1127. *Gas-phase Eliminations. Part IV.* The Pyrolyses of Isopropyl and s-Butyl Iodide.*

By J. L. Holmes and Allan Maccoll.

Pyrolysis of isopropyl iodide in a static system from 240° to 357° yielded only iodine, propane, and propene, in equimolar proportions. The reaction was homogeneous and of the first order from 290° to 357°. The Arrhenius parameters were log A 14·79 and E 47·96 kcal. mole^{-1}. Iodine-catalysed decomposition became important below 290°. The effects of adding iodine, propene, and nitric oxide suggested that the first-order process was unimolecular elimination of hydrogen iodide, and that this was followed by a rapid reaction between hydrogen iodide and isopropyl iodide to yield the observed products. The kinetics of the gas-phase reactions between hydrogen iodide and iso-propyl iodide, and between hydrogen iodide and propene, are also reported.

The pyrolysis of s-butyl iodide was also studied, from 250° to 330°. Above 290° the reaction was homogeneous and of the first order, with log A 15·20 and E 47·91 kcal. mole^{-1}. Calculation of the first-order rates was complicated by the fact that hydrogen iodide was found in amounts up to 50% of the iodine produced. It was concluded that the first-order rate represented that of the reaction s-$C_4H_9I \longrightarrow C_4H_8 + HI$. Below 290° an autocatalytic reaction became of increasing kinetic importance, as in the case of isopropyl iodide. The nature of the olefinic products and the possibility of catalysis by hydrogen iodide were also studied.

On pyrolysis, monochloro- and monobromo-alkanes yield a halogen acid and an olefin. With the chlorides, radical-chain processes are absent and the mechanism is unimolecular elimination of hydrogen chloride. The bromides display three reaction mechanisms, namely, a radical-chain process, a radical-non-chain process, and unimolecular elimination of hydrogen bromide. Alkyl iodides, on pyrolysis, yield iodine, an olefin, and the corresponding paraffin; the mechanisms of these reactions are not well established. Other

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* Part III, *J.*, 1962, 335. For a preliminary account see *Proc. Chem. Soc.*, 1957, 175.

authors[1] have shown that for n-propyl, n-butyl, isopropyl, s-butyl, and isobutyl iodide unimolecular elimination of halogen acid and iodine-catalysed decompositions are both feasible, but they were unable to prove unequivocally the mechanisms of these processes.

It seemed possible from Ogg's work[1b] that isopropyl iodide decomposed by unimolecular elimination of hydrogen iodide, so we chose this compound for initial investigation. Ogg had rejected this mechanism on the grounds that the reaction $C_3H_7I + HI \longrightarrow C_3H_8 + I_2$, would be slower than $C_3H_7I \longrightarrow C_3H_6 + HI$, thus prohibiting the observed formation of iodine and propane. He based this argument on his own earlier work[2] on the kinetics of the gas-phase reactions of methyl, ethyl, and n-propyl iodide with hydrogen iodide (see also Benson and O'Neal[3]). We investigated first, therefore, the reaction between isopropyl iodide and hydrogen iodide.

EXPERIMENTAL

Materials.—Isopropyl iodide (commercial) was freed from iodine by shaking it with mercury, dried, and fractionated twice. It then had b. p. 89·0°/738 mm., n_D^{25} 1·4966, d^{20} 1·705 (cf. Timmermans *et al.*[4] 89·45°/760 mm., n_D^{25} 1·4970, d^{20} 1·704).

Anhydrous hydrogen iodide was prepared from the concentrated aqueous solution (commercial) by Dillon and Young's method[5]

Iodine was of " AnalaR " purity. It was sublimed and degassed *in vacuo*.

" Pure " propene, from a cylinder, was passed over phosphorus pentoxide and degassed before use. Gas chromatography showed the absence of propane and lighter or heavier hydrocarbons up to C_6.

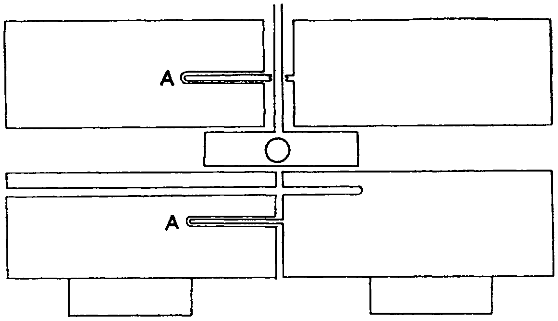

FIG. 1. The thermostat and reaction vessel.
A, Thermocouple well.

Nitric oxide was prepared by the reaction of a nitrite on acidified ferrous sulphate.[6]

Commercial s-butyl iodide was shaken with mercury to remove iodine, dried, and fractionated from pure, dry sodium hydrogen carbonate. The fraction with b. p. 119·6—119·7°/764 mm. and n_D^{25} 1·4973, was collected and used in the kinetic experiments (lit., b. p.[4] 120·0°, n_D^{25} 1·4974 [7]).

