Organosilicon Compounds. Part L.[1] Kinetics of the Thermal Decomposition of Bis(trimethylsilyl)mercury in Solution

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The thermal decomposition of solutions of bis(trimethylsilyl)mercury in benzene or cyclohexane shows second-order kinetics, except that a small first-order contribution appears at very low concentrations in cyclohexane. In toluene mixed second- and (pseudo)-first-order kinetics are observed, and in anisole, (pseudo)-first-order kinetics only. Bis(trimethylsilyl)mercury appears to decompose mainly by bimolecular reactions, either with itself or with the solvent, with unimolecular homolysis seemingly unimportant. From the small first-order contribution to the reaction in cyclohexane, a rough lower limit of 200 kJ mol^{-1} for $D(\text{Me}_3\text{Si–HgSiMe}_3)$ can be derived.

PHOTOLYSIS of bis(trimethylsilyl)mercury appears to provide a convenient source of trimethylsilyl radicals,[2] but product studies indicate that the thermal decomposition of bis(trimethylsilyl)mercury in at least some solvents occurs by molecular processes.[3,4] We present below kinetic evidence that (except possibly in very dilute solutions) bis(trimethylsilyl)mercury does not decompose significantly by unimolecular homolysis to mercury and trimethylsilyl radicals even in inert solvents such as toluene or cyclohexane, but undergoes bimolecular reactions, either with itself or with the solvent.

EXPERIMENTAL

Bis(trimethylsilyl)mercury was prepared as described previously.[3] Extinction coefficients (measured by Dr. A. R. Bassindale) were 290, 260, and 290 at 330 nm, and 92, 85, and 90 at 390 nm, in cyclohexane, benzene, and toluene, respectively. Solvents were distilled immediately before use from sodium or from lithium aluminium hydride as appropriate, and degassed; the solutions of the mercurial were made up in a nitrogen-filled glove box.

Kinetic Experiments.—Solutions of bis(trimethylsilyl)-mercury in the appropriate solvent were prepared in Pyrex ampoules, which were then degassed and sealed. The ampoules were heated in a metal block, the temperature of which was maintained within ±0·3°. Ampoules were withdrawn at intervals, and cooled, and after any mercury had been shaken to the bottom, the ampoules were placed in the cell holder of a Unicam SP 500. The disappearance of the bis(trimethylsilyl)mercury was followed by measuring the absorption of light at 330 and 386 or 390 nm. After each measurement, the ampoules were returned to the heated block. Care was taken to ensure that the ampoules were always placed in the cell holder in the same orientation, although changes in the orientation in fact caused little change in the optical density recorded. At the end of some runs, the ampoules were opened, and the internal diameter measured with calipers; values very close to 1·00 cm were normally found.

Products.—Ampoules which had been used for kinetics (*i.e.* solutions initially containing bis(trimethylsilyl)mercury of concentration *ca.* 2×10^{-2}M which had been heated at a temperature within the range of 189—246°) were opened, and the contents were analysed by g.l.c. The cyclohexane and benzene solutions contained hexamethyldisilane as the only major organic product, with a small amount of trimethylsilane and traces of high boiling material. In toluene, comparable amounts of trimethylsilane, hexamethyldisilane, and benzyltrimethylsilane were formed, along with a trace of bibenzyl. More concentrated solutions (*ca.* 0·2 g mercurial in 1·0 ml toluene) kept at 190° for 7 days gave mercury (100%), hexamethyldisilane (80—90%), hexamethyldisiloxane † (2—4%), and trimethylsilane (1%), along with benzyltrimethylsilane (0·2—0·6%), and bibenzyl (trace).

