Formation of $HHgC_2H_5$ in the Hg-Sensitized Photolysis of H_2/C_2H_4 Mixtures

C. Kerst, I. Lein, P. Potzinger,* and H. G. Wagner

Max-Planck-Institut für Strömungsforschung, Bunsenstrasse 10, 37073 Göttingen, Germany

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In the Hg-sensitized photolysis of H_2 in the presence of C_2H_4 the sensitizer Hg is consumed under formation of a metastable compound. The rate of formation and the steady-state concentration of this compound have been studied as a function of Hg, H_2, and C_2H_4 concentration, absorbed light intensity, temperature, and in the presence of radical scavengers. All these experiments ask for the participation of HgH and C_2H_5 in the formation of the Hg compound. We therefore suggest that these two radicals combine under formation of $HHgC_2H_5$. Further support comes from two color photolysis experiments where HgH and C_2H_5 radicals have been generated independently. $HHgC_2H_5$ decomposes under 206 nm irradiation and much slower in the dark. It is also very easily attacked by radicals.

Introduction

Mercury atoms excited to the $^3P_1$ state may undergo an energy transfer to, or a photoreaction with, a substrate molecule, depending on the chemical nature of the substrate. If the substrate provides a suitable state which accepts the energy, an energy transfer will occur. Otherwise a photoreaction will take place which can be further subdivided into metathetical and addition reactions.[1] A typical example of an energy-transfer reaction is the reaction of $Hg(^3P_1)$ with *cis*-butene leading to a cis−trans isomerization.[2] The reaction of $Hg(^3P_1)$ with H_2 is a well-known example of a metathetical reaction.[3] The HgH formed in this photoreaction has a low bond dissociation energy[4] and leads to a fast collisionally induced decomposition which restores the original Hg concentration.[5] In other cases, such as the reaction of $Hg(^3P_1)$ with oxides, chlorides, or sulfides, stable mercury compounds are formed.[6] Pimentel and co-workers[7] have shown that $Hg(^3P_1)$ atoms insert into the C−Cl bond of a chloride, and the addition product was observed in a matrix at low temperature. A very detailed account of the reaction mechanism of excited Hg atoms with H_2, the C−H and Si−H bond has recently been given by Breckenridge.[8]

With the exceptions mentioned above, it is always assumed that in Hg-sensitized gas-phase reactions Hg atoms are regenerated very quickly independent of the type of reaction they undergo. Surprisingly, in the case of the Hg-sensitized photolysis of Me_3SiH a moderately stable mercury compound is formed.[9] Further experiments showed that this phenomenon is not limited to silanes but can also be observed with other classes of substrates.[10]

Here we report the Hg-sensitized photolysis of H_2 in the presence of ethylene leading to the removal of Hg. We discuss our attempts to unravel the nature of the metastable Hg compound, as well as the pathways leading to its formation.

Experimental Section

All substances were of commercial origin and used without further purification. Azoethane contained a large ethanol impurity.

Gas handling was performed on a conventional vacuum line. Reactant pressures were determined by capacitance manometers (MKS Baratron 220 and 122A). The Hg concentration was determined by an absorption experiment.

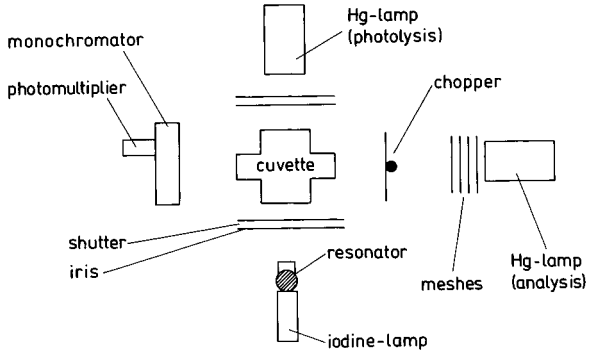

Figure 1. Experimental setup of the two color photolysis experiments.

Some of the photolysis experiments were carried out as described in ref 9, the low-pressure Hg lamp acted as photolysis source as well as analysis lamp. Photolysis experiments were performed at room, elevated, and low-temperatures. In the low temperature setup we used a double-walled cuvette thermostated by a cryostat (Lauda, RM6T).

In another series of experiments we carried out two color photolysis experiments as shown in Figure 1. The reaction mixture was photolyzed by a low-pressure Hg lamp ($\lambda = 254$ nm) and/or by a microwave driven iodine lamp ($\lambda = 206$ nm). The second low pressure Hg-arc served as an analysis lamp. The intensity of the monitoring light was attenuated by wire meshes to avoid photochemical reactions. The monitoring light, modulated by a chopper (HMS 220), passed the cuvette at right angle to the photolyzing light, was dispersed by a monochromator and detected by a photomultiplier. The signal was amplified by a lock-in amplifier (Ithaco Dynatrac 399) and finally recorded.

The intensity of the low-pressure Hg-lamps was determined by *cis*-butene (Φ(*trans*-butene) = 0.5[11]) as well as N_2O ($\Phi(N_2) = 1.0$[12]) actinometry. The values of the two actinometers agreed within 1.6%. The intensity of the iodine lamp was determined by HBr-actinometry ($\Phi(H_2) = 1.0$[13]).

Endproduct analyses by GC and MS were performed as described in ref 14.

The conversion of Hg-resonance radiation absorption values into Hg-concentration values was determined through the use of calibration plots described in ref 10.

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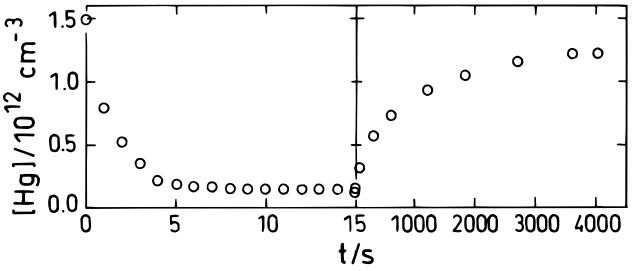

Figure 2. Change of the Hg concentration as a function of time (a) 254 nm light on and (b) 254 nm light off (exp 16, Table 1).

