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Kinetics of Gas Phase Addition Reactions of Trichlorosilyl Radicals. VIII. Reinvestigation of Addition to Ethylene

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The addition of $\cdot SiCl_3$ radicals to ethylene has been reinvestigated using a large conversion method. The amended values are $\log(k_3/k_5) = -0.17\pm0.05-(0.80\pm0.10)$ kcal mol^{-1}/2.303 RT and $\log\{k_{-5}/k_6\ (\text{mol cm}^{-3})\} = 3.4\pm0.3-(22.5\pm0.7)$ kcal mol^{-1}/2.303 RT where the reactions involved are $\cdot SiCl_3 + CH_3COCH_3 \xrightarrow{3} (CH_3)_2\dot{C}OSiCl_3$, $\cdot SiCl_3 + C_2H_4 \underset{-5}{\overset{5}{\rightleftarrows}} \cdot CH_2CH_2SiCl_3$ and $\cdot CH_2CH_2SiCl_3 + HSiCl_3 \xrightarrow{6} C_2H_5SiCl_3 + \cdot SiCl_3$.

Silyl radical chemistry is now in the stage where any kinetic data leading to precise rate constants involving silyl radicals or silicon-containing compounds are in urgent need.

In the course of our kinetic study of addition of $\cdot SiCl_3$ radicals to olefins we found[1] that the A-factor of reaction (-5) for ethylene (see synopsis, $\log(A_{-5}/\text{s}^{-1}) = 12.8$) was too small compared with the ones for other 1-alkenes ($\log(A_{-5}/\text{s}^{-1}) = 14.8$—$16.3$. There is no convincing elucidation that the transition state of decomposition of the adduct radical for ethylene should be so tight while those for the other 1-alkenes are very loose. Further, transition state theory requires that $\log(A_{-5}/\text{s}^{-1}) \geq 13.4$.

In view of these facts we attempted to reinvestigate the addition to ethylene using a large conversion method (*vide infra*). In the previous study[2] there was a very small amount of impurity (possibly$(CH_3)_2CHOSiCl_2H$ by GC–MS analysis) which could not be separated completely from $C_2H_5SiCl_3$ by GLC analysis and which arised only when CH_3COCH_3 and $HSiCl_3$ were mixed. We purified CH_3COCH_3 but failed to reduce the amount of the impurity. Although we ascertained that the impurity itself did not participate in the reaction, it may have caused some systematic errors during the analytic process.

In this study we allowed the reaction to proceed to the extent that the yield of $C_2H_5SiCl_3$ is 10 times larger than the amount of the impurity.

Experimental

Materials and procedures are essentially similar to those described earlier.[2] Mixtures of CH_3COCH_3, C_2H_4, and $HSiCl_3$ were introduced into a cylindrical Pyrex cell of 137 cm^3 which was heated in an electric oven. The light source was a 50 W medium pressure mercury arc. After photolyzed, the reaction mixture was passed to a gas sampling loop and was immediately analyzed by GLC on a 2m SE 30 column.

Kinetic Equation. Photolysis of acetone in the presence of $HSiCl_3$ and C_2H_4 can be interpreted by the following chain reaction;[2] Eqs. 1 and 2, Eqs. 3 to 6, and Eqs. 7 to 9 are initiation, propagation and termination steps, respectively.

$$CH_3COCH_3(Ac) \xrightarrow{h\nu} 2\cdot CH_3 + CO \tag{1}$$

$$\cdot CH_3 + HSiCl_3(TCS) \longrightarrow CH_4 + \cdot SiCl_3 \tag{2}$$

$$\cdot SiCl_3 + CH_3COCH_3 \longrightarrow (CH_3)_2\dot{C}OSiCl_3 \tag{3}$$

$$(CH_3)_2\dot{C}OSiCl_3 + HSiCl_3 \longrightarrow (CH_3)_2CHOSiCl_3(A) + \cdot SiCl_3 \tag{4}$$