Analysis of Results.—Orders of reaction were determined from rates of reactions obtained by drawing tangents to the curve of a graph of optical density, D, against time. First- and second-order kinetic analyses were done by standard log D and $1/D$ plots. The mixed first- and second-order decompositions were analysed in two ways. (*a*) Rates of reaction ($-\mathrm{d}D/\mathrm{d}t$) were obtained by taking tangents to the curve of a plot of optical density against time, and $\mathrm{d}D/D^2 . \mathrm{d}t$ was plotted against $1/D$. The slope of this graph gives k', and the intercept is proportional to k''. (*b*) A computer programme using (arbitrary) initial estimates of k', and k'', and D_0 (optical density at time zero) provided 'calculated' values for the various readings. These initial estimates were systematically varied to produce a minimum value of $\Sigma(D_{\text{obs.}} - D_{\text{calc.}})^2$, using Powell's method.[5] The observed infinity value of the optical density (usually very close to zero) was treated as a constant in these calculations. This method works best when there are significant contributions from both first- and second-order components to the rate. In three experiments at 191·7 and 220·6° where both methods of analysis were used the results agreed to within an average of 4% for k' and 11% for k''.

RESULTS AND DISCUSSION

The results of the kinetic experiments are summarized in Table 1. There is good agreement between the results at 330 and at 390 nm. Since ε_{330} is three to four times the value of ε_{390}, use of both wavelengths allows a wider range of concentrations to be studied, thereby lending extra confidence to the results, particularly when both first- and second-order reactions are taking place.

In benzene and cyclohexane, the reactions were of second order, and the rate constants were effectively the

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† Hexamethyldisiloxane could never be completely eliminated as a product in these reactions. The small quantities formed probably arise from traces of oxygen or water present in the atmosphere of the glove box or in the solvents used.

[1] Part XLIX, C. Eaborn, R. A. Jackson, and M. T. Rahman, *J.C.S. Perkin II*, 1972, 55.

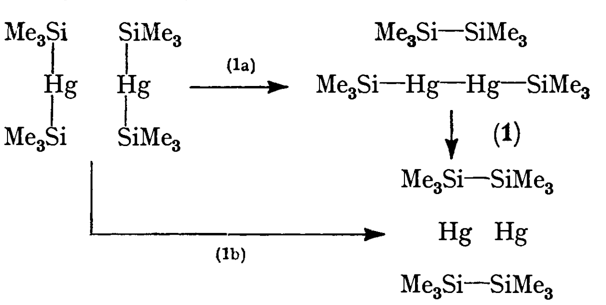
[2] C. Eaborn, R. A. Jackson, and R. Pearce, *Chem. Comm.*, 1967, 920; S. W. Bennett, C. Eaborn, and R. A. Jackson, *J. Organometallic Chem.*, 1970, **21**, 79.

[3] C. Eaborn, R. A. Jackson, and R. W. Walsingham, *J. Chem. Soc.* (*C*), 1967, 2188.

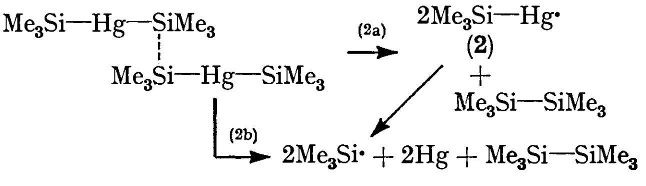
[4] R. Fields, R. N. Haszeldine, and R. E. Hutton, *J. Chem. Soc.* (*C*), 1967, 2559.

[5] M. J. D. Powell, *Computer J.*, 1965, **7**, 155.

same in the two solvents at 245·8 °C. These results can be accounted for most simply in terms of a simple bimolecular decomposition to give mercury and hexamethyldisilane (reaction 1). However, the observed *A*



factor for the decomposition in cyclohexane (see Table 2), even allowing for uncertainties due to the fact that experiments were only carried out at two temperatures, is rather large for a bimolecular reaction in which considerable entropy is lost in the transition state. It is possible that the initial reaction gives two trimethylsilyl radicals, a hexamethyldisilane molecule, and two mercury atoms [reaction (2)] * which is then followed by reactions (3)—(5). This sequence would lead to overall second-



$$\mathrm{Me_3Si\cdot + Me_3Si{-}Hg{-}SiMe_3 \longrightarrow Me_3Si{-}SiMe_3 + Hg + \cdot SiMe_3} \quad (3)$$

