COMPARATIVE STUDY OF cw CO₂ LASER INDUCED AND SF₆ SENSITIZED DECOMPOSITION OF METHYL IODIDES CH₃I AND CD₃I

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Received December 22nd, 1983

The decomposition of methyl iodide- d_3 initiated by the irradiation of a $cw CO_2$ laser in the presence of SF₆ proceeds under comparable conditions faster, particularly in the shorter wavelength region of the CO₂ laser spectrum, than the decomposition of methyl iodide. The differences can be explained by the different distribution of energy levels of both reactants. Observable differences are also in the composition of the reaction products. All these facts indicate the participation of at least two reaction mechanisms, a radical one and a molecular one, which can probably proceed via the collision of two vibrationally excited molecules of CX₃I.

Chemical reactions induced by the $cw \operatorname{CO}_2$ laser radiation in the presence of SF₆ as a sensitizer are usually supposed to be thermal. The SF₆ molecules, absorbing extraordinarily strongly the radiation, can transform the obtained vibrational energy into the thermal energy by a very fast relaxation process so that certain authors denote these reactions as a "homogeneous pyrolysis" (LIHP method – Laser Induced Homogeneous Pyrolysis). It was therefore surprising that the decomposition of CH₃I molecule sensitized by SF₆ depends in a certain degree on the excitation level^{1,2}, chosen from the set of emission lines of the CO₂ laser. In order to explain this fact the decomposition of CD₃I was also studied. To be able to compare the decompositions of both isotopomers of methyl iodide the decomposition of CH₃I was studied again under the same conditions as those used³ for the decomposition of CD₃I.

The analysis of the experimental results indicates that the explanation of the decomposition of CH_3I and CD_3I molecules initiated by the irradiation with the $cw CO_2$ laser requires to take into consideration not only the kinetic energy of translation but also their vibrational temperature. If the vibrational temperature of the irradiated mixture is successfully maintained at a level higher than the equilibrium one or if it increases by suitable relaxation mechanisms, the reaction proceeds faster as is the case of the induced decomposition of CD_3I .

EXPERIMENTAL

The reagents used, the experimental arrangement, and the analytical procedures are described in our previous $papers^{2,3}$.

RESULTS

The decomposition of CH_3I yields² methane, ethane, ethene, and ethyne, in the decomposition of CD_3I methane- d_4 , ethane- d_6 , ethene- d_4 , and ethyne- d_2 are formed³. The formation of molecular iodine is typical for both cases. Table I summarizes the results obtained in the studies of CH_3I decomposition under the same conditions under which the decomposition of CD_3I was studied³. It also illustrates the effect of the reaction mixture composition and of the irradiation time on the course of CH_3I decomposition and on the reaction product distribution. The decomposi-

TABLE I

The effect of the reaction mixture composition and of the irradiation time on the reaction course and on the product distribution^{*a*} for the decomposition of CH_3I

Total pressure in reactor kPa	Volume %	Irradiation	CH ₃ I	Products distribution ^d , %			
	mixture	s	conversion ^{b,c}	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₂ H ₂
9.3	0.3	30	44.5 (4)	73	5	20	2
	0.3	300	77 (3)	82	1	15	2
	0.01	30	36 (2)	68	11.5	19.5	1
	0.02	300	57 (3)	70	10	18	2
	0.03	30	17 (2)	72	16	11	1
	0.03	300	60 (2)	72	3.5	22	2.5
2.6	0.3	30	13 (2)	64.5	23.5	11	1
	0.3	300	47.5 (2)	72	5	22	1
	0.1	30	18 (2)	67	15	17	1
	0.1	300	53 (2)	68	3	28	1
1.3	0.2	30	8 (3)	50.5	33.5	15	1
	0.5	300	21 (3)	79	2	18	1
	0.1	30	9 (2)	60	26	14	e
	0.1	300	16 (3)	75.5	13.5	11	e

^{*a*} CH₃I decomposed by the excitation line P(32) (transition $00^{\circ}1-10^{\circ}0$) from the *cw* CO₂ laser (output 8 W) in the presence of SF₆; ^{*b*} the amount of decomposed CH₃I in %; ^{*c*} average from experiments, the number of which is given in the parentheses; ^{*d*} average from the experiments, the number of which is given in parentheses in the previous column; ^{*e*} the amount of C₂H₂ formed is at the detection limit.

