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Hg-sensitized photolysis of Me_3SiH II. The role of the sensitizer

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Abstract

In the mercury-sensitized photolysis of Me_3SiH, it was found that the mercury concentration does not remain constant during photolysis, and mercury forms an unidentified compound. The compound decomposes to elemental mercury by radical attack and in the dark by a surface-catalysed reaction. Experiments suggest that mercury atoms in the ground state are involved in compound formation.

Keywords: Mercury-sensitized photolysis; Me_3SiH; Photolysis; Radical attack; Surface catalysed reaction

1. Introduction

Cario and Franck [1] showed that excited Hg atoms can transfer their energy to an acceptor atom (or molecule), and since then Hg has been frequently used as a sensitizer in photochemical studies. Subsequent studies have shown that excited mercury is not just a carrier of energy, but can form complexes and undergo chemical reactions. A well-known example is the reaction of $Hg(^3P_1)$ with H_2 which leads to the formation of the intermediate HgH [2]. With certain classes of compounds, such as chlorides, oxides and sulphides, stable mercury compounds are formed [3].

More recently, mercury-sensitized reactions have been studied in matrices at low temperatures. Cartland and Pimentel [4] have shown that $Hg(^3P_1)$ inserts into a C–Cl bond and that this insertion product can be stabilized at very low temperatures. Brown and Willard [5] observed that mercury dissolved in 3-methyl-pentane glass disappears on illumination with Hg resonance radiation. A non-paramagnetic Hg species is formed. As a working hypothesis, it was assumed that excited Hg atoms insert into R–H bonds.

In this paper, we report a similar effect, but this time in the gas phase, i.e. the disappearance of Hg during the mercury-sensitized photolysis of Me_3SiH.

2. Experimental details

The experimental apparatus used in this work is the same as that described in part I [6] and the photolyses were carried out in the same way. Contrary to the work in part I, we focused our attention on the change in sensitizer concentration during photolysis. For this purpose, the intensity of the Hg resonance line (253.7 nm) transmitted through the photolysis cell was measured. The signal from the photomultiplier was amplified and then recorded either by an x–t recorder or a multichannel scaler.

The concentration of Hg atoms in the photolysis cell, which was low for the absorption experiment, was determined by assuming that it was equal to a known vapour pressure of a thermostatically controlled Hg reservoir. The temperature of the reservoir, which varied in the range 240.4–279.9 K, was measured by calibrated thermometers.

The experiments were performed in the temperature range 298–373 K. Two copper blocks sliding on a track perpendicular to the optical axis allowed installation of the oven without destroying the optical alignment. The temperature was constant to better than 0.5 K.

3. Results and discussion

In Fig. 1, the following experiment is documented. The photolysis cell is filled with a certain small concentration of Hg atoms. A transmitted light intensity I_{Hg} of mercury resonance radiation at 253.7 nm corresponds to this known Hg concentration. After addition of Me_3SiH, the shutter is opened and the transmitted light intensity changes from $I=0$ to I_{sample}, a value in the vicinity of I_{Hg}. However, the intensity does not remain at this value, as would be expected if Hg acts

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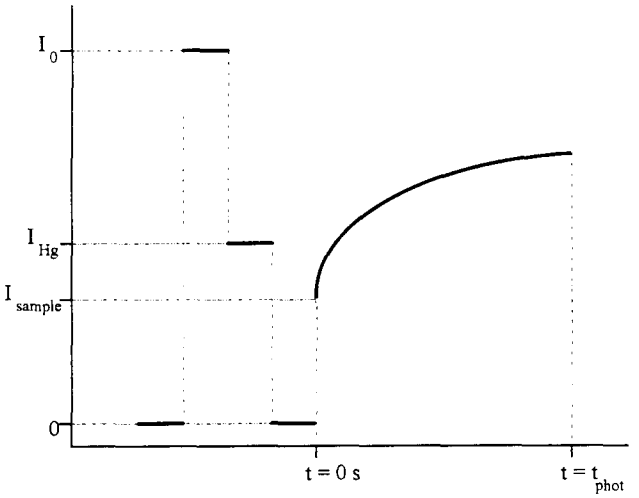

Fig. 1. Change in the transmitted resonance radiation with time in a typical experiment.

solely as a sensitizer, but increases until it reaches a stationary value. Because no other absorber, except for Hg, is present at this wavelength, we can conclude that the mercury concentration decreases at the expense of a non-absorbing or only weakly absorbing Hg compound. The attainment of a stationary intensity value shows that this compound is not stable under the applied conditions but decomposes to Hg.