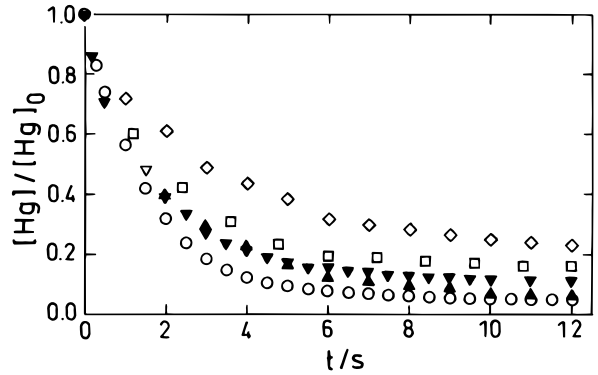

Figure 3. Change of the Hg concentration as a function of time for different initial Hg concentrations (exp 1 (○), 2 (▼), 3 (□), 4 (▲), 5 (◇), Table 1).

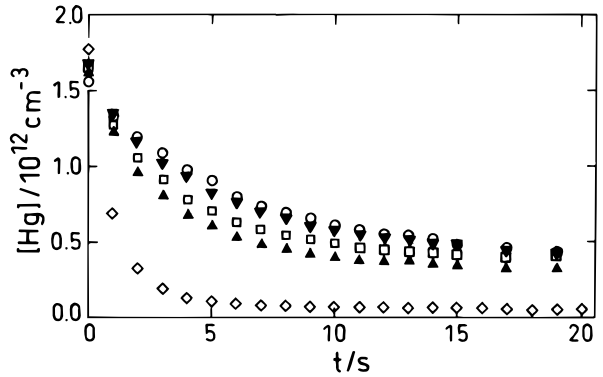

Figure 4. Change of the Hg concentration as a function of time for different 254 nm light intensities (exp 6 (○), 7 (▼), 8 (□), 9 (▲), 10 (◇), Table 1).

Results

Hg-sensitized photolysis of H_2 in the presence of C_2H_4 results in an almost complete loss of Hg. The Hg-concentration recovers quite slowly when the resonance radiation is shut off (Figure 2). A metastable mercury compound X must be formed which does not absorb at all or only weakly at 254 nm. Hg-sensitized photolysis of pure C_2H_4 or pure H_2 does not result in any reduction of the Hg-concentration. The rate of Hg-removal and to a lesser extent the stationary Hg-concentration depends on the initial Hg-concentration, light intensity, H_2-concentration, and temperature. The rate of Hg-disappearance increases with increasing initial Hg-concentration (Figure 3). This is also observed for the absorbed intensity of the Hg-resonance radiation (Figure 4). H_2 inhibits the formation of X to such an extent, that its formation comes to an almost complete halt at high H_2 pressure (Figure 5). The temperature was varied between −1.5 °C and 100 °C and had a large effect on the formation of X, i.e., it decreased with increasing temperature and was almost negligible at 100 °C (Figure 6). The experiments were repeated after a dark period in which the Hg-

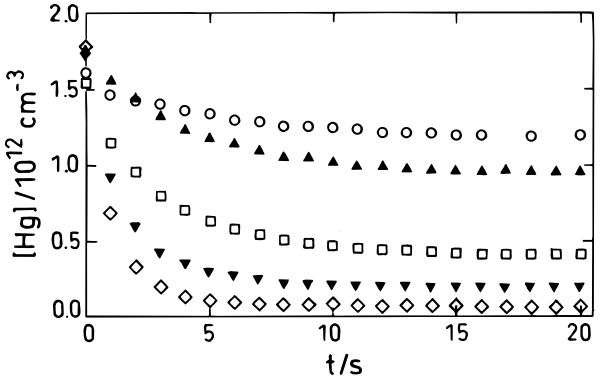

Figure 5. Change of the Hg concentration as a function of time for different H_2 concentrations (exp 11 (○), 12 (▲), 13 (□), 14 (▼), 15 (◇), Table 1).

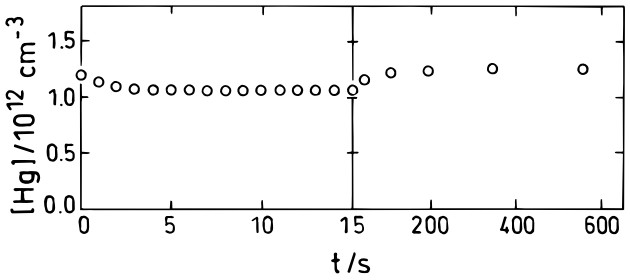

Figure 6. Change of the Hg concentration as a function of time at 373 K: (a) 254 nm light on and (b) 254 nm light off (exp 20, Table 1).

concentration recovered to its original value. The reproducibility can be seen from the two values given for α and β in Table 1, experiments 16−20. Adding O_2 to the reaction mixture inhibits the disappearance of Hg until all the O_2 has reacted (Figure 7). Similar results were obtained with NO.[10] Changing the C_2H_4-concentration by a factor of almost one hundred had only a very minor effect (Figure 8). The mercury concentration − time profiles shown in Figure 3 may be the result of the change in the Hg-concentration and/or the change in the absorbed light intensity. To check specifically the influence of ground-state mercury concentration on the formation of X, the following experiment was performed: Change in the Hg-concentration is accompanied by a change in the absorbed light intensity, therefore the incident light was adjusted so that the absorbed light intensity was kept constant, at least at the beginning of the photolysis (Figure 9). All the experiments reported so far were carried out with the simple one lamp arrangement of.[9] Experimental details are given in Table 1.

To elucidate the reaction paths leading to the metastable Hg-compound other sources of H-atoms and radicals were utilized. The photolysis of NH_3 at 206 nm was used as an alternative H-atom source. The primary step is the formation of an H-atom and a NH_2-radical.[15] Similarly, azoethane was used as an alternative ethyl-radical source. Photolysis of pure Et_2N_2 at 206 nm produced mainly N_2 and C_4H_{10}, as well as small amounts of C_2H_6, C_2H_4 and C_3H_8. Reactant concentrations, experimental conditions, and results are compiled in Table 2 and Table 3.

