

Journal of Organometallic Chemistry, 381 (1990) 155–164
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20386

γ -Ray induced reduction of acid chlorides with trichlorosilane

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(Received July 18th, 1989)

Abstract

The γ -ray induced reduction of various acid chlorides (RCOCl) with trichlorosilane was studied at ambient temperature. Trichlorosilyl radicals were found to attack acid chloride selectively at chlorine atom to produce acyl radicals at the first step. The preference of chlorine-atom attack to carbonyl-oxygen-atom attack is explained in terms of molecular orbital calculations (STO-3G); the SOMO (singly occupied molecular orbital) of trichlorosilyl radicals is more likely to interact with the energetically closer σ -HOMO (C-Cl) than π -HOMO (C=O) of acid chlorides. The acyl radicals thus formed yield two kinds of products depending on the nature of the alkyl moiety involved. When the alkyl moiety (R) is tertiary, the acyl radical undergoes decomposition into carbon monoxide and an alkyl radical which finally yields an alkane (RH). When R is primary, the acyl radical abstracts a hydrogen atom from trichlorosilane producing an aldehyde, which, by subsequent hydrosilation, gives an alkoxysilane ($\text{RCH}_2\text{OSiCl}_3$) as a final product. Thus, the present reaction can be used as a complementary synthesis to the reported method in which initiators are used.

Introduction

Trichlorosilane has been used as a versatile reducing reagent for a variety of organic substrates such as alkyl halides [1], olefinic compounds [2], carbonyl compounds [3], and other functional groups [4^{*}] under free-radical reaction conditions. The main reactions of trichlorosilyl radicals are the abstraction of halogens and the addition to unsaturated bonds.

An acid chloride has two sites that are open to attack in the molecule, and it can be a convenient substrate with which to study an intramolecular competition reaction between two functional groups toward trichlorosilyl radicals. The free-radi-

^{*} Reference number with asterisk indicates a note in the list of references.

cal reaction of acid chlorides with silane that has been reported is the reduction with tripropylsilane initiated by di-*t*-butyl peroxide (DTBP) to give alkanes (eq. 1) [5].



Trialkylsilyl radicals are regarded as nucleophiles [6] whereas trichlorosilyl radicals are seen as electrophiles [7]. Furthermore, γ -ray induced free-radical reduction sometimes results in the formation of a different product from that formed by the conventional method [8]. So it was of interest to see that changes in reactivity are brought about by changing the polarity of silyl radicals and initiation method. Thus, we have studied γ -ray induced reduction of acid chlorides with trichlorosilane.

Results and discussion

A degassed mixture of pivaloyl chloride and trichlorosilane in an NMR tube was subjected to γ -ray irradiation at room temperature. The NMR spectrum of the irradiated (2 kGy) sample (Fig. 1B) indicates new sets of signals: a doublet ($\delta = 0.89$, J 6.7 Hz) and a multiplet ($\delta = 1.71$, J 6.7 Hz) which are reasonably assigned to those of isobutane [9]. Further irradiation (at 6 kGy) increased the signals of isobutane while the starting material disappeared almost completely (Fig. 1C).

A degassed mixture of pivaloyl chloride and trichlorosilane in a sealed Pyrex tube with a breakable tip was irradiated at 8 kGy. An uncondensable gas at -196°C was introduced into the IR gas cell. The IR spectrum of the gas showed an absorption centered at 2145.9 cm^{-1} with PR branches characteristic of carbon monoxide. GLPC analysis of the gas showed that it consisted solely of CO. The