Apparatus.—The vacuum-system was of conventional design. Silicone grease was used on all heated stopcocks as it was little affected by iodine vapour. A Pyrex-glass Bourdon gauge was used for pressure measurements, the " spoon " being heated by a closely wound nichrome coil which surrounded but did not touch it.

Fig. 1 shows the thermostat which consisted of two cylindrical aluminium blocks, joined

[1] Jones and Ogg, *J. Amer. Chem. Soc.*, 1937, **59**, (*a*) 1931, 1934, (*b*) 1939; (*c*) Jones, *ibid.*, 1938, **60**, 1877; Ogg and Polanyi, *Trans. Faraday Soc.*, 1935, **31**, 482; Butler and Polanyi, *ibid.*, 1943, **39**, 19.

[2] Ogg, *J. Amer. Chem. Soc.*, 1934, **56**, 526.

[3] Benson and O'Neal, *J. Chem. Phys.*, 1962, **34**, 514.

[4] Timmermans and Delcourt, *J. Chim. Phys.*, 1934, **31**, 85.

[5] Dillon and Young, *J. Amer. Chem. Soc.*, 1929, **51**, 2389.

[6] *Inorg. Synth.*, Vol. II, p. 126.

[7] Audsley and Goss, *J.*, 1942, 358.

endwise by four steel pins. Each block was wound with nichrome wire, giving zero temperature-gradient in the central half of the combination, and then lagged with asbestos. The blocks were drilled in two directions at right angles to each other to allow beams of light to be passed either lengthwise (6 cm. path) or across the vessel (2 cm. path).

The optical system is shown in Fig. 2. The lamp was a 100-w projection lamp, cooled by compressed air. The photo-cells were two Cintel VB 39 photometric photoelectric cells, and the cathodes were connected to the grids of two pentodes. The valve cathodes were connected across a spot galvanometer of sensitivity 113 mm./mA. A variable shunt allowed up to a ten-fold reduction of sensitivity. The lenses were of glass. The filters G were two Ilford 604 Spectrum green, gelatin-in-glass filters. They were protected by Chance ON20 heat-absorbing filters H. The iris diaphragm D was calibrated for percentage transmission. The sizes of the lamp-house windows were such that light of approximately equal intensity fell on the photo-cells when the reaction vessel was empty. The spectrophotometric apparatus was calibrated for iodine by introducing known amounts into a removable, heated side-arm of the reaction vessel. Galvanometer deflections were read for various concentrations of iodine. By using the calibrated iris diaphragm it was shown that for 12 mg. of iodine (the maximum used), absorption was only about 20%.

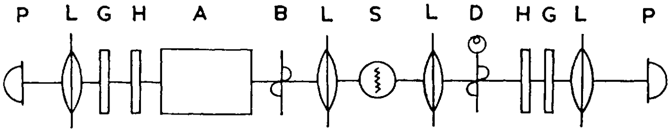

FIG. 2. The optical system.

A, reaction vessel; B, iris diaphragm; D, calibrated iris; H and G, heat and green filters; L, collimating lens; P, photo-cells; S, projection lamp.

PROCEDURE AND RESULTS

The Reaction between Isopropyl Iodide and Hydrogen Iodide.—Procedure. Isopropyl iodide and hydrogen iodide were degassed before each run. Hydrogen iodide was admitted to the reaction vessel, the pressure was noted, and then the gas was frozen out by liquid nitrogen into a side-arm in the reaction vessel. Some of the alkyl iodide was then allowed to distil into the cooled side-arm, and the initial steady galvanometer reading noted. The vacuum-flask containing liquid nitrogen was removed from the side-arm which was then quickly flamed and covered with its auxiliary heater, and a stop-clock was started. The total pressure of the reactants was noted and the isopropyl iodide pressure obtained by difference. Galvanometer readings were taken at regular time intervals, the final pressure was noted, the reaction-vessel tap was opened, and the products were pumped away to a trap cooled in liquid nitrogen. No change in pressure was observed in any of the runs. All the products were completely condensed by liquid nitrogen. In one run the reactants were left together for several hours; the products were condensed into a trap cooled in liquid nitrogen and containing a few pieces of soda-lime, to absorb the excess of hydrogen iodide. The refrigerant was replaced by solid carbon dioxide–acetone, and the gas liberated was condensed in a sampling tube cooled by liquid nitrogen. The collected material was then analysed by gas chromatography, for C_1—C_5 hydrocarbons. Only propane was found.

Results. Analytical results for this reaction were obtained solely from the spectrophotometric measurements. Fig. 3 shows two typical iodine-pressure–time curves at the single temperature investigated (216°). The results fitted the autocatalytic rate expression

$$d[I_2]/dt = k_{1\cdot5}[C_3H_7I][I_2]^{\frac{1}{2}}.$$

Fig. 4 shows the plot of the logarithmic fraction of the integrated rate equation, against time for the runs shown in Fig. 3. The integrated rate equation is

$$k_{1\cdot5} = \{2\cdot303/t[C_3H_7I]_0^{\frac{1}{2}}\}\log([C_3H_7I]_0^{\frac{1}{2}} + [I_2]^{\frac{1}{2}})/([C_3H_7I]_0^{\frac{1}{2}} - [I_2]^{\frac{1}{2}}).$$

The rate constants (Table 1) varied between the limits 2·6—6·9 × 10^{-5} sec.$^{-1}$ mm.$^{-\frac{1}{2}}$ but did not depend in any simple way on the partial pressures of the reactants.

