation energies.

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Palladium Catalyzed Carbonylative Vinylation of Aryl Halides with Olefins and Carbon Monoxide

Jin Il Kim*

Department of industrial Chemistry, Hanyang University, Seoul 133

Cheol Mo Ryu

Department of Chemical Engineering, Kyonggi National Open University, Seoul 132. Received February 16, 1987

The reaction of aryl iodides or bromides with olefins in the presence of 1 mol % of $\text{PdCl}_2(\text{PPh}_3)_2$ and 3 equiv. of $n\text{-Bu}_3\text{N}$ at 100°C in carbon monoxide atmosphere gave the corresponding aryl vinyl ketones in good yields with small amount of vinylated 1-aryl olefins. But, when the reaction was proceeded under the 10 atm of carbon monoxide, aryl vinyl α -diketones and aryl vinyl ketones were obtained in moderate to good yields. The reaction was tolerant of a wide variety of functional groups on either the aryl halides or olefin compounds. Reactivity of aryl halide decrease in the order; aryl iodide > aryl bromide >> aryl chloride. In general, the reaction proceeded well and gave good yields of aryl vinyl ketones and aryl vinyl α -diketones when reactants are substituted with electron withdrawing groups.

Introduction

Aryl vinyl ketones^{1,2} and aryl vinyl α -diketones^{3,5} are im-

portant intermediates in the synthesis of a wide variety of organic compounds.

The palladium catalyzed aryl halide reaction with olefins