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Isothermal Pyrolysis of Iodomethanes in Gases

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Abstract—The fact was established that the pyrolysis of gaseous iodomethanes RI yields methane and non traces of recombination products R_2 . A pyrolysis mechanism was proposed and rate constants of limiting stages of the pyrolysis of iodomethane, trideuteroiodomethane, and diiodomethane over the range of 500–1500 K were determined.

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The method of isochore isothermal pyrolysis was applied [1–4] to the study of thermal gas-phase reactions involving perfluoroalkyliodides (CF₃I, C₂F₅I, C₃F₇I, ...) and -bromides (CF₃Br). In this method a perfluoroalkylhalide RX is subjected to pyrolysis (1) at a fixed temperature under mild conditions. The detailed mechanism of the pyrolysis is presented by reactions (2)–(5).

$$RX \rightarrow 1/2R_2 + 1/2X_2, \tag{1}$$
$$RX \leftrightarrow R' + X',$$

$$(K_{c,2} = k_2/k_{-2} = [R]_{eq}[X]_{eq}/[RX]_{eq}),$$
 (2)
X' + RX \leftrightarrow R' + X₂

$$(K_{c,3} = k_3/k_{-3} = K_{c,2}/K_{c,4}),$$
 (3)

$$2 X' + (Y) \leftrightarrow X_2 + (Y),$$

$$(K_{c,4} = k_4 / k_{-4} = [X]_{eq}^2 / [X_2]_{eq}),$$
(4)
2R' + (Y) \rightarrow R₂ + (Y),

$$(k_5 = -\frac{1}{2}(d[\mathbf{R}]/dt)[\mathbf{R}]^{-2}).$$
 (5)

Here Y are particles of any third agent, i.e. of Y = RX, R_2 , X_2 , R', X', or an inert diluent (Ar, He,...); $[R]_{eq}$, $[X]_{eq}$, and $[RX]_{eq}$ are equilibrium concentrations of corresponding components; k_i (k_{-i}) is a rate constant of a direct (inverse) elementary reaction, and $K_{c,i}$ is a constant of the *i*th equilibrium.

The process rate is limited by irreversible (under conditions of our experiments) reaction (5) that allows us to determine the rate constant k_5 from the accumulation rate of the recombination product R₂ or, which is more convenient, from the rate of molecular halogen X₂ accumulation. Kinetic Eqs. (6) correspond to reactions (2)–(5).

$$\frac{d[\mathbf{R}]}{dt} = \frac{k_2[\mathbf{RX}] - k_{-2}[\mathbf{R}][\mathbf{X}] + k_3[\mathbf{X}][\mathbf{RX}]}{-k_{-3}[\mathbf{R}][\mathbf{X}_2] - 2k_5(\mathbf{P}, T)[\mathbf{R}]^2 - k_{\text{diff}, \mathbf{P}}[\mathbf{R}],$$
 (6¹)

$$(d[X])/(dt) = k_2[RX] - k_{-2}[R][X] - 2k_4[M][X]^2 2k_{-4}[M][X_2],$$
(6²)

$$(d[R_2])/(dt) = k_5(P,T)[R]^2.$$
 (6³)

Three Eqs. (6^1) – (6^3) are sufficient for the unambiguous solution of the kinetic problem, because concentrations [Eq. (7)] of remaining components can be found from conservation laws.

$$[RX]_{t} = [RX]_{0} - 2[X_{2}]_{t},$$
$$[X_{2}]_{t} = [R_{2}]_{t}.$$
(7)

Concentrations of intermediate active species fast reach almost equilibrium values constant at a specified temperature, which slowly vary as the initial substance RX is consumed. Therefore, bypassing the integration procedure, we find concentrations of the intermediate particles in explicit form (8), (9) from Eqs. (6^1) and (6^2) (Bodenstein–Semenov approximation of quasistationary concentrations).

$$[\mathbf{X}]_t = \sqrt{K_{\mathrm{c},4}[\mathbf{X}_2]_t},\tag{8}$$

$$[\mathbf{R}]_{t} = K_{c,2}([\mathbf{R}\mathbf{X}]_{0} - 2[\mathbf{X}_{2}]_{t})/(K_{c,4}[\mathbf{X}_{2}])^{0.5}.$$
 (9)

The necessity for integrating Eq. (6^3) also disappears, for the rate of increasing r(t) [Eq. (10)] of the concentrations of a molecular halogen is measured directly under isochorically-isothermal pyrolysis conditions.

$$r(t) = (d[X_2])/(dt) = (d[R_2])/(dt) = k_5(P,T)[R]^2.$$
(10)

Substituting functions (8), (9) in Eq. (10), we obtain explicit expression (11) for k_5 .

$$k_5(\mathbf{P},T) = \alpha(T)(K_{\rm c,4})/(K_{\rm c,2}^2), \tag{11}$$

$$\alpha(T) = r(t)[X_2]_t ([RX]_0 - 2[X_2]_t)^{-2}.$$
 (12)

Here $[RX]_0$ is the initial concentration, $[X_2]_t$ is the measured concentration of the molecular halogen to an instant *t*, and $\alpha(T)$ is kinetic invariant (12) independent of current concentration of components. The constant $K_{c,4}(T)$ is known for all halogens, that is why for the halides CF₃I,C₂F₅I, C₃F₇I, and CF₃Br, for which $K_{c,2}(T)$ values are known, we can find $k_5(P, T)$ values from the measured invariant $\alpha(T)$ by formula (11) [1–4].

