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THE THERMOLYSIS OF ETHYLTRICHLOROSILANE AND ETHYLTRIMETHYLSILANE

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SUMMARY

The thermal decompositions of ethyltrichloro- and ethyltrimethyl-silane have been studied in the gas phase at 823 K. The main primary process in each case is the dehydrosilylation reaction $X_3SiCH_2CH_3 \rightarrow X_3SiH + CH_2{=}CH_2$ (X = Cl or Me), though several additional products are formed, mainly in secondary reactions. It is concluded that the dehydrodesilylations involve a radical chain sequence, and that the formation of vinyl chloride by dehydrosilylation during the thermolysis of (2-chloroethyl)trichlorosilane probably also follows a radical pathway rather than the four-centre molecular process previously suggested.

The following reactions at ca. 823 K have also been briefly examined: (*i*) the thermal decomposition of trichlorosilane; (*ii*), the interaction of ethylene and trichlorosilane; (*iii*) the thermal decomposition of vinyltrichlorosilane.

INTRODUCTION

Addition of silicon hydrides to olefins, hydrosilylation, occurs under a very wide range of conditions, but there is no evidence that it ever occurs by a four-centre molecular process[1]; such a process under thermal activation would be "forbidden" on the basis of orbital symmetry conservation for first-row elements, but not necessarily so for reactions involving second-row or heavier elements (see *e.g.* ref. 2). The reverse reaction, dehydrosilylation, is also known[3], and in one case, namely the formation of some vinyl chloride in the thermal decomposition of (2-chloroethyl)trichlorosilane, it was suggested that it probably involved a four-centre molecular process, as does the main reaction, which produces tetrachlorosilane and ethylene[4]. The evidence indicating this was: (*i*) that both the main reaction and the dehydrosilylation were clean first-order processes, and (*ii*), that the presence of nitric oxide had little effect on the overall rate of disappearance of the ethyltrichlorosilane or the proportion of vinyl chloride formed. It was puzzling, however, that no appreciable quantities of vinyl chloride were formed in the thermal decompositions of the closely related compounds $EtCl_2SiCH_2CH_2Cl$, $Et_2ClSiCH_2CH_2Cl$, $Me_3SiCH_2CH_2Cl$, and $Me_2PhSiCH_2CH_2$-

Cl[5], since there seems no good reason why the four-centre elimination of an R_xCl_{3-x}-SiH species should occur significantly less readily than that of Cl_3SiH.

In a study of the nature of thermal dehydrosilylation, we have now examined the thermolysis of ethyltrichloro- and ethyltrimethyl-silane in the gas phase at 823 K. We find that the dehydrosilylations involve radical chain sequences, as described below. To throw further light on the nature of the reaction of ethyltrichlorosilane, we have also briefly examined, under similar conditions, three associated reactions, namely: (*i*) the decomposition of trichlorosilane; (*ii*), the interaction of ethylene and trichlorosilane; and (*iii*), the decomposition of vinyltrichlorosilane.

EXPERIMENTAL

The static system employed for the thermolyses has been described[6]; a reaction temperature of 823 ± 5 K was used. Products were analysed by GLC (kathometer detector; column 2.35 m, 10% w/w squalane on 60–85 mesh Embacel), after calibration with authentic samples in the case of major products, but assuming proportionality between the peak areas and concentrations in the case of some minor products. Products were mainly identified by comparison of their retention times with those of authentic samples, complemented by IR and mass spectral examination of isolated samples. Methane and ethane were not separated from ethylene in the GLC analysis, but their presence in some cases was revealed by mass spectra.