To evaluate plots of the type shown in Fig. 1, the relationship between the optical density and concentration must be known. It is well known [7] that the Beer–Lambert law is not valid for line absorption and that the functional relationship between the atom concentration and absorbance depends on the presence of added gases. For all experimentally utilized reaction mixtures, we have therefore recorded calibration plots of the type shown in Fig. 2. In all cases, the relationship between the Hg pressure and $\ln(I_0/I_{Hg})$ can be described satisfactorily by

$$\ln\left(\frac{I_0}{I_{Hg}}\right) = \frac{a[Hg]}{b + [Hg]} \quad (I)$$

Attempts have been made to determine the nature of the unknown mercury compound X by mass spectrometry. These experiments have been unsuccessful and we are forced to draw rather indirect conclusions about compound X and the mechanism of its formation.

The formation of compound X requires both Hg and Me_3SiH. With Hg alone, no change in the transmitted intensity is observed. In the presence of both compounds, there is a dependence of the rate of X formation as well as the stationary X concentration on the initial Hg concentration (Fig. 3). The higher the mercury concentration, the larger the amount of X formed and the larger its rate of formation. At high mercury concentrations, we observe an exponential decrease in the Hg concentration, while at low mercury concentrations, a more complex behaviour is noted.

The Me_3SiH concentration has a weak influence on the Hg–time profiles (Fig. 4). The amount of X formed does not depend on the Me_3SiH concentration; only a retarding effect on the rate of X formation with increasing [Me_3SiH] is noted.

The experimental results presented so far are in agreement with two essentially different reaction mechanisms:

(1) the involvement of an electronically excited Hg atom;
(2) the reaction of a reactive intermediate with Hg in the ground state.

To date, only excited Hg atoms have been reported to be involved in the formation of stable mercury compounds [3,4]. The disappearance of mercury on irradiation with resonance radiation in 3-methyl-pentane glass at 77 K was explained by an insertion reaction of $Hg(^3P_1)$ into a C–H bond [5]. This suggestion is also attractive for our experiments because it is known that RHgH compounds are only moderately stable [8].

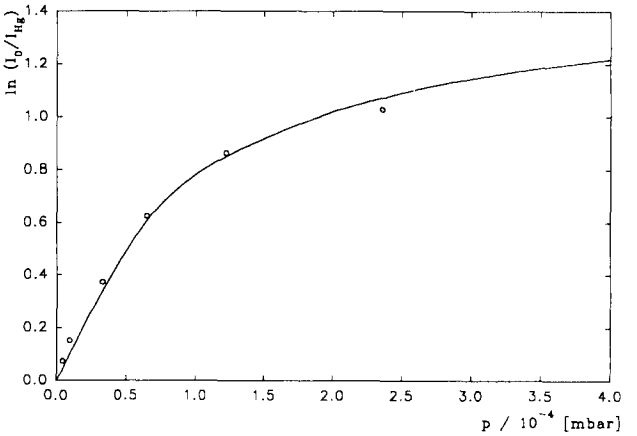

Fig. 2. Relationship between absorbance at 253.7 nm and mercury pressure.

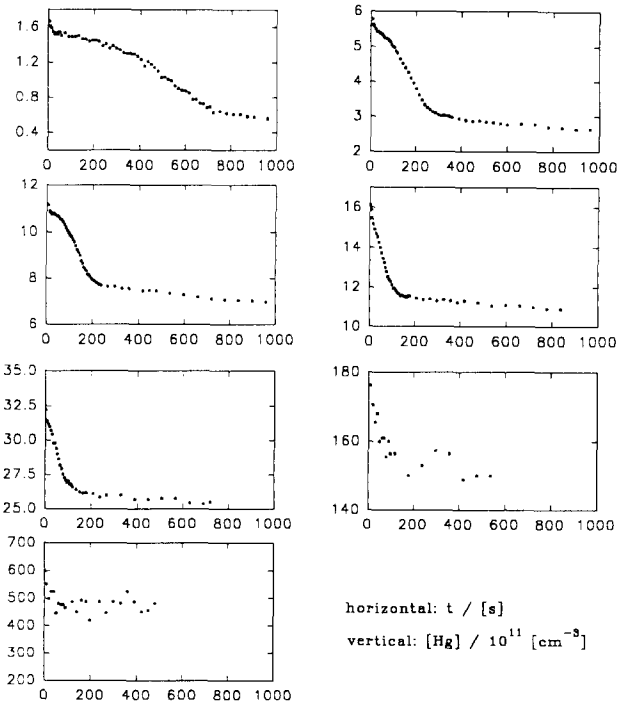

Fig. 3. [Hg] vs. time plot for different mercury concentrations; [Me_3SiH] = 2×10^{18} cm^{-3}, T = 298 K.