TABLE 1.

The reaction between isopropyl iodide and hydrogen iodide at 216°.

Pressure (mm.) C_3H_7I	Pressure (mm.) HI	10^5k (sec.$^{-1}$ mm.$^{-\frac{1}{2}}$)	Pressure (mm.) of I_2 at zero time	Pressure (mm.) C_3H_7I	Pressure (mm.) HI	10^5k (sec.$^{-1}$ mm.$^{-\frac{1}{2}}$)	Pressure (mm.) of I_2 at zero time
58·3	182·2	6·03	0·17	66·3	67·5	4·80	—
54·2	125·0	6·43	0·17	27·5	186·0	2·63	0·07
49·2	79·8	6·20	—	110·3	46·7	4·60	0·29
53·0	62·2	6·50	0·14	34·9	16·2	3·25	0·09
50·4	57·6	6·05	0·13	42·2	55·2	4·85	0·11
49·5	88·1	6·90	0·13	53·8	139·5	5·30	0·14
61·3	79·7	6·61	0·16	16·9	184·3	2·88	—
71·6	69·0	5·67	0·18	24·4	26·1	9·07 (236°)	0·07
50·0	42·1	5·55	0·17				

The iodine necessary to initiate this autocatalysis was probably introduced as impurity in one of the reactants. Extrapolation of the log plots to zero time allowed calculation of the concentrations of the initiating iodine; these were of the order of 0·1 mm.

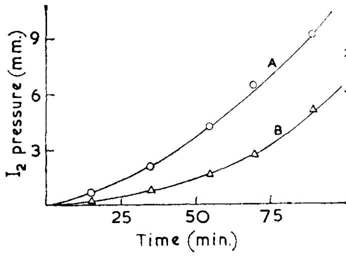

FIG. 3.

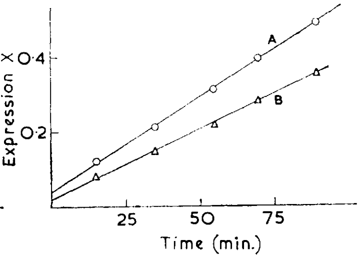

FIG. 4.

FIG. 3. Iodine pressure–time curves for the reaction of isopropyl iodide and hydrogen iodide.

(A) Pr^{i}I 42·2 mm., HI 55·2 mm.
(B) Pr^{i}I 27·5 mm., HI 186 mm.

FIG. 4. Logarithmic plots for the runs shown in Fig. 3.
$X = \log([RI]^{\frac{1}{2}} + [I_2]^{\frac{1}{2}})/([RI]^{\frac{1}{2}} - [I_2]^{\frac{1}{2}})$.

The reactions

$$2HI \longrightarrow H_2 + I_2 \quad \ldots \ldots \quad (3)$$

$$2Pr^iI \longrightarrow C_3H_8 + C_3H_6 + I_2 \quad \ldots \ldots \quad (4)$$

would necessarily give rise to long induction periods and production of hydrogen and propene accompanied by a pressure increase; none of these was observed and so these reactions were discounted as possible sources of iodine. Also, since pressure changes were not observed, reactions such as

$$C_3H_7\cdot + C_3H_7\cdot \longrightarrow C_6H_{14} \quad \ldots \ldots \quad (5)$$

$$C_3H_7\cdot + C_3H_7I \longrightarrow C_3H_8 + C_3H_6 + I\cdot \quad \ldots \ldots \quad (6)$$

can be neglected.

The single result at 236° suggested that the reaction had a small temperature coefficient. The following mechanism is proposed:

$$I\cdot + C_3H_7I \longrightarrow C_3H_7\cdot + I_2 \quad \ldots \ldots \quad (7)$$

$$C_3H_7\cdot + HI \longrightarrow C_3H_8 + I\cdot \quad \ldots \ldots \quad (8)$$

$$I\cdot + I\cdot + X \rightleftharpoons I_2 + X \quad \ldots \ldots \quad (9)$$

Reaction (7) is the rate-determining step. By means of the thermochemical data,[8] $\Delta H_f^{298}\text{I}\cdot = 25\cdot5$, $\Delta H_f^{298}\text{C}_3\text{H}_7\cdot = 17$, $\Delta H_f^{298}\text{C}_3\text{H}_7\text{I} = -10\cdot5$, $D(\text{HI}) = 71$, and heat of sublimation $\Delta H_f^{298}\text{I}_2 = 15$ kcal. mole^{-1}, the heat of reaction (7) was found to be 17 kcal. mole^{-1}, which is a lower limit for the activation energy of that reaction. Reaction (8), however, is exothermic to the extent of 23 kcal. mole^{-1}, and the work of Ogg and Williams [9] on the photolysis of alkyl iodides in the presence of hydrogen iodide suggests that $E_8 \approx 0$.