RESULTS

(1). *Thermolysis of ethyltrichlorosilane*

Initial pressures ranged from 44 to 176 mmHg. In a typical experiment, 87 mmHg of ethyltrichlorosilane after 66 min gave unchanged $EtSiCl_3$ (43), C_2H_4 (11.1), $SiCl_4$ (9), $CH_2{=}CHSiCl_3$ (1.5), and $HC{\equiv}CSiCl_3$ (0.8 mmHg); these gaseous products accounted for only 56% of the $EtSiCl_3$ decomposed. All the products mentioned were positively identified by comparison of their GLC retention times and IR spectra with those of authentic samples, except for $HC{\equiv}CSiCl_3$, which has not been isolated previously (*cf.* refs. 7 and 8); its structure was inferred from its retention time (a little longer than that of $SiCl_4$, indicating a b.p. in the region of 60°C) and from the presence of strong sharp peaks in the IR spectrum at 673 cm^{-1}. (Monosilylacetylenes have[8] H–C bonding deformations at 670–680 cm^{-1}.) An additional product, (A), formed in smaller quantity than $HC{\equiv}CSiCl_3$, had a retention time between that of the latter and that of $CH_2{=}CHSiCl_3$ (closer to the latter), and may have been $EtCl_2SiH$. The concentration–time curves for ethylene and trichlorosilane were of a shape consistent with their being primary products, while the curve for tetrachlorosilane had the distinctive sigmoid shape characteristic of a secondary product. The curve for vinyltrichlorosilane passed through a flat maximum.

When the initial pressure of $EtSiCl_3$ was varied over a 4-fold range, the ratio $C_2H_4/EtSiCl_3$ after a given time was independent of the initial pressure, indicating that the conversion of $EtSiCl_3$ into ethylene was a first-order process; the rate constant was about 10^{-4} sec^{-1}. Addition of nitric oxide (11 with 25.5 mmHg of $EtSiCl_3$) lowered the rate of decomposition by at least 25%, and possibly by as much as 90% in the very early stages; no new products were observed, but the formation of trichlorosilane was almost completely suppressed.

(2). *Related reactions*

(*i*). Trichlorosilane decomposed at a rate of the same order of magnitude as that for ethyltrichlorosilane. Hydrogen and silicon tetrachloride were the main gaseous products; dichlorosilane, identified by its IR spectrum, was a minor product, its concentration going through a maximum as the reaction progressed.

(*ii*). Vinyltrichlorosilane decomposed at a rate comparable with that for ethyltrichlorosilane, to give ethylene, trichlorosilane, and tetrachlorosilane as major products; once again the products included small quantities of ethynyltrichlorosilane and compound (A) ($EtSiHCl_2$?), an even smaller quantity of ethyltrichlorosilane, and a trace of methane.

(*iii*). Ethylene and trichlorosilane reacted together to give mainly ethyltrichlorosilane, but also a substantial quantity of vinyltrichlorosilane; there were smaller amounts of tetrachlorosilane and ethynyltrichlorosilane, and traces of hydrogen, methane, ethane, hydrogen chloride and two other volatile species. In reactions involving initially 47.3 mmHg of ethylene and 39.5 mmHg of trichlorosilane, ca. 16.9 mmHg of ethylene and 12.9 mmHg of trichlorosilane had disappeared after 20 min, and 7.7 mmHg of ethyltrichlorosilane and 3.3 mmHg of vinyltrichlorosilane had appeared, along with ca. 3.5 mmHg of a mixture of tetrachlorosilane and ethynyltrichlorosilane. The amounts of ethyl- and vinyl-trichlorosilane passed through maxima. Increase in the initial ratio of ethylene to trichlorosilane caused an increase in the $Et_3SiCl_3/CH_2{=}CHSiCl_3$ ratio after reaction for 20 min.

(3). *Thermolysis of ethyltrimethylsilane*

Thermolysis of ethyltrimethylsilane gave ethylene and trimethylsilane as the greatly predominant products, along with small quantities of tetramethylsilane, methane, and a further product, (B), and trace amounts of two additional products with retention times between those of ethylene and trimethylsilane. Product (B) had a retention time (and thus probably a b.p.) intermediate between that of tetramethylsilane and ethyltrimethylsilane, and was assumed to be vinyltrimethylsilane*. The methane and ethylene were not resolved on the column, but from the mass spectrum and IR spectrum of the mixed fraction the methane was estimated to contribute less than 5 % of this fraction. In a typical experiment, 22.5 mmHg of ethyltrimethylsilane after 66 min gave unchanged ethyltrimethylsilane (11.6 mmHg), ethylene (+a little methane) (10.5 mmHg, including < 0.5 mmHg of methane), trimethylsilane (8.4 mmHg), vinyltrimethylsilane, (1.6 mmHg), and tetramethylsilane (0.4 mmHg), plus traces of the two additional products mentioned above (together less than 0.5 mmHg). The material balance was thus satisfactory, in contrast to that observed with ethyltrichlorosilane. In the early stages of the reaction, ethylene and trimethylsilane were formed at approximately equal rates. As the reaction proceeded the concentration of vinyltrimethylsilane passed through a shallow maximum.

