

PHOTOLYSIS OF CH_2I_2 AND $1,1\text{-C}_2\text{H}_4\text{I}_2$ AT 300 nm

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Summary

Absorption of UV light ($\lambda = 300$ nm) by diiodomethane (CH_2I_2) and 1,1-diiodoethane ($1,1\text{-C}_2\text{H}_4\text{I}_2$) results in photodissociation. In both cases molecular iodine can be excluded as a photofragment. However, I_2 was found to be a significant photoproduct and plays an important role in the chemical reactions of the photofragments. I_2 strongly enhances the re-formation of CH_2I_2 molecules. Addition of oxygen to CH_2I_2 decreases the percentage of re-formed parent molecules because of reactions of the fragments with O_2 . The primary step in the photolysis of CH_2I_2 and $1,1\text{-C}_2\text{H}_4\text{I}_2$ is the formation of iodine atoms which are partially in the excited state. For $1,1\text{-C}_2\text{H}_4\text{I}_2$ the formation of stable molecular photofragments (H_2 , HI) is also possible. In the photolysis of $1,1\text{-C}_2\text{H}_4\text{I}_2$ the formation of I_2 was found to be of minor importance, compared with that in the CH_2I_2 photolysis, and consequently the fraction of re-formed parent molecules is smaller.

1. Introduction

The maximum of the bell-shaped absorption continuum in the near UV for monoiodoalkanes occurs at about 260 nm [1, 2]. This energy exceeds the energy required to break a carbon-iodine bond. The dissociation into the corresponding alkyl radical and an iodine atom occurs readily [3]; the excess energy is distributed among the photofragments.

Porret and Goodeve [4] have proved in experiments with methyl iodide that excited iodine atoms are formed preferentially after absorption of UV photons. The branching ratio between the number of electronically excited iodine atoms and the number of ground state iodine atoms is very large in experiments with perfluorinated monoiodo compounds [5]. This inverted population has been used by Kasper *et al.* [6] to produce stimulated laser emission at $1.315 \mu\text{m}$. Reactive and non-reactive collisions between excited iodine atoms in the $^2\text{P}_{1/2}$ state and the parent molecules or added gases have been studied [7, 8]. Also reactions of both "hot" and non-excited alkyl radicals produced in the photolysis with many other compounds have been

observed [9 - 12]. One result is that the alkyl radicals can abstract hydrogen atoms in their collisions with the parent molecules. Photofragment studies [13] have shown that the rotational and vibrational excitation of these radicals increase with the complexity of the fragment. The fraction of available excess energy deposited in the alkyl radical is up to 50% in the photolysis of *n*-propyl iodide.

Diiodomethane (CH_2I_2) and 1,1-diiodoethane ($1,1\text{-C}_2\text{H}_4\text{I}_2$), investigated in this work, show strong absorption continua with intensities even higher than those of the monoiodides with two relative maxima between 200 and 400 nm. Here also a strong rovibrational excitation has been observed in the corresponding monoiodomethyl radical after photolysis of CH_2I_2 [14, 15]. Using the wavelength 266 nm of the fourth harmonic of a neodymium-yttrium aluminium garnet laser, Kroger *et al.* [15] have observed that 90% of the total excess energy appears as rovibrational excitation of the fragment CH_2I . Vibrational excitation has also been detected in a study of the IR emission of these radicals [16]. The other important fragments in the UV photolysis of CH_2I_2 are the iodine atoms which, similar to experiments with alkyl iodides, appear partly in the excited state. Although a quantum yield measurement has not been made, emission at $1.315 \mu\text{m}$ after the photolysis at 308 nm has been detected [16]. Chemical reactions of the photofragments after the dissociation of CH_2I_2 have only been observed in the presence of a large excess of oxygen [17].

In this work the primary steps and the subsequent chemical reactions of the fragments of CH_2I_2 and $1,1\text{-C}_2\text{H}_4\text{I}_2$ after absorption at 300 nm are discussed. Iodine and oxygen were added to CH_2I_2 in some experiments before irradiation to exclude chemical reactions of excited iodine atoms. The variations in the concentrations of the iodo compounds were observed by absorption measurements.

2. Experimental

CH_2I_2 was obtained commercially. After a fractional distillation at reduced pressure with a spinning band column of length 1.5 m, the purity of the CH_2I_2 was controlled by gas chromatography. The preparation of $1,1\text{-C}_2\text{H}_4\text{I}_2$ from the reaction of 1,1-dichloroethane with an excess of ethyl iodide catalysed by AlCl_3 was first described by Letsinger and Kammeyer [18]. After distillation, which was carried out in the same manner as that described for CH_2I_2 , a gas chromatographic analysis confirmed the purity of the $1,1\text{-C}_2\text{H}_4\text{I}_2$. Both diiodo compounds were stored over copper in a darkened glass bulb to prevent further decomposition. Iodine and oxygen, which were added in some experimental runs, were obtained commercially and were used without further purification. All the iodo compounds were outgassed at liquid nitrogen temperature before use.

The photolysis source was a commercial dye laser (Chromatix CMX 4). Using Rhodamin 6G the output was frequency doubled to yield the radiation

at 300 nm. The validity of the assumption of linear absorption was monitored by running the experiments at various laser energies (0.3 - 0.5 mJ pulse⁻¹). Using a beam diameter of 0.2 cm, saturation effects were found to be negligible.

The wavelength of 300 nm was chosen for two reasons: (1) the absorption coefficients of the diiodo compounds are close to their respective maxima in the UV (the maxima occur at about 290 nm); (2) the absorption coefficients of potential photoproducts such as monoiodo compounds or I₂ are very small. The repetition rate was always 5 pulses s⁻¹.