The Pyrolysis of Isopropyl Iodide.—In these experiments the reaction vessel was given a thin carbonaceous coating as described by Maccoll,[10] to eliminate heterogeneous processes. Gases uncondensable by liquid nitrogen were never observed. Analysis of the light hydrocarbons by gas–liquid chromatography showed only the presence of propane and propene, in equimolar amounts. The reaction was studied by measuring the pressure increase and titrating the iodine produced at the end of each run. The iodine was washed out of the trap, into which it had been condensed, by means of potassium iodide solution and was then titrated with 0·02N-sodium thiosulphate, starch being used as indicator. At the end point a few c.c. of potassium iodate solution were added and the mixture was left in the dark for 2 min. If the blue starch–iodide colour had returned, the iodine was titrated and this figure was reported as hydrogen iodide. Hydrogen iodide was never found in the products from runs below 320°, but it was observed at higher temperatures. At 343° the amount of hydrogen iodide produced tended to increase with decrease of initial isopropyl iodide pressure. However, the fraction of hydrogen iodide appearing at the half-life was only ~0·5% of the products, and so it was not necessary to correct the kinetic results. Added iodine had no effect on the rate except at temperatures below 290°, as described below. In a number of runs the pressure change and the amount of iodine were measured simultaneously, the latter by spectrophotometry; in these experiments a reaction vessel which had only been very lightly "coated" was used. The agreement between the analyses (Fig. 5) was good. Iodine titrations agreed well with the pressure increase up to the half-life of the reaction.

TABLE 2.

The decomposition of isopropyl iodide.

Temp.	Initial pressure (mm.) of C_3H_7I	Final pressure (mm.)	I_2 (by titre, mm.)	10^5k (sec.$^{-1}$)
357·0°	10·25	13·50	3·1	164·0
	21·85	28·40	6·5	155 0
	34·10	46·35	12·9	147·0
	58·90	73·30	—	162·0
343·0	13·55	17·60	3·5	58·1
	44·35	60·75	15·2	61·0
	67·40	85·10	—	56·6
342·5	26·50	34·60	8·4	54·1
333·8	9·70	11·80	2·1	32·9
	33·40	41·65	8·6	32·8
	57·60	70·70	—	34·3
325·0	13·35	17·45	—	16·9
	26·90	35·05	—	16·4
	43·60	57·00	—	16·7
314·2°	8·30	11·60	—	7·24
	31·15	39·85	—	8·52
	86·90	116·50	—	7·89
306·0	12·75	16·05	3·35 (3·35 *)	4·22
	20·77	27·10	5·90 (5·35 *)	4·59
	44·55	58·20	13·60	4·87
301·0	11·30	14·60	3·15	3·31
	26·65	34·20	7·75	3·25
	60·35	76·55	16·40	3·40
295·1	11·80	14·50	—	2·11
	25·50	32·15	—	2·11
	37·05	46·55	10·70	2·36
	69·90	88·00	18·60	1·94

* Iodine by spectrophotometry.

The kinetics were calculated on the basis of equation (4). That the reaction was of the first order over the temperature range 290—357° is shown by the lack of change of rate constant with initial iodide pressure (Table 2). The first-order rate constants were calculated from the expression

$$k = \{2\cdot303/t\}\log P_0/(P_0 - 2\Delta P),$$

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[8] Trotman-Dickenson, "Gas Kinetics," Butterworths, London, 1955, pp. 12, 15.

[9] Ogg and Williams, *J. Chem. Phys.*, 1937, **15**, 691.

[10] Maccoll, *J.*, 1955, 965.

ΔP being the pressure increase after time t, and the equation was followed up to ~40% decomposition.

In the above temperature range the reaction was homogeneous. A vessel packed with silica wool was "seasoned" by the method used previously.[10] The results are shown in Table 3.

TABLE 3.

The homogeneity of the reaction.

	10^4k (sec.$^{-1}$) at		
Temperature	343°	310°	286°
Surface/Volume 1·2 cm.$^{-1}$ (unpacked vessel)	57·5	6·38	1·05
Surface/Volume ∞ (packed vessel)	61·6	6·85	1·4

At 286° the first-order plots in the packed vessel were poor, the rate being somewhat pressure-dependent.

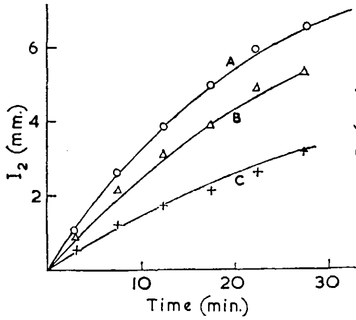

FIG. 5.

