BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 2660—2661 (1972)

Photolytic Addition of Trichlorosilane to Acetone in the Gas Phase

Takaaki DOHMARU, Yoshio NAGATA, and Jitsuo TSURUGI
Radiation Center of Osaka Prefecture, Shinke-cho, Sakai, Osaka

(Received May 1, 1972)

Although silyl radicals have long been known to add to a C=O bond of ketones,[1–5] detailed kinetics of this reaction has never been studied. Our previous works[6,7] on the reduction of alkyl aliphatic carboxylates with trichlorosilane (TCS), reported that the first step of this reaction is addition of trichlorosilyl radical to carbonyl of carboxylates. In connection with these works, we have examined the kinetic behavior of the photolytic addition of TCS to acetone in the gas phase. Using a gaschromatograph directly attached to a vacuum line, the reaction mixture was kept completely free from contact with air during analyses.

Experimental

Apparatus and Procedure. Photolyses and analyses were carried out on a conventional Pyrex vacuum line. The full light from a 50 W medium pressure mercury arc was admitted into a Pyrex reaction vessel of 5.88 cc which cuts off the light of a wavelength region shorter than about 2700 Å to prevent absorption by TCS. The reaction vessel was heated in an electrical furnace controlled to better than ±1°C. After the photolysis, the reaction mixture was transferred by a Toepler pump to a gas sampler which is directly connected to a gaschromatograph equipped with a Gow-Mac thermister detector. A 1 m glass column of 30% SE-30 on Chromosorb W was used at 43°C. Before a series of runs, the column was siliconized by TCS until a reproducible peak height of TCS was obtained.

Material. TCS was treated with quinoline to remove hydrogen chloride and distilled under atmospheric pressure. The distillate (bp 31.8—32.2°C) was further purified by vacuum distillation. Acetone was dried with anhydrous magnesium sulfate and distilled through a 50 cm fractionation column packed with glass Raschig rings. Isopropoxytrichlorosilane prepared previously in this laboratory[6] was used after degassing. All the materials were stored on the vacuum line at −78°C.

Results and Discussion

Rates, and hence quantum yields for product formation and reactant consumption were determined from concentration-time curves at various temperatures. A typical analytical curve at 253°C is shown in Fig. 1.

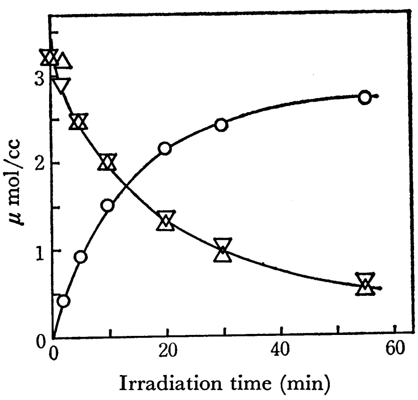

Fig. 1. Plots of the concentration of adduct, $(CH_3)_2CHOSiCl_3$ (○) and of reactants, TCS (△) and acetone (▽) with irradiation time at 253°C.

From Fig. 1, each one mole of acetone and TCS is consumed and one mole of adduct (isopropoxytrichlorosilane) is formed; the following stoichiometric relation holds within the experimental error.

$$(CH_3)_2CO + HSiCl_3 = (CH_3)_2CHOSiCl_3 \qquad (A)$$

The initial rate of reaction was obtained from the initial slope of a concentration-time curve of adduct at a given temperature. The results were summerized in Table 1. Activation energy was calculated to be 6.7 kcal/mol.

In order to obtain the kinetic orders of the reaction, the variations in rate with the reactant concentration were examined at 125°C. The results are presented in Fig. 2 in which (a) shows a run with a constant TCS pressure of 50 Torr (2.01 μmol/cc) and acetone pressure of 50—150 Torr, and (b) with a constant acetone pressure of 50 Torr and TCS pressure of 50—150 Torr. Fairly good linear plots were obtained in both runs and the slopes of (a) and (b) were calculated to be 0.40 and 1.0, respectively. The rate of

TABLE 1. RATES OF REACTION AT VARIOUS TEMPERATURE

$[TCS]_0 = [Acetone]_0 = 3.27$ μmol/cc

Temp. (°C)	253[a]	188	138	78
Rate (μmol/cc min)	0.202	0.071	0.032	0.0075
Quantum Yield[b]	90	32	14	3

a) At this temperature, the mixture was allowed to stand in the reaction cell for about 30 min without irradiation, but no detectable reaction product was observed in spite of the possible molecular reaction between acetone and TCS.[8]

b) Acetone photolysis was used for actinometry.[9]

---

1) For a reviw see for example, R. A. Jackson, *Adv. Free Radical Chem.*, **3**, 231 (1969).