Because of the values of the diffusion coefficients of the various species in the photolysis cell, the mixing of the particles should be completed 200 ms after the photolysis flash. The reaction cell was a glass tube of length 10 cm with two suprasil windows.

The initial concentration of the diiodo compounds in the various experimental runs was varied between 0.1 and 1 Torr. Higher sample pressures are not obtainable at room temperature because the vapour pressures of CH₂I₂ and 1,1-C₂H₄I₂ are about 1 Torr at 25 °C.

To determine the variation in the concentrations of the iodo compounds in the photolysis, we studied the absorption at different wavelengths in the visible and near UV. To calculate the concentrations according to the Lambert-Beer law, it is necessary to know the absorption coefficients of the alkyl iodides as a function of wavelength. These gas phase absorption coefficients, reported in the literature, are only given with sufficient accuracy at a few wavelengths [12, 14, 19]. Therefore a redetermination was performed and the results for CH₂I₂ and 1,1-C₂H₄I₂ in the range from 200 to 400 nm are given in Table 1. The absorption coefficients of 1,1-C₂H₄I₂ are shown in Fig. 1 as a function of wavelength. The absorption coefficients for I₂ in the visible were taken from ref. 20. All absorption measurements were obtained using a double-beam spectrometer (Zeiss DMR 10). The absolute concentrations of the gas samples were determined with a U-shaped paraffin manometer and a capacity manometer.

3. Results

3.1. Concentrations of I₂ and CH₂I₂ or 1,1-C₂H₄I₂

In all the photolysis experiments carried out with CH₂I₂ a decrease in the parent molecule concentration with irradiation time and a simultaneous increase in the I₂ concentration were observed. One result is shown in Fig. 2. Experiments were carried out using various initial parent molecule concentrations and different irradiation times and power.

The concentration of parent molecules was always maintained so that there was no total absorption of the laser pulse. I₂ was always observed as a product of the photolysis, even when CH₂I₂ was mixed with different gases such as I₂ or O₂ before irradiation. However, when I₂ was used as an additive the variation in the concentrations of the two molecules considered was much

TABLE 1

Extinction coefficients of CH_2I_2 and $1,1\text{-C}_2\text{H}_4\text{I}_2$

λ (nm)	ϵ ($\text{l mol}^{-1} \text{ cm}^{-1}$)	
	CH_2I_2	$1,1\text{-C}_2\text{H}_4\text{I}_2$
220	764	795
225	518	629
230	347	473
235	286	377
240	333	361
245	406	396
250	422	410
255	366	375
260	315	347
265	343	380
270	488	479
275	701	636
280	915	795
285	1030	921
290	1063	979
295	1022	958
300	977	887
305	922	798
310	850	714
315	756	645
320	668	581
325	548	527
330	424	457
335	311	360
340	216	280
345	142	198
350	81	129
355	50	83
360	23	50

smaller for the same number of quanta absorbed. Whereas the effect of the addition of I_2 to the photolysis gas was to decrease the total CH_2I_2 decomposition, the addition of O_2 increased the total amount of parent molecule decomposition. In order to compare these results and to illustrate the origin of this differing behaviour in the photolysis of CH_2I_2 , the total decomposition of CH_2I_2 caused by the number of absorbed quanta was calculated. The following assumptions were made:

(1) the quantum yield for the photodissociation of CH_2I_2 at 300 nm is unity;

(2) none of the photofragments reacts with the parent molecule to decompose CH_2I_2 further.

From this calculation (see curve IV in Fig. 3) it follows that in every case the decrease in concentration of the parent molecules is much lower

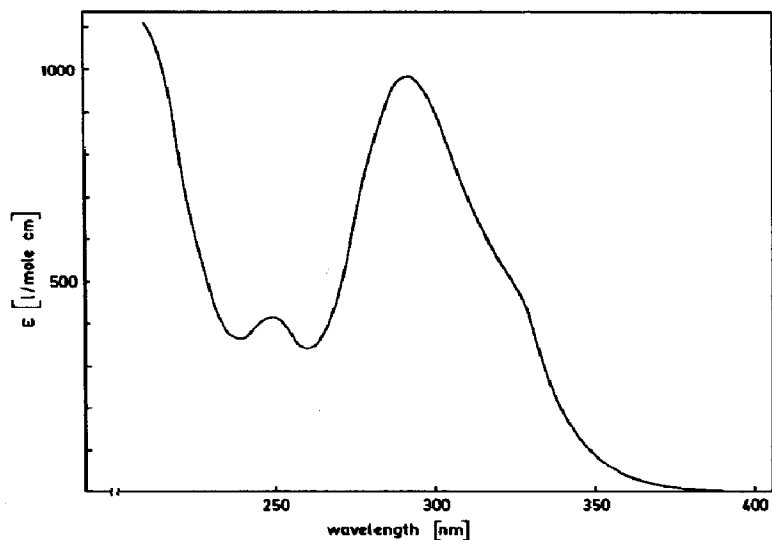


Fig. 1. Extinction coefficients of gaseous 1,1-C₂H₄I₂.