When the reaction mixture $Hg/H_2/C_2H_4/NH_3$ was photolyzed at 206 nm, no decrease in the Hg concentration was observed (Table 2, exp 33). Photolysis of the above mixture at 254 nm radiation leads to the known almost complete disappearance of Hg. Upon irradiation with both wavelengths, 206 and 254 nm, an increase of the stationary Hg concentration is observed (Figure 10). In a similar experiment the same reaction mixture was photolyzed by 254 nm light until the stationary Hg

TABLE 1: Experimental Conditions and Results of the 254 nm Photolysis of $Hg/H_2/C_2H_4/O_2$/Mixtures

exp	$[Hg]_0/10^{12}$ cm^{-3}	$[C_2H_4]/10^{15}$ cm^{-3}	$[H_2]/10^{18}$ cm^{-3}	$[O_2]/10^{14}$ cm^{-3}	$I_0/10^{13}$ cm^{-3} s^{-1}	T/K	results	$\alpha/10^{-1}$	$\beta/10^{-7}$ cm$^{3/2}$ s^{-1}
1	1.9	3.04	1.19		3.36	298	s, Figure 3	1.31	6.13
2	0.65	3.15	1.19		3.35	298	s, Figure 3	3.06	9.28
3	0.35	3.22	1.19		3.55	298	s, Figure 3	3.74	10.63
4	0.26	3.17	1.20		3.41	298	s, Figure 3	1.76	11.49
5	0.14	3.27	1.19		3.42	298	s, Figure 3	4.40	10.66
6	1.5	2.57	1.22		0.89	298	s, Figure 4	4.67	1.52
7	1.6	2.57	1.24		1.17	298	s, Figure 4	4.88	1.98
8	1.6	2.51	1.24		1.40	298	s, Figure 4	4.83	2.74
9	1.6	2.51	1.23		1.54	298	s, Figure 4	4.42	3.13
10	1.5	2.48	1.21		3.42	298	s, Figure 4	3.23	6.33
11	1.6	3.13	23.8		3.41	298	s, Figure 5	8.64	1.72
12	1.7	3.14	11.8		3.64	298	s, Figure 5	7.28	2.11
13	1.5	3.22	5.91		3.60	298	s, Figure 5	5.06	3.32
14	1.8	3.15	2.33		3.67	298	s, Figure 5	3.29	6.70
15	1.8	3.11	1.19		3.69	298	s, Figure 5	1.76	10.46
16	1.5	2.49	1.22		3.11	298	s, Figure 2	2.82	7.30
								3.97[a]	8.07[a]
17	1.3	2.52	1.22		3.10	313		4.86	4.64
								5.34[a]	5.26[a]
18	1.4	2.48	1.22		3.25	333		7.35	5.13
								7.55[a]	3.92[a]
19	1.6	2.52	1.22		3.21	353		8.42	4.16
								8.74[a]	3.75[a]
20	1.2	2.49	1.22		3.29	373	s, Figure 6	9.39	6.27
								9.53[a]	5.04[a]
21	1.9	2.72	2.62	5.23	3.42	298	s, Figure 7		
22	1.6	2.71	2.65	0.34	3.34	298	s, Figure 7		
23	1.9	3.04	1.19		3.36	298	s, Figure 8		
24	1.7	24.44	1.17		4.10	298	s, Figure 8		
25	1.8	122.1	1.07		4.16	298	s, Figure 8		
26	1.9	244.1	0.95		4.18	298	s, Figure 8		
27	0.24	2.54	1.24		3.00	298	s, Figure 9	5.47	11.86
28	0.40	2.49	1.22		1.63	298	s, Figure 9	4.22	5.99
29	0.51	2.43	1.22		1.43	298	s, Figure 9	4.67	5.91
30	0.64	2.48	1.23		1.14	298	s, Figure 9	4.72	2.88
31	1.2	2.45	1.22		0.86	298	s, Figure 9	5.30	1.90
32	1.9	2.50	1.22		0.70	298	s, Figure 9	6.16	1.28

[a] Experiment repeated after a dark period.

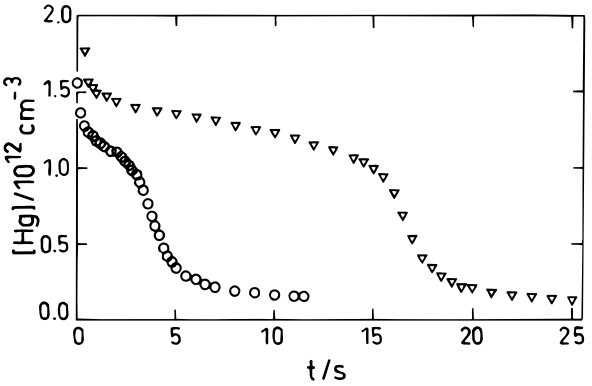

Figure 7. Change of the Hg concentration as a function of time in the presence of O_2 (exp 21 (▽) and 22 (○), Table 1).

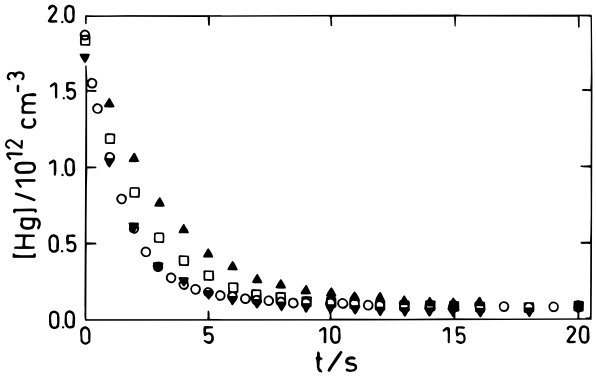

Figure 8. Change of the Hg concentration as a function of time for different C_2H_4 concentrations (exp 23 (○), 24 (▼), 25 (□), 26 (▲), Table 1).

concentration was reached; then the iodine lamp was turned on. An increase in the stationary Hg concentration is observed, the extent of which depends on the intensity of the two light sources (Figure 11).

Hg-sensitized photolysis of NH_3 in the presence of C_2H_4 did not result in any Hg-removal (Table 2, exp 39, 40).

The slow increase in Hg concentration after 254 nm photolysis of a $Hg/H_2/C_2H_4$ mixture could be accelerated by illuminating the product mixture with 206 nm radiation (Figure 12).

Simultaneous photolysis of a Hg/Et_2N_2 mixture at 254 and 206 nm caused no loss of Hg (Table 3, exp 42).

Photolysis of a $Hg/H_2/Et_2N_2$ mixture at 206 nm or 254 nm had no effect on the Hg concentration, while simultaneous irradiation with light of both wavelengths resulted in a loss of Hg (Figure 13).

An attempt to characterize the metastable Hg compound by mass spectrometry failed.

The $[C_2H_6]/[C_4H_{10}]$ ratio was determined in the photolysis of Et_2N_2 at 366 nm to be 0.124 ± 0.005, whereas in our standard system $Hg/H_2/C_2H_4$ at 254 nm we determined $[C_2H_6]/[C_4H_{10}] = 0.16 \pm 0.01$.