$$\mathrm{2Me_3Si\cdot \longrightarrow Me_3Si{-}SiMe_3} \quad (4)$$

$$\mathrm{Me_3Si\cdot + H{-}R \longrightarrow Me_3SiH + R\cdot} \quad (5)$$

order kinetics. We have independent indications that reaction (3) takes place at lower temperatures in photolytic experiments,[6] while reaction (5) would account for the formation of some trimethylsilane. We should not expect significant amounts of aromatic substitution by trimethylsilyl radicals at temperatures above 200 °C.[6] This reaction scheme also provides an explanation for the smaller second-order rate constant found in the toluene reaction, since toluene should act as a better trap for trimethylsilyl radicals than either benzene or cyclohexane, and thus the chain length, and hence the apparent second-order rate constant, would be reduced.

TABLE 1

Kinetic data for the decomposition of bis(trimethylsilyl) mercury in organic solvents *

	Cyclohexane	Benzene	Toluene		Anisole
t/°C	$10^4k''$	$10^4k''$	$10^6k'$	$10^4k''$	$10^6k'$
189·0					67 ± 4
191·7			1·8 ± 0·3	1·7 ± 0·2	
			2·0 ± 0·2	*1·4 ± 0·4*	
220·6	27 ± 7 †		15 ± 3	10 ± 2	
	25 ± 8 †		*15 ± 4*	—	
245·8	143 ± 14	133 ± 28	116 ± 12	30 ± 9	
	123 ± 22	*130 ± 35*	*140 ± 14*	—	

* Data obtained at 386 or 390 nm (normal type) and at 330 nm (italic). k' (in s^{-1}) and k'' (in $l\ mol^{-1}\ s^{-1}$) represent first- and second-order contributions to the rate. Error limits are standard deviations. † Data obtained at 219·7 °C.

TABLE 2

Arrhenius parameters for the decomposition of bis(trimethylsilyl)mercury in toluene and in cyclohexane *

Solvent	λ/nm	First-order component		Second-order component	
		$\log_{10}(A/s^{-1})$	E/kJ mol^{-1}	$\log_{10}(A/l\ mol^{-1}\ s^{-1})$	E/kJ mol^{-1}
Toluene	386	11·69 ± 0·50	155·5 ± 4·8	7·94 ± 0·79	104·0 ± 7·5
	330	11·74 ± 0·83	155·6 ± 7·8		
Cyclohexane	286			11·89 ± 1·27	136·4 ± 12·1
	330			11·56 ± 1·57	133·9 ± 15·1

* Error limits are standard deviations.

The decomposition of bis(trimethylsilyl)mercury in toluene was analysed in terms of a first-order and a second-order contribution. (This analysis gave a better fit to the results than an alternative scheme involving first-order and 1·5-order contributions.) The contribution from the second-order reaction was greater at lower temperatures. Arrhenius parameters are given in Table 2. The low *A* factor for the second-order reaction is to be expected if a bimolecular reaction with a ' tight ' transition state [reaction (1)] is occurring, while the fact that the activation energy is relatively low even though the reaction is symmetry-forbidden, could be explained by a development of the arguments in ref. 7.

The ' first-order ' component of the toluene reaction is almost certainly pseudo-first-order, since if a genuine first-order reaction took place in toluene, it would also be expected to take place in benzene, in which no appreciable contribution from a first-order reaction was

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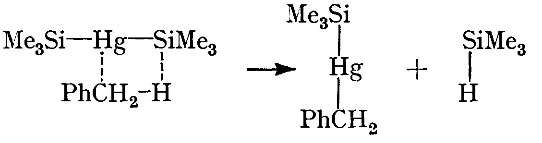
* Mechanisms (1a) and (2a) are more reasonable from the point of view of the principle of microscopic reversibility than the ' direct ' reactions (1b) and (2b). We have, however, no independent evidence for intermediates (**1**) or (**2**): if formed, they probably decompose rapidly.

[6] S. W. Bennett, C. Eaborn, R. A. Jackson, and R. Pearce, *J. Organometallic Chem.*, 1971, **28**, 59.