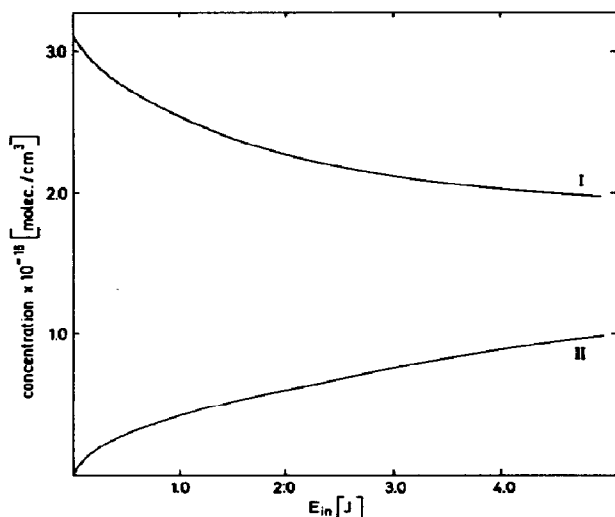


Fig. 2. The CH₂I₂ concentration (curve I) and the I₂ concentration (curve II) as functions of the laser energy E_{in} in the photolysis of pure CH₂I₂. (E_{in} = number of laser pulses \times energy per laser pulse at 300 nm; in the figures given in this work the energy per laser pulse is not always the same.)

than that calculated and thus the re-formation of CH₂I₂ must be an important step in the reaction mechanism. This effect is obviously enhanced by the presence of I₂ molecules, whereas O₂ molecules seem to suppress it.

The results of such photolysis experiments are shown in Fig. 3. Pure CH₂I₂ (curve II) at an initial concentration of 3.1×10^{16} molecules cm⁻³ was photolysed with a laser pulse power of 0.35 mJ. The actual concentration is shown as a function of the number of photons in the beam. When I₂ at a concentration of 4.0×10^{15} molecules cm⁻³ was added before irradiation

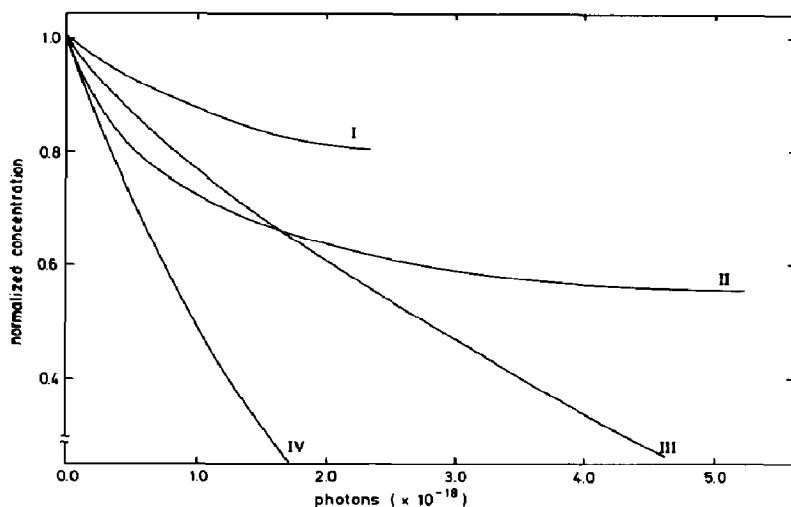


Fig. 3. The normalized CH_2I_2 concentration as a function of the laser energy: curve I, $\text{CH}_2\text{I}_2 + \text{I}_2$; curve II, pure CH_2I_2 ; curve III, $\text{CH}_2\text{I}_2 + \text{O}_2$; curve IV, CH_2I_2 concentration calculated assuming that no parent molecules are re-formed.

(curve I in Fig. 3), a remarkable decrease in the total decomposition of parent molecules was observed. This effect is dependent on the concentration of I_2 ; at higher I_2 concentrations the change in CH_2I_2 concentration per laser pulse is decreased. However, O_2 (curve III) gives rise to a different effect; the decomposition by irradiation of the probe is much more effective. Nevertheless, the decrease is still less than that calculated without considering recombination (curve IV).

It is interesting to compare curves II and III in more detail. At the beginning of the photolysis the decrease of CH_2I_2 per laser pulse is greater when pure CH_2I_2 is photolysed (curve II). This means that the extent of re-formation of the parent molecules is more important if oxygen is added. It must be mentioned that for added oxygen the total pressure in the reaction cell was higher by a factor of 40; therefore re-formation by three-body collisions is more probable. Also reaction of a CH_2I radical with a potential $(\text{O}_2-\text{I})^*$ intermediate complex, discussed previously for the photolysis of $\text{CF}_3\text{I}-\text{O}_2$ [21] and CHI_3-O_2 [22] mixtures, supports re-formation of the parent molecule in the photolytic experiments with $\text{CH}_2\text{I}_2-\text{O}_2$.

However, the total depletion of parent molecules is smaller if pure CH_2I_2 is photolysed. This means that re-formation becomes more important during the photolysis, which is certainly an effect of the photoproduct I_2 . The other possibility would be a recombination by a three-body collision. Such a possibility can be excluded since the total pressure changes only slightly during the experiment. Although the increase in I_2 concentration per laser pulse is greater for added O_2 , competitive reactions of the photofragments with oxygen lead to a nearly constant fraction of re-formed parent molecules. Therefore the effect of an increase in the I_2 concentration is greater if pure CH_2I_2 is photolysed.

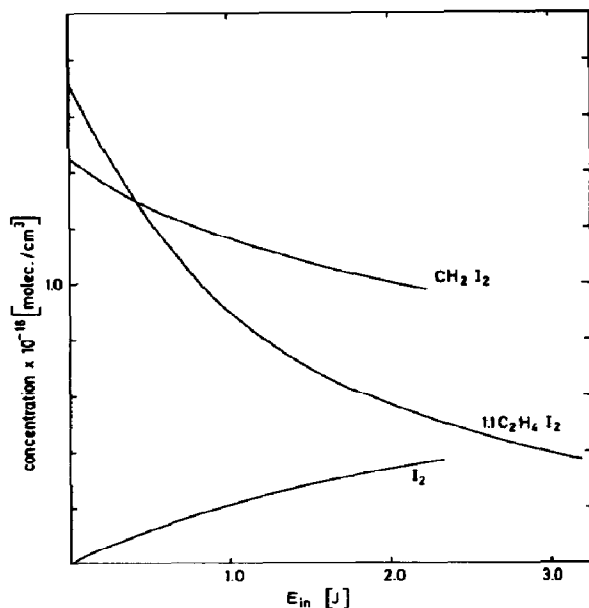


Fig. 4. Parent molecule concentrations as functions of the laser energy E_{in} . The I_2 concentration in both cases is nearly identical.