Discussion

In recent publications[16−19] it has been shown that reactions of excited metal atoms such as $Mg(^1P)$, $Zn(^3P_1)$, and $Hg(^3P_1)$

TABLE 2: Experimental Conditions and Results of the Photolysis of $Hg/H_2/C_2H_4/NH_3$ Mixtures at the Two Wavelengths 254 and 206 nm

exp	$[C_2H_4]/10^{15}$ cm^{-3}	$[NH_3]/10^{16}$ cm^{-3}	$[H_2]/10^{18}$ cm^{-3}	t/s	$I_0(\lambda = 254$ nm)/%	$I_0(\lambda = 206$ nm)/%	results
33	4.72	6.34	1.20		0	100	[Hg] $\neq f(t)$
34	4.45	6.25	1.19	0−30.5	100	0	s, Figure 10
				30.5−661.2	0	0	
35	4.71	6.73	1.20	0−30.3	100	100	s, Figure 10
				30.3−605.6	0	0	
36	4.67	6.55	1.21	0−31.8	10.5	0	s, Figure 11
				31.8−46.8	10.5	100	
37	4.75	6.66	1.20	0−25.4	52.6	0	s, Figure 11
				25.4−40.3	52.6	100	
38	4.66	6.37	1.20	0−25.1	100	0	s, Figure 11
				25.1−40.0	100	100	
39	4.66	24.76	0		100	0	[Hg] $\neq f(t)$
40	4.72	74.29	0		100	0	[Hg] $\neq f(t)$
41	4.69	0	1.19	0−30.2	100	0	s, Figure 12
				30.2−115.2	0	0	
				115.2−220.5	0	100	

TABLE 3: Experimental Conditions and Results of the Photolysis of $Hg/H_2/Et_2N_2$ Mixtures at the Two Wavelengths 254 and 206 nm

exp	$[Et_2N_2]/10^{16}$ cm^{-3}	$[H_2]/10^{18}$ cm^{-3}	t/s	$I_0(\lambda = 254$ nm)/%	$I_0(\lambda = 206$ nm)/%	results
42	9.50	0	0−28.2	100	100	[Hg] $\neq f(t)$
43	9.89	1.19	0−10.0	0	100	s, Figure 13
			10.0−39.5	100	100	
			39.5−73.5	0	100	
			73.5−423.9	0	0	

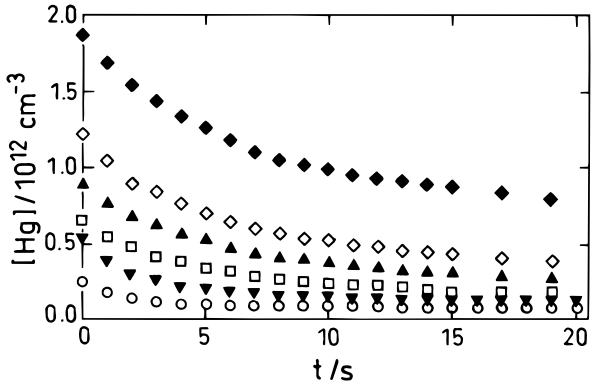

Figure 9. Change of the Hg concentration as a function of time for different Hg concentrations under the condition of constant absorbed lightintensity (exp 27 (○), 28 (▼), 29 (□), 30 (▲), 31 (◇), 32 (◆), Table 1).

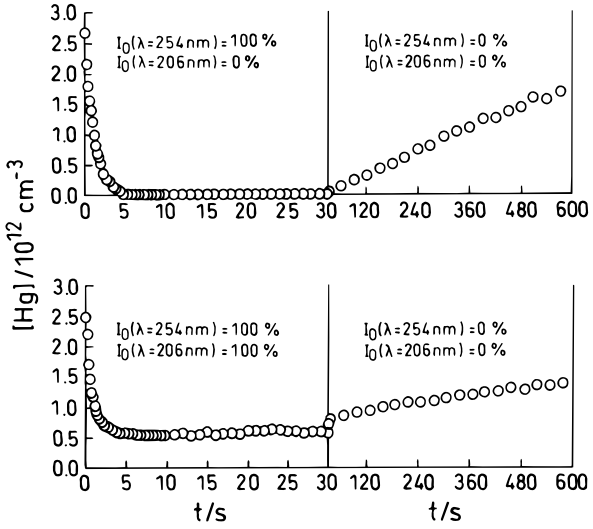

Figure 10. Hg concentration−time profiles in the two color photolysis of $Hg/H_2/C_2H_4/NH_3$ mixtures and in the dark periods (exp 34, 35, Table 2).

with H_2 and CH_4 in a solid matrix result in the formation of MgH_2, ZnH_2, HgH_2, $HMgCH_3$, and $HHgCH_3$. It is suggested[20] that these compounds are formed by direct insertion of the excited metal atom into the H−H and C−H bond, respectively. A similar mechanism was discussed in the Hg-sensitized photolysis of silanes[9] as a possible explanation for the formation of the unknown Hg containing product X, namely, the addition of excited mercury atoms to the substrate:

$$Hg(^3P_1) + R_3SiH \rightarrow X \quad (1)$$

$$Hg(^3P_0) + R_3SiH \rightarrow X \quad (2)$$

These reactions can be immediately discarded in the Hg-sensitized photolysis of the H_2/C_2H_4 mixture. The $Hg(^3P_1)$ is quenched predominantly by H_2 under our experimental conditions, and no decrease of the Hg concentration was observed in a Hg/H_2 (or a Hg/C_2H_4) system. The mechanism of the Hg-sensitized photolysis of H_2 has been carefully studied by Callear and co-workers,[3] and the mechanism is as follows:

$$Hg(^1S_0) + h\nu \rightarrow Hg(^3P_1) \quad (3)$$

$$Hg(^3P_1) + H_2 \rightarrow HgH + H \quad (4)$$

$$\rightarrow Hg(^1S_0) + 2H \quad (5)$$

$$\rightarrow Hg(^3P_0) + H_2 \quad (6)$$

The H atoms are scavenged by C_2H_4:

$$H + C_2H_4 \rightarrow C_2H_5 \quad (7)$$

It seems therefore likely that H atoms and/or ethyl radicals are involved in the formation of the metastable compound X. These

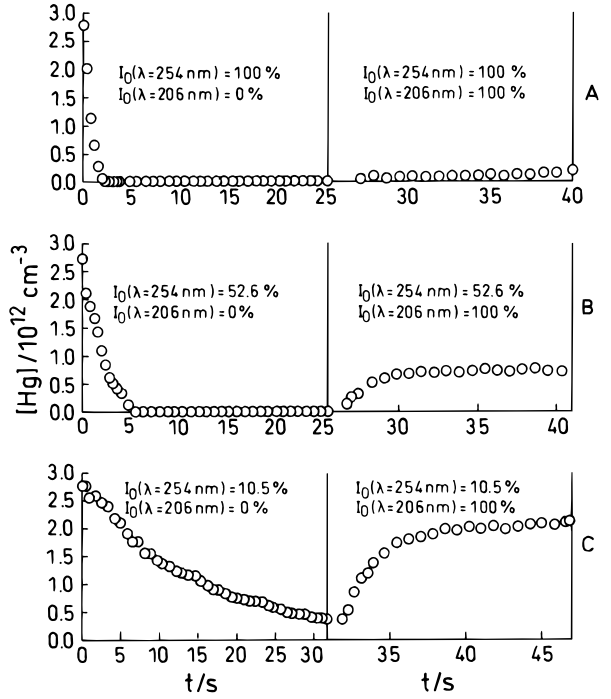

Figure 11. Decomposition of the Hg compound by 206 nm irradiation in the 254 nm photolysis of a $Hg/H_2/C_2H_4/NH_3$ mixture (exp 36−38, Table 2).

