CW CO_2 LASER-INDUCED AND SF_6-SENSITIZED DECOMPOSITION OF METHYL IODIDE-d_3

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The decomposition of CD_3I initiated by the irradiation of a *cw* CO_2 laser was studied in the presence of the SF_6 sensitizer. The first reaction step of the decomposition produces $CD_3^{\bullet}$ radical that yields either methane-d_4 (the abstraction reaction of "hot" radicals), or ethane-d_6 (the recombination reaction of "cold" radicals). The effect of the total pressure and the composition of the reaction mixture, that of the laser excitation line and output and that of the irradiation time upon the decomposition rate and the product distribution was examined.

Recently, the results on the decomposition of methyl iodide induced with *cw* CO_2 laser in the presence of the SF_6 sensitizer were published in this journal[1]. It was shown that the first step of the decomposition produces methyl radical,

$$CH_3I + SF_6^* \rightarrow CH_3^{\bullet} + I + SF_6 \qquad (A)$$

this species initiating, depending upon reaction conditions in a reaction zone, either abstraction (CH_3 radical having sufficient translational or vibrational energy),

$$CH_3^{\bullet} + CH_3I \rightarrow CH_4 + {}^{\bullet}CH_2I \qquad (B)$$

leads to the formation of methane, or undergoes in the presence of moderator M the recombination affording ethane.

$$2\,CH_3^{\bullet} + M \rightarrow C_2H_6 + M \qquad (C)$$

Both reactions occur concurrently and give thus rise to both hydrocarbons. The iodine liberated from methyl iodide in the course of the step *A* undergoes recombination to I_2. Apart from it, both ethene and ethyne appear amongst reaction products. The dual behavior of methyl radical which depend on the radical kinetic and vibrational energy enables to follow conditions in a reaction zone of irradiated samples. We presumed that products' distribution will noticeably vary depending on the experimental conditions, which will make possible to draw inferences on both the reaction mechanism and the ways of the energy distribution.

The aim of this work is a detailed study of the *cw* CO_2 laser-induced decomposition of methyl iodide-d_3 in the presence of the SF_6 sensitizer.

EXPERIMENTAL

The experimental set-up and the chemicals used are analogous to those described previously[1] In an effort to prove the reproducibility of the results all the runs were at least twice repeated (tables give average values). Some irregularities in the course of a few runs turned out to stem from leaky cells-reactors. The air penetrating into the reaction space was, however, discernible based on the presence of CO and CO_2 absorption bands in the IR spectrum of the mixture of reaction products; these runs were, of course, not taken into account. The relative error of the GC determination of the reaction products quantities was 3%, the numerical evaluation of areas was performed by means of the Robotron KSR 4100 computer.

RESULTS

Most of all the data on the conversion and the composition of the reaction products obtained by the GC analysis are considered. The conversion was calculated from the intensity decrease of the CD_3I infrared ν_2 absorption band at 950 cm^{-1}. Using the GC and IR spectroscopy we also followed the formation of major products, *i.e.* methane-d_4, ethane-d_6, ethene-d_4, and ethyne-d_2, the relative amounts of those are given.

Table I gives the results of the basic runs performed with the CD_3I–SF_6 mixture and shows how is the CD_3I decomposition influenced by the total pressure, molar ratio and the irradiation time. The decomposition was carried out by irradiation of the gaseous mixtures with the P(32) line of the $00^01 \rightarrow 10^00$ CO_2 laser transition at 932·96 cm^{-1} with the output 8 W. It appears that amount of CD_3I decomposed (conversion) increases with increasing total pressure of the gas in the reactor and it is not noticeably affected with the $SF_6 : CD_3I$ ratio. The irradiation time being prolonged (30 to 300 s), the amount of CD_3I reacted increases as expected (roughly by one-third). Further data concern the way in which the reaction products composition is affected by experimental conditions. Thus, e.g. with total pressure 9·3 kPa the formation of CD_4 is almost unaltered with variation of the reaction mixture composition and irradiation time. With lower total pressure 2·6 kPa more apparent variations are observed, mainly the increase of CD_4 with longer irradiation time. With total pressure 9·3 kPa the amount of C_2D_6 increases as the concentration of SF_6 decreases; there is no variation in C_2D_6 amount with lower total pressures and the same irradiation time. The prolongation of irradiation brings about the depletion of ethane-d_6. The opposite situation is seen with C_2D_4, the concentration of that decreases with the decrease of total pressure and increases with longer irradiation times.