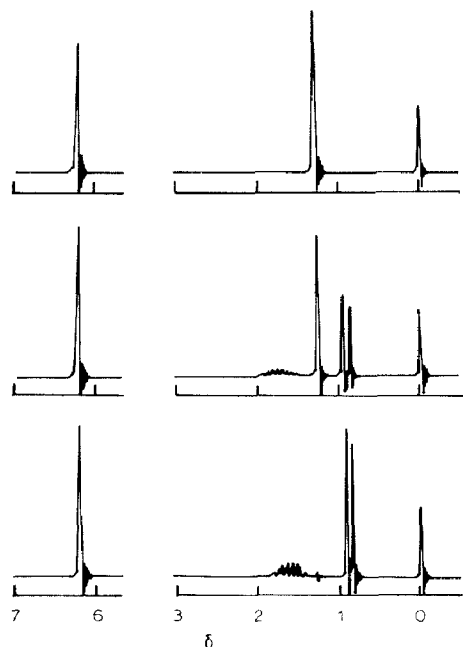
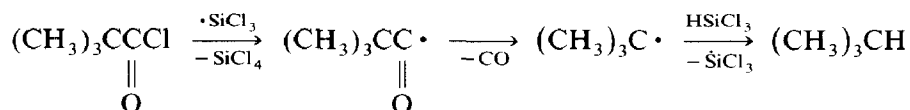


Fig. 1. NMR spectra of a mixture of pivaloyl chloride and trichlorosilane (molar ratio, 1:7). (A) Before irradiation. (B) Irradiated at 2 kGy. (C) Irradiated at 6 kGy.



Scheme 1

yield of the evolved CO gas was nearly quantitative based on the amount of pivaloyl chloride fed in.

Quantitative production of CO and isobutane was also observed in the reaction of pivaloyl chloride and dimethylchlorosilane or dichloromethylsilane, suggesting that the process for the production of CO and isobutane was independent of the nature of silyl radicals.

The production of CO serves as a good probe for the involvement of pivaloyl radicals [10]. This fact combined with the large *G*-value* (ca. 800) of the consumed pivaloyl chloride suggests the occurrence of an efficient free-radical chain reaction.

These results may be rationalized as the sequence of reactions shown in Scheme 1; the initial dechlorination of pivaloyl chloride by trichlorosilyl radicals yields pivaloyl radicals which subsequently decompose into tert-butyl radicals and carbon monoxide. The alkyl radicals thus produced abstract a hydrogen atom from trichlorosilane yielding the corresponding alkane as a final product.

To compare the ease of this chlorine abstraction with the well-established addition to carbonyl oxygen in methyl acetate by trichlorosilyl radicals [11], the competition between pivaloyl chloride and methyl acetate for trichlorosilyl radicals was evaluated. The rate of the chlorine abstraction from pivaloyl chloride relative to the addition to carbonyl group in the methyl acetate was 24.5, suggesting that chlorine abstraction from pivaloyl chloride is far more feasible than the addition to the carbonyl group.

To examine the general applicability of this reaction, γ -ray induced reactions of various kinds of acid chlorides with trichlorosilane were studied. The results are summarized in Table 1.

As shown in Table 1, CO was formed in all cases. Here, the fact that the yields of CO were nearly equal to those of RH in most cases lends support to the mechanism outlined in Scheme 1. But alkoxytrichlorosilanes ($\text{RCH}_2\text{OSiCl}_3$) were formed in addition to CO and alkanes in all cases, except for that of pivaloyl chloride (Table 1). Here, the production of alkoxytrichlorosilane was not predicted from Scheme 1. There are two possible routes for the formation of alkoxytrichlorosilanes, viz., by Scheme 2 or by Scheme 3. The latter Scheme involves an initial addition of trichlorosilyl radicals to the carbonyl oxygen atom, a reaction which may be facilitated by the formation of a strong Si–O bond of 128 kcal/mol [12].

To find out which site (Cl or O) in an acid chloride is more open to attack by trichlorosilyl radicals, we performed molecular orbital calculations. The molecular orbital calculations (STO-3G) for the trichlorosilyl radicals and acetyl chloride, which was chosen for convenience of calculation, gave an energy diagram of frontier orbitals as shown in Fig. 2. The energy level of SOMO (singly occupied molecular orbital) in trichlorosilyl radicals (-9.04 eV) resembles more closely those of the trichloromethyl radicals (-8.8 eV) and the methyl radicals (-9.8 eV) than the

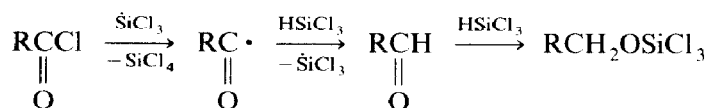
* The number of molecules consumed or formed per 100 eV absorbed radiation energy.