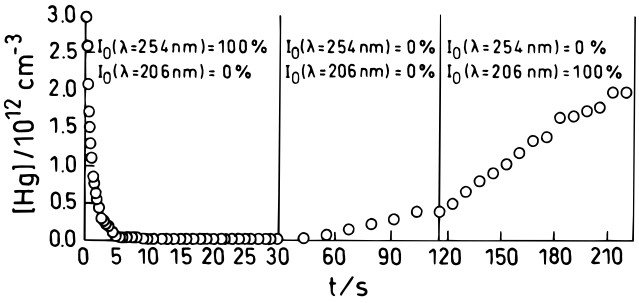

Figure 12. Dependence of the lifetime of the Hg compound on 206 nm irradiation (exp 41, Table 2).

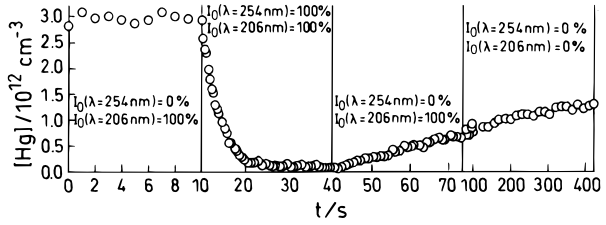

Figure 13. Dependence of the rate of formation and rate of decomposition of the Hg compound on the wavelength in the two color photolysis experiments of $Hg/H_2/Et_2N_2$ mixtures (exp 43, Table 3).

considerations are supported by the observation that typical radical scavengers such as O_2 and NO inhibit the formation of X.

In the following experiments we examined which of the Hg species $Hg(^3P_1)$, $Hg(^3P_0)$, $Hg(^1S_0)$, and HgH and which of the reactive species H and C_2H_5 are responsible for the formation of X and the removal of Hg.

The reaction of $Hg(^3P_1)$ with either H or C_2H_5 as the rate-determining step in the formation of X

$$Hg(^3P_1) + H \longrightarrow\!\!\!\!\!\rightarrow X \tag{8}$$

$$Hg(^3P_1) + C_2H_5 \longrightarrow\!\!\!\!\!\rightarrow X \tag{9}$$

can be dismissed for the reasons given below. The stationary concentrations of $Hg(^3P_1)$, C_2H_5, and H, given approximately by $[Hg(^3P_1)]_{ss} \approx I_{abs}/\{(k_4 + k_5 + k_6)[H_2]\}$, $[C_2H_5]_{ss} \approx \{2I_{abs}/(k_{10} + k_{11})\}^{1/2}$, and $[H]_{ss} \approx 2I_{abs}/k_7[C_2H_4]$ have the following values under the conditions of experiment 1: $[Hg(^3P_1)]_{ss} \approx 10^5$ cm^{-3}, $[C_2H_5]_{ss} \approx 10^{12}$ cm^{-3} and $[H]_{ss} \approx 10^{10}$ cm^{-3}. Even if we assume the rate of reactions 8 and 9 to be collision controlled, it would take orders of magnitude longer to build up X than is experimentally observed. These considerations are in agreement with exp 42 where $Hg(^3P_1)$ and ethyl radicals were generated by two independent light sources. Reactions 10 and 11 describe two important reactions of C_2H_5:

$$2C_2H_5 \rightarrow C_4H_{10} \tag{10}$$

$$\rightarrow C_2H_6 + C_2H_4 \tag{11}$$

A similar calculation for $Hg(^3P_0)$ predicts an even smaller stationary concentration for $Hg(^3P_0)$ than for $Hg(^3P_1)$. The rate of formation of $Hg(^3P_0)$ is more than a factor of 30 smaller than for $Hg(^3P_1)$, outweighing the 1 order of magnitude smaller rate constant for $Hg(^3P_0)$ with H_2.[21] This calculation is supported by an experiment in which excited Hg atoms react with NH_3 in the presence of C_2H_4. The following two reactions occur:

$$Hg(^3P_1) + NH_3 \rightarrow H + NH_2 + Hg(^1S_0) \tag{12}$$

$$\rightarrow Hg(^3P_0) + NH_3 \tag{13}$$

The H atoms are scavenged by C_2H_4 (reaction 7). In this system similar stationary concentrations of H and C_2H_5 are generated as in our standard system; in this case, however, the $Hg(^3P_0)$ stationary concentration is larger. No removal of Hg was observed in these experiments.

In a previous publication[9] it has been proposed that the reaction of ground-state mercury atoms with radicals is the crucial step in the formation of X. Two experiments argue against such an explanation. The initial rate of Hg removal as a function of Hg concentration at constant absorbed light intensity (Figure 9) does not show the 1.5 order dependence on light intensity which one would expect if the reaction of Hg with C_2H_5 is the rate determining step in the formation of X. Experiment 33 shows that mercury atoms in the ground state and C_2H_5 radicals do not react to form X.