$$\cdot SiCl_3 + C_2H_4(Et) \rightleftarrows \cdot CH_2CH_2SiCl_3 \tag{5}$$

$$\cdot CH_2CH_2SiCl_3 + HSiCl_3 \longrightarrow C_2H_5SiCl_3(E) + \cdot SiCl_3 \tag{6}$$

$$2(CH_3)_2\dot{C}OSiCl_3 \longrightarrow \text{Products} \tag{7}$$

$$2\cdot CH_2CH_2SiCl_3 \longrightarrow \text{Producrs} \tag{8}$$

$$(CH_3)_2\dot{C}OSiCl_3 + \cdot CH_2CH_2SiCl_3 \longrightarrow \text{Products} \tag{9}$$

Assuming long reaction chains,[3] we obtain the following rate equation by the conventional steady state treatment of the scheme.

$$(R_A/R_E)([\text{Et}]/[\text{Ac}]) = (k_3/k_5)\{1 + (k_{-5}/k_6)[\text{TCS}]^{-1}\}, \tag{10}$$

where R, k, and [ ] have usual meanings of rate, rate constant, and concentration, respectively.

In a study where the conversion of the reactants can be kept small, we may make an approximation:

$$R_A/R_E = [\text{A}]/[\text{E}]. \tag{11}$$

Previously,[2] we used Eqs. 10 and 11 to obtain k_3/k_5 and k_{-5}/k_6.

When the conversion of the reactants can not be assumed small, however, we must find out an alternative to Eq. 11. Equation 10 itself applies at any time during the course of reaction, so the simplest solution to this problem is to obtain the initial rate ratio, *i.e.* $(R_A/R_E)_0$.

First-order approximation can be made to R_A and R_E, when reactant conversions are not very large.

Then, $$R_A/[\text{Ac}] = a_0 + a_1 t, \tag{12}$$

and $$R_E/[\text{Et}] = b_0 + b_1 t. \tag{13}$$

Here the problem is to evaluate a_0 and b_0. Integration of Eq. 12 gives

$$\ln([\text{Ac}]_0/[\text{Ac}]) = a_0 t + a_1 t^2/2. \tag{14}$$

From the mechanism we obtain

$$[\cdot SiCl_3] = (k_1/k_7)^{1/2}(k_4/k_3)[\text{Ac}]^{1/2}[\text{TCS}] \times \{[\text{Ac}] + [\text{Et}](\lambda_4/\lambda_6 p)\}^{-1}, \tag{15}$$

where λ is a kinetic chain length and p stands for $(R_A/R_E)([\text{Et}]/[\text{Ac}])$. On the other hand, $R_A/[\text{Ac}] = k_3[\cdot SiCl_3]$, so that

$$a_0 = k_4(k_1/k_7)^{1/2}[\text{Ac}]_0^{1/2}[\text{TCS}]_0 \times \{[\text{Ac}]_0 + [\text{Et}]_0(\lambda_4/\lambda_6 p)\}^{-1}, \tag{16}$$

and

$$a_1/a_0 = 1/t\left[\frac{[\text{Ac}]^{1/2}[\text{TCS}]\{[\text{Ac}]_0 + [\text{Et}]_0(\lambda_4/\lambda_6 p)\}}{[\text{Ac}]_0{}^{1/2}[\text{TCS}]_0\{[\text{Ac}] + [\text{Et}](\lambda_4/\lambda_6 p)\}} - 1\right]. \tag{17}$$

Substitution of Eqs. 16 and 17 into Eq. 14 gives

$$a_0 = \frac{2}{t}\left[\frac{[\text{Ac}]^{1/2}[\text{TCS}]\{[\text{Ac}]_0 + [\text{Et}]_0(\lambda_4/\lambda_6 p)\}}{[\text{Ac}]_0{}^{1/2}[\text{TCS}]_0\{[\text{Ac}] + [\text{Et}](\lambda_4/\lambda_6 p)\}} + 1\right]^{-1} \times \ln\frac{[\text{Ac}]_0}{[\text{Ac}]}. \tag{18}$$