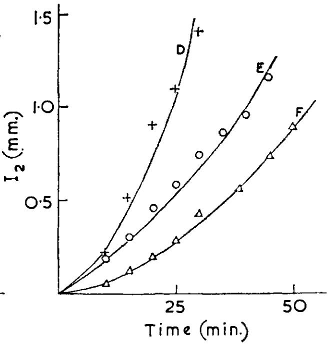

FIG. 6.

FIG. 5. Iodine analyses.

Lines denote pressure readings; points denote spectrophotometer readings.

Initial iodine pressure: (A) 24·4 mm.; (B) 20·77 mm.; (C) 12·75 mm.

FIG. 6. Pyrolysis of isopropyl iodide at 257°.

Initial iodide pressure: (D) 68·9 mm.; (E) 31·9 mm. + 1·4 mm. of iodine; (F) 31·4 mm.

The temperature-dependence of the homogeneous first-order rate constant is shown in Table 4. These figures were fitted to the Arrhenius equation:

$$\log k = 14{\cdot}793 - (47{,}960 \pm 80)/2{\cdot}303RT;$$

a least-squares calculation gave the standard deviation shown.

TABLE 4.

The temperature dependence of k_1.

Temp.	275·3°	295·1°	301·0°	306·0°	314·2°	325·0°	333·8°	343·0°	357·0°
No. of runs	9	31	15	17	19	15	10	22	10
10^5k (sec.$^{-1}$)	4·62	22·7	33·0	46·7	81·5	176	342	575	1520

At temperatures below about 290°, an autocatalytic decomposition became of increasing kinetic importance, and addition of iodine accelerated the reaction.

Some pressure–time curves at 257° are shown in Fig. 6; here the kinetics fitted the differential equation

$$d[I_2]/dt = k[C_3H_7I] + k_7[C_3H_7I][I_2]^{\frac{1}{2}}.$$

Fig. 7 shows the results obtained when values for $\{1/[C_3H_7I]\}d[I_2]/dt$ are plotted against $[I_2]^{\frac{1}{2}}$. Values for k_7 at 240° and 257° were 3·48 and $10{\cdot}0 \times 10^{-6}$ $mm.^{-\frac{1}{2}}$ $sec.^{-1}$, respectively. The activation energy derived from these results is about 20 kcal. $mole^{-1}$ for reaction (7).

To investigate the mechanism of the first-order decomposition, the effects of propene and nitric oxide were examined. The effect of propene was studied at 295°, at which temperature the pyrolysis was conveniently slow and the autocatalytic reaction undetectable. The propene : isopropyl iodide ratio was varied in each run. Every experiment was stopped after 50 min. and the iodine produced estimated by titration. The pressure increase was always less than the iodine measured by titre (see Table 5). The end-point of the titres was not sharp, the starch–iodide colour slowly returning after the first end-point had been reached. Approximate first-order rate constants were calculated from these iodine determinations, as shown in Table 5; the average value of 10^5k_1 (the last entry being excluded) was 21·1 $sec.^{-1}$, in reasonable agreement with the value 22·7 $sec.^{-1}$, observed (Table 4) in the absence of propene.

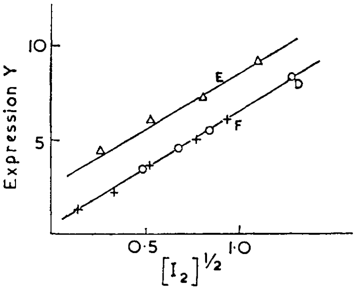

FIG. 7.

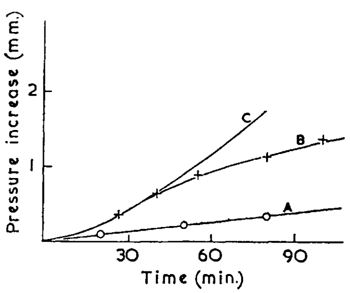

FIG. 8.

FIG. 7. Rate plots for runs (D), (E), and (F) of Fig. 6.
$Y = (d[I_2]/dt).1/[C_3H_7I]_t$ (10^{-4} $min.^{-1}$).

FIG. 8. Effect of nitric oxide on pyrolysis of isopropyl iodide at 257°.
(A) Pr^iI 32 mm., NO 8·3 mm.; (B) Pr^iI 33 mm., NO 2·8 mm.; (C) Pr^iI 31 mm.

TABLE 5.

The effect of propene on the decomposition of isopropyl iodide at 295°.

C_3H_6/C_3H_7I	0	1·74	3·77	4·55	5·64	10·1
Pressure increase/Iodine by titre	1·0	0·73	0·67	0·53	0·47	0·00
10^5k ($sec.^{-1}$) (calc. from I_2 titres)	22·7	24·1	21·6	18·1	20·7	14·4

Iodine and propene were left together under the same conditions for 50 min.; 80% of the iodine was recovered by titration, no non-condensable gas was found, and the iodine titration end-point did not wander.

At 334° and 295° nitric oxide, in concentration from 2% to 30% of the total initial pressure, had no effect on the kinetics of the pyrolysis of isopropyl iodide. At 257°, where the autocatalytic decomposition was important, nitric oxide had a marked effect as is shown in Fig. 8. Here, the pressure change was substantially reduced.