tion was initiated by the irradiation of the gaseous mixtures of CH_3I/SF_6 by the P(32) line using the laser output of 8 W. The beam was focused to the cell center using a lens with the focal length of 0.25 m. The conversion of methyl iodide (the amount of methyl iodide that entered into the reaction as given by the decrease of the v_2 -band intensity of CH₂I observed at 1 251 cm⁻¹ in the IR spectrum) increases with the increasing total pressure of the gases in the reactor and is only slightly dependent on the participation of gases in the reaction mixture (at the same total pressure). As expected, the amount of decomposed methyl iodide increases with the increasing time of irradiation. The amount of methane in the product mixture depends very little on the reaction mixture composition before irradiation and also on the time of irradiation. This is true for experiments carried out at the total pressure of 9.3 kPa. At lower pressures larger changes were observed, particularly at prolonged irradiation. The content of ethane in the product mixture at 9.3 kPa increases with the decreasing amount of SF_6 . At low total pressures and at the same irradiation time its amount remains nearly constant (unchanged), prolonged irradiation decreases the amount of ethane. The content of ethene in the reaction mixture is nearly

TABLE II

Dependence of the conversion degree and of the products distribution for the decomposition products of CH_3I in the presence of SF_6^a on the excitation line P^b

Excitation line P	CH ₃ I conversion	Produc	ucts distribution ^c , %		
 $00^{\circ}1 - 10^{\circ}0$	°⁄0	CH ₄	C ₂ H ₆	C ₂ H ₄	
P (16)	1.5	38	50	12	
P(18)	2	47	41	12	
P(20)	3	47	38	15	
P(22)	4	51.5	32	16.5	
P(24)	9	56	22	22	
P(26)	10	59	19	22	
P(28)	10	58	18	24	
P(30)	13	57	20	23	
P(32)	12.5	65.5	10	24.5	
P(34)	10	63.5	13	23.5	
P(36)	11.5	60	14.5	25.5	
P(38)	11.5	69	9	22	
P(40)	11.5	68	8	24	
P(42)	11	70	10	20	
P(44)	4	60	15	25	

^a The ratio of the CH_3I/SF_6 pressures was 6.64/2.66 kPa; ^b the output at each line was 5 W, irradiation time 5 s; ^c the amount of ethyne formed is at the detection limit.

constant, moderately decreases with the decrease of the total pressure, increases for longer irradiations. The yield of ethyne is negligible for the CH_3I decomposition induced by the laser irradiation with the output of 8 W.

Table II gives the results of experiments in which various excited lines were used for the initiation of CH_3I decomposition in the presence of SF_6 . The results obtained with the addition of buffer gases are given in Table III. In the irradiation with the P(32) line and with the output of 8 W helium and xenon were used as inert gases. Table IV presents the results of the measurements of the dependence of the amount of decomposed CH_3I and of the reaction product composition on the laser output (3-13 W).

To determine the effect of the CO_2 laser radiation on the reactivity of hydrocarbons formed in the decomposition of CH_3I a series of control experiments was carried out under the standard conditions, when the reactor was filled either with a model mixture of hydrocarbons or with its individual components and SF_6 . It has been found that ethane undergoes most easily the consecutive secondary reaction which gives very little of methane and ethyne, the amounts of which are measurable only at irradiation times substantially exceeding those used in the methyl iodide decomposition. In the last series of experiments a rotating chopper (with a variable frequency) was placed between the lens and the reactor. The conversion of CH_3I is little dependent on the chopper frequency, the maximum value is achieved at 100 Hz. With the increasing frequency it moderately decreases.