Similar experiments were performed with 1,1- $C_2H_4I_2$ and the results are compared with those obtained with CH_2I_2 (Fig. 4). It is interesting to note that the amount of I_2 production is very much alike for the two compounds while the parent molecule decomposition is very different. The influence of I_2 on the re-formation of the parent molecules, which was so clearly demonstrated for CH_2I_2 , is obviously less important for the higher alkane.

3.2. Re-formation of the parent molecules

As discussed in Section 3.1, re-formation of the parent molecules is an important step in the photochemistry of these diiodo compounds. This chemical reaction becomes more important with increasing irradiation time, as shown by the fact that the change in the concentration of CH_2I_2 per single laser pulse decreases with the irradiation time. A computer was used to calculate the extent of the re-formation of the parent molecule. This was necessary because the change in concentration per single laser pulse is very low and a particular value can only be obtained by interpolation. For this reason the following recursion formula was used:

$$[CH_2I_2]_{n+1} = [CH_2I_2]_n - (1 - R)N_0 \{1 - \exp(-\sigma [CH_2I_2]_n l)\} / V_0$$

where $[CH_2I_2]_{n+1}$ is the concentration after $n + 1$ laser pulses, $[CH_2I_2]_n$ is the concentration after n laser pulses, R is that fraction of dissociated parent molecules which are re-formed, σ is the absorption coefficient of CH_2I_2 at 300 nm, l is the length of the reaction cell and V_0 is the volume of the reaction cell.

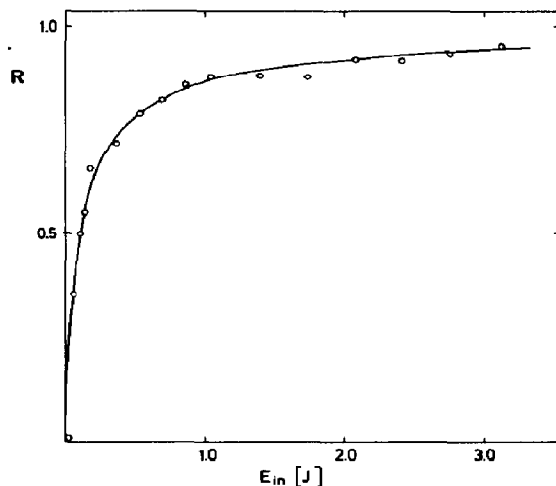


Fig. 5. The variation of R with the laser energy E_{in} . R represents the ratio of re-formed to photolysed CH_2I_2 molecules.

The calculated concentrations of CH_2I_2 (or $1,1\text{-C}_2\text{H}_4\text{I}_2$) for constant R are compared with measured values. From the coincidence of these values a resultant R is obtained. The R values are found to increase with the irradiation time (Fig. 5).

In particular, the re-formation is very weak at the beginning of the photolysis and increases rapidly. The example given in Fig. 5 corresponds to an experiment with pure CH_2I_2 . For added I_2 , R has high values initially, but the behaviour at longer irradiation times is similar to that shown in Fig. 5: R approaches a constant value close to unity. $R = 1$ would mean that every molecule photodissociated by the absorption of a UV quantum will be re-formed. (The factor $1 - R$ in the recursion formula is equal to zero.) This is the case when a sufficient amount of I_2 is present.

We can summarize the results for the various cases as follows.

(1) If pure CH_2I_2 or $\text{CH}_2\text{I}_2\text{-I}_2$ mixtures are photolysed, re-formation is the most important reaction and the re-formation factor R approaches unity for high I_2 concentrations.

(2) If $\text{CH}_2\text{I}_2\text{-O}_2$ mixtures are photolysed the maximum value of R is smaller and depends markedly on the O_2 mixing ratio; high O_2 concentrations lead to smaller values of R .

(3) If $1,1\text{-C}_2\text{H}_4\text{I}_2$ is photolysed the maximum value of R is close to 0.8.

3.3. Formation of I_2

We have shown that the decomposition of the parent molecule is accompanied by a simultaneous formation of I_2 . Denoting the respective diiodo compound by RI_2 the decrease in RI_2 concentration with irradiation time is given by $-\Delta[\text{RI}_2]$. The increase in I_2 concentration is then given by $\Delta[\text{I}_2]$. The quantity $K = -\Delta[\text{RI}_2]/\Delta[\text{I}_2]$ designates the number of decomposed

parent molecules divided by the number of generated I_2 molecules. K has characteristic values for different experimental conditions.

(1) If CH_2I_2 or $CH_2I_2-I_2$ mixtures are photolysed, the value of K observed shows no dependence on the laser energy: $K = 1.3$.

(2) If $CH_2I_2-O_2$ mixtures are photolysed, K is also found to be a constant: $K = 1.0$.

(3) If $1,1-C_2H_4I_2$ is photolysed, there is a dependence on the laser energy; this is shown in Fig. 6.

It can be seen from Fig. 6 that for $1,1-C_2H_4I_2$ K' decreases to $K' = 3$ during the photolysis. Such a behaviour indicates that other iodo compounds as well as I_2 are formed and that the formation of I_2 as a photoproduct becomes more and more important.