The Pyrolysis of s-Butyl Iodide.—This reaction has been briefly studied over the temperature range 250—330° with iodide pressures of 8—120 mm. Gases uncondensable by liquid nitrogen were not observed at any temperature. The hydrocarbon products were analysed by vapour-phase chromatography. Butane, but-1-ene, and *cis-* and *trans*-but-2-ene were found; the paraffin and total olefins were in approximately equimolar proportions. Iodine and hydrogen iodide were determined by titration. The amount of hydrogen iodide produced decreased with increase of initial iodide pressure and tended to increase with rise of temperature (Table 6).

In the temperature range 290—330°, the pyrolysis was found to be of the first order and essentially homogeneous. No change of rate was observed when the surface : volume ratio was increased seven-fold. Addition of iodine did not accelerate the decomposition, but addition of hydrogen iodide did cause a slight acceleration.

Results were calculated as for isopropyl iodide, that is, from the reaction

$$\text{s-C}_4\text{H}_9\text{I} \longrightarrow \text{C}_4\text{H}_8 + \text{C}_4\text{H}_{10} + \text{I}_2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (11)$$

and the equation

$$k_{11} = \{2{\cdot}303/t\}\log P_0/(P_0 - 2\Delta P).$$

Pressure–time curves and the corresponding log plots were similar to those obtained for isopropyl iodide, except that the log plots were slightly concave upwards. This non-linearity is attributed to the fact that $(P_0 - 2\Delta P)$ does not represent exactly the amount of iodide remaining since some hydrogen iodide escaped reaction, and so this method exaggerates the degree of decomposition. Initial rates were therefore found by plotting $\mathrm{d}\{\log P_0/(P_0 - 2\Delta P)\}/\mathrm{d}t$ against t and extrapolating the lines to zero time. Some rate constants obtained in this way are shown in Table 6.

TABLE 6.

Rate constants and products of the pyrolysis of s-butyl iodide.

	s-C_4H_9I (mm.)			Titrations				
				HI		I_2		
Temp.	P_0	ΔP	Time (sec.)	mm.	%	mm.	%	10^4k_{11} (sec.$^{-1}$)
295·1°	3·25	0·80	600	0·80	61	0·50	39	—
	8·60	1·70	600	0·60	36	1·15	64	5·57
	18·60	3·75	600	0·80	22	2·90	78	5·53
	31·65	5·75	600	1·00	16	5·20	84	5·57
	52·05	10·90	600	1·20	12	9·15	88	5·49
	87·40	17·30	480	1·40	8	15·60	92	—
305·5	10·60	2·50	360	0·90	37	1·55	63	13·00
	31·05	6·90	330	0·85	15	5·20	85	12·40
	75·05	13·25	240	1·20	9	11·80	91	12·70
314·2	9·15	2·75	300	0·50	24	1·60	76	24·30
	19·30	5·90	300	1·65	30	3·90	70	26·40
	34·75	11·35	300	1·10	13	7·60	87	24·30
321·0	9·80	2·75	180	1·20	40	1·80	60	35·50
	18·50	5·60	180	1·90	35	3·50	65	34·90
	29·10	7·90	180	1·40	18	6·20	82	30·50
	62·90	13·80	180	—	—	—	—	—
330·0	15·55	3·70	80	1·25	33	2·50	67	67·90
	25·30	6·20	80	1·40	24	4·40	76	71·40
	40·65	10·90	95	2·35	22	8·40	78	67·00

An Arrhenius plot was drawn from the results in Table 7. The parameters were log A 15·20 and E 47·91 ± 0·160 kcal. mole^{-1}.

TABLE 7.

Variation of first-order rate constant with temperature for s-butyl iodide.

Temp.	330·0°	320·0°	314·2°	305·5°	295·1°
No. of runs	8	8	11	9	12
10^4k_{11} (sec.$^{-1}$)	67·2	35·1	23·9	12·5	5·67

Some runs were performed at 250°. At this temperature the decomposition is essentially autocatalytic, as was found for isopropyl iodide at 257°. The results fitted the kinetic expression

$$-\mathrm{d}[\mathrm{C_4H_9I}]/\mathrm{d}t = k_{11}[\mathrm{C_4H_9I}] + k_{12}[\mathrm{C_4H_9I}][\mathrm{I_2}]^{\frac{1}{2}},$$

where reaction (12) is

$$\text{I}\cdot + \text{s-C}_4\text{H}_9\text{I} \longrightarrow \text{s-C}_4\text{H}_9\cdot + \text{I}_2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (12)$$

The value for k_{12} was found to be $\sim 1 \times 10^{-5}$ mm.$^{-\frac{1}{2}}$ sec.$^{-1}$.