DISCUSSION

The aim of this study is to compare the experimental results for the decomposition of CH_3I and CD_3I induced by the cw CO_2 laser radiation in the presence of SF_6 . $CH_{3}I$ and $CD_{3}I$ interact with the infrared radiation by means of different vibrational modes. CH_3I interacts with the v_6 mode of the E symmetry (CH_3 rocking) while CD_3I interacts with the v_2 mode of the A_1 symmetry (CD_3 deformation vibration). While CH₃I has in the region 950-900 cm⁻¹ only bunches of the Q branches with distances of about 8 cm⁻¹, CD₃I possesses a higher density of rotational-vibrational lines⁴. The pattern of the spectrum is also evident from the measurement of the radiation absorption using discrete lines of the CO_2 laser. Fig. 1 gives the absorption of IR radiation in CH_3I , CD_3I , and SF_6 measured⁵ at a higher laser radiation density (8 W focused by a lens with the focal length of 0.25 m). While the absorption of CD₃I in the region of measurement does not reveal any large changes of the intensity, in the case of CH_3I a strong absorption is observed on the R_0 (6,0) line, which is in good coincidence with the laser line P(32) of the $00^{\circ}1 - 10^{\circ}0$ transition. In the case of SF_6 the absorption is substantially shifted towards longer wavelengths due to the absorption in hot bands. Because the spectra of SF_6 were measured at a pressure lower than 1/30 of the pressure of CH₃I and CD₃I it can be stated that under the

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TABLE III

The effects of buffer gases on the reaction course and on the product distribution for CH_3I decomposition^{*a*}

Gas	Total pressure	Volume % of the inert gas	CH ₃ I	Products distribution, %			
	kPa		%	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₂ H ₂
Helium	9.3	0	44·5	73	5	20	2
	13.3	0.3	43	68	7	24	1
	18.5	0.2	9	54	26	18	2
	27.9	0.66	10	42	40	16	2
Xenon	9.3	0	44.5	73	5	20	2
	13.3	0.3	77	74	2	18	6
	18.5	0.66	50	71	2	22	5
	27.9	0.86	25	72	3	21	4

^a CH₃I decomposed by the P(32) excitation line (transition $00^{\circ}1-10^{\circ}0$) from the $cw CO_2$ laser (output 8 W) in the presence of SF₆ and inert gas, irradiation time 30 s; ^b the amount of the decomposed CH₃I in %.

TABLE IV

The dependence of the amount of decomposed CH_3I and of the products distribution^{*a*} on the laser output

	Laser output W	Decomposed CH ₃ I Pa	Conversion	Products distribution ^b , %			
			%	CH ₄	C ₂ H ₆	C ₂ H ₄	
	3	110	1.6	42.4	49.2	8∙4	
	4	170	2.5	50.4	33.1	16.5	
	5	180	2.7	54.9	28.4	16.7	
	6	367	5.5	57.4	22.4	20.2	
	7	380	5.7	60.5	14.4	25.1	
	8	520	7.8	82.5	17.3	20.2	
	9	600	9	65.6	12.2	22.2	
	10	787	11.8	75-4	6.4	18.2	
	12	947	14.2	80.1	4.8	15.1	
	13	1 566	23.5	84.8	2.4	12.8	

^a The mixture of 6.64 kPa of CH_3I and 2.66 kPa of SF_6 excited by the excitation line P(32) for one second; ^b the ethyne amounts are in all cases beyond the limit of reliable determination.

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conditions of the experiment the radiation is preferentially absorbed by SF_6 and the other gases participate only negligibly on the total absorption of the mixture. From this it follows that in the case of a pure thermal process the dependence of the CX_3I conversion on the radiation wavelength will follow the absorption curve for SF_6 . These dependences are given in Fig. 2. The comparison with Fig. 1 reveals substantial differences between the dependences of the decomposition rate on the wavelength. First of all, the decomposition rate of CD_3I is slightly higher than that of CH_3I , particularly in the shorter wavelength region, and it follows more closely the absorption of SF_6 (it differs less from the absorption curve of SF_6). The differences between the two dependences can be explained by the different distribution of the energy levels of both reactants. While CD_3I has in the region of the laser tuning a high density of the CD_3 symmetric deformation vibration levels with the center at 950.7 cm⁻¹, the center of CH_3 rocking vibration lies at 882 cm⁻¹, *i.e.*, the center is shifted in agreement with the experiment towards longer wavelengths, where the decomposition rate of CH_3I is higher than that of CD_3I .