To prove or disprove the involvement of excited Hg atoms in the formation of compound X, we studied the 254 nm photolysis of the system Hg–H_2–Me_3SiH. No loss of Hg was

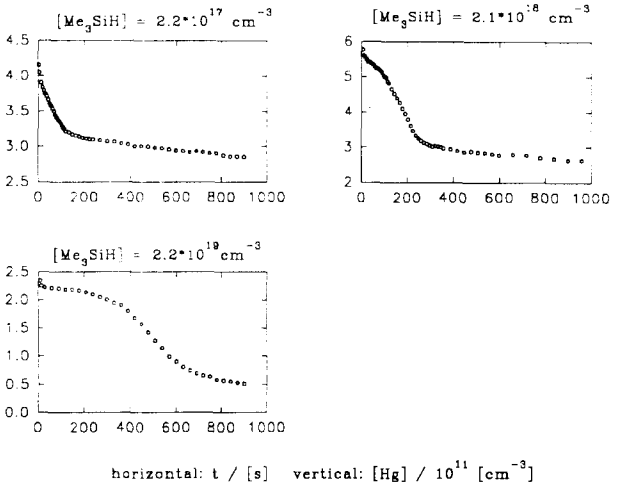

Fig. 4. Influence of the Me_3SiH concentration on the change in Hg concentration with time; $T = 298$ K.

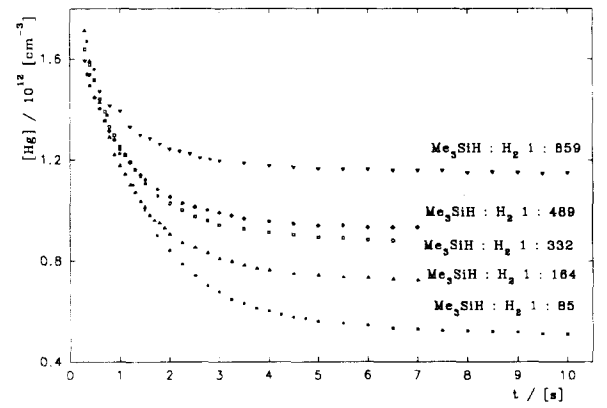

Fig. 5. Influence of the H_2 concentration on the change in Hg concentration with time; $[Me_3SiH] = 3 \times 10^{15}$ cm^{-3}, $T = 298$ K.

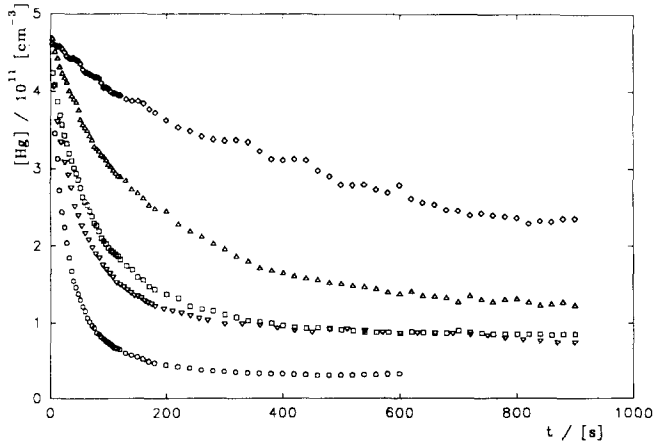

Fig. 6. Influence of the incident light intensity on the change in Hg concentration with time; $[Me_3SiH] = 2 \times 10^{18}$ cm^{-3}, $T = 353$ K. ○, $I_0 = 4.18 \times 10^{13}$ cm^{-3} s^{-1}; ▽, $I_0 = 2.23 \times 10^{13}$ cm^{-3} s^{-1}; □, $I_0 = 1.67 \times 10^{13}$ cm^{-3} s^{-1}; △, $I_0 = 0.94 \times 10^{13}$ cm^{-3} s^{-1}; ◇, $I_0 = 0.53 \times 10^{13}$ cm^{-3} s^{-1}.