DISCUSSION

The experiments with isopropyl iodide over the temperature range 290—357° showed that the pyrolysis was homogeneous, of the first order, and of stoicheiometry $2C_3H_7I \longrightarrow C_3H_8 + C_3H_6 + I_2$. The following reactions have been considered [1b] as possibly playing some part in the pyrolysis mechanism:

$$C_3H_7I \longrightarrow C_3H_6 + HI \tag{2}$$

$$C_3H_7I \longrightarrow C_3H_7\cdot + I\cdot \tag{13}$$

$$C_3H_7I + HI \longrightarrow C_3H_8 + I_2 \tag{1}$$

$$\left.\begin{aligned} C_3H_7I + C_3H_7\cdot &\longrightarrow C_3H_8 + C_3H_6I\cdot \\ C_3H_6I\cdot &\longrightarrow C_3H_6 + I\cdot \end{aligned}\right\} \tag{6}$$

$$C_3H_7\cdot + C_3H_7\cdot \longrightarrow C_3H_8 + C_3H_6 \tag{5a}$$

$$\longrightarrow C_6H_{14} \tag{5b}$$

$$C_3H_7\cdot + I_2 \longrightarrow C_3H_6 + HI + I\cdot \tag{14}$$

$$C_3H_7I + I\cdot \longrightarrow C_3H_7\cdot + I_2 \tag{7}$$

$$I\cdot + I\cdot + X \rightleftharpoons I_2 + X \tag{9}$$

Experiments with added propene did not show a marked decrease in rate of decomposition of the iodide, as measured by iodine titres (Table 5). Pressure changes were decreased to a greater extent. It is suggested that the main effect of propene is to retard the pyrolysis by means of the back-reaction:

$$C_3H_6 + HI \longrightarrow C_3H_7I \tag{-2}$$

This may account for the fall-off of first-order rate constants beyond the half-life. Some addition of iodine to propene may also take place, partially accounting for the drop in iodine production. If some process involving radicals took an important part in the pyrolysis more marked effects would have been observed. That nitric oxide had no effect on the pyrolysis in the above temperature range strongly suggests that free-radical processes can be neglected. These conclusions eliminate all the above reactions except (2) and (1). The mechanism of the first-order, homogeneous decomposition of isopropyl iodide is therefore a unimolecular elimination of hydrogen iodide followed by a rapid reaction between the alkyl iodide and hydrogen iodide.

The results of experiments at lower temperatures have shown that free-radical processes must occur and that the rate-determining process under these conditions was the autocatalytic reaction (7). When nitric oxide was added, the pressure increase was much reduced, indicating the presence of free radicals. In the absence of nitric oxide, the following reaction scheme

$$I\cdot + C_3H_7I \longrightarrow C_3H_7\cdot + I_2 \tag{7}$$

$$C_3H_7\cdot + C_3H_7I \longrightarrow C_3H_8 + C_3H_8 + I\cdot \tag{6}$$

$$2C_3H_7\cdot \longrightarrow C_3H_8 + C_3H_6 \tag{5a}$$

$$2C_3H_7\cdot \longrightarrow C_6H_{14} \tag{5b}$$

$$I\cdot + I\cdot + X \rightleftharpoons I_2 + X \tag{9}$$

represents the mechanism of the low-temperature autocatalysed pyrolysis. Pressure changes were found to give results some 5—10% lower than iodine analyses. This could be attributed to the occurrence of 10—15% of reactions (5a and b), the latter producing a net pressure change of zero; the disproportionation : combination ratio for isopropyl radicals [11] is about 0·64. Homolysis of the C–I bond can be discounted on energetic

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[11] Kerr and Trotman-Dickenson, "Progress in Reaction Kinetics," Pergamon Press, Oxford, 1961, p. 111.

grounds. Thermodynamic data [8] give a value for $D(\mathrm{Pr^i{-}I})$ of $\sim$53 kcal. mole^{-1} and therefore at 250° the rate of reaction (13) would be negligible compared with that found experimentally.

The difference in values for k_7 obtained from the study of the reaction between isopropyl iodide and hydrogen iodide (236°; $k_7 = 9 \times 10^{-5}$ sec.$^{-1}$ mm.$^{-\frac{1}{2}}$) and from the autocatalysed pyrolysis can be accounted for, since in the first case the removal of isopropyl radicals from the equilibrium, $\mathrm{I\cdot + C_3H_7I \rightleftharpoons C_3H_7\cdot + I_2}$, was greatly facilitated by the presence of an excess of hydrogen iodide.

The results obtained with s-butyl iodide were very similar to those obtained with isopropyl iodide. It was concluded, therefore, that the mechanisms are essentially the same, namely:

$$\mathrm{Bu^sI \longrightarrow C_4H_8 + HI} \tag{17}$$

$$\mathrm{HI + Bu^sI \longrightarrow C_4H_{10} + I_2} \tag{18}$$

being the reactions occurring in the first-order temperature range 290—330°; reaction (17) is the rate-determining unimolecular elimination.