2) R. Calas and N. Duffant, *Compt. Rend.*, **245**, 906 (1957).

3) R. Calas, J. Valade, and J. C. Miléo, *Bull. Soc. Chim. France*, **1961**, 2213.

4) H. Sakurai, A. Hosomi, and M. Kumada, This Bulletin, **40**, 1551 (1967).

5) A. G. Beaumont, C. Eaborn, and R. A. Jackson, *J. Chem. Soc.*, *B*, **1970**, 1624.

6) J. Tsurugi, R. Nakao, and T. Fukumoto, *J. Amer. Chem. Soc.*, **91**, 4587 (1969).

7) Y. Nagata, T. Dohmaru, and J. Tsurugi, submitted for publication.

8) J. A. Kerr, D. H. Slater, and J. C. Young, *J. Chem. Soc.*, *A*, **1966**, 104.

9) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry", John Wiley & Sons, Inc. New York (1966), p. 782.

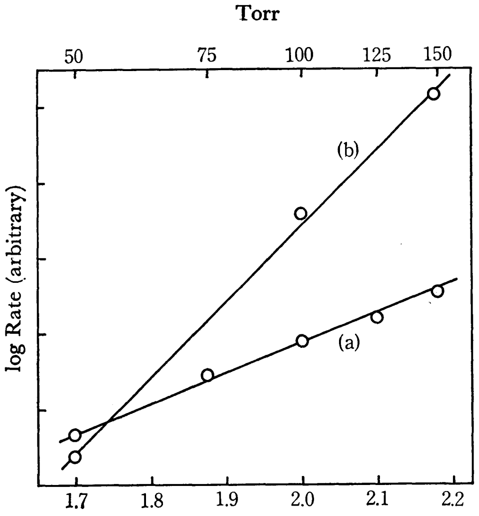

Fig. 2. Variation of rates of adduct formation with acetone concentration (a), and with TCS concentration (b) at 125°C.

adduct formation may be expressed by Eq. (B);

$$R_{adduct} \propto [\text{Acetone}]^{0.4}[\text{TCS}] \qquad \text{(B)}$$

The results mentioned above are consistent with the following mechanism.

$$\text{CH}_3\text{COCH}_3 \longrightarrow 2\cdot\text{CH}_3 + \text{CO} \qquad (1)$$

$$\cdot\text{CH}_3 + \text{HSiCl}_3 \longrightarrow \text{CH}_4 + \cdot\text{SiCl}_3 \qquad (2)$$

$$\cdot\text{SiCl}_3 + \text{CH}_3\text{COCH}_3 \longrightarrow (\text{CH}_3)_2\dot{\text{C}}\text{OSiCl}_3 \qquad (3)$$

$$(\text{CH}_3)_2\dot{\text{C}}\text{OSiCl}_3 + \text{HSiCl}_3 \longrightarrow (\text{CH}_3)_2\text{CHOSiCl}_3 + \cdot\text{SiCl}_3 \qquad (4)$$

$$2(\text{CH}_3)_2\dot{\text{C}}\text{OSiCl}_3 \longrightarrow \text{products} \qquad (5)$$

In our experimental conditions, TCS does not absorb light and only acetone contributes to an initiation reaction (1). Reactions (3) and (4) constitute chain propagating steps. Reaction (5) was assumed as a termination step, and will be seen to lead to the correct kinetic behavior. The steady-state treatment of the scheme leads to rate Eq. (C), where k_x denotes a rate constant of a reaction (x) and I_a does a rate of absorption of light. I_a may be considered to be directly proportional to an acetone concentration. Then, Eq. (C) leads to Eq. (D), which is in reasonable agreement with the observations. The reaction chain is adequately long at 253°C, so that the overall variations of the concentration of the reactants and product may be explained in terms of reactions (3) and (4), the inspection of which leads to the stoichiometric Eq. (A). This was also confirmed by the result of Fig. 1. From Eq. (C), overall activation energy E_0 is equal to $E_4 - {}^1/_2E_5$. The activation energy of a radical combination reaction such as reaction (5) may be generally assumed to be ~0 in the gas phase, so $E_4 \simeq E_0 = 6.7$ kcal/mol.

$$R_{adduct} = k_4 k_5^{-1/2} I_a^{1/2}[\text{TCS}] \qquad \text{(C)}$$

$$R_{adduct} \propto [\text{Acetone}]^{0.5}[\text{TCS}] \qquad \text{(D)}$$