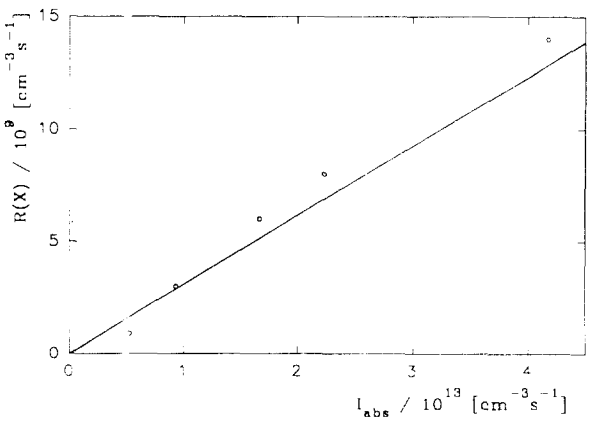

Fig. 7. Initial rate of mercury disappearance vs. absorbed intensity.

found if Hg was irradiated in the presence of H_2 only. Adding a small amount of Me_3SiH, however, caused a very fast decrease in the Hg concentration (Fig. 5).

If the mechanism is analogous to that in the 3-methylpentane system [5], the following process should occur

$$Hg(^3P_1) + Me_3SiH \longrightarrow X \qquad (1)$$

and the rate of X formation, $R(X)$, is proportional to

$$R(X) \propto [Hg(^3P_1)][Me_3SiH]$$

In the presence of a large excess of H_2, most of the excited mercury atoms will be quenched by H_2

$$Hg(^3P_1) + H_2 \longrightarrow \text{products} \qquad (2)$$

the quenching rate constants for H_2 and Me_3SiH being almost the same [9,10].

The stationary concentration of $Hg(^3P_1)$ is then given by

$$[Hg(^3P_1)]_{ss} = \frac{I_{abs}}{k_2[H_2]}$$

and we finally obtain

$$R(X) \propto I_{abs} \frac{[Me_3SiH]}{[H_2]} \qquad (II)$$

The dependence on light intensity has been investigated at an elevated temperature (353 K) and is shown in Fig. 6. Under these conditions, the Hg concentration decreases exponentially and the initial rate is directly proportional to the light intensity (Fig. 7), as required by relation (II). However, the expected dependence on the reactant ratio $[Me_3SiH]/[H_2]$ is not borne out by experiment. This is clearly seen in Fig. 5, where the initial rate is independent of the reactant ratio. We therefore conclude that reaction (1) does not properly describe the formation of compound X.

It is known that mercury in the $^3P_0$ state attaches to other molecules [9], and we therefore examine the possibility that X is formed via $Hg(^3P_0)$. There are a number of arguments against such a reaction path. Firstly, collisional relaxation of $Hg(^3P_1)$ to $Hg(^3P_0)$ by H_2 is very small [9]. Secondly, the $^3P_0$ state is also efficiently quenched by H_2, and therefore we

again expect a dependence on the $[Me_3SiH]/[H_2]$ ratio. Thirdly, the addition of N_2, which is a very efficient quencher of the $^3P_1$ state to the $^3P_0$ state [9], does not lead to an increased rate of Hg loss. On the contrary, X formation comes to a complete halt. For the same reason, the involvement of Hg dimers and trimers [9] can be ruled out.

A more indirect involvement of excited mercury atoms would be the participation of HgH in the formation of X. HgH is a major primary product in the Hg-sensitized photolysis of H_2, formed by reaction (1a)

$$Hg(^3P_1) + H_2 \longrightarrow HgH + H \quad (1a)$$

HgH disappears by collision-induced decomposition

$$HgH + M \longrightarrow Hg + H + M \quad (3)$$

and reactive collision with other intermediates

$$HgH + R \longrightarrow \text{products} \quad (4)$$

In the presence of Me_3SiH, the most abundant intermediate will be the Me_3Si radical

$$2Me_3Si \longrightarrow \text{products} \quad (5)$$

In addition to reaction (5), an abstraction reaction from and a combination reaction with HgH must be taken into consideration

$$HgH + Me_3Si \longrightarrow Hg + Me_3SiH \quad (4a)$$

$$HgH + Me_3Si \longrightarrow X \quad (4b)$$

The rate of X formation is given by

$$R(X) = \frac{k_{4b}\Phi_{1a}\sqrt{I_{abs}^3}}{\sqrt{k_5}k_3[H_2] + k_4\sqrt{I_{abs}}} \quad (III)$$