Table 1

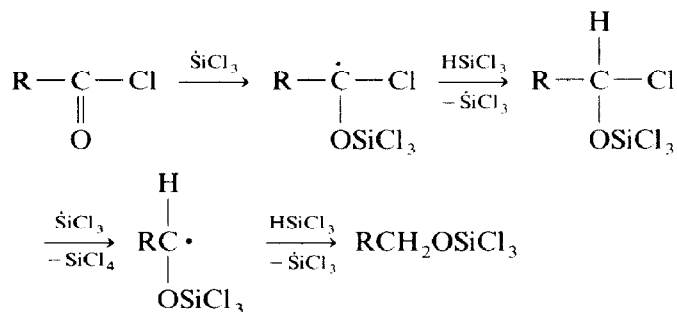
Reduction of acid chlorides with trichlorosilane ^a

$\text{RCOCl} + \text{HSiCl}_3 \xrightarrow{\gamma\text{-Rays}} \text{RH} + \text{RCH}_2\text{OSiCl}_3$				
R	dose (kGy)	Yield(%) ^b		
		CO	RH	$\text{RCH}_2\text{OSiCl}_3$
C_2H_5	490	22.1	15.3	70.8
$n\text{-C}_4\text{H}_9$	490	15.7	2.4	80.7
$n\text{-C}_5\text{H}_{11}$	490	12.6	7.2	83.6
$n\text{-C}_7\text{H}_{15}$	490	11.4	11.8	86.6
$n\text{-C}_9\text{H}_{19}$	490	11.7	10.0	81.2
$n\text{-C}_{13}\text{H}_{27}$	490	11.4	— ^c	89.0
$(\text{CH}_3)_2\text{CH}$	350	60	52.1	30.5
$(\text{C}_2\text{H}_5)_2\text{CH}$	350	55.8	42.3	37.2
$\text{C}_4\text{H}_9\text{CH}$	490	41	12.8	31.9
$n\text{-C}_6\text{H}_{11}$	490	12	10.0	84.5
$(\text{CH}_3)_3\text{C}^d$	8	98	100	0
1-Ad ^e	350	11.5	12.0	— ^c
C_6H_5	490	10.2	4.0	trace
$\text{C}_6\text{H}_5\text{CH}_2$	490	4.1	6.7	trace
$o\text{-CH}_3\text{C}_6\text{H}_4$	490	8.7	trace	trace
$\text{C}_6\text{H}_5\text{CH}=\text{CH}$	490	7.8	28.6	— ^c
$\text{CH}_3\text{O}_2\text{C}(\text{CH}_2)_2$	350	26	38.6	— ^c
$\text{ClCO}(\text{CH}_2)_4$	350	36.7	trace	— ^c

^a $[\text{HSiCl}_3]/[\text{RCOCl}] = 6$, Dose rate, 70 kGy/hr. ^b Based on the amount of acid chloride fed in. ^c Not determined. ^d Dose rate, 8 kGy/hr. ^e Ad = adamantyl.



Scheme 2



Scheme 3

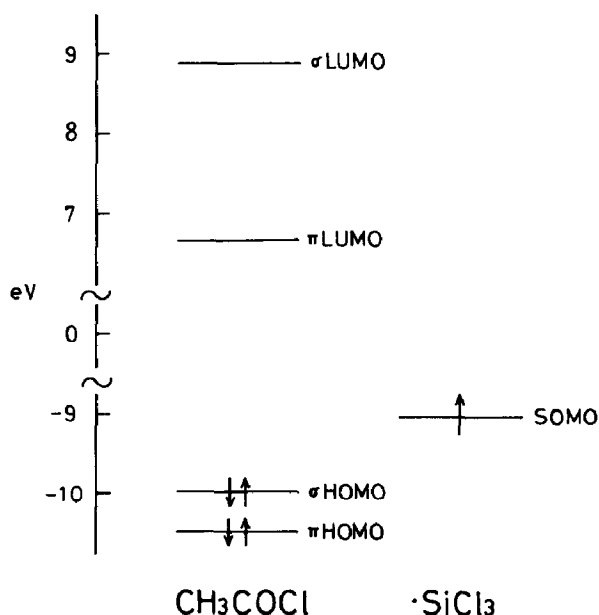
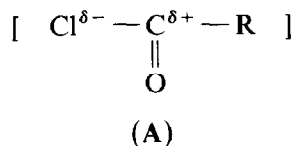