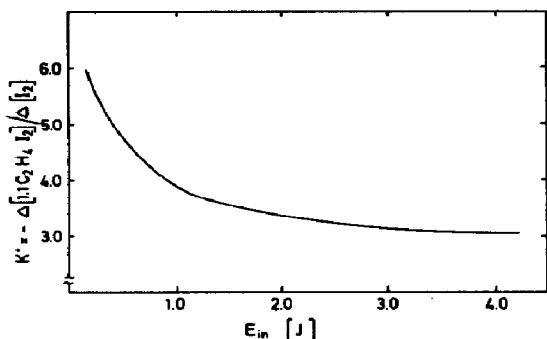


Fig. 6. The variation of K' with the laser energy E_{in} in the photolysis of $1,1-C_2H_4I_2$.

In addition to K a second quantity was determined which describes the I_2 formation in the photolysis of CH_2I_2 in more detail, *i.e.* the quantum yield $\phi(I_2)$ of I_2 formation. $\phi(I_2) = N(I_2)/N_{abs}$, where $N(I_2)$ is the number of I_2 molecules formed and N_{abs} is the number of absorbed quanta. Since the re-formation of the parent molecule becomes more and more important during the photolysis, as shown in Section 3.2, $\phi(I_2)$ will decrease with laser energy. Considering that part of the CH_2I_2 initially photolysed is re-formed, given by R , and therefore does not contribute to the products, we introduce a modified quantum yield in the following way:

$$(1 - R)\phi_{mod}(I_2) = \phi(I_2)$$

$$\phi_{mod}(I_2) = \frac{N(I_2)/(1 - R)}{N_{abs}}$$

Calculated values of $\phi_{mod}(I_2)$ show the following behaviour.

(1) $\phi_{mod}(I_2)$ decreases in the presence of O_2 from 1.3 to 1.0 during the photolysis.

(2) For pure CH_2I_2 , $\phi_{mod}(I_2)$ starts with a value greater than 1.0 and decreases to a value of 0.76. The latter value is the constant quantum yield $\phi_{mod}(I_2)$ found for $CH_2I_2-I_2$ mixtures.

From these observations it follows that I_2 counteracts the formation of I_2 .

3.4. Formation of monoiodo compounds

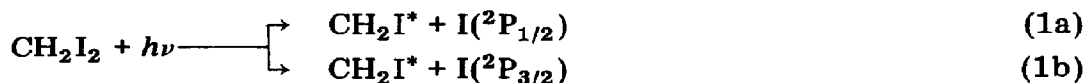
As mentioned in the experimental section, concentrations were determined by measuring the absorption in the visible and near UV. The absorption spectra of the monoiodo and the diiodo compounds in the near UV are quite different. The position of the absorption coefficient maximum for the monoiodoalkanes is near the position of the absorption coefficient minimum of the two diiodo compounds used in the experiments. From the known absorption coefficients we determine the sensitivity of the method for CH_3I detection to be 5%. For this reason the absorption is determined at three positions in the absorption continua of both CH_2I_2 and $1,1\text{-C}_2\text{H}_4\text{I}_2$, e.g. at 320, 290 and 250 nm. Whereas the first two positions are located in the region of strong absorption of the diiodo compounds the last is near the absorption coefficient maximum of the monoiodoalkanes. The results of the measurements for CH_2I_2 and $1,1\text{-C}_2\text{H}_4\text{I}_2$ are shown in Fig. 7. The ratio E_{290}/E_{320} , where E_{290} is the extinction measured at 290 nm, does not change during the photolyses of CH_2I_2 and $1,1\text{-C}_2\text{H}_4\text{I}_2$. For the ratio E_{290}/E_{250} , this is also true for CH_2I_2 but not for $1,1\text{-C}_2\text{H}_4\text{I}_2$.

From the behaviour of these ratios for CH_2I_2 , we conclude that monoiodo compounds are not important products of the photolysis. This is not true for $1,1\text{-C}_2\text{H}_4\text{I}_2$. If we subtract the specific absorption of the $1,1\text{-C}_2\text{H}_4\text{I}_2$ molecules from the total absorption, we obtain a residual absorption which is due to the newly formed products; this residual absorption has a peak at about 255 nm, indicating an absorption typical for monoiodo compounds. The variation of this residual absorption as a function of wavelength and irradiation energy is shown in Fig. 8.

4. Discussion

4.1. Photolysis of CH_2I_2

The photodissociation of CH_2I_2 has been observed recently by photofragment spectroscopy [14, 15] as well as by time-resolved emission spectroscopy [16]. A result which is common to these observations is that diiodomethane dissociates after absorption in the UV into a monoiodomethyl radical and an iodine atom according to the following scheme:



where the asterisk indicates rovibrational excitation of the radical.

From thermodynamic considerations [14] it follows that direct production of methylene and I_2 according to reaction (2) is also possible:



Gregory and Style [17] favour reaction (2) from their results of the photochemistry of CH_2I_2 in the presence of O_2 .