[7] R. A. Jackson, *J. Chem. Soc.* (*B*), 1970, 58.

observed. Hence the reaction is almost certainly a bimolecular reaction with the solvent, which is present at effectively the same concentration throughout. Thus the observed first-order Arrhenius parameters (Table 2) should probably be converted into second-order parameters by dividing A by the toluene concentration. The bimolecular reaction of a mercurial molecule with a toluene molecule may be strictly molecular [reaction (6)] or may give radicals (7). These possibilities are not easily distinguished, since if the molecular reaction (6) takes place, homolysis of the carbon–mercury bond of the intermediate (**3**) will be rapid at these temperatures, and radical products will still be observed. However, the derived A factor (A_{obs}/[toluene]) seems rather large for a reaction of type (6), and would be more appropriate for the looser transition state involved in (7).

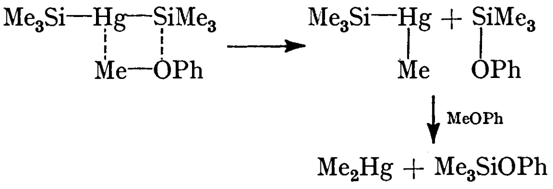


$$Me_3Si{-}Hg{-}SiMe_3 + PhCH_2{-}H \longrightarrow Me_3Si{-}Hg{-}CH_2Ph + Me_3Si{-}H \quad (6)$$

(**3**)

$$Me_3Si{-}Hg{-}SiMe_3 + H{-}CH_2Ph \longrightarrow Me_3SiHg\cdot + Me_3SiH + \cdot CH_2Ph \quad (7)$$

We studied the decomposition in anisole at a rather lower temperature. Only first-order kinetics were observed, and, as in the toluene reaction, we believe that a bimolecular reaction with the solvent is taking place. Evidence from product studies [*e.g.* the isolation of phenoxytrimethylsilane (70—88%) and dimethylmercury [3]] allows us to be fairly confident that this is a true bimolecular 4-centre reaction, and the enhancement of the rate, in comparison with that of decomposition in other solvents, can be attributed at least in part to the strength of the silicon–oxygen bond formed during the reaction (8). Analogous molecular reactions occur with halogen compounds.[4]



$$Me_3Si{-}Hg{-}SiMe_3 + Me{-}OPh \longrightarrow Me_3Si{-}Hg{-}Me + Me_3Si{-}OPh \quad (8)$$

$$Me_3Si{-}Hg{-}Me \xrightarrow{MeOPh} Me_2Hg + Me_3SiOPh$$

The Mercury–Silicon Bond Dissociation Energy in $(Me_3Si)_2Hg$.—A value for $D(Me_3SiHg{-}SiMe_3)$ would be very useful in interpreting the radical and molecular reactions of bis(trimethylsilyl)mercury, and we had hoped that the thermal decomposition of the mercurial in inert solvents such as cyclohexane would involve unimolecular homolysis, so that study of the kinetics would yield an activation energy, and hence a value for $D(Me_3SiHg{-}SiMe_3)$. In the event, the decomposition in cyclohexane was of second order (see Table 1), with deviations only after a substantial amount of reaction had taken place. However, when plots of $1/[Hg(SiMe_3)_2]$ against time were made for reactions at 245·8° in which the weakest solutions of the mercurial had been used (*i.e.* readings taken at 330 nm), progressively greater deviations were noted at low optical densities, in the direction to be expected from a reaction component of less than second order.

If the deviation from second-order behaviour is due to the homolysis of the mercurial [reaction (9)], the kinetic consequences will depend on the mechanism

$$Me_3Si{-}Hg{-}SiMe_3 \longrightarrow 2Me_3Si\cdot + Hg \text{ (1 or 2 steps)} \quad (9)$$

of the second-order reaction.