Table II gathers the results on the decomposition of the mixture CD_3I/SF_6 using different *P* lines. In all the runs the mixtures were irradiated for 15 s with the laser output 8 W. It was observed that the CD_3I conversion increases with decreasing wavenumber of the excitation line (from the $P(10)$ at 952·88 cm^{-1} to the $P(30)$ at 934·90 cm^{-1}), then slowly decreases to the $P(42)$ at 922·92 cm^{-1}. More apparent are, however, the variations in the composition of the reaction products as the energy of a different excitation line is used. The concentration of methane increases from the $P(10)$ to the $P(30)$, the further shift to higher P lines results only in irregular alteration of the CD_4 quantities. The concentration of ethane-d$_6$ varies in the opposite way – the highest concentration of C_2D_6 relates to the $P(12)$ line, then there is an apparent decrease to the $P(30)$ and irregular distributions to the $P(42)$. The C_2D_4 formation turns out to be independent of the line used, while C_2D_2 is formed only in negligent quantities under used conditions (compare Table II).

The decomposition of CD_3I as dependent upon the laser output (2–14 W) was followed, too. In order to do so the reactor was filled with the CD_3I/SF_6 mixture in

TABLE I

The effect of the reaction mixture composition and the irradiation time upon the reaction course and the products distribution of the CD_3I decomposition[a]

Total pressure in reactor kPa	Volume % of SF_6	Irradiation time s	Conversion[b,c] of CD_3I %		Products distribution volume %			
					CD_4	C_2D_6	C_2D_4	C_2D_2
9·3	0·3	30	51	(3)	72	5	20	3
	0·3	300	80	(3)	74·5	6·5	16·5	2·5
	0·07	30	56	(2)	60·5	17·5	21	1
	0·07	300	68	(2)	64·5	25·5	9	1
	0·03	30	46	(2)	67	17	15	1
	0·03	300	72	(2)	68	12·5	19·5	0·5
2·6	0·3	30	40	(3)	52·5	30	16·5	1
	0·3	300	79	(3)	72	4·5	22	1·5
	0·1	30	44	(2)	61	19	20	1
	0·1	300	78	(2)	78	2	19	1
1·3	0·2	30	23	(2)	69	17·5	12·5	1
	0·2	300	31	(2)	27	16·5	56·5	d
	0·1	30	15	(2)	65	21	14	d
	0·1	300	28	(2)	48	16	35	d

[a] CD_3I decomposition induced with the P (32) line in the presence of SF_6 sensitizer; [b] the amount of CD_3I in %; [c] average value from runs the number of those is given in parentheses; [d] the quantitative determination of C_2D_2 limited by the sensitivity of the method used.

ratio 6·64/2·66 kPa, the mixture being irradiated by the $P(28)$ line for 1 s. The laser beam was focussed by a Ge lens (f.l. 0·25 m). Table III shows that the conversion significantly increases with higher laser outputs. This is also true for the CD_4 amount formed; contrarily, the amount of C_2D_6 continuously decreaes. The same dependence on the laser output is exhibited (from the output being 4 W) by the formation of ethene-d_4. The threshold laser output can be estimated using the results of Table III by their extrapolation.

We have also tried to determine how the decomposition of CD_3I progresses using the laser output 8 W with different excitation lines (the $P(18, 26, 28, 30)$). It turned out (Table IV) that the CD_3I decomposition occurs with the highest rate (the highest conversion) with infrared irradiation at 938·69 cm^{-1} (the $P(26)$ line), *i.e.* the wavenumber at which CD_3I exhibits the highest absorptivity. Among the reaction products the major one is, again, methane-d_4, the amount of that increases with longer irra-

TABLE II

Conversion and product distribution of the CD_3I decomposition in the presence of SF_6[a] as dependent upon the excitation line[b] P

P line of $00^{0}1 \rightarrow 10^{0}0$ transition	CD_3I conversion %	Products distribution, %			
		CD_4	C_2D_6	C_2D_4	C_2D_2
10	11	19	61·5	19·5	[c]
12	10	26	65·5	8·5	[c]
14	18	34	48	18	[c]
16	18	41	43·5	15·3	0·2
18	31	45	36	18·8	0·2
20	30	44	34	22	[c]
22	37	58	24	17·5	0·5
24	46·5	55	26	18·7	0·3
26	52	58	19·5	22·5	[c]
28	54	58	16	25·5	0·5
30	63	66	9	24	1
32	53	63	12·5	23	1·5
34	56	63	11	24·5	1·5
36	55	69	8·5	21	1·5
38	50	63·5	9	25·5	2
40	47	71	8	19	2
42	33	67·5	11·5	21	[c]

[a] The pressure ratio CD_3I/SF_6 was 6·64/2·66 kPa; [b] the laser output on each line was 8 W, the irradiation time was 15 s; [c] the quantitative determination of C_2D_2 hampered by the sensitivity of the method used.

diation period. On the contrary, the amount of ethene-d_4 is with longer irradiation time decreased. As for ethane-d_6, its dependence of the formation upon time is difficult to determine unambiguously. The least amount of this hydrocarbon is obviously, however, formed when using the excitation $P(26)$ line.