Fig. 2. Energy levels of frontier orbitals of acetyl chloride and trichlorosilyl radicals.

triethylsilyl radicals (-7eV) [13], indicating the electrophilic character of trichlorosilyl radicals [7]. The energy level of the SOMO of the trichlorosilyl radical lies closer to the σ -HOMO (C-Cl) than to the π -HOMO of the carbonyl group. This fact also predicts the preferential interaction of the SOMO with the σ -HOMO (C-Cl).

A contour map of the σ -HOMO of acetyl chloride is shown in Fig. 3. The orbital of the C-Cl bond is bonding while the in-plane π -orbital of the C-O bond is antibonding. Thus, it is obvious that trichlorosilyl radicals exclusively attack the chlorine atom of acetyl chloride to give acetyl radicals and tetrachlorosilane.

The charge distribution of trichlorosilyl radicals and acid chloride is shown in Fig. 4. The preferential attack at the more negative chlorine atom than at the carbonyl oxygen in the acid chloride by electrophilic trichlorosilyl radicals can be predicted from electrostatics. Polarization of the acid chloride, as shown (A), is important.



Furthermore, we have found that γ -ray irradiation of a mixture of aldehydes and trichlorosilane gives the corresponding alkoxytrichlorosilanes, as in the photochemical reaction [3].

Thus the initial site where the trichlorosilyl radicals attack the acid chloride is the chlorine atom rather than the oxygen atom (Scheme 2).

The ratio of the yields of CO or RH to that of $\text{RCH}_2\text{OSiCl}_3$ reflects the rate of the decomposition of acyl radicals into alkyl radicals and CO (Scheme 1) relative to that of the hydrogen abstraction from trichlorosilane (Scheme 2), i.e., the ratio of