Addition of nitric oxide (ca. 10 with 22 mmHg of ethyltrimethylsilane) had a considerable effect on the reaction, viz., (*a*), the rate of disappearance of the ethyltrimethylsilane was approximately doubled; (*b*), the rate of formation of trimethylsilane

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* Unfortunately, although an authentic sample of vinyltrimethylsilane could have been easily obtained, this minor product was not positively identified, its mechanistic significance not being appreciated at the time of the experiments.

was approximately halved; and (*c*), two new products appeared, one of which was positively identified from its retention time as hexamethyldisiloxane, and the other of which had a retention time consistent with its being trimethylsilanol.

DISCUSSION

The thermolysis of ethyltrichlorosilane is complicated by the instability of trichlorosilane under the reaction conditions. A small part of the tetrachlorosilane found may have been formed in primary reactions (see below), but the concentration–time curve indicated that it was mainly a secondary product; if, for simplicity, it is assumed to have been formed entirely from trichlorosilane in secondary reactions, with the overall stoichiometry: $4\,HSiCl_3 \rightarrow 3\,SiCl_4 + H_2 + Si$, then the total pressure of trichlorosilane formed in the example given above would be 23.1 mmHg, virtually equal to the pressure of ethylene formed (viz. 22.7 mmHg). Hence, in the initial stages ethylene and trichlorosilane seem to be formed in roughly equal amounts, as are ethylene and trimethylsilane in the thermolysis of ethyltrimethylsilane. The greatly dominant course of both thermolyses in their early stages thus appears to be the dehydrosilylation reaction (1) ($X = Cl$ or Me), which is, of course, reversible, as illustrated by the observed reaction between ethylene and trichlorosilane.

$$C_2H_5SiX_3 \rightarrow C_2H_4 + HSiX_3 \tag{1}$$

In each case the vinylsilicon species $CH_2{=}CHSiX_3$ is also produced, however, and this is mechanistically very significant, since it is difficult to visualize a plausible route to such a species except through the radical intermediate $\cdot C_2H_4SiX_3$,which could give rise to the vinyl–silicon product by one or more of reactions (2)–(4)

$$\cdot C_2H_4SiX_3 \rightarrow CH_2{=}CHSiX_3 + H\cdot \tag{2}$$

$$2\,\cdot C_2H_4SiX_3 \rightarrow CH_2{=}CHSiX_3 + C_2H_5SiX_3 \tag{3}$$

$$X_3Si\cdot + \cdot C_2H_4SiX_3 \rightarrow X_3SiH + CH_2{=}CHSiX_3 \tag{4}$$

From the initially produced $CH_2{=}CHSiX_3$, the ethynyl species $CH{\equiv}CSiX_3$, which was also produced, could then be formed analogously via the radical $\cdot C_2H_2SiX_3$, and it is noteworthy that the amounts of $CH_2{=}CHSiCl_3$ and $CH_2{=}CHSiMe_3$ went through maxima as the reaction progressed.

The substantial effect of nitric oxide on the rates and on the product compositions of the thermolyses is also evidence for a radical mechanism, and we suggest the chain sequence (5)–(8) + (4) for the gas phase dehydrosilylation, the choice of (8) and (4) as termination steps being dictated by the observation of first-order kinetics for the ethyltrichlorosilane reaction

$$C_2H_5SiX_3 \rightarrow \cdot C_2H_5 + \cdot SiX_3 \tag{5}$$

$$X_3Si\cdot + C_2H_5SiX_3 \rightarrow X_3SiH + \cdot C_2H_4SiX_3 \tag{6}$$

$$\cdot C_2H_4SiX_3 \rightarrow C_2H_4 + \cdot SiX_3 \tag{7}$$

$$X_3Si\cdot + \cdot C_2H_4SiX_3 \rightarrow X_3SiC_2H_4SiX_3 \tag{8}$$

$$X_3Si\cdot + \cdot C_2H_4SiX_3 \rightarrow X_3SiH + CH_2{=}CHSiX_3 \tag{4}$$

The chain-propagating reactions (6) and (7) are essentially the reverse of those which occur in additions of silicon hydrides to olefins under free radical conditions[9]. The addition of the $Me_3Si\cdot$ radical to ethylene [the reverse of reaction (7) with $X = Me$] has been shown to be essentially irreversible in solution at temperatures up to 413 K[10], but reasonable estimates[11] for ΔH_7 indicate that reaction (7) would be adequately fast at 823 K.