In none of the experiments the quantity of ethyne-d_2 was determined due to insufficient sensitivity of the used analytical (GC) method.

DISCUSSION

Wigh regard to the fact that the reaction products of the CD_3I decomposition consist of hydrocarbons CD_4, C_2D_6, C_2D_4, and C_2D_2 (small quantity), together with iodine, we assume that the CD_3I decomposition can be described, similarly as the decomposition of CH_3I (ref.[1]), by the following reaction scheme:

$$SF_6 \xrightarrow{h\nu} SF_6^* \qquad (D)$$

$$CD_3I + SF_6^* \longrightarrow SF_6 + CD_3^{\bullet} + I \qquad (E)$$

$$CD_3^{\bullet} + CD_3I \longrightarrow CD_4 + {}^{\bullet}CD_2I \qquad (F)$$

$$CD_3^{\bullet} + CD_3^{\bullet}) \longrightarrow C_2D_6 \qquad (G)$$

$${}^{\bullet}CD_2I + {}^{\bullet}CD_2I \longrightarrow C_2D_4 + I_2 \qquad (H)$$

$$I + I \longrightarrow I_2 \qquad (I)$$

No reverse reaction (mainly reaction of species with I and I_2) are included therein similarly as reactions leading to larger molecules. The former are not included because they do not affect qualitative composition of the products (having had impact solely upon the reaction rate), the latter were not incorporated due to the fact that the sensitivity of the analytical methods used was not sufficient to detect more complicated compounds, which therefore suggests that the compounds can be formed just in only negligent amounts. There is also quite useless to assume the mechanism of the C_2D_2 formation; this compound is a product of high-temperature reactions (abstractions) and considering not high energies used for the initiation of the decomposition (the laser output did not usually exceeded 8 W), it was ascertained among other reaction products only in negligent amounts. There appears (Tables I and II and Fig. 1) that the product ratio CD_4/C_2D_6 noticeably varies. Thus, *e.g.* when using the $P(12)$ line a large quantity of ethane and only little amount of methane is formed, while the opposite situation – 10% of ethane and almost 70% of methane – is arrived at when using some line between the $P(30)$ and $P(42)$ lines. The conversion of CD_3I decomposition shows apparent maximum with the $P(30)$ excitation line

TABLE III

The effect of the laser output[a] upon the amount of the CD_3I reacted and the products distribution

Laser output W	Conversion %	CD_3I reacted kPa	Products distribution[b], %		
			CD_4	C_2D_6	C_2D_4
2	1·1	75	[c]	[c]	[c]
3	2	133	12	45·4	42·6
4	3·1	210	12·1	44·1	43·8
5	4·2	279·9	28	31·5	40·5
6	5	330	45	21·1	33·9
7	6·7	446·6	52	13·5	34·5
8	8·2	546·6	60	10	30
9	11·1	739·9	64·3	9·2	26·5
10	11	733·3	69·5	8·2	22·2
11	12·8	853·3	75·2	5	19·9
12	17·1	1 139·8	78·6	5·3	16·2
14	25·9	1 726·5	80	4·4	15·6

[a] The P (28) line, irradiation time 1 s, reaction mixture 6·64 kPa of CD_3I and 2·66 kPa of SF_6; [b] quantitative determination of C_2D_2 by GC not possible; [c] quantitative determination of the products limited by the analytical method used.

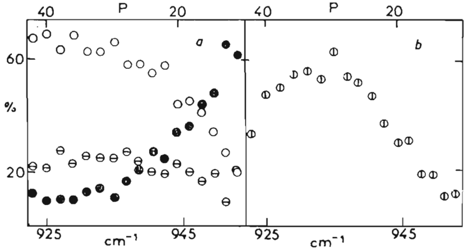

FIG. 1

The dependence of the conversion CD_3I (*b*) and the reaction products amounts (*a*) upon the wavenumber of IR radiation (line *P*) inducing the CD_3I decomposition

a ○ CD_4; ● C_2D_6; ⊖ C_2D_4;
b ⦶ CD_3I conversion

(Fig. 1*b*). We can therefore state that $CD_3^\bullet$ radicals possessing an excess of translational or vibrational energy are not procuded inside the hot zone when using the *P*(12) line but are formed there when the *P*(30) to *P*(42) lines were chosen for the irradiation.