(a) If the second-order reaction is molecular [reaction (1)] and the radicals formed by (9) undergo rapid combination by reaction (4), then the rate expression will be given by (10) and (11), where k_9 and k_1 refer to the first- and second-order contributions respectively. Provided that the first-order contribution is small compared

$$\frac{-\mathrm{d}[Hg(SiMe_3)_2]}{\mathrm{d}t} = k_9[Hg(SiMe_3)_2] + k_1[Hg(SiMe_3)_2]^2 \quad (10)$$

or

$$\frac{-\mathrm{d}[Hg(SiMe_3)_2]}{k_1[Hg(SiMe_3)_2]^2\left\{1 + \dfrac{k_9}{k_1[Hg(SiMe_3)_2]}\right\}} = \mathrm{d}t \quad (11)$$

with the second-order term at all concentrations considered, the above expression can be expanded binomially, truncated after the second term, and integrated to give equation (12).

$$\frac{1}{[Hg(SiMe_3)_2]} = k_1t + \frac{k_9}{2k_1[Hg(SiMe_3)_2]^2} + \text{constant} \quad (12)$$

Plots of $1/[Hg(SiMe_3)_2]$ against t were made: deviations from the initial straight line were determined for the lower concentrations, and the deviations $k_9/2k_1[Hg(SiMe_3)_2]^2$ were themselves plotted against $1/[Hg(SiMe_3)_2]^2$ to give reasonable straight lines from which the ratio $k_9/2k_1$ was obtained. Since k_1 is known, k_9 could be estimated as $(3{\cdot}2 \pm 1{\cdot}3) \times 10^{-6}\ s^{-1}$. We emphasize that this is only a very rough figure, being based, as it is, on differences between reciprocals of low optical density values; it corresponds to a value for the activation energy for the first-order reaction of between 204 and 223 kJ mol^{-1}, if $\log_{10} A$ factors of between 15 and 17 are assumed, as is usual in unimolecular homolyses. The true value of k_9 is unlikely to be more than 3 standard deviations above the mean value; use of this maximum value leads to slightly lower activation energy limits of 200—220 kJ mol^{-1}. If the dissociation is to two $Me_3Si\cdot$ radicals and a mercury atom, the A factor would be expected to be greater, and consequently the activation energy would be greater as well. Hence the activation energy for the unimolecular decomposition is unlikely to be less than 200 kJ mol^{-1}, a value which we can equate with a minimum estimate for $D(Me_3SiHg{-}SiMe_3)$. An upper limit of 307 kJ mol^{-1} for this bond dissociation energy can be based on the fact that the mercurial is readily decomposed photolytically by light of 390 nm wavelength, but this is likely to be a considerable overestimate, since energy in excess of the bond dissociation energy is normally needed in photolytic dissociations.

(*b*) Various other possibilities for the mechanism may be envisaged. For example, the reaction may involve the radical-chain sequence (2)—(4) with a contribution from (9). Perhaps less likely would be the radical sequence (9), (3), (4) with an independent molecular component from reaction (1). In each of these cases, analysis along the lines carred out in (*a*) suggests that the first-order rate constant will not have a value greater than that inferred above. If the first-order contribution corresponds to a molecular reaction such as (13), the rate constant for the (unobserved) homolysis [reaction (9)] will clearly be smaller than k_{13}. Thus the minimum value for $D(\mathrm{Me_3SiHg{-}SiMe_3})$ derived above will still hold for these other mechanistic possibilities.

$$\mathrm{Hg(SiMe_3)_2} \longrightarrow \mathrm{Hg} + \mathrm{Me_3Si{-}SiMe_3} \qquad (13)$$

Finally, the upper limit for the rate of unimolecular homolysis allows a comparison to be made with bis(triphenylsilyl)mercury, which decomposes at 219·5° by a first-order process, which is believed to be the unimolecular homolysis.[1] [The large phenyl groups will hinder bimolecular reactions of bis(triphenylsilyl)mercury]. The first-order rate constant for $\mathrm{(Ph_3Si)_2Hg}$ decomposition at 219·5° is $4 \times 10^{-6}\ \mathrm{s^{-1}}$, which approximates to the upper limit for the first-order decomposition of $\mathrm{(Me_3Si)_2Hg}$ at 245·8°. This implies that the activation energy for $\mathrm{(Ph_3Si)_2Hg}$ decomposition is less than that for its methyl analogue, albeit probably by only a small amount. Such a difference could be due to a small amount of resonance stabilization of the $\mathrm{Ph_3Si\cdot}$ radical.

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