where the stationary concentrations of Me_3Si and HgH have been approximated by

$$[Me_3Si]_{ss} \approx \sqrt{\frac{I_{abs}}{k_5}}$$

$$[HgH]_{ss} \approx \frac{\Phi_{1a}I_{abs}}{k_3[H_2] + k_4[Me_3Si]}$$

Only if the first term in the denominator of Eq. (III) could be neglected would the rate law be in agreement with the experiment, namely direct proportionality to I_{abs} and independence of $[H_2]$. With the known values for the rate constants $k_3 = 3 \times 10^{-16}$ cm^3 s^{-1} [11] and $k_5 = 3 \times 10^{-11}$ cm^3 s^{-1} [12], $I_{abs} = 1 \times 10^{13}$ cm^{-3} s^{-1} and assuming a large value for $k_4 = 1 \times 10^{-10}$ cm^3 s^{-1}, we calculate that neither of the two terms in the denominator can be neglected and increasing the H_2 pressure in the system should have a distinct influence on the initial rate of Hg disappearance. For the conditions given in Fig. 5, we expect a decrease in the initial rate by a factor of 6–7 when $[H_2]$ is increased by a factor of 10. This is obviously not the case. A further argument against such a mechanism concerns the availability of HgH in the absence of H_2. The results of Brix et al. [13] suggest that no or very little HgH is formed in the Hg-sensitized photolysis of Me_3SiH.

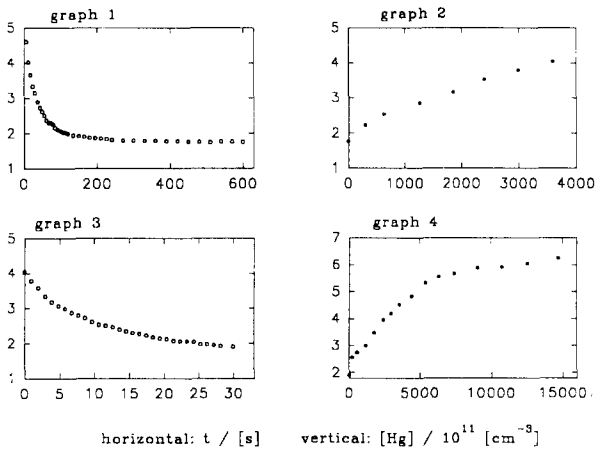

Fig. 8. [Hg]–time plots during illuminated and dark phases at 298 K; $[Me_3SiH] = 2 \times 10^{18}$ cm^{-3}, $I_0 = 4.90 \times 10^{13}$ cm^{-3} s^{-1}.

We conclude that an insertion reaction of the excited mercury atom into the Si–H bond, as has been proven for the C–Cl bond [4] and postulated for the C–H bond [5], must be abandoned as an explanation for the disappearance of Hg in our case.

We are left with the second possibility, the reaction of ground state mercury atoms with a reactive intermediate. Such an explanation does not seem to be very attractive. Mercury atoms in the ground state are considered to be chemically fairly inert because of their $(6s)^2$ valence occupancy. However, if the potential energy surface of a mercury–radical system, Hg–R, resembles that of HgH, we can expect a third- or second-order, non-activated combination reaction

$$M + Hg + Me_3Si \longrightarrow Me_3SiHg + M \quad (6)$$

The concentration of the Me_3SiHg radical could be very small if the radical only has a very small dissociation energy and the back reaction of Eq. (6) is rapid

$$Me_3SiHg + M \longrightarrow M + Hg + Me_3Si \quad (-6)$$

If the rate-determining step is the reaction with a further Me_3Si radical

$$Me_3SiHg + Me_3Si \longrightarrow X \quad (7)$$

the initial rate should be proportional to the absorbed light intensity, independent of the H_2 concentration and directly proportional to the Hg concentration. The first two consequences of this mechanism are in agreement with experiment. The third is more difficult to test because a change in the Hg concentration also affects the absorbed intensity. However, the time dependence of the Hg concentration in Figs. 5, 6, 8 and 9 suggests a pseudo-first-order disappearance of Hg (see below) in agreement with the demanded mercury dependence of the rate law. One consequence of this mechanism seems to be in contradiction with experiment. In reaction (7), we expect the formation of a stable compound $(Me_3Si)_2Hg$ [14] and a permanent loss of Hg, while Figs. 8 and 9 show the