This leaves us with HgH. Indeed, if we look through Tables 2 and 3 Hg removal is observed only in the presence of HgH. In Figure 13 it is quite clearly demonstrated that besides HgH, C_2H_5 radicals have to be present to form the Hg compound under investigation. We suggest that X is formed by the combination reaction

$$HgH + C_2H_5 \rightarrow HHgC_2H_5 \tag{14}$$

Thus, the overall mechanism of the Hg-sensitized photolysis of H_2 in the presence of C_2H_4 is made up of reactions 3−5, 7, 10, and 11 as the main steps. Furthermore it is known that HgH decomposes in a collision-induced process:[22]

$$HgH + M \rightarrow Hg + H + M \tag{15}$$

For $M = H_2$, the main collision partner in our system, the rate constant is known.[22] It has been suggested by Callear et al.[23] that HgH is also attacked by H atoms and radicals in the manner of an abstraction reaction:

$$HgH + H \rightarrow H_2 + Hg \quad (16)$$

$$HgH + C_2H_5 \rightarrow C_2H_6 + Hg \quad (17)$$

We now add reaction 14 to this mechanism. $HHgC_2H_5$ is not stable and decomposes slowly in the dark and rather quickly under irradiation. This can be accounted for by a unimolecular step

$$HHgC_2H_5 \rightarrow C_2H_6 + Hg \quad (18)$$

and by abstraction processes with the radicals present. If only C_2H_4 is present besides Hg and H_2 the abstraction pathway will be dominated by C_2H_5:

$$HHgC_2H_5 + C_2H_5 \rightarrow C_2H_6 + HgC_2H_5 \quad (19)$$

In the presence of other substances, e.g., NH_3, other radicals such as NH_2 will undergo a reaction equivalent to (19). HgC_2H_5 radicals are not characterized in the literature and are thought to have a very small bond dissociation energy[24] so that a fast further decomposition is quite likely:

$$HgC_2H_5 \rightarrow Hg + C_2H_5 \quad (20)$$

To account for our experimental results we have to assume that reaction 15 is the main process for the destruction of HgH. Hence, the rate of Hg disappearance should be inhibited by H_2. There should also be a temperature and intensity dependence. Reaction 15 has an appreciable activation energy[22] and it will therefore be favored over reaction 14 at higher temperatures. The intensity dependence arises from the different orders in the radical concentration in reaction 14 and 15.

A more quantitative comparison is possible by examining the integrated rate equation for $HHgC_2H_5$:

$$R(HHgC_2H_5) = -R(Hg) = k_{14}[HgH][C_2H_5] - k_{19}[C_2H_5]\{[Hg]_0 - [Hg]\} \quad (I)$$

For HgH and C_2H_5 approximate steady-state expressions will be inserted:

$$[HgH]_{ss} \approx \frac{k_4}{k_4 + k_5}\frac{I_{abs}}{k_{15}[M]} \approx \frac{k_4}{k_4 + k_5}\frac{\kappa I_0}{k_{15}[M]}[Hg] \equiv A[Hg] \quad (II)$$

$$[C_2H_5]_{ss} \approx \left(\frac{k_4 + 2k_5}{k_4 + k_5}\frac{I_{abs}}{2(k_{10} + k_{11})}\right)^{1/2} \approx \left(\frac{k_4 + 2k_5}{k_4 + k_5}\frac{\kappa I_0}{2(k_{10} + k_{11})}\right)^{1/2}[Hg]^{1/2}$$

$$\equiv B[Hg]^{1/2} \quad (III)$$

In the two expressions II and III it has been assumed that the absorbed light intensity I_{abs} [cm^{-3} s^{-1}] can be approximated by κI_0[Hg], where κ [cm^3] is the product of the absorption cross section σ of Hg atoms for 254 nm resonance radiation and the optical path length d. $I_0{*}d$ is the light intensity [cm^{-2} s^{-1}] at the entrance window of the cuvette.

We obtain the following expression for the mercury concentration as a function of time:

$$[Hg] = [Hg]_0\alpha^2\left(1 - \frac{2(\alpha - 1)}{(\alpha + 1)\exp([Hg]_0^{1/2}\alpha\beta t) + \alpha - 1}\right)^2 \quad (IV)$$

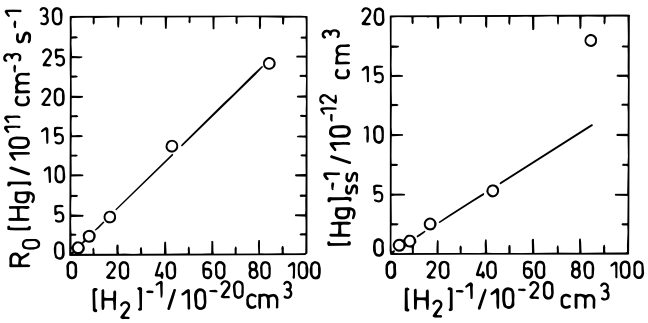

Figure 14. Dependence of the initial reaction rate and the steady-state concentration of Hg on the reciprocal H_2 concentration.

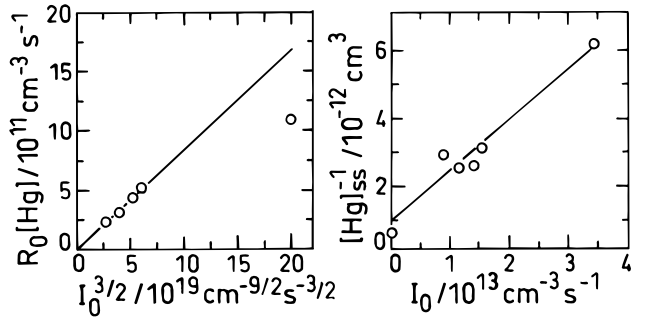

Figure 15. Dependence of the initial reaction rate and the steady-state concentration of Hg on the 254 nm absorbed light intensity.

with

$$\alpha = \left(\frac{k_{19}B}{k_{14}AB + k_{19}B}\right)^{1/2} \quad (V)$$

$$\beta = k_{14}AB + k_{19}B \quad (VI)$$

$[Hg]_0$ and t denote the initial mercury concentration and time, respectively. Expression IV was fitted to our experimental [Hg] versus time curves with α and β as parameters. These parameters are also given in Table 1.

The initial rate R_0 of the Hg reaction is given by

$$R_0(Hg) = \lim_{t \rightarrow 0} d(Hg)/dt = \beta(\alpha^2 - 1)[Hg]_0^{3/2} = -\text{const}\frac{I_0^{3/2}[Hg]_0^{3/2}}{[M]} \quad (VII)$$

The stationary Hg-concentration $[Hg]_{ss}$ is given by

$$[Hg]_{ss} = \alpha^2[Hg]_0 = [Hg]_0\frac{[M]}{\text{const}I_0 + [M]} \quad (VIII)$$

Equations VII and VIII express the quantitative dependence of initial rate and stationary Hg concentration on H_2 concentration, light intensity, and initial Hg concentration.

The dependence of R_0(Hg) and $[Hg]_{ss}$ on $[H_2]$ are depicted in Figure 14, and in both cases a straight line is obtained as predicted by the mechanism. The data point for the smallest H_2 concentration in the $1/[Hg]_{ss}$ vs $1/[H_2]$ plot is in error due to the very small Hg concentration (Figure 5).