We can discuss now the dependence of CH_3I and CD_3I decomposition on the laser output. Mixtures containing in all cases 2.66 kPa of SF_6 and 6.64 kPa of CX_3I (where X = H or D) were irradiated by the P(32) line for one second. As it is evident from the dependence of Fig. 3 the decomposition rate is nearly comparable in both





IR radiation absorption in CH₃I, CD₃I, and SF₆ in dependence on the excitation line *P* of the $00^{\circ}1-10^{\circ}0$ transition of the CO₂ laser. Output 8 W, focused by a lens 0.25 m; 6.64 kPa of CX₃I and 0.2 kPa of SF₆. 1 CH₃I; 2 CD₃I; 3 SF₆





Dependence of the CX_3I conversion K (%) on the wavelength of the CO_2 laser. Experiment conditions *cf.* Fig. 1, irradiation time 15 s. 1 X = H, 2 X = D

cases. In spite of that, observable differences in the product distribution were found (Fig. 4). At low radiation outputs the mechanism of methane formation is preferred in the CH₃I decomposition while in the decomposition of CD₃I only minor amounts of CD₄ are formed and the yield of CD₄ increases substantially only at higher outputs of the laser. Still more pronounced difference between the two reactions can be observed in the formation of ethene. In the case of CH₃I decomposition the yield of ethene at first increases, reaches a maximum at 7 W, and then decreases with the increasing output. In the case of $CD_{3}I$ decomposition the yield of $C_{2}D_{4}$ monotonously decreases. It is evident that two mechanisms should be considered for the formation of C_2X_4 (X = H, D). One of them is the radical mechanism described already in the paper³ which takes place at higher outputs. The second mechanism could probably proceed via the collision of two vibrationally excited molecules of CX₃I, the excitation energy of which is insufficient for the radical dissociation. The final products of this reaction are ethene and hydrogen iodide, which forms – under the conditions of the experiment – molecular iodine and hydrogen. The realization of this mechanism in CD_3I is probably due to the more effective



FIG. 3

Conversion K (%) of CH₃I and CD₃I in dependence on the laser output N. The values for CD₃I were taken from ref.³; the reaction mixture composition: 6.64 kPa of CX₃I: 2.66 kPa of SF₆; irradiation time 1 s; decomposition by the infrared P(32)line of the CO₂ laser (transition $00^{\circ}1-10^{\circ}0$); a CH₃I: b CD₃I

FIG. 4

Distribution of the CX_3I (X = H, D) decomposition products in dependence on the laser output. Experiment conditions *cf.* Fig. 3. *a* CH₃I; *b* CD₃I; 1 CX₄; 2 C₂X₆; 3 C₂X₄

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$$\begin{bmatrix} \mathbf{C} \mathbf{X}_{2} \\ \mathbf{X} \\ \mathbf{C} \mathbf{X}_{2} \end{bmatrix}^{+} \rightarrow \mathbf{C} \mathbf{X}_{2} = \mathbf{C} \mathbf{X}_{2} + 2 \mathbf{X} \mathbf{I}$$

vibrational energy transfer from SF₆ to CD_3I . The energy of CD_3I molecules is distributed over a higher number of molecules so that it contains a lower portion of molecules with energy higher than the dissociation energy. On the other hand CH_3I , which receives the energy from SF₆ with a lower probability, is excited only by highly excited SF₆ molecules and the energy transfer is immediately followed by the dissociation giving the methyl radical and iodine atom. In the case of CD_3I the dependence of the relative amount of ethene- d_4 has a character of a monotonously decreasing function because the molecular mechanism predominates while a competition of both mechanisms takes place in CH_3I . The dependence with a distinct maximum is a consequence of this competition.

The question whether the methyl radicals formed in the radical decomposition of CX₃I have an excess of kinetic or vibrational energy could be solved using the results of the experiments in which CH₃I decomposition proceeds in the presence of buffer gases (Table III). Addition of helium which has a high thermal conductivity, decreased very rapidly the conversion of methyl iodide. However, addition of higher amounts of helium led to a higher formation of ethane and to a lower yield of methane. It can be therefore deduced that helium cooled down the hot reaction zone, decreased the reaction rate, and preferred the recombination reaction of methyl radicals. On the other hand the addition of xenon, of a gas the molecules of which have an approximately equal relative mass as the molecules of CX₃I and SF₆, did not affect the composition of the reaction mixture up to rather high concentrations. Xenon does not allow any large escape of the excited molecules from the reaction zone. The coolling effect of helium is corroborated by the thermovisual observations⁶ that bear out the dwindling away of the hot zone and the decrease of the vibrational temperature of excited molecules. On the other hand, the addition of xenon affects the hot zone only negligibly.

The authors would like to express their thanks to Dr Z. Papoušková for her help with the evaluation of the analyses with the KSR 4100 computer and to Dr J. Pola for his valuable comments.

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Translated by Z. Prášil.