We could expect that the iodomethane pyrolysis would follow simple gross-scheme (1), however even the first experiments have shown [5, 6] that the volatile products of the iodomethane pyrolysis are presented exclusively by methane and contain no ethane at all (Table 1). Therefore, recombination (5) is completely eliminated during iodomethane pyrolysis ($R = CH_3$), and the detailed mechanism of this process includes reactions (2), (4), and (13).

$$CH_3 + CH_3I \longrightarrow CH_4 + CH_2I + 18 \text{ kJ mol}^{-1}.$$
(13)

Iodomethane thermal reactions were studied even in the first half of the last century [7, 8], however the principal attention was paid to obtaining information on kinetic constants of reactions (3) ($R = CH_3$) and (14), and for which purpose the iodide was diluted by hydrogen iodide.

$$CH_3 + HI \rightleftharpoons CH_4 + \Gamma.$$
 (14)

The resulting information was not highly reliable, as added hydrogen iodide increased the number of the elementary reactions from 8 up to 12 that did not allow unambiguous calculating any rate constant from a unique kinetic curve of the molecular iodine accumulation. Furthermore, the authors of [7, 8] did not use the advantage of the Bodenstein-Semenov approximation. In our experiments we did not add HI to initial iodomethane, but it could be generated during the pyrolysis, so generally it is necessary to suppose a possibility of occurring reactions (15^1) – (15^6) and (16), (17).

CH₃I + I'
$$\xrightarrow{k_{1m}}$$
 CH₃' + I₂ - 84.1 kJ mol⁻¹,
($K_{c,1m} = k_{1m}/k_{-1m}$), (15¹)

CH₃I
$$\xrightarrow{k_{2m}}$$
 CH₃' + I' - 232.9 kJ mol⁻¹,
($K_{c,2m} = k_{2m}/k_{-2m}$), (15²)

CH₃' + CH₃I
$$\xleftarrow{k_{3m}}{\leftarrow}$$
 CH₄ + CH₂I' + 18.1 kJ mol⁻¹,
 $(K_{c,3m} = k_{3m}/k_{-3m}),$ (15³)

$$CH_{3}' + CH_{2}I' \xleftarrow{k_{4m}} CH_{4} + CHI'' - 1.3 \text{ kJ mol}^{-1},$$

 $(K_{c,4m} = k_{4m}/k_{-4m}),$ (15⁴)

Haloalkane	Supposed radical R and its $\Delta_{\rm f} H_{298}^0$, kJ mol ⁻¹	Found product of recombinations of radicals (R ₂)	Others pyrolysis products		
CF ₃ I ^a	CF ₃ (-471)	C ₂ F ₆ (100%)	I ₂		
$C_2F_5I^a$	C ₂ F ₅ (-921)	C ₄ F ₁₀ (100%)	I ₂		
$C_3F_7I^a$	C ₃ F ₇ (-1283)	C ₆ F ₁₄ (98%)	I_2, C_3F_6, C_3F_8		
CF_3Br^a	CF ₃ (-471)	C ₂ F ₆ (100%)	Br ₂		
$C_2H_5I^a$	C ₂ H ₅ (+125)	Absent	$I_2, C_2H_4, C_2H_6, C_6H_6$		
CF_2HBr^b	CF ₂ H [·] (–243)	$C_2F_4H_2$ (2%)	Br ₂ , HBr, C ₃ F ₆ H ₂ , C ₃ F ₅ H, C ₂ F ₅ H, C ₂ F ₄		
CF_2ClBr^b	CF ₂ Cl [·] (-280)	$C_2F_4Cl_2$ (3%)	Br ₂ , HBr, C ₂ F ₄ , C ₂ F ₄ ClBr, C ₃ F ₆ ClBr, C ₄ F ₈ ClBr, C ₃ F ₆		
CH_3I^b	CH ₃ : (+147)	Absent	I ₂ , CH ₄ , C _{solid}		
CD_3I^b	CD ₃ . (+137)	Absent	I ₂ , CD ₄ , C _{solid}		
CH ₂ I ₂ ^b	CH ₂ I (+230)	Absent	I ₂ , CH ₄ , C _{solid}		
CHI ₃ ^b	CHI ₂ (+334)	Absent	I ₂ , CH ₄ , C _{solid}		

Table 1. Products of pyrolysis (at 500-800 K) of certain haloalkanes

^a Published data [1-4]. ^b Found in the present work.

CH₃I + I
$$\xrightarrow{k_{5m}}$$
 CH₂I + HI - 115.0 kJ mol⁻¹,
 $(K_{c,5m} = k_{5m}/k_{-5m}),$ (15⁵)

CH₄ + I'
$$\stackrel{k_{6m}}{\longleftarrow}$$
 CH₃ + HI - 137.7 kJ mol⁻¹,
($K_{c,6m} = k_{6m}/k_{-6m}$), (15⁶)

where index "*m*" indicates that the constants refer to a usual methyl group.

Resulting diradical CHI^{••} is capable to disappear fast either in volume due to irreversible dissociative recombination (16) or in heterogeneous process (17).

2CHI^{••}
$$\stackrel{k_0}{\longrightarrow}$$
 $\left[\begin{array}{c} \longrightarrow \text{HI} + \text{HC} \equiv \text{CI} + 550 \pm 30 \text{ kJ mol}^{-1}, \\ \longrightarrow 2 \text{ HI} + \text{C}_2 + 15 \pm 10 \text{ kJ mol}^{-1}, \quad (16) \\ \text{CHI}^{••} \quad \stackrel{k_{\text{diff}}}{\longrightarrow} \quad \text{CHI (surface)} \\ \longrightarrow \text{C}_{\text{solid}} + \text{HI(gas)} + 414 \pm 5 \text{ kJ mol}^{-1}. \quad (17) \end{array} \right]$

The enthalpies of reactions (15)–(17) were calculated by means of the tables [9]. The aim of the present study was to detect a limiting stage among reactions (15)–(17) and to measure its rate constant. A similar problem was solved also for the diiodomethane pyrolysis.

Thermal experiments. A kinetic pyrolysis scheme of any substance should be first of all coordinated with the composition of observed final products. Therefore we have determined final products of the pyrolysis gross-process for a series of halides by the methods of gas chromatography and mass spectrometry. In the case of gaseous CH₃I ethane (as well as diiodoethane at the pyrolysis of CH_2I_2), i.e. the product of the CH_3 (or CH₂I[·]) radical recombination, was completely absent. Instead of it in the both cases exclusively methane CH₄ and molecular iodine were present in the volume, and a carbon polymer, on the cell walls (Table 1). The schemes of CF₂HBr and CF₂ClBr pyrolysis also were not limited by reactions (2)-(5), unlike perfluoroalkyliodides, for which pyrolysis grossscheme (1) with reactions (2)–(5) is fully suitable.