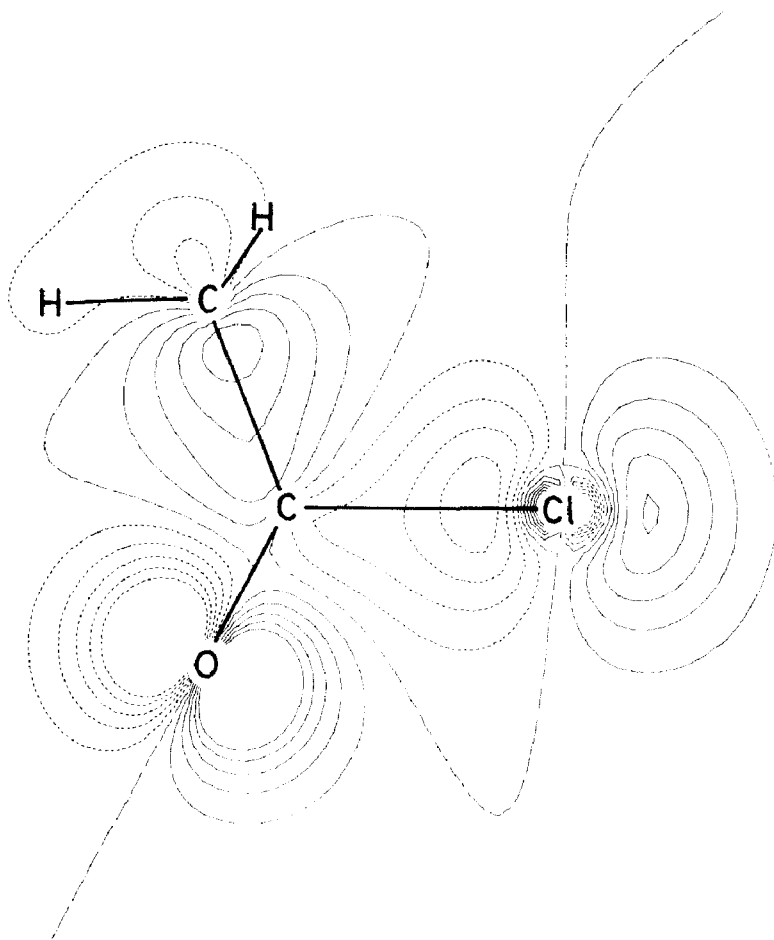


Fig. 3. Contour map of σ -HOMO of acetyl chloride.

$[RH \text{ or } CO]/[RCH_2OSiCl_3]$ depends on the stability of alkyl radicals. Table 1 shows that the yield of decarbonylation products (CO or RH) is high when the alkyl moiety is tertiary and secondary but it is low when the alkyl is a primary group. The present result is consistent with the order of the stabilities of the alkyl radicals unlike the DTBP-initiated reaction from which the yield of t-alkanes is poor [5].

The dependence of CO yield on molar ratios of $[HSiCl_3]/[\text{acid chloride}]$ for pivaloyl, 2-ethylbutyryl, and n-decanoyl chlorides, which were chosen as examples

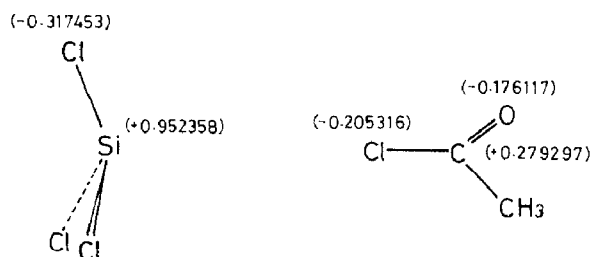


Fig. 4. Net charge distribution in acetyl chloride and trichlorosilyl radicals.

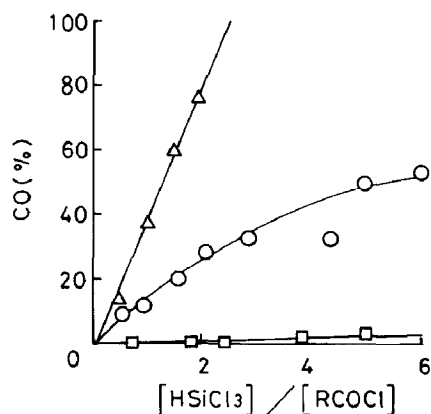


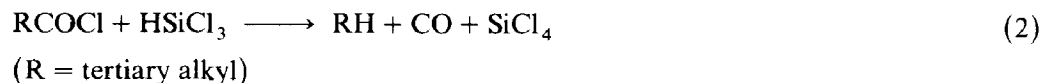
Fig. 5. Effect of the molar ratio of $[\text{HSiCl}_3]/[\text{RCOCl}]$ on CO yield from acid chloride. (Δ) Pivaloyl chloride; dose, 73 kGy. ($\circ$) 2-Ethylbutyryl chloride; Dose, 511 kGy. ($\square$) n-Decanoyl chloride; Dose, 511 kGy. Dose rate, 73 kGy/hr.

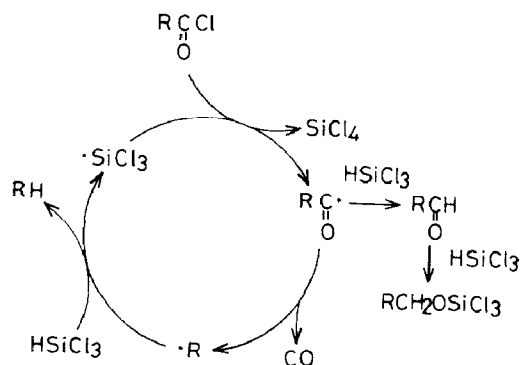
having tertiary, secondary, and primary alkyl groups in acid chlorides, were studied. The results are shown in Fig. 5.