TABLE IV

The effect of the irradiation time[a] and the excitation line upon the reaction course of the CD_3I decomposition[b] and products distributions

Excitation line	Irradiation time s	Conversion Pa	CD_3I %	Products distribution[c] %		
				CD_4	C_2D_6	C_2D_4
P (18)	0·5	240	3·6	49·3	20·6	30
	1	633·3	9·5	57·1	25·2	17·7
	3	1 180	17·7	64·7	19·3	16
	6	1 933	29	69	17·1	13·9
	9	2 213	33·2	74·4	12·9	12·7
	12	2 497	37·5	74·6	13·4	12
	15	2 700	40·5	76·2	13·8	10
	18	2 860	42·9	75·6	14·7	9·7
	24	3 240	48·6	75	13·8	11·2
	30	3 480	52·2	75·3	13	11·7
P (26)	0·5	447	6·7	66·4	4·8	28·8
	1	1 000	15	73·4	4	22·6
	3	1 533	23	79·5	4·8	15·7
	6	2 320	34·8	81·2	5	13·8
	9	2 766	41·5	81·3	5·2	13·5
	12	3 266	49	82·7	5·3	12
	15	3 565	53·5	82·5	5·1	12·4
	18	3 820	57·3	81·7	5·9	12·4
	24	4 130	61·1	81·6	6·5	11·9
	30	4 360	65·4	82	5·4	12·6
P (28)	0·5	327	4	61·5	18·2	20·3
	1	507	8·6	70·6	17·8	11·6
	3	1 123	16·8	72·5	16·9	10·6
	6	1 548	23·2	73·1	16·5	10·4
	9	2 320	34·8	72·5	18·3	9·2
	12	2 332	35	72·9	16·9	10·2
	15	2 635	39·4	71·7	18·9	9·4
	18	2 866	43	74·9	16·8	8·3
	24	2 942	44·1	71	18·8	10·2
	30	3 351	50·5	72·8	17·5	9·7

TABLE IV

(*Continued*)

Excitation line	Irradiation time s	Conversion Pa	CD_3I %	Products distribution[c] %		
				CD_4	C_2D_6	C_2D_4
P (30)	0·5	533·3	7·9	55·5	9·2	35·3
	1	709	10·7	65·6	7·4	27
	3	1 333	20	72·9	6·5	20·6
	6	2 200	33	77·7	4·6	17·7
	9	2 815	42·2	77·8	4·4	17·8
	12	3 158	47·3	83·3	3·6	13·1
	15	3 533	53	78·6	3·9	17·5
	18	3 793	56·9	84·7	3·7	11·6
	24	3 946	59·2	85·7	3·3	11
	30	4 200	63	82·8	4·6	12·6

[a] The laser output 8 W; [b] reaction mixture 6·64 kPa CD_3I and 2·66 kPa SF_6; [c] quantitative determination of C_2D_2 not possible.

Similar conclusions were arrived at also by the authors of works on flash photolysis of methyl iodide[2-6].

The formation of unusually high quantity of C_2D_4 (>40%) when decomposing the CD_3I/SF_6 mixture at very low total pressures (around 1·3 kPa) sounds interesting. It appears that this high yield necessitates to use other model of the CD_3I decomposition. This is the fact known also from other initiated reactions[7,8] that can take place at different pressures by different manners. The only relevant mechanism[9] is the one assuming the decomposition of CD_3I to biradical $:CD_2$, the latter species undergoing the recombination to C_2D_4:

$$CD_3I \xrightarrow{h\nu} :CD_2 + DI \qquad (J)$$

$$2\ :CD_2 \longrightarrow C_2D_4 \qquad (K)$$

$$2\ DI \longrightarrow D_2 + I_2 \qquad (L)$$

Such a mechanism is undoubtedly operating concurrently with the decomposition described by the Eqs (*D*)–(*I*). Not being sufficiently stable at high temperatures DI decomposes in the reaction zone immediately according to Eq. (*L*). To determine the iodine produced by this decomposition is not, however, possible due to the fact that this compound is also produced during the decomposition of CD_3I *via* CD_3 radical; the analytical determination of D_2 by the methods used in this work is hampered chiefly by the fact that the reaction occurs at low pressures of the reactants.

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