Thus, according to pyrolysis results, all iodides (bromides) are broken up into three groups.

(1) Perfluoroalkyliodides and -bromides, for which gross-scheme (1) is obeyed and the method of

isothermal pyrolysis makes it possible to measure rate constants k_5 ;

(2) Remaining haloalkanes, except for iodomethanes, for which gross-scheme (1) is not obeyed and kinetic measurements by the isothermal pyrolysis method are impossible;

(3) Iodomethanes, for which gross-scheme (1) is not obeyed, but the set of final pyrolysis products is so simple that there is a chance to discover the mechanism of their pyrolysis.

In the previous work [6] we have shown by an example of CF_3I that the isochore isothermal pyrolysis method allows us to measure confidently the rate constant of radical R recombination (5), but only if two conditions are obeyed. First, radical R in a gas should behave as a quasi-atom (i.e. not be split); second, for the iodide RI under study all thermodynamic parameters of equilibria (2)–(4) should be known. It is seen from Table 1 that perfluoroalkyliodides (bromides), but not the iodomethanes CH_3I , CH_2I_2 , and CHI_3 , meet the first condition. However for the last-named compounds the set of pyrolysis products is very simple, and below we shall reveal the mechanism of their low-temperature pyrolysis.

Photolytic experiments. The absence of C_2H_6 from the iodomethane pyrolysis products sharply contrasts with the fact that the pulse photolysis of CH₃I in Ar excess leads exclusively to the formation of ethane [10]. On the contrary, the stationary CH₃I photolysis in Ar excess (λ 230–300 nm, [CH₃I] 8.9×10¹⁷ molecule/cm³, [Ar] 1.97×10¹⁹ molecule/cm³, *T* 343 K, Δt 30 min) leads only to the formation of CH₄, I₂, and pyrocarbon on quartz cell walls.

To reveal the contribution of reactions of CH_3 radicals on a quartz cell surface in comparison with the processes in a reactor volume, we have studied the photolysis of gaseous acetone (CH_3)₂CO under conditions when generated radicals CH_3 [•] certainly have a possibility to contact with a quartz wall of a reaction cell.

It was reliably estimated [11] that the photolysis of acetone at *T* 398 K and λ 250–320 nm gives the acetone quantum yield φ (CO) equal to one.

$$CH_3COCH_3 \longrightarrow CO + 2 CH_3$$
 (18)

$$2 \operatorname{CH}_3^{\cdot} \xrightarrow{k_{19}} \operatorname{C}_2 \operatorname{H}_6 \tag{19}$$

However, recently it has been shown by the method of molecular beams [12] that at λ 193 nm the carbonyl amide photodissociation yields oxalonitrile with a probability of 6% by the intramolecular rearrangement mechanism (20).

$$CO(CN)_2 \xrightarrow{hv} COCN^{\bullet} + CN^{\bullet},$$

$$(20)$$

$$(6 \pm 2)\% CO + NCCN.$$

Therefore it is logical to add one more reaction (predissociation) (21) to stages (18), (19) of the gaseous acetone photolysis, as it is possible that this stage was not noticed in ordinary photochemical experiments.

$$CH_3COCH_3 \xrightarrow{hv} CO + C_2H_6.$$
(21)

To measure the quantum yield φ_{predis} of reaction (21), we have fulfilled experiments with multiplelabelled acetone (containing isotope molecules in extremely nonequilibrium concentrations). The deuterium analog (CD₃)₂CO is indistinguishable in photochemical properties from ordinary acetone. Free radicals CD₃ recombine by scheme (19a) with almost the same rate constant (22) as their protium analogs.

$$CD_3^{\cdot} + CD_3^{\cdot} \xrightarrow{k_{19d}} C_2D_6,$$
 (19a)

$$k_{19d} = (15/18)^{1/2} k_{19} = 0.913k_{19}.$$
 (22)

Therefore in the case of the photolysis of multiplylabelled acetone [$(CH_3)_2CO + (CD_3)_2CO$] reaction (21) should result in the formation of only C_2H_6 and C_2D_6 molecules, whereas reactions (18), (19) produce three isotope varieties of ethane molecules (C_2H_6 , C_2D_6 , and $C_2H_3D_3$), their amounts being highly accurate defined [13] by combinatorial formulae (23).

$$[C_2H_6] = 1/2x_0^2, [C_2H_3D_3] = x_0y_0, [C_2D_6] = 1/2y_0^2.$$
(23)

Here x_0 is a mole fraction of initial radicals CH₃; $y_0 = (1 - x_0)$ is a mole fraction of initial radicals CD₃. As a result the excess of C₂H₆ and C₂D₆ molecules above combinatorial distribution (23) in the photogenerated ethane is entirely defined by the contribution of predissociation (21).

The isotope composition of the ethane formed after the photolysis of an acetone and deuteroacetone mixture is presented in Table 2 together with the calculated fraction of molecules formed by intramolecular mechanism (21). This fraction is independent of pressure and temperature of photolyzed acetone and has value (24).

$$\varphi_{21} = 0.26 \pm 0.02. \tag{24}$$

It follows from the value (24) that with a probability of 74% acetone photolysis generates free methyl radicals, which inevitably contact a quartz cell wall in the conditions of a stationary photolysis. However, within the limits of measuring errors ($\pm 0.1\%$) methane was not detected among the photolysis products, though its formation is energy more favorable.

$$4 \text{ CH}_3 \rightarrow 2 \text{ C}_2 \text{H}_6 + 760 \text{ kJ mol}^{-1},$$
 (25)

$$4 \text{ CH}_3 \rightarrow 3 \text{ CH}_4 + \text{C}_{\text{solid}} + 821 \text{ kJ mol}^{-1}, \qquad (26)$$