An approximate value of p can be obtained using Eq. 11 and λ_4/λ_6 is easily calculated since $\lambda_4/\lambda_6=(k_4/k_6)(k_8/k_7)^{1/2}$, where log $(k_4/k_6)=-1.2$ kcal mol^{-1}/2.3 RT[1] and $(k_8/k_7)^{1/2}=1.04$ (calculated based upon the mass difference between the terminating radicals). Also a concentration of each reactant obeys the stoichiometric Eq. 19.

$$\begin{aligned}[\mathrm{Ac}] &= [\mathrm{Ac}]_0-[\mathrm{A}]\\ [\mathrm{Et}] &= [\mathrm{Et}]_0-[\mathrm{E}]\\ [\mathrm{TCS}] &= [\mathrm{TCS}]_0-[\mathrm{A}]-[\mathrm{E}] \end{aligned} \tag{19}$$

In the similar way b_0 can be derived using Eqs. 10, 12, and 13.

$$b_0=\frac{2}{t}\left[\frac{(a_0+a_1t)\{1+(k_{-5}/k_6)[\mathrm{TCS}]_0{}^{-1}\}}{a_0\{1+(k_{-5}/k_6)[\mathrm{TCS}]^{-1}\}}+1\right]^{-1}\ln\frac{[\mathrm{Et}]_0}{[\mathrm{Et}]} \tag{20}$$

An approximate value of k_{-5}/k_6 can be obtained from the plot of ([A]/[E])([Et]/[Ac]) *vs.* [TCS]$^{-1}$. Thus we obtain a_0 and b_0. At the initial stage of reaction, Eq. 10 is expressed as

$$(R_\mathrm{A}/R_\mathrm{E})_0([\mathrm{Et}]_0/[\mathrm{Ac}]_0)=(k_3/k_5)\{1+(k_{-5}/k_6)[\mathrm{TCS}]_0{}^{-1}\}, \tag{21}$$

where $(R_\mathrm{A}/R_\mathrm{E})_0([\mathrm{Et}]_0/[\mathrm{Ac}]_0)=a_0/b_0$.
In this study we employed Eq. 21 to obtain k_3/k_5 and k_{-5}/k_6.

Results and Discussion

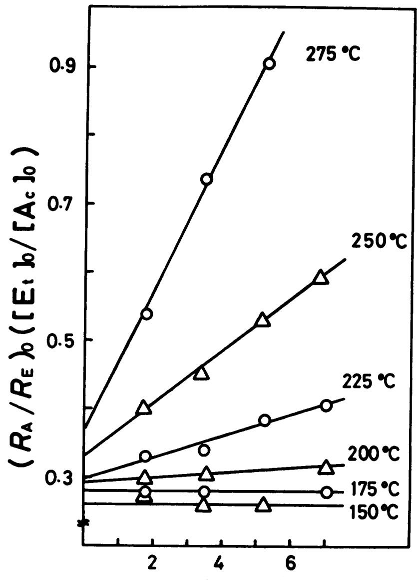

Fig. 1. Plot of Eq. 21.

Table 1. Yields of the adducts in the photolysis[a] of mixtures of CH_3COCH_3, C_2H_4, and $HSiCl_3$