From our calculations of K values it is easy to exclude the dissociative process reaction (2) as a possible primary reaction. Another reason for the

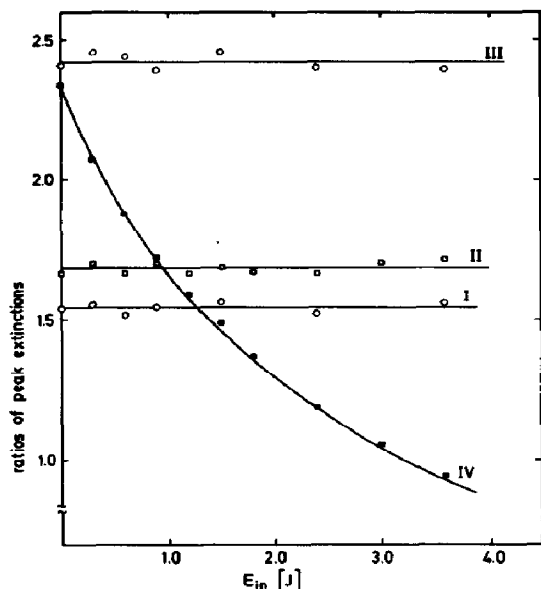


Fig. 7. Ratios of the peak extinctions as a function of the laser energy E_{in} taken at wavelengths of 250, 290 and 320 nm: curve I, $E_{290}(\text{CH}_2\text{I}_2)/E_{320}(\text{CH}_2\text{I}_2)$; curve II, $E_{290}(1,1\text{-C}_2\text{H}_4\text{I}_2)/E_{320}(1,1\text{-C}_2\text{H}_4\text{I}_2)$; curve III, $E_{290}(\text{CH}_2\text{I}_2)/E_{250}(\text{CH}_2\text{I}_2)$; curve IV, $E_{290}(1,1\text{-C}_2\text{H}_4\text{I}_2)/E_{250}(1,1\text{-C}_2\text{H}_4\text{I}_2)$.

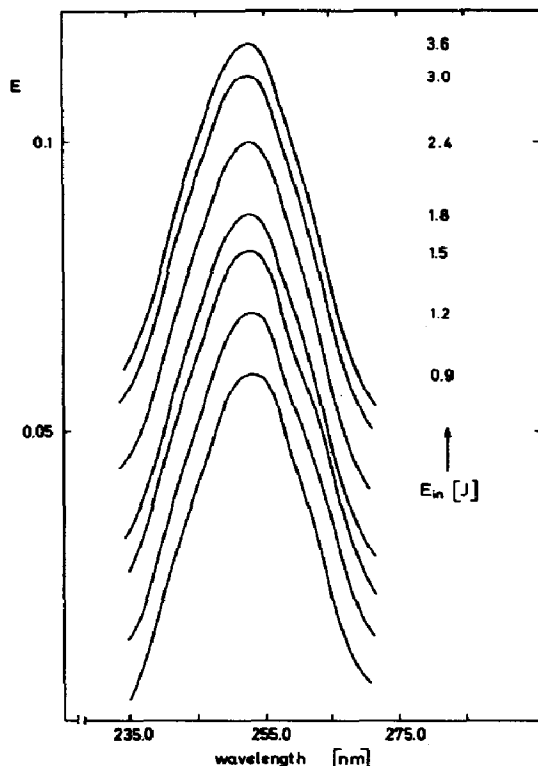


Fig. 8. The extinction as a function of the laser exposure (right-hand column) showing increasing formation of photoproducts in the photolysis of $1,1\text{-C}_2\text{H}_4\text{I}_2$.

unimportance of the dissociative process reaction (2) is the fact that the quantum yield $\phi_{\text{mod}}(\text{I}_2)$, which is found to be 0.76, should be larger because the most probable reaction of CH_2 in the system, *i.e.*



is a source of additional I_2 . Reactions (2) and (3) together lead to a quantum yield $\phi_{\text{mod}}(\text{I}_2) = 2$, in contrast with the measured value $\phi_{\text{mod}}(\text{I}_2) = 0.76$. A further important argument against the dissociative process reaction (2) is that recombination of the two fragments of reaction (2) in a three-body collision is highly improbable, which is in contrast with the observed large extent of re-formation of parent molecules. These arguments are in excellent agreement with the observations of Kawasaki *et al.* [14] who did not find molecular iodine in their photofragment spectra of CH_2I_2 .

Thermodynamic calculations show that the photofragments formed in reactions (1a) and (1b) must have external and/or internal energy. The formation of rovibrationally excited CH_2I^* [14 - 16] as well as the formation of excited iodine atoms $\text{I}(^2\text{P}_{1/2})$ [16] is well established. To what extent

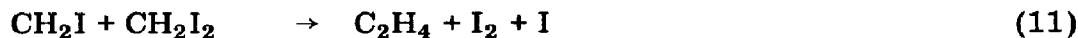
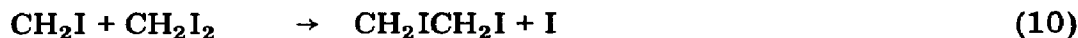
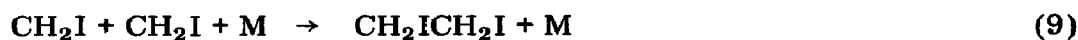
$I(^2P_{1/2})$ atoms are formed in the UV photolysis of CH_2I_2 is still an unanswered question.

Both species, the excited radicals CH_2I^* and the excited atoms $I(^2P_{1/2})$, are effectively deactivated in collisions:



The measured rate constants for these reactions are $k_4 = 6.6 \times 10^{-13}$ and $k_5 = 3.2 \times 10^{-11}$ molecules $cm^{-3} s^{-1}$ with $M \equiv CH_2I_2$ [16].

To discuss the results given in Section 3 we propose the following reaction mechanism:



It should be noted that internal energy of CH_2I is not indicated in this scheme but may be present in all the reactions (7) - (12). Because of the high efficiency of the relaxation process reaction (5), hot CH_2I radicals will only contribute for a short time immediately after the laser flash.