Therefore, the formation of methane at the iodomethane pyrolysis is defined not by the contact of

photolysis of multiply-labelled acetoneInitial concentration
of acetone,
molecule/cm³Photolysis product
(isotope molecule)Measured isotope com-
position of ethane,
mole fractionContribution of recombi-
nation of CH3 and CD3,
mole fractionContribution of
predissociation,
mole fractionEthane formed in
an intramolecular
regrouping, %

Table 2. Fraction of ethane formed as a result of intramolecular rearrangement (21) (induced predissociation) at a stationary

molecule/cm ³	(isotope molecule)	mole fraction	mole fraction [by formulae (23)]	mole fraction	regrouping, %
9.7×10 ¹⁷	CH ₃ CH ₃	0.477±0.001	0.3065	0.170±0.002	
(64.4% H,	CH ₃ CD ₃	0.337±0.001	0.3373	0	26.3±0.4
35.6% D)	CD_3CD_3	$0.186{\pm}0.001$	0.0928	0.093 ± 0.002	
3.9×10^{18}	CH ₃ CH ₃	0.487 ± 0.001	0.3265	0.161±0.015	
(64.4% H,	CH ₃ CD ₃	$0.340{\pm}0.001$	0.3402	0	24.5±2.4
35.6% D)	CD_3CD_3	0.173 ± 0.001	0.0886	$0.084{\pm}0.009$	
3.9×10^{18}	CH ₃ CH ₃	$0.360{\pm}0.001$	0.2088	0.151 ± 0.002	
(53.8% H,	CH ₃ CD ₃	0.357±0.001	0.3573	0	28.1±0.4
46.2% D)	CD_3CD_3	0.283 ± 0.001	0.1528	0.130 ± 0.002	
	1		1		1



Fig. 1. Absorption cross sections (σ) of photons published and measured in the present work. The left-hand scale: I₂ (λ 500 nm) and CH₂I₂ (λ 251 nm). The right-hand scale: CH₃I (258 nm), CD₃I (λ 257 nm), CF₃I (267.8 nm), and C₃F₇I (270 nm). Data of: (1) [14], (2) [15], (3) [16], (4) [17], and (5) our measurements.

methyl radicals with a wall, but by the presence of iodine-containing molecules (radicals) in the gas.

Kinetics of iodomethane pyrolysis. Current concentrations of components in a reaction vessel were found in the kinetic experiments by a signal of the current optical density of a mixture under pyrolysis (by the Bouguer–Lambert–Beer law) from the extinction of each component depending on temperature (Fig. 1). We have found a part of the data on the extinctions in the literature [14–17] and determined a part by ourselves.

To elucidate the mechanism of iodomethane pyrolysis, we have recorded kinetic curves $[I_2]_t$ in the course of the isochore isothermal pyrolysis of pure CH_3I (Fig. 2) and the $CH_3I + CD_3I$ (50:50) mixture based on the mass-spectral analysis of the pyrolysis products (Fig. 3 and Table 3). To minimize a diffusion drift of free radicals to a wall, the initial pressure of iodomethane was set at a level of 2 atm. The anomalous mutual arrangement of the kinetic curves has come to light: the molecular iodine is accumulated faster in the case of the pyrolysis trideuteroiodomethane, though the iodide CD₃I, being more stable thermodynamically [9] than CH₃I, should be pyrolyzed more slowly. It is easy to calculate from the data of Table 3 that in the 25th minute of the pyrolysis the atomic fraction of D in formed methane is equal to



Fig. 2. Kinetics of the I₂ accumulation in the isochore isothermal pyrolysis of iodomethane: (1) $[CH_3I]_0 5.7 \times 10^{19}$, (2) $[CH_3I]_0 5.45 \times 10^{19}$ molecule/cm³; $T_1 588 \pm 1$, $T_2 615 \pm 1$, $T_3 633 \pm 1$ K.

0.5065 (i.e. is greater than a half) and the atomic fraction of H is 0.4935; in the 195-th minute the atomic fraction of D in methane is 0.5775, and the fraction of H, 0.4225 that agrees within the limits of the errors with the data of the kinetic measurements (Fig. 3).

The data of Tables 2 and 3 essentially differ from each other owing to the fact that only molecules with the number of deuterium atoms multiple of three are



Fig. 3. Kinetics of the I₂ accumulation in the isochore isothermal pyrolysis of gaseous methyliodide CH₃I or CD₃I. T_1 599 and 588 K, respectively; T_2 625, T_3 652 K. [CH₃I]₀ 5.7×10¹⁹; [CD₃I]₀ 2.25×10¹⁹ molecule/cm³.

Isotope	Experiment		Calculation by combi	natorics formulae [18]	Deviation of the experiment from the calculation, rel %		
molecule	25 min	195 min	25 min	195 min	25 min	195 min	
CD_4	20.5±0.8	16.1±0.2	6.58	11.11	+212±12	$+44\pm3$	
CD_3H	32.4±0.1	32.5±0.2	25.65	32.54	+26±1	0±1	
CD_2H_2	5.5±0.3	25.5±0.3	37.49	35.72	$-85{\pm}1$	-29±1	
CDH ₃	12.4±0.3	18.1±0.2	24.35	17.43	-49±1	$+4{\pm}1$	
CH_4	29.2±0.1	7.8±0.3	5.93	3.19	+392±2	$+144{\pm}10$	
CD_3I	44.1±2.0	18.5±1.5	12.02	7.54	+267±17	145±20	
CD ₂ HI	1.2±0.3	6.3±0.5	37.00	30.93	-97±1	-80 ± 2	
CDH_2I	13.3±1.5	58.7±2.5	37.97	42.27	-65±4	+39±6	
CH ₃ I	41.4±2.0	16.5±1.5	12.99	19.26	+216±18	-14±7	