Temp °C	Time min	Reactant (μmol cm^{-3}) [Ac]$_0$	[Et]$_0$	[TCS]$_0$	Product (μmol cm^{-3}) [A]	[E]
275	7	2.854	0.571	5.708	0.1410	0.0510
275	14	2.854	0.571	2.854	0.1444	0.0383
275	27	2.854	0.571	1.904	0.1828	0.0391
250	12	2.932	0.586	5.864	0.1483	0.0708
250	20	2.932	0.586	2.932	0.1208	0.0518
250	31	2.922	0.584	1.949	0.1290	0.0471
250	40	2.922	0.584	1.461	0.1212	0.0394
225	19	2.864	0.573	5.728	0.1553	0.0892
225	33	2.864	0.573	2.864	0.1311	0.0737
225	43	2.854	0.571	1.904	0.1128	0.0563
225	37	2.854	0.571	1.427	0.0714	0.0342
200	18	2.845	0.569	5.690	0.0976	0.0630
200	32	2.836	0.567	2.836	0.0853	0.0543
200	46	2.836	0.567	1.418	0.0566	0 0351
175	22	2.845	0.569	5.690	0.0714	0.0496
175	45	2.845	0.569	2.845	0.0712	0.0493
175	74	2.845	0.569	1.423	0.0577	0.0404
150	21	2.845	0.569	5.690	0.0421	0.0302
150	64	2.845	0.569	2.845	0.0643	0.0481
150	87	2.845	0.569	1.900	0.0583	0.0428

a) The volume of the cell was 137 cm^3 and the rate of absorption of light by 3 μmol cm^{-3} of acetone was *ca.* 7 × 10^{-12} einstein cm^{-3} min^{-1}.

Mixtures of CH_3COCH_3, C_2H_4 and varying amounts of $HSiCl_3$ were photolyzed in the gas phase between 150 and 275 °C. Reaction conversions of C_2H_4 were *ca.* 10%. The results are shown in Table 1.

The data in Table 1 were used to calculate $(R_\mathrm{A}/R_\mathrm{E})_0$, which are then plotted according to Eq. 21 (Fig. 1). The linearity of the plot at each temperature is excellent. Eq. 21 shows that the intercept of each line gives k_3/k_5 and its slope divided by the intercept value gives k_{-5}/k_6.

The least-mean-squares treatment of the Arrhenius plots of these rate constant ratios provides the Arrhenius parameters, which are shown in Table 2.

In Table 2 are compared the Arrhenius parameters obtained in this work with the previous values for 1-alkenes. The values of k_5/k_3 and k_{-5}/k_6 at 200 °C (middle temperature) in this work (3.5, 1.0 × 10^{-7} mol cm^{-3}) are in good agreement with those (3.2, 0.96 × 10^{-7} mol cm^{-3}) of the previous work.[2] Comparison of the values of log (A_{-5}/A_6) shows that the present value seems more reasonable, since there is no convincing

Table 2. Comparison of Arrhenius parameters with the previous values

	log (A_5/A_3)	$\frac{E_5-E_3}{\text{kcal mol}^{-1}}$	$\log\frac{A_{-5}/A_6}{\text{mol cm}^{-3}}$	$\frac{E_{-5}-E_6}{\text{kcal mol}^{-1}}$
Ethylene[a]	0.17 ± 0.05	−0.8 ± 0.1	3.4 ± 0.3	22.5 ± 0.7
Ethylene[b]	−0.14 ± 0.6	−1.4 ± 0.1	1.3 ± 0.4	18.0 ± 1.0
Propylene[c]	0.46 ± 0.09	−1.2 ± 0.04	3.3 ± 0.2	19.9 ± 0.4
1-Butene[c]	0.44 ± 0.05	−1.4 ± 0.1	3.8 ± 0.2	21.0 ± 0.4
1-Pentene[c]	0.51 ± 0.07	−1.4 ± 0.1	3.3 ± 0.6	19.6 ± 1.2
2-Methylpropene[c]	0.52 ± 0.41	−2.4 ± 0.8	4.8 ± 1.1	21.3 ± 2.3

a) This work. b) Ref. 2. c) Ref. 1.

elucidation that the transition state of only ethylene should be so tight while those of the other 1-alkenes are very loose.

References

1) T. Dohmaru and Y. Nagata, *J. Chem. Soc., Faraday Trans. 1*, **75**, 2617 (1979).

2) T. Dohmaru, Y. Nagata, and J. Tsurugi, *Chem. Lett.*, **1973**, 1031.

3) Since the rate of absorption of light was kept very small, *ca.* 7×10^{-12} einstein cm^{-3} min^{-1}, the kinetic chain length at the lowest temperature would exceed 50.