The effect of nitric oxide on the ethyltrimethylsilane reaction can be readily explained in terms of reactions postulated by Gunning and his co-workers to explain the results of reactions between nitric oxide and $Me_3Si\cdot$ radicals generated by photosensitization of trimethylsilane[12]. They found that the main products were nitrogen and hexamethyldisiloxane, and suggested that these arise by initial combination of an $Me_3Si\cdot$ radical with a nitric oxide molecule to give the biradical $Me_3Si\dot{\underset{\cdot}{N}}$, which then gives N_2 and $Me_3SiO\cdot$ via a dimeric intermediate; the $Me_3SiO\cdot$ radical would then abstract hydrogen to give trimethylsilanol, which would undergo self-condensation to give hexamethyldisiloxane and water. A simplified version of this scheme applied to the reaction between ethyltrimethylsilane and nitric oxide can be represented as follows:

$$C_2H_5SiMe_3 \rightarrow \cdot C_2H_5 + \cdot SiMe_3 \tag{5}$$

$$Me_3Si\cdot + NO \rightarrow Me_3SiO\dot{\underset{\cdot}{N}} \tag{9}$$

$$2\,Me_3SiO\dot{\underset{\cdot}{N}} \rightarrow 2\,Me_3SiO\cdot + N_2 \tag{10}$$

$$Me_3SiO\cdot + C_2H_5SiMe_3 \rightarrow Me_3SiOH + \cdot C_2H_4SiMe_3 \tag{11}$$

$$\cdot C_2H_4SiMe_3 \rightarrow C_2H_4 + \cdot SiMe_3 \tag{7}$$

$$2\,Me_3SiOH \rightarrow Me_3SiOSiMe_3 + H_2O \tag{12}$$

The chain-propagating reaction (11) would be faster than reaction (6), and this could account for the increased rate of decomposition of ethyltrimethylsilane in the presence of nitric oxide. Reaction (9), by competing with reaction (6) for $Me_3Si\cdot$ radicals, would reduce the rate of formation of trimethylsilane. It should be noted that reaction (7) features in the mechanism whether or not nitric oxide is present, and that, since the $\cdot C_2H_4SiMe_3$ radical is present, vinyltrimethylsilane will still be formed.

It has recently been shown that $Me_2ClSi\cdot$ and $MeCl_2Si\cdot$ radicals abstract chlorine atoms more rapidly than hydrogen atoms from silicon compounds[13]. If $Cl_3Si\cdot$ radicals behaved similarly, tetrachlorosilane would be expected to be a primary product in the thermolysis of ethyltrichlorosilane as a consequence of reaction (13); some tetrachlorosilane may, indeed, be formed as a primary product [and we have