Table 3. Isotope composition (mole fraction, %) of methane obtained on the pyrolysis (708 K) of the 50 mol % CH_3I + 50 mol % CD_3I mixture and also of residual initial methyliodide

present in Table 2, i.e. a nonequilibrium distribution of deuterium over methyl radicals is retained on the acetone photolysis. On the contrary, in the case of the iodomethane pyrolysis the isotope composition of both final methane and initial iodomethane points to intensive hydrogen exchange between methyl groups. It follows from these facts that at least reactions (2), (4), and (13) occur in the starting phase of the iodomethane pyrolysis. It was the consideration of possible reactions (3) and (14) that has led us to the adoption of kinetic scheme (15)–(17). Kinetic equations (27¹)–(27⁶) correspond to this scheme.

$$d[CH_3]/dt = k_{2m}[CH_3I] - k_{-2m}[CH_3][I] + k_{1m}[CH_3I][I] - k_{-1m}[I_2][CH_3] - k_{3m}[CH_3I][CH_3] + k_{-3m}[CH_4][CH_2I] - k_{4m}[CH_3][CH_2I] + k_{-4m}[CH_4][CHI] k_{-6m}[HI][CH_3] + k_{6m}[CH_4][I],$$
(27¹)

$$d[CH_2I]/dt = k_{3m}[CH_3I][CH_3] - k_{-3m}[CH_4][CH_2I] - k_{4m}[CH_2I][CH_3] + k_{-4m}[CH_4][CHI],$$
(27²)

$$d[\text{CHI}]/dt = k_{4m}[\text{CH}_2\text{I}][\text{CH}_3] - k_{-4m}[\text{CH}_4][\text{CHI}]$$

$$-2k_0[CHI]^2 - k_{diff}[CHI], \qquad (27^2)$$

$$d[II]/dt = k_0 [CH_0] - k_0 [II][CH_0]$$

-3

$$\begin{array}{l} u_{[1]}(u_{1} - \kappa_{2m}[\text{CH}_{3}\text{I}] - \kappa_{-2m}[1][\text{CH}_{3}] \\ - k_{1m}[\text{CH}_{3}\text{I}][\text{I}] + k_{-1m}[\text{I}_{2}][\text{CH}_{3}], \end{array}$$
(27⁴)

$$d[\text{HI}]/dt = -k_{-6}[\text{HI}][\text{CH}_3] + k_6[\text{CH}_4][\text{I}] + 2k_0[\text{CHI}]^2 + k_{d:\text{ff}}[\text{CHI}], \qquad (27^5)$$

$$d[I_2]/dt = 2/3d[CH_4]/dt = 2/3k_{3m}[CH_3][CH_3I].$$
 (27⁶)

Concentrations of the remaining macrocomponents can be calculated highly accurate from conservation laws (28).

$$[CH_{3}I]_{t} = [CH_{3}I]_{0} - 2 [I_{2}]_{t},$$

$$[CH_{4}]_{t} = 3/2[I_{2}]_{t}.$$
 (28)

The first equality in equation (27^6) is written according to gross-scheme (29) of the pyrolysis, and

the second equality, on the ground that this is reaction (15^3) in scheme (15) generating radicals CH₂I which is the limiting stage of the pyrolysis.

$$4/3$$
CH₃I \rightarrow CH₄ + $2/3$ I₂ + $1/3n$ C_n + 61.8 kJ mol⁻¹. (29)

The previous stages (generating I atoms and CH_3 radicals) fast come to a quasistationary mode, therefore the necessity of integrating equations (27¹), (27⁴), and (27⁵) disappears, and expressions (30)–(32) are obtained from the right-hand parts of these equations.

$$[I]_t = \sqrt{K_{c,4}}[I_2]_t, \tag{30}$$

$$[CH_3]_t = \frac{K_{c,2m}[CH_3I] - 3r(t)/k_{-2m}}{\sqrt{K_{c,4}[I_2]}}$$
(31)

[HI] =
$$\frac{\{2/3[I_2]K_{c,6m}\sqrt{K_{c,4}[I_2]} + 2r(t)/k_{-6m}\}\sqrt{K_{c,4}[I_2]}}{\{K_{c,2m}[CH_3I] - 3r(t)/k_{-2m}\}}.$$
 (32)

Rate constants of reactions (15^5) are absent from equations (30)–(32), because the effect of these reactions in a quasiequilibrium is doubled by reactions (15^3) and (15^6) , as is seen from the following relationship.

$$K_{c,5m} = K_{c,3m} K_{c,6m}$$

Equations (30)–(32) also contain no parameters of reactions (15^1) , as reactions (15^2) and (4) lead to the same effect.

$$K_{c,1m} = K_{c,2m}K_{c,4}$$

In the kinetic experiment (Figs. 2 and 3) we measured initial concentration of $[CH_3I]_0$ and current concentration $[I_2]_t$, and found directly the process rate $r = d[I_2]/dt$ from these data. As a result, the necessity

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of integrating Eq. (27^6) also disappears. Substituting expression (31) in Eq. (27^6) , we obtain working formula (33).

$$k_{3m} = \frac{3\sqrt{K_{c,4}}}{2K_{c,2m}} \frac{r\sqrt{[I_2]_t}}{([CH_3I]_0 - 2[I_2]_t)^2}.$$
 (33)

We find equilibrium constant (34) on the basis of the tabular data [9] for the range of 500–700 K.

$$K_{c,2m}(T) = 10^{25.00\pm0.03} \exp(-28013 \text{K/T}) \text{ molecule/cm}^3.$$
 (34)

The data on k_{-2m} and k_{-6m} are taken from the literature [19, 20]. Now, using formulas (30)–(33), we can calculate the concentrations of [I⁻], [CH₃], and [HI] and the rate constant k_{3m} (Table 4) for five experimental situations presented in Figs. 2 and 3. In the same table we presented the calculated time of the half-consumption of CH₃⁻ radicals in reactions with CH₃I and CH₃⁻.