The formation of iodo compounds such as 1,1- $C_2H_4I_2$ or monoiodoalkanes is excluded. 1,1- $C_2H_4I_2$, if formed in the photolysis, is easily dissociated in UV light so that its contribution should appear in the typical absorption region of the monoiodo compounds. However, such an absorption was not observed in the photolysis experiments with CH_2I_2 , but it appeared readily when pure 1,1- $C_2H_4I_2$ was photolysed.

Similar to the photolysis of pure CH_3I , in which methane was found as a photoproduct [9, 11], we expect the formation of monoiodoalkanes from the reaction of CH_2I radicals with the parent molecules. But our results favour an iodine exchange reaction in the collision of the two molecules, as no CH_3I was detected.

The reaction scheme starts with the iodine atom reactions (reactions (6) and (7)). Then reactions of the CH_2I radicals are considered (reactions (7) - (12)). The last of these reactions, reaction (12), describes the very efficient re-formation of the parent molecules.

The most important reaction of ground state iodine atoms is the three-body recombination reaction (6) forming I_2 . Iodine atoms in the excited state $^2P_{1/2}$ are effectively deactivated according to reaction (4) both with $M \equiv CH_2I_2$ [16] and with $M \equiv I_2$ [8]. Another reaction of ground state iodine atoms is reaction (7) which leads to the re-formation of CH_2I_2 in a three-body collision. This reaction is always possible in the system but it is

certainly of minor importance, because its contribution to the re-formation of CH_2I_2 is very small in the early stages of the photolysis (Fig. 5). Other reactions of the iodine atoms $\text{I}(^2\text{P}_{3/2})$ are not possible from energy considerations.

Since most of the reactions in the scheme reactions (6) - (12) are molecular-iodine-forming processes, consideration of the quantum yield, or better the modified quantum yield $\phi_{\text{mod}}(\text{I}_2)$, is important for a discussion of the scheme. This yield starts with a value of approximately unity at the beginning of the photolysis. As $\phi_{\text{mod}}(\text{I}_2)$ approaches a constant value of 0.76 we have to look for reactions with $\phi_{\text{mod}}(\text{I}_2) > 1$ and which contribute to I_2 formation in the early stages of the photolysis.

One candidate is reaction (11). A further possibility is a reaction between the two primary photoproducts CH_2I and I , both of which have to be in an excited state from energy considerations:



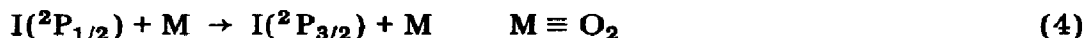
Methylene can react further according to reaction (3), thus forming an additional I_2 molecule. Such a reaction is possible because immediately after the photolysis flash the concentration of radicals is comparatively high (one part in seven). It is expected that the main contribution to the higher I_2 formation in the early stages is from reaction (13), because the observed decrease in $\phi_{\text{mod}}(\text{I}_2)$ with irradiation time cannot be explained by a competition between reactions (11) and (12) as an influence of reaction (12) on $\phi_{\text{mod}}(\text{I}_2)$ does not exist.

As the number of laser pulses increases the contribution from reactions (13) and (3) to I_2 formation decreases because of competition from reaction (4) ($\text{M} \equiv \text{I}_2$), the deactivation of $\text{I}(^2\text{P}_{1/2})$ by molecular iodine. A clear evidence for this mechanism is the observation that photolyses of $\text{CH}_2\text{I}_2\text{-I}_2$ mixtures do not show this effect. They start with $\phi_{\text{mod}}(\text{I}_2) = 0.76$ immediately at the beginning of the photolysis with no obvious change during the photolysis.

From the decrease $-\Delta[\text{CH}_2\text{I}_2]$ in the concentration of the parent molecules and the simultaneous increase $\Delta[\text{I}_2]$ in molecular iodine concentration K is computed. This K value was found to be constant with respect to laser energy when pure CH_2I_2 and $\text{CH}_2\text{I}_2\text{-I}_2$ mixtures were photolysed. Whereas a value $K = 2$ would indicate that in total only one carbon-iodine bond is broken, the measured value of $K = 1.3$ shows that to some extent the second carbon-iodine bond of CH_2I_2 is also broken. Reactions (8) and (11) give rise to such an effect. Since $\text{CH}_2\text{I}\text{CH}_2\text{I}$, formed in reactions (9) and (10), has a very low vapour pressure, its absorption spectrum, which is known to occur in the absorption region of the monoiodo compounds [23], cannot be observed. $K = 1.3$ means that about 30% of the parent molecules consumed react according to reactions (9) and (10).

The addition of oxygen strongly suppresses reactions of excited iodine atoms because O_2 deactivates I^* effectively in collisions with a rate constant $k = 8.6 \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ [24]. For the photolysis of $\text{CF}_3\text{I-O}_2$

mixtures Strong *et al.* [21] have observed a fast rise in I_2 production which they discuss as being caused by the formation of the $(O_2I)^*$ intermediate.



The formation of this complex could effectively enhance the formation of I_2 and the subsequent re-formation of CH_2I_2 by reactions (6a) and (6b) and (11a) respectively.

The results of the photolysis of CH_2I_2 in the presence of excess O_2 are explained by the following reaction scheme, which is also partially supported by results of Gregory and Style [17] who identified I_2 , $(CH_2O)_2$, HCHO and CHOOH as photoproducts in the photolysis of $CH_2I_2-O_2$.