The yield of CO in the case of pivaloyl chloride increased linearly with increasing ratios; a relation, which can be explained by an increase in the initial concentration of trichlorosilyl radicals with an increase in the $[\text{HSiCl}_3]/[\text{acid chloride}]$ ratio. In view of the strict linearity of the CO yield vs. the relative $[\text{HSiCl}_3]$ concentration, the pivaloyl radicals may be regarded exclusively as decomposing in accordance with Scheme 1; deviation from the linearity indicates the contrary (i.e. hydrogen atom abstraction depicted in Scheme 2). On the other hand, the yield of CO in the case of decanoyl chloride did not exceed 3%, suggesting that the initially formed acyl radicals are resistant to decomposition and mainly undergo hydrogen abstraction. The CO yield was observed to deviate from linearity in the case of 2-ethylbutyryl chloride. This deviation can be accounted for by the occurrence of a hydrogen atom abstraction, since the higher ratio of $[\text{HSiCl}_3]/[\text{acid chloride}]$ facilitates the bimolecular reaction in Scheme 2.

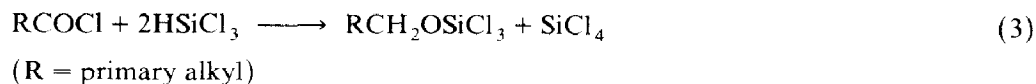
In conclusion, γ -ray induced reduction of acid chlorides with trichlorosilane proceeds by an initial attack at a chlorine atom to give acyl radicals. Subsequent reactions of the acyl radicals occur in two ways, viz., decomposition and hydrogen atom abstraction from HSiCl_3 , the relative importance depending on the stability of the particular acyl radicals. The overall reaction mechanism is depicted in Scheme 4.

Billingham et al. [5] reported that DTBP initiated reductions of acid chlorides with tripropylsilane produced primary and secondary alkanes in high yields but tertiary alkanes in low yields. In contrast, tertiary and secondary alkanes can be produced by our method (eqs. 2 and 3) and would, thus, be a useful synthetic alternative to Billingham's method [5].





Scheme 4



A low yield of aromatic products is observed in the reduction of carboxylic acid chlorides and is attributed to the scavenging effect of the aryl groups similar to the reduction of aromatic esters [11]. The low yield of adamantane, though the alkyl is tertiary, suggests the importance of electronic effects on the unimolecular decomposition of acyl radicals; the adamantyl group is poorly electron-releasing. Complex products were obtained in the reactions of adipoyl chloride and succinoyl chloride derivatives.

Experimental

Materials. Acid chlorides were prepared by the reaction of thionyl chloride with carboxylic acid or they were obtained commercially, and used after distillation. Trichlorosilane was purified as reported previously [15]. Alkoxytrichlorosilanes as authentic samples for GLPC analysis were prepared by γ -ray induced hydrosilation reaction of the corresponding aldehyde [3,11].

Instruments. Infrared spectra were recorded on a JASCO DS-705 spectrophotometer in a liquid cell (KBr window) for liquid samples and in a 10-cm gas cell (NaCl window) for gaseous samples. Mass spectra were recorded with a Shimadzu LKB 9000 gaschromatograph-mass spectrometer. NMR spectra were obtained with a JEOL NM-100 spectrometer; chemical shifts are in δ unit using tetramethylsilane as an internal standard. GLPC analyses were performed on Shimadzu GC6AM-PrTF using a thermal conductivity detector and a flame ionization detector. Molecular Sieves (5A) or Porapak Q columns (2 m $\times$ 4 mm) for gas samples and 25% Silicon DC 200, 20% Dioctyl Phthalate, 15% Silicon OV 27 and 30% SE 30 on Celite 545 columns (2 m or 3 m $\times$ 4 mm) for liquid samples were used. Peak areas were automatically calculated by a Shimadzu Chromatopack CR-1A integrator. The products were identified by comparison of their retention times with those of authentic samples. The quantities of volatile materials including CO gas were measured by a Senso Pressure Transducer Model A instrument coupled with a Sokken Model SPX-A Amplifier which was attached to a vacuum line of a known volume. γ -Rays were from a 10-kCi ^{60}Co source.