The dependence of the initial rate on light intensity shows the expected order of 3/2 but only at the low intensity experiments. The experimental data in the plot $1/[Hg]_{ss}$ vs I_0 are quite scattered; however, in a linear fit we obtain an intercept which agrees quite well with the value of $1/[Hg]_0$, predicted by the mechanism (Figure 15).

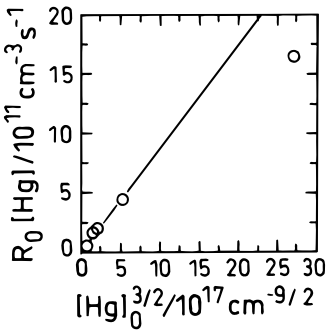

Figure 16. Dependence of the initial reaction rate of Hg on the 3/2 power of the initial Hg concentration.

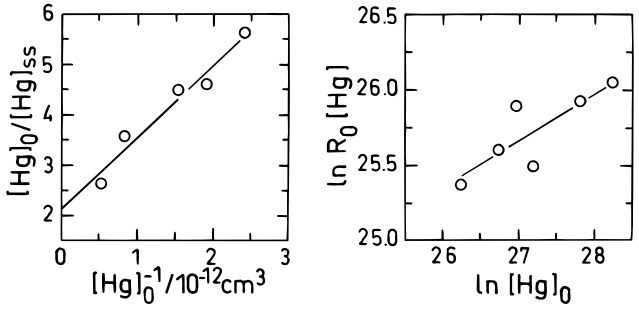

Figure 17. (a) Dependence of the reciprocal steady-state Hg concentration on the reciprocal initial Hg concentration. (b) Double-logarithmic plot of initial reaction rate of Hg on the initial Hg concentration.

The dependence on the initial mercury concentration can only be evaluated for R_0(Hg). The stationary Hg concentrations are quite small (Figure 3) and are associated with large errors which prevent an accurate determination. For R_0(Hg) the 3/2 power dependence is in very good agreement for the low Hg concentration experiments (Figure 16).

By keeping the absorbed light intensity I_{abs} constant while changing the initial mercury concentration $[Hg]_0$, we deduce from our mechanism (equation VII) that R_0(Hg) should be independent of $[Hg]_0$. However, this is not completely exemplified by our experiments, since a double logarithmic plot ln(R_0(Hg)) vs ln($[Hg]_0$) yields a slope of 0.3 ± 0.1 (Figure 17). For $[Hg]_{ss}$ we derive the following relation under the condition of constant absorbed light intensity:

$$[Hg]_0/[Hg]_{ss} = 1 + \frac{\text{const}}{[Hg]_0} \qquad \text{(IX)}$$

A plot of the experimental data according to IX yields a straight line with an intercept of 2.1 ± 0.3 (Figure 17), rather than 1.0. The discrepancy between predicted and experimental result is in large parts due to the assumption of a linear dependence of I_{abs} on [Hg].

It remains to be shown that the quantity const in eq VII has the same value in all three relations R_0(Hg) versus $I_0^{3/2}$, $[Hg]_0^{3/2}$, and $1/[H_2]$. The slope of the straight line in the last case (Figure 14) amounts to $m = \text{const } I_0^{3/2}[Hg]_0^{3/2} = (2.92 \pm 0.07) \times 10^{30}$ cm^{-6} s^{-1}. With $I_0 = (3.60 \pm 0.11) \times 10^{13}$ cm^{-3} s^{-1} and $[Hg]_0 = (1.68 \pm 0.13) \times 10^{12}$ cm^{-3}, we arrive at const $= (6.2 \pm 0.8) \times 10^{-9}$ cm^3 s$^{1/2}$. In the case of the I_0 dependence we obtain const $= (5.3 \pm 0.3) \times 10^{-9}$ cm^3 s$^{1/2}$, whereas in the case of the $[Hg]_0$ dependence const $= (5.2 \pm 0.3) \times 10^{-9}$ cm^3 s$^{1/2}$. Taking the weighted mean of these three values yields

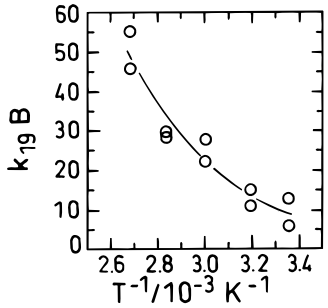

Figure 18. Arrhenius plot for $k_{19}B$.

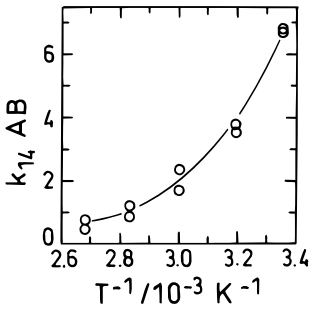

Figure 19. Arrhenius plot for $k_{14}AB$.

$$\text{const} = \frac{k_{14}}{k_{15}} \frac{k_4(k_4 + 2k_5)^{1/2}}{(k_4 + k_5)^{3/2}} \frac{\kappa^{3/2}}{(2(k_{10} + k_{11}))^{1/2}} = (5.3 \pm 0.2) \times 10^{-9} \text{ cm}^3 \text{ s}^{1/2} \qquad \text{(X)}$$

From (X) we can derive an approximate value for k_{14}/k_{15}. The rate constants k_4, k_5,[3] and k_{10}, k_{11}[25] are known, only κ is not a very well-defined quantity which depends on the experimental conditions. From our own absorption measurements[10] we derive a value of $\kappa \approx 5 \times 10^{-13}$ cm^3. From this it follows that

$$k_{14}/k_{15} = 1.2 \times 10^5$$

With the known rate constant for (15), $k_{15} = 3 \times 10^{-16}$ cm^3 s^{-1},[22] we obtain a value of $k_{14} = 3.7 \times 10^{-11}$ cm^3 s^{-1}, which has the correct order of magnitude for a radical combination reaction.