The experiments show that in the presence of O_2 the value for K is constant, e.g. $K = 1$, which means that in total two carbon-iodine bonds are broken. Although a contribution to this effect can be expected from one of the reactions of the scheme reactions (6) - (12) a more probable contribution is from reaction (14). The formation of I_2 in this case will readily occur by reactions (6), (6a) and (6b). Methylene peroxide can either rearrange, forming formic acid (reaction (15)), or react with the parent molecule (reaction (16)). This latter reaction is a source of a second I_2 molecule and explains why $\phi_{mod}(I_2)$ is 1.3 at the beginning of the photolysis. This value for $\phi_{mod}(I_2)$ of 1.3 is in good agreement with the results of Gregory and Style [17]. The decrease of $\phi_{mod}(I_2)$ from about 1.3 to 1.0 is the result of different competing processes in the system: increasing I_2 concentration favours reaction (12) and the consumption of CH_2I_2 favours reaction (15).

The contribution of I_2 to the re-formation of parent molecules in the photolysis of $CH_2I_2-O_2$ mixtures is less effective than in the photolysis of pure CH_2I_2 and $CH_2I_2-I_2$ mixtures (Fig. 3), although the total amount of I_2 formed is larger. This effect is certainly a consequence of reaction (14) which competes strongly with the re-formation processes (11), (11a) and (12).

4.2. Photolysis of 1,1-C₂H₄I₂

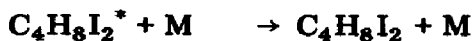
Similar to the discussion for CH₂I₂ we will consider four different pathways which are possible from thermodynamic calculations for the photodissociation of 1,1-C₂H₄I₂ at 300 nm.



This proposed scheme parallels results from the photolyses of 1,1-C₂H₄Cl₂ [25] and 1,1-C₂H₄F₂ [26]. Hitherto no formation of excited iodine atoms I(²P_{1/2}) has been detected. As the observation of I(²P_{1/2}) is a result which is common to the photolysis of iodoalkanes we have to take this possibility into consideration. According to the discussion in Section 4.1 excited iodine atoms I(²P_{1/2}) are quickly deactivated with increasing I₂ concentration.

From the results we calculate a *K'* value (*K'* = -Δ[C₂H₄I₂]/Δ[I₂]) which is always greater than 3. This implies that the formation of I₂ is rather improbable. Ground state iodine atoms, formed either by photolysis (reaction (18)) or by deactivation of excited atoms (reaction (4)), will only react by recombination. The main formation mechanism of I₂ molecules will be the three-body recombination reaction (6). This leads us to the conclusions (1) that the dissociation of 1,1-C₂H₄I₂ into an iodine molecule and a CH₃CH radical (reaction (20)), with the subsequent rearrangement reaction forming an ethylene molecule, is of minor importance and (2) that the reaction of two photofragments (reaction (22)), forming C₂H₄ and I₂, is also of no importance.

Possible reactions of the alkyl fragments are summarized in the following scheme:



All the compounds formed in reactions (23) - (25) will have absorption maxima in the near UV at about 255 nm. At this position an increase in absorption was detected during the photolysis of 1,1-C₂H₄I₂. Furthermore the formation of these compounds will result in large *K'* values, which is observed. The re-formation reactions (26) and (27) are similar to those discussed in considering the re-formation of CH₂I₂. The increasing importance of re-formation during the photolysis of 1,1-C₂H₄I₂ is expected from the increase

in I_2 concentration which favours reaction (27). But the fraction of re-formed parent molecules never exceeds 80% of the molecules photolysed, which is contrary to the results from the photolysis of CH_2I_2 . We therefore come to the conclusion that about 20% of the molecules dissociate into iodoethene and hydriodic acid according to reaction (21). Support for this comes from the photolysis of 1,1- $C_2H_4Cl_2$ [25] and 1,1- $C_2H_4F_2$ [26] which show the analogous products C_2H_3Cl , C_2H_3F , HCl and HF^* .

A direct recombination of these fragments leading to re-formation of the parent molecule in a three-body collision (reaction (28)) is rather improbable:



A further result of the measurements is the temporal increase in the importance of I_2 formation as shown from the K' values in Fig. 6. One possibility for this is the reaction of excited iodine atoms at the beginning of the photolysis, when the concentration of I_2 is very low. If $I(^2P_{1/2})$ reacts with a CH_3CHI radical, iodoethene and hydriodic acid can be formed. With increasing I_2 concentration such reactions will become very improbable because of the fast deactivation of $I(^2P_{1/2})$ by I_2 (reaction (4)). The ground state iodine atoms formed further increase I_2 formation by reaction (6).

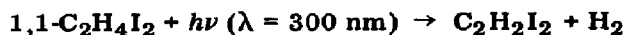
5. Summarizing remarks

For the photochemical systems studied molecular iodine plays the most important role. It is not formed in the primary photolysis step. Therefore I_2 must be formed in chemical reactions of the photofragments, the most probable reaction being the three-body recombination of ground state iodine atoms. Molecular iodine influences more and more the chemical reactions of the photofragments for two reasons: (1) I_2 is an excellent quencher of excited iodine atoms in the $I(^2P_{1/2})$ state, therefore making reactions of these species improbable; (2) I_2 supports the recombination of the parent molecules in a collision with the monoiodoalkyl fragment.

Comparing CH_2I_2 and 1,1- $C_2H_4I_2$, the fraction of re-formed parent molecules is smaller for the latter compound. This is certainly the consequence of two properties of the photolysis: the smaller amount of I_2 formation and the primary dissociation into C_2H_3I and HI .

The analytical procedure is, as far as the hydrocarbons are concerned, concentrated only on the parent molecules. However, for 1,1- $C_2H_4I_2$ an increasing effect from those species absorbing in the typical absorption region of the monoiodoalkanes could be observed. Experiments are in progress to

*1,2-Elimination of molecular hydrogen was observed in these experiments so that in addition to reactions (18) - (21) the following primary dissociation process has to be considered:



identify these compounds and to determine their contribution to the overall photolysis.

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