It is seen from Table 4 that the rate of consuming CH₃ radicals in reaction (15^3) exceeds the rate of their consuming in the recombination by 2–3 orders, i.e. the methane generation occurs hundreds times faster than the ethane generation, which explains the absence of ethane in the products of the iodomethane pyrolysis (Table 1). This conclusion does not depend on the ambiguity of the mechanism of radicals CHI disappearance [in reactions (16) or (17)], because rate constants k_0 or k_{diff} are absent from formulae (30)–(33), which contain only a changed rate of process r(t) independent of the knowledge of the gross-process (29) detailed mechanism.

The data of the last column in Table 4 are graphically presented in Fig. 4. Analytical representa-

tion (35) follows from our data (for 567–672 K) and available published data (for 1050–1500 K).

$$k_{\rm H} \equiv k_{3m} = 10^{-11.3 \pm 0.3} \exp[-(8060 \pm 700) \text{K}/T] \text{ cm}^3/(\text{molecule s}),$$

(500 K $\leq T \leq 1500$ K). (35)

In the case of deuterated molecules reaction (36) proceeds instead of process (15^2) .

CD₃I
$$\xleftarrow{k_{2d}}{k_{-2d}}$$
 CD₃' + I' - 241.4 kJ mol⁻¹,
($K_{c,2d} = k_{2d}/k_{-2d}$). (36)

We calculate equilibrium constant (37) for reaction (36) from the thermodynamic tables [9].

$$K_{c,2d}(T) = 10^{25.5 \pm 0.1} \exp(-29040 \text{K}/T) \text{ molecule/cm}^3.$$
 (37)

Similarly in the case of completely deuterated molecules instead of reaction (15^3) reaction (38) proceeds.

$$CD_{3}' + CD_{3}I \xrightarrow{k_{D}} CD_{4} + CD_{2}I' + (18\pm10) \text{ kJ mol}^{-1},$$

 $(K_{c,3d} = k_{3d}/k_{-3d}).$ (38)

Rate constants for direct reaction (38) (Table 4) were found from the kinetic curves of iodine accumulation at the trideuteroiodomethane pyrolysis (Fig. 3). Table 4 shows that the rate of consuming radicals CD₃ in reaction (38) exceeds the rate of their consuming in recombination by 2–3 orders, which explains the complete absence of C_2D_6 from the products of CD₃I pyrolysis (Table 1). Analogously to expression (35) we present rate constant k_{3d} in analytical form (39) (Fig. 4).

Table 4. Quasistationary concentrations of particles Z during the pyrolysis of iodomethane ($[CH_3I]_0 \times 10^{19.41}$ molecule/cm³) or deuteroiodomethane ($[CD_3I]_0 \times 10^{19.35}$ molecule/cm³); at 600 K; $k_{rec} \times 10^{-10.1}$ [cm³/(molecule·s)] for R = CH₃ and $10^{-10.2}$ for R = CD₃

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- 5									
R <i>T</i> , K		log [I ₂]/	$\log r(T)$	log {[Z]/(molecule/cm ³)}			Half-lifetime, ms		$\log k_{3i}$
	(molecule/cm ³)	[molecule/(cm3 s)]	Ľ	R	HI	$1/k_{3i}[RI]$	$1/k_{\rm rec}[\mathbf{R}]$	[cm ³ /(molecule·s)] [Eq. (33)]	
CH ₃	567	15.30	11.64	13.0	10.1	7.3	15	940	-17.6±0.3
2	599	15.72	12.60	13.5	10.7	8.3	7	230	-17.2±0.3
i = m	619	16.19	13.12	14.0	11.0	9.4	3.5	140	-17.0±0.3
644	644	16.60	13.64	14.4	11.3	10.4	2.3	63	-16.8±0.3
	672	17.33	14.61	15.0	11.5	12.0	0.4	40	-16.0±0.3
CD_3	599	15.7±0.10	12.62	13.5	10.3		2.8	790	-16.8 ± 0.2
62:	625	16.3±0.20	13.02	14.1	10.6		1.8	400	-16.6±0.2
i = d	652	16.6±0.12	13.70	14.5	11.1		1.4	130	-16.5±0.2
		1							1



Fig. 4. Temperature dependence of the rate constant of reaction (15^3) and analogous reactions of trideuteroiodomethane and diiodomethane: (1) k_{3m} according to Table 4; (2) k_{3m} according to the reference [21]; (3) k_{3d} according to Table 5; (4) k'_3 according to Table 6; (5, 6) data of [22] for analogous reaction (15³) of the bromo- and chloroderivatives, respectively.

$$k_{\rm D} = k_{3d} = 10^{-11.3\pm0.3} \exp[-(7600\pm400) \text{ K}/T] \text{ cm}^3/(\text{molecule s}),$$

(500 K $\leq T \leq$ 700 K). (39)

It follows from expressions (39) and (35) that the activation energy $[(63\pm3) \text{ kJ mol}^{-1}]$ of limiting stage (38) of the CD₃I pyrolysis is lower by 4 kJ mol⁻¹ than the activation energy $[(67\pm6) \text{ kJ mol}^{-1}]$ of limiting stage (15³) of the iodomethane pyrolysis.

Kinetics of the gaseous CH_2I_2 pyrolysis. The kinetic curves of the molecular iodine accumulation in the diiodomethane pyrolysis are presented in Fig. 5. We conclude from the kinetic experiments that the limiting stage of the diiodomethane pyrolysis is reaction (40³).

$$CH_{2}I_{2} + I' \xrightarrow{k_{1}^{\prime}} CH_{2}I' + I_{2} - 57.6 \text{ kJ mol}^{-1},$$
$$(K_{c,1}^{\prime} = k_{1}^{\prime}/k_{-1}^{\prime}), \qquad (40^{1})$$

CH₂I₂
$$\xrightarrow{k_2}$$
 CH₂I⁻ + I⁻ - 206.4 kJ mol⁻¹,
 $(K_{c,2}^{\prime} = k_2^{\prime}/k_{-2}^{\prime}),$ (40²)