Reaction of pivaloyl chloride with trichlorosilane

A mixture of pivaloyl chloride, trichlorosilane and tetramethylsilane (1 : 7 : 0.5) in an NMR tube was degassed by a number of freeze-and-thaw cycles. An NMR signal from the pivaloyl group was located at δ 1.28(s) (Fig. 1A). After irradiation (dose rate, 2 kGy/h; dose, 2 kGy) new signals appeared. These signals were assigned to those of isobutane as follows [9]: δ = 0.98(d, J 6 Hz, $(\text{CH}_3)_3\text{CH}$) and 1.7–1.9(m, J 6 Hz, $(\text{CH}_3)_3\text{CH}$). Further irradiation of this sample (6 kGy) almost totally suppressed the signals from the acid chloride and enhanced those from isobutane.

A mixture of pivaloyl chloride and trichlorosilane was irradiated (dose rate, 8 kGy/h; dose, 8 kGy) in a Pyrex tube with breakable seal, and the sample was frozen at -196°C . The seal was broken, and the gas that had evolved from the sample during the freeze-and-thaw cycles, was introduced into an IR gas cell. After an IR measurement, the gas sample was transferred to a GLPC gas sampler and then subjected to GLPC analysis. The solidified mixture was found to contain appreciable amounts of the gas.

Reaction of pivaloyl chloride with methyldichlorosilane or dimethylchlorosilane

A degassed mixture of pivaloyl chloride, dimethylchlorosilane (or methyldichlorosilane) and tetramethylsilane (1 : 10 : 0.5) in an NMR tube or a Pyrex tube was exposed to γ -rays (15 kGy) as described above. Isobutane and carbon monoxide were generated quantitatively.

Reaction of trichlorosilane and various kinds of acid chlorides

Each of the acid chlorides listed in Table 1 was mixed with trichlorosilane in a Pyrex tube with breakable seal, degassed, sealed, and irradiated. The evolved carbon monoxide was measured by the same method as described above and the components, non-volatile at liquid nitrogen temperature, were analysed by GLPC.

Preparation of alkoxytrichlorosilanes as authentic samples

An aldehyde was mixed with trichlorosilane in a Pyrex tube, degassed, sealed, and irradiated. The tenfold excess of trichlorosilane was distilled from the sample and the resulting residue was used as an authentic sample for GLPC analysis.

Competitive reaction

An equimolar mixture of pivaloyl chloride, methyl acetate and a sixfold excess of trichlorosilane in an NMR tube was degassed and subjected to γ -ray irradiation (dose rate 2kGy/h). Use of the Ingold–Show's equation [16], showed the rate of the abstraction of chlorine atom in pivaloyl chloride by trichlorosilyl radicals relative to that of the addition to carboxyl oxygen in methyl acetate to be 24.5.

Molecular orbital calculation

Molecular orbital calculations were carried out by use of restricted Hartree–Fock STO-3G for acetyl chloride and unrestricted Hartree–Fock STO-3G for trichlorosilyl radicals. Published parameters for acetyl chloride [17] and for the trichlorosilyl radicals [18] were used in the calculations.

Dependence of the carbon monoxide yield on molar ratio

Pivaloyl, 2-ethylbutyryl, and n-decanol chlorides were chosen as the examples of the tertiary, secondary and primary alkyls of the acid chlorides. Each acid chloride

was mixed with trichlorosilane at a known molar ratio in a Pyrex tube with a breakable seal by use of the conventional vacuum technique. The samples were irradiated (pivaloyl chloride, dose, 73 kGy. 2-ethylbutyryl chloride and n-decanol chloride, dose, 511 kGy) and the volume of the evolved carbon monoxide was measured.

Acknowledgement

The authors thank the Computer Center, Institute for Molecular Science, Okazaki National Research Institute for the use of the HITAC M-820/80 computer and Library Program Gaussian 82.

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