From the experiments in Table 1 it is also possible to derive a value for k_{19}. The product $\alpha^2\beta$ contains only k_{19} as an unknown rate constant

$$\alpha^2\beta = k_{19}B = k_{19}\left(\frac{k_4 + 2k_5}{k_4 + k_5} \frac{1}{2(k_{10} + k_{11})}\right)^{1/2} I_0^{1/2}\kappa^{1/2} \qquad \text{(XI)}$$

With the values for α and β given in Table 1, the value for κ, and the known rate constants, we arrive at a value of $k_{19} = (1.1 \pm 0.2) \times 10^{-13}$ cm^3 s^{-1} from the intensity dependence experiments. Similarly, the H_2 dependence yields $k_{19} = (1.3 \pm 0.3) \times 10^{-13}$ cm^3 s^{-1}. From the $[Hg]_0$ dependence experiments a value of $k_{19} = (1.3 \pm 1.1) \times 10^{-13}$ cm^3 s^{-1} is obtained, which is in good agreement with the above results, however, with a larger uncertainty. The value of about 1×10^{-13} cm^3 s^{-1} for a hydrogen abstraction reaction by an alkyl radical at room temperature is rather large, suggesting that the C_2H_5Hg-H bond energy is quite weak. The temperature dependence of $\alpha^2\beta$ can be mainly attributed to reaction 19. From Figure 19 we derive an activation temperature of 2500 ± 300 K for k_{19}. These results together with the value for k_{19} yields an A factor $\log(A(19)/\text{cm}^3\text{ s}^{-1}) = -9.3 \pm 0.8$. This value is too large, but

taking into account the complex analysis and the large errors involved, the result does not argue against the proposed mechanism.

Combining α and β in the following way

$$\beta(1 - \alpha^2) = k_{14}AB \qquad \text{(XII)}$$

provides a quantity which contains only one rate constant, namely, k_{15}, with an appreciable temperature dependence. Because k_{15} is part of the denominator, we expect a negative activation energy when plotting $\ln(k_{14}AB)$ vs $1/T$. This is in fact the case, and from Figure 19 we derive an activation energy for reaction 15, $E_a(15) = 29.9 \pm 1.7$ kJ/mol. This value is in good agreement with the value given in ref 22 for the collision-induced decomposition of HgH by H_2.

A few reactions have to be added to the suggested mechanism to explain the experimental results in Tables 2 and 3. The increased rate of Hg formation when the sample is irradiated with 206 nm radiation can be rationalized by a direct photolytic decomposition of $HHgC_2H_5$.

$$HHgC_2H_5 + h\nu \rightarrow Hg + C_2H_6\,(C_2H_5 + H) \qquad (21)$$

From Figure 12 it can be deduced that the absorption cross section for 206 nm photons is $\sigma \approx 3 \times 10^{-17}$ cm^2 taking into account $I_0(\lambda = 206\text{ nm}) = 4.2 \times 10^{13}$ cm^{-3} s^{-1} and $d = 6$ cm. This result agrees with the spectroscopic properties of mercury compounds. HgH_2 absorbs at 193 nm[26] but not at 254 nm. The maximum of the first absorption band of $(CH_3)_2Hg$ is located at ~200 nm, the cross section at the maximum amounts to 3×10^{-17} cm^2.[27,28] The absorption maximum of $(C_2H_5)_2Hg$ is slightly shifted toward longer wavelengths.[29]

Addition of NH_3 to our standard reaction system $Hg/H_2/C_2H_4$ has no effect. However, simultaneous photolytic decomposition of NH_3 leads to a substantial reduction of the stationary $HHgC_2H_5$ concentration. This can be explained by the three reactions

$$NH_3 + h\nu \rightarrow NH_2 + H \qquad (22)$$

$$NH_2 + R \rightarrow \text{products} \qquad (23)$$

$$NH_2 + HHgC_2H_5 \rightarrow NH_3 + HgC_2H_5 \qquad (24)$$

The two photolysis products of NH_3, H, and NH_2 have opposing effects with respect to the stationary concentration of $HHgC_2H_5$. The H atoms form mainly C_2H_5 radicals which favor $HHgC_2H_5$ formation via reaction 14 while NH_2 radicals have the opposite effect: reaction 24 directly affects the concentration of the mercury compound, while reaction 23 reduces the HgH and C_2H_5 radicals which are precursors to the mercury compound. Computer simulations suggest that the rate constant for reaction 24 is larger than k_{19} by approximately a factor of 2.

For the experiments given in Table 3 the photolytic decomposition of $(C_2H_5)_2N_2$

$$(C_2H_5)_2N_2 + h\nu \rightarrow 2\,C_2H_5 + N_2 \qquad (25)$$

is essential for the formation of $HHgC_2H_5$. Without the simultaneous irradiation of the $Hg/H_2/(C_2H_5)_2N_2$ system with 254 and 206 nm light, no mercury compound is formed. The absorbed light intensity of the two light sources is roughly the same, and we expect similar rates of formation for HgH and C_2H_5, as in the 254 nm/$Hg/H_2/C_2H_4$ system. In contrast to the last system, there exists no large sink for the H atoms, like C_2H_4, and they will therefore react with HgH and C_2H_5, inhibiting the formation of $HHgC_2H_5$. This explains qualitatively the much smaller rate of formation of $HHgC_2H_5$ in the 254 nm/$Hg/H_2/(C_2H_5)_2N_2$/206 nm system (Figure 13) compared to the 254 nm/$Hg/H_2/C_2H_4$ system (Figure 2).

We have also addressed the question whether the proposed reactions 17 and 19 can be directly demonstrated. If these two reactions are of any importance, then the product ratio $[C_2H_6]/[C_4H_{10}]$ should be different in the experiments where the C_2H_5 radicals are generated by direct photochemical or thermal means and in experiments where they are generated in a system such as $Hg/H_2/C_2H_4$. Direct photolysis of $(C_2H_5)_2N_2$ at 366 nm yielded a $[C_2H_6]/[C_4H_{10}]$ ratio of 0.124 ± 0.005, while in the other system a value of 0.16 ± 0.01 has been found.

Conclusion

In the Hg-sensitized photolysis of H_2 in the presence of ethylene, as well as in the presence of other alkenes[10] and in the Hg-sensitized photolysis of silanes[9,10] or alkanes,[10] it was observed that the sensitizer is consumed under formation of a metastable mercury compound. The experiments presented here show that HgH and C_2H_5 or more generally HgH and a radical are involved in the formation of this metastable compound. Concerning the structure of this compound, we have made the simplest assumption, namely, that it results directly from the combination of HgH with C_2H_5. Proof in the form of a mass spectrometric experiment failed. Indirect support for the suggested structure comes from more recent publications.[30−34] In these works various organomercury hydrides have been prepared and characterized, a type of Hg compound which was thought to be unstable. Of importance to us is the finding that $HHgCH_3$ decomposes slowly at room temperature.[30]

What are the consequences of this hitherto overlooked effect?

(i) If a low sensitizer concentration is chosen, e.g., to achieve a more uniform absorption of the resonance radiation, a systematic error in the quantum yield may result.

(ii) Disproportionation to recombination ratios of radicals will be too high, as demonstrated above.

(iii) This is a sensitive method to show the formation of HgH in the photochemical reaction between an excited Hg atom and a substrate.

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