Fig. 5. Kinetics of I_2 accumulation in the isochoric-isothermal pyrolysis of diiodomethane [CH₂I₂]₀: (*I*) 2.35× 10¹⁸, (*2*) 4.06×10¹⁸, (*3*) 2.11×10¹⁹ molecule/cm³; *T*₁ 587±1, *T*₂ 610±1, *T*₃ 571±1, *T*₄ 590±1, *T*₅ 615±1, *T*₆ 617±1, *T*₇ 636±1 K.

$$CH_{2}I + CH_{2}I_{2} \xrightarrow{k_{3}} CH_{3}I + CHI_{2} + 28.2 \text{ kJ mol}^{-1},$$

 $(K_{c,3} = k_{3}/k_{-3}).$ (40³)

The gross-scheme of the pyrolysis looks like (41).

$$CH_2I_2 \rightarrow 1/2CH_4 + I_2 + 1/2C_{sol.} - 22.0 \text{ kJ mol}^{-1}.$$
 (41)

This implies that the rate equation for $[I_2]$ concentration looks like (42).

$$r = d[I_2]/dt = 2d[CH_4]/dt = 2k'_3[CH_2I][CH_2I_2].$$
(42)

The remaining equations are analogous to Eqs. (27), so, by-passing the integration operation, we obtain Eqs. (31^*) and (33^*) for the calculation of the required parameters in the quasistationary approximation.

$$[CH_2I]_t = \frac{K_{c,2}[CH_2I_2]}{\sqrt{K_{c,4}[I_2]}}$$
(31*)

$$k_{3}^{*} = \frac{r\sqrt{K_{c,4}[I_{2}]}}{2K_{c,2}([CH_{2}I_{2}]_{0} - [I_{2}])^{2}}$$
(33*)

Using thermodynamic tables [9], we calculate constant (34^*) of equilibrium (40^2) .

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$$K_{c,2m}(T) = 10^{25.00\pm0.03} \exp(-28013 \text{K/}T) \text{ molecule/cm}^3, (34^*)$$

The calculated data given in Table 5 allow us to present analytical expression (35^*) for the kinetic constant k'_3 (Fig. 4).

$$k_{\rm H} \equiv k_{3m} = 10^{-11.3 \pm 0.3} \exp[-(8060 \pm 700) \text{K}/T] \text{ cm}^3/(\text{molecule s}),$$

(500 K $\leq T \leq 1500$ K). (35*)

It follows from Table 5 that the $[CH_3]$ concentration is lower by 1–3 orders than the concentrations of other intermediate particles, which suppress the formation of ethane, but do not hinder the formation of methane from iodomethane formed in reaction (40³).

In our experiments we added neither hydrogen iodide nor other reagents to initial iodomethane, so the kinetic scheme of the pyrolysis was limited to three pairs of independent reactions (15^1) , (15^2) , and (15^3) . The reverse reaction in the last pair has appeared unessential, and in the first two pairs of reactions a quasistationary regime was established. Therefore, only one (required) rate constant k_{3m} and two equilibrium constants ($K_{c,2m}$ and $K_{c,4}$), which both can be calculated from the thermodynamic tables [9], enter into working formula (33). In such situation it is possible to find unambiguously the rate constant k_{3m} from the unique kinetic curve of I₂ accumulation, as it is demonstrated in Table 4.

So, it is possible to measure rate constants of limiting elementary reactions in the isochore isothermal pyrolysis of not only perfluoroalkyliodides [1– 4, 6], but also iodomethanes. Everything that occurs after a limiting stage, is a "black box" for a researcher, who limits himself by kinetic measurements of macrocomponents. However, something can be said about these reactions. So, in the pyrolysis of iodomethanes, reactions (15⁴) and (16), in which radicals CH₂I are "utilized", should be sufficiently fast as otherwise they would be limiting stages instead of reaction (15³). The rate constant k_{4m} should be greater than the kinetic constant k_{3m} by a factor of millions, lest the course of the is constrained in stage (15^4) . Analogously dissociative recombination (16) should proceed with a great (almost gas-kinetic) cross section. We note that in the previous work [5] it was reaction (16) {reaction (55) in the notations of [5]} which was accepted as a limiting stage, and therefore the kinetic constant k_{55} found there is underestimated by almost an order as compared to the true (almost gas-kinetic) k_0 value.

Reaction (16) of dissociative recombination is analogous to recombination (43) yielding the trifluroethane molecule, which is so high-energy [23] that in the very first vibration splits out one or two HF molecules in reactions (44).

$$CH_{3}^{'} + CF_{3}^{'} \rightarrow (CH_{3}CF_{3})^{*} + 424 \text{ kJ mol}^{-1}, \quad (43)$$

$$CH_{3}^{'} + CF_{3}^{'} \rightarrow CH_{2}=CF_{2} + HF(\nu=0) + 285 \text{ kJ mol}^{-1}, \quad \rightarrow CH_{2}=CF_{2} + HF(\nu=1) + 235 \text{ kJ mol}^{-1}, \quad \rightarrow CH_{2}=CF_{2} + HF(\nu=2) + 186 \text{ kJ mol}^{-1}, \quad \rightarrow CH_{2}=CF_{2} + HF(\nu=0) + 192 \text{ kJ mol}^{-1}, \quad CH_{3}^{'} + CF_{3}^{'} \rightarrow CH \equiv CF + 2HF(\nu=0) + 192 \text{ kJ mol}^{-1}, \quad \rightarrow CH \equiv CF + 2HF(\nu=1) + 93 \text{ kJ mol}^{-1}. \quad (44)$$

Basically all the elementary processes are reversible, but reaction (16) appears practically irreversible as C_2 molecules are condensed fast and irreversibly (at T 800 K) immediately in a gas phase [24].

$$C_{2} + C_{2} \rightarrow C_{4} + 620 \text{ kJ mol}^{-1},$$

$$C_{2} + CHI^{"} \rightarrow C_{3} + HI + 394 \text{ kJ mol}^{-1},$$

$$C_{2} + C_{3} \rightarrow C_{5} + 613 \text{ kJ mol}^{-1},$$

$$C_{4} + CHI^{"} \rightarrow C_{5} + HI + 390 \text{ kJ mol}^{-1},$$
..... etc. (45)