$$Cl_3Si\cdot + C_2H_5SiCl_3 \rightarrow SiCl_4 + C_2H_5Cl_2Si\cdot \tag{13}$$

seen that one of the products which was not positively identified could have been $C_2H_5Cl_2SiH$, some of which should be formed from the $C_2H_5Cl_2Si\cdot$ radicals produced in reaction (13)], but it appears to be predominantly a secondary product. This may well reflect a significant difference in behaviour between the radicals $Cl_3Si\cdot$ and $R_xCl_{3-x}Si\cdot$ (R=alkyl, $x = 1–3$). Trichlorosilyl radicals are known to be less reactive than $Me_3Si\cdot$ radicals in chlorine-abstractions, possibly because of electron delocalization[14], and a sharp difference between $Cl_3Si\cdot$ and $Me_xCl_{3-x}Si\cdot$ radicals ($x = 1–3$) was revealed in sodium flame studies[15]; in the latter it was shown that the rate of the gas phase reaction $Na + Me_xSiCl_{4-x} \rightarrow NaCl + Me_xCl_{3-x}Si\cdot$ changed little along the series with $x = 3$, 2, and 1, but rose sharply when $x = 4$, tetrachlorosilane being about 100 times more reactive than the other compounds. It was suggested that $p \rightarrow d$ interactions reach a maximum when 3 chlorine atoms are attached to silicon, and that the stabilization is disrupted by a fourth chlorine atom, leading to an unusually weak $Cl_3Si{-}Cl$ bond in tetrachlorosilane[15]. This explanation would account for the low reactivity of $Cl_3Si\cdot$ radicals in chlorine abstraction, and hence for the relative unimportance of reaction (13). It would also follow that $Cl_3Si\cdot$ radicals would not necessarily be unreactive in hydrogen abstraction, since the $p \rightarrow d$ interactions in the radical would be much less disturbed by formation of an Si–H bond; indeed, there is spectroscopic evidence[16] that the Si–H bond is stronger in trichlorosilane than in silane or trimethylsilane, possibly because of increased *s*-character in the relevant hybrid orbital of silicon. Thus, $Cl_3Si\cdot$ radicals could abstract hydrogen, even from C–H bonds, in preference to chlorine from Si–Cl bonds, an inversion of the reactivity pattern observed for $Me_3Si\cdot$ radicals. It is noteworthy that chlorine abstraction by $Cl_3Si\cdot$ radicals has been extensively studied in solution[17] and in the gas phase[18], but since trichlorosilane was invariably the source of the $Cl_3Si\cdot$ radicals, hydrogen abstraction would simply have regenerated the trichlorosilane, and thus have gone undetected.

The reaction of ethyltrichlorosilane in the presence of nitric oxide may now be interpreted in terms of a scheme analogous to that proposed above for ethyltrimethylsilane. Nitric oxide would resemble chlorine rather than hydrogen in its reaction with $Cl_3Si\cdot$ radicals, and thus disturb the $p \rightarrow d$ interactions in the radical. Consequently, the condensation reaction analogous to (9) would be relatively slow, and the presence of nitric oxide would not lead to an increase in the rate of decomposition of ethyltrichlorosilane. The failure to observe new products in the presence of nitric oxide is also readily explained, since the species Cl_3SiOH and $Cl_3SiOSiCl_3$ formed in reactions analogous to (11) and (12) would be hydrolysed by the water formed in (12), and thus converted into involatile polymeric siloxanes*. Some trichlorosilane should still be formed in the presence of nitric oxide, since the reaction of type (9) would not compete effectively with that of type (6), but the trichlorosilane would also be hydrolysed, and so its yield would be substantially reduced, as observed.

In the light of the findings above, we must now conclude that the formation of vinyl chloride during the thermolysis of (2-chloroethyl)trichlorosilane probably also involves a radical process, rather than the previously suggested four-centre molecular elimination of Cl_3SiH[4]. At the time, the observation that nitric oxide had little effect on the rate of formation of vinyl chloride seemed good evidence in favour of a simple unimolecular elimination, but we can now see it was probably fortuitous. The vinyl chloride is probably produced in the reaction sequence (14) and (15) [the

$$Cl_3Si\cdot + ClCH_2CH_2SiCl_3 \rightarrow HSiCl_3 + Cl\dot{C}_2H_3SiCl_3 \qquad (14)$$

$$Cl\dot{C}_2H_3SiCl_3 \rightarrow CH_2{=}CHCl + Cl_3Si\cdot \qquad (15)$$

latter being analogous to reaction (7)], and there is now no reason to believe that nitric oxide would compete effectively with reaction (14) for the chain-propagating

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* Neither nitrogen nor hydrogen chloride would have been detected in our GLC system.

$Cl_3Si\cdot$ radicals, while we have seen that reactions of type (7) still occur in the presence of nitric oxide.

We can also now understand why, in the thermolysis of $R_xCl_{4-x}SiCH_2CH_2Cl$ species, vinyl chloride is formed only when $x=0$. With the species having $x=1-3$, if a few silyl radicals are generated concurrently with the main molecular reaction the chlorine-abstraction reaction (16) would be much faster than hydrogen abstraction of the type involved in reaction (14), and this would lead, via reaction (17), to the same products as the main molecular reaction:

$$Me_xCl_{(3-x)}Si\cdot + ClCH_2CH_2SiMe_xCl_{3-x} \rightarrow Me_xCl_{3-x}SiCl + \cdot C_2H_4SiMe_xCl_{3-x} \quad (16)$$

$$\cdot C_2H_4SiMe_xCl_{3-x} \rightarrow C_2H_4 + \cdot SiMe_xCl_{3-x} \quad (17)$$

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