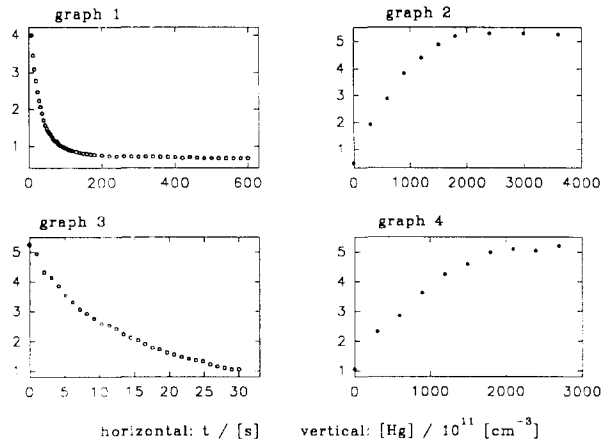

Fig. 9. [Hg]–time plots during illuminated and dark phases at 373 K; $[Me_3SiH] = 2 \times 10^{18}$ cm^{-3}, $I_0 = 4.20 \times 10^{13}$ cm^{-3} s^{-1}.

recurrence of Hg in the dark. As discussed below, the decomposition of X could be totally caused by heterogeneous processes.

In a series of experiments, the behaviour of the system as a function of temperature was studied in the range 298–373 K. Only the results at 298 and 373 K are shown in Figs. 8 and 9. The Hg concentration was measured on irradiation and in the dark. Both figures consist of four graphs. In graph 1, the normal dependence of the Hg concentration on time during photolysis is plotted. After 10 min of irradiation, the system was kept in the dark for 60 min. During this time, the absorption was measured with short light pulses (50 ms) at regular time increments (graph 2). Then followed a second irradiation (graph 3) and, finally, a dark period until the Hg concentration became constant (graph 4).

The time required to reach this constant Hg concentration in graph 4, which is identical to the original Hg concentration within error limits, lies between 30 min at 373 K and 100 min at 298 K. The dependence of the Hg concentration on time in Figs. 8 and 9, as well as in Figs. 5 and 6, in the presence of light can be described by a two-parameter equation

$$[\mathrm{Hg}] = \frac{b}{a+b}[\mathrm{Hg}]_0 + [\mathrm{Hg}]_0\left(1 - \frac{b}{a+b}\right)e^{-(a+b)t} \qquad \text{(IV)}$$

The initial rate and stationary concentration are given by

$$-R(\mathrm{Hg}) = a[\mathrm{Hg}]_0$$

$$[\mathrm{Hg}]_{ss} = \frac{b}{a+b}[\mathrm{Hg}]_0$$

The pseudo-first-order rate constant for the disappearance of X is part of parameter b

$$\mathrm{X} \longrightarrow \mathrm{Hg} + \text{products} \qquad (8)$$

Parameter b is always larger in the illuminated system than in the dark system. We therefore add another reaction, the decomposition of X by the attack of radicals

$$\mathrm{Me_3Si} + \mathrm{X} \longrightarrow \mathrm{Hg} + \text{products} \qquad (9)$$

The decomposition of the mercury compound in the dark can be described by a simple first-order rate law

$$[\mathrm{Hg}] = [\mathrm{Hg}]_0 - ([\mathrm{Hg}]_0 - [\mathrm{Hg}]_{ss})e^{-bt}$$

From the temperature dependence, we obtain the following values for the activation energy and A factor: $E_A = 30 \pm 5$ kJ mol^{-1} and $A = 1 \times 10^2$ s^{-1}.

The A factor indicates a wall participation in the decomposition of the Hg compound. There is additional evidence that the mechanism is more complicated than suggested here. Neither the specific influence of H_2 on the stationary X concentration (Fig. 5) nor the non-exponential behaviour shown in Figs. 3 and 4 can be explained by the proposed mechanism.

Without identification of the mercury compound it is difficult to assess the importance of this compound on the mechanism of the Hg-sensitized photolysis of Me_3SiH. Support for such an involvement comes from the experiments in Ref. [5]. It is therefore tempting to speculate that the reaction of X with radicals or H atoms regenerates the substrate and is responsible for the low primary quantum yield reported in part I.

Preliminary experiments, e.g. with Hg–H_2–C_2H_4 systems, have shown that the involvement of Hg is a ubiquitous phenomenon and work is in progress to increase our understanding of these processes.

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