If C_2 HI molecules are formed in recombination (16) they also do not come back in scheme of reactions (15), being released from HI molecules either in a gas phase [see the bottom line in scheme (16)] or on reactor walls according to scheme (46).

$$C_2$$
HI (on a surface)
→ 2 C_{solid} + HI ↑ + 280±30 kJ mol⁻¹. (46)

Table 5. Parameters of the isochore isothermal pyrolysis of diiodom	ethane
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[CH ₂ I ₂] ₀ .	<i>T</i> , K	$log \{[I_2]/(molecule/cm^3)\}$	$\frac{\log [r(T)/(molecule/cm^3 s)]}{(molecule/cm^3 s)]}$	log {[Z]/(molecule/cm ³)}		Half-life time, ms		$\log \{k_3^\prime\}$
molecule/cm ³				I.	CH ₂ I	1/(k ₃ [CH ₂ I ₂])	$1/(k_{\rm rec}[CH_2\Gamma])$	[cm ³ /(molecule·s)]} [Eq. (33*)]
1018.37	587	16.2±0.1	13.93	13.6	12.4	65	400	-17.2±0.2
	610	16.9±0.1	14.15	14.2	12.5	50	350	-17.1±0.2
$10^{18.61}$	571	16.1±0.1	13.46	13.4	12.4	40	400	-17.8±0.2
	590	16.5±0.1	13.73	13.9	12.6	30	300	-17.7±0.2
	615	16.9 ± 0.1	14.18	14.3	12.8	20	200	-17.5 ± 0.2



Fig. 6. Scheme of a kinetic experimental installation. (1) DDS-30 or DVS-25 lamp; (2) quartz lenses; (3) quartz windows-stoppers; (4) metal thermostat-heater (accuracy of ± 1 K); (5) diaphragms; (6) quartz reaction vessel (diameter *d* 30 mm, length *l* 100-150 mm); (7) PP-63 potentiometer; (8) switch of monochromator working frequency; (9) MDR-3 monochromator; (10) FEU-18A photomultiplier; (11) self-recorder.

Biradicals CI₂^{\cdot} formed next after reaction (40³) in process (47) also do not come back in scheme of reactions (40), as they generate a cascade of energy favorable (and consequently irreversible at *T* 800 K) reactions (48).

$$CH_{2}I' + CHI_{2} \rightarrow CH_{3}I + CI_{2}^{2} + 80 \text{ kJ mol}^{-1}, \quad (47)$$

$$CI_{2}^{2} + C_{2} \rightarrow C_{3} + I_{2} + 285 \text{ kJ mol}^{-1}, \quad \dots \quad C_{2} + C_{2} \rightarrow C_{4} + 620 \text{ kJ mol}^{-1}, \quad \dots \quad \text{etc.} \quad (48)$$

Carbon clusters (45) formed in reactions (45) and (48) diffuse to reaction vessel walls, on which they are deposited in the form of a pyrocarbon layer.

The isochore isothermal pyrolysis method is not direct unlike pulse methods (pulse photolysis and pressure-jump methods [25]), so the rate constant to be determined definitely depends on the correctness of a postulated gross-process mechanism. However, direct methods have their imperfections. So, in a direct pressure-jump method (in a shock tube) temperature in a shock wave is calculated by a Hugoniot adiabat or by a deformation of spectral lines, the temperature and gas density in a shock wave being fast changed. On the contrary, in the isochore isothermal pyrolysis method, though intermediate particles are not directly recorded, the temperature and density of a pyrolyzed gas are strictly constant and are reliably measured by a thermometer and a manometer. Therefore, if stages of mechanism (2)–(5) and gross-scheme (1) of the pyrolysis correspond to a reality, it is possible to calculate unambiguously required kinetic constant k_5 from the kinetic curves of the accumulation-expenditure of macrocomponents by formula (11). Recently [6] we have applied such method to the iodide CF_3I that has allowed us to measure the rate constant k_5 in a transition region of pressures, and in the present work we have applied the isochore isothermal pyrolysis method to the compounds CH_3I and CH_2I_2 .

EXPERIMENTAL

The scheme of an experimental installation for kinetic studies by the isochore isothermal pyrolysis method is presented in Fig. 6. The iodides and bromides under study were purified from air oxygen by triple vacuum distillation, and from water admixtures by a 24-hour exposure above zeolite 4-5 Å, beforehand degassed in vacuum at 400°C. Solid triiodomethane was not dried, but only degassed. A reaction vessel (Fig. 6, position 6) was filled with an iodide under study on an OM-2 under a control of a standard manometer on a vacuum installation allowing vacuum from 10^{-2} up to 10^{-4} torr to be created, then was sealed off from the installation and placed in a thermostatic furnace (Fig. 6, position 4). Temperature in the furnace was maintained during pyrolysis accurate to ± 1 K, and the temperature gradient along a tube axis did not exceed 1 K on the length of 250 mm. The initial mixture of CH_3I (50 mol %) + CD_3I (50 mol %) in the isotope experiment was prepared by a gravimetric technique, then dried and degassed as described above.

In some experiments a cell was cooled by liquid nitrogen on the pyrolysis termination and then shaken, and a I₂ content was measured by thiosulfate titration that allowed us to check the reliability of published data on the gaseous iodine extinction with an accuracy of $\pm 3\%$. The iodide extinction was found from its optical density on a required wave length, if its concentration was measured beforehand (on an OM-2 manometer). The used extinction values are presented in Fig. 1.

The optical scheme of the kinetic installation allows us (alternately, with a resolution of ± 1 nm) to record optical density of a reaction vessel content either on an absorption wave length of a consumable iodide or on an absorption wave length of arising molecular iodine. Usually the kinetic experiment at a higher temperature was carried out in the same quartz cell and with the same mixture, which was studied at a lower temperature.

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