At the lower temperature, 250°, the autocatalytic reaction

$$\mathrm{I\cdot + Bu^sI \longrightarrow C_4H_9\cdot + I_2} \tag{14}$$

was rate-determining, this reaction being followed by

$$\mathrm{C_4H_9\cdot + C_4H_9I \longrightarrow C_4H_{10} + C_4H_8 + I\cdot} \tag{19}$$

The similarity of these elimination reactions to those obtaining with the isopropyl and s-butyl chloride and bromide, is shown in Table 8, where relative rates at 600°K are given. This correlation is further evidence for a common mechanism of elimination of halogen acid.

TABLE 8.

Relative rates of decomposition of isopropyl and s-butyl halide at 600°K.

	Chloride	Bromide	Iodide
Isopropyl	1 [12]	16 [13]	210
s-Butyl	1 [13]	13 [14]	180
Isopropyl/s-Butyl	0·31	0·39	0·37

Since this work was completed, a paper appeared by Bose and Benson [15] dealing with the equilibrium between hydrogen iodide, propene, and isopropyl iodide, and the kinetics of the addition reaction over the temperature range 209—249°. The equilibrium constant was measured at 238·5° and used in conjunction with the rate constant for addition, to give a value of $10^{-5\cdot08}$ (later [16] corrected to $10^{-4\cdot75}$). This they said was in better agreement with the value of Jones and Ogg,[1b] calculated from $k_1 = 1{\cdot}59 \times 10^{13} \exp(-42{,}900/\boldsymbol{R}T)$, namely, $10^{-5\cdot15}$ than with our value, namely, $10^{-6\cdot14}$. The last-mentioned value was calculated from the Arrhenius parameters given by us in the preliminary note; using the results reported here gives the value $10^{-5\cdot68}$. If the reaction is molecular, then it is difficult to put forward a mechanism for lowering the rate, so it appears that the slowest rate should be the most reliable. A possible explanation of Jones and Ogg's and Benson's results is that the reaction they followed occurred in part on the walls of the reaction vessel, thus leading to enhanced rates. This would, of course, not affect the equilibrium constant.

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[12] Howlett, *J.*, 1952, 3695.
[13] Stone, M.Sc. Thesis, University of London, 1958.
[14] Maccoll and Thomas, *J.*, 1955, 2445.
[15] Bose and Benson, *J. Chem. Phys.*, 1962, **37**, 1081.
[16] Bose and Benson, *J. Chem. Phys.*, 1962, **37**, 2935.

APPENDIX

The Reaction between Hydrogen Iodide and Propene.—A brief investigation was made of the reaction between hydrogen iodide and propene at 295°, which was accompanied by a pressure drop. The products were propane and iodine, and the stoicheiometry of the reaction was represented by the equation, $C_3H_6 + 2HI \longrightarrow C_3H_8 + I_2$. Kinetics measured by the pressure change fitted the second-order rate equation

$$k_{10} = \{2{\cdot}303/t(p^{\circ}_{C_3H_6} - p^{\circ}_{HI})\} \log(p^{\circ}_{C_3H_6} - P)p^{\circ}_{HI}/(p^{\circ}_{HI} - 2P)p^{\circ}_{C_3H_6} \text{ (mm.}^{-1}\text{ sec.}^{-1}),$$

where P is the pressure decrease. A typical pressure–time curve and the corresponding plot of log $(p^{\circ}_{C_3H_6} - P)/(p^{\circ}_{HI} - 2P)$ against t, are shown in Fig. 9. The rate constants k_{10} (Table 10) are pressure-dependent. No simple explanation for this result could be found. It has been suggested by M. Back[17] that this may be due to addition of hydrogen iodide to propene, occurring inadvertently when the reactants are being introduced into the reaction vessel and giving randomly inaccurate values for the initial pressures of the reactants. The mechanism proposed for this reaction was:

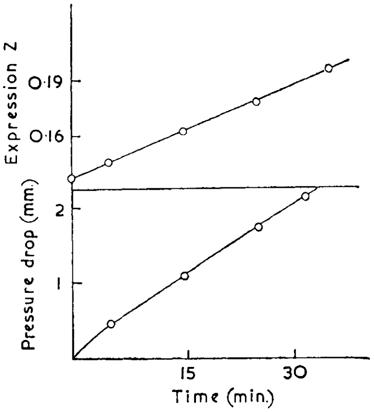

FIG. 9. Pressure–time curve and log plot for the reaction between propene and hydrogen iodide at 295°. Initial reaction pressures: C_3H_6, 35·8 mm.; HI, 26·1 mm.

$Z = \log (p^{\circ}_{C_3H_6} - P)/(p^{\circ}_{HI} - 2P)$.

TABLE 10.

The reaction between propene and hydrogen iodide.

C_3H_6 (mm.)	HI (mm.)	P (mm.)	Titration I_2	10^6k_{10} (mm.$^{-1}$ sec.$^{-1}$)	C_3H_6 (mm.)	HI (mm.)	P (mm.)	Titration I_2	10^6k_{10} (mm.$^{-1}$ sec.$^{-1}$)
231·0	35·1	8·30	6·35	0·56	22·8	99·15	4·20	2·75	1·23
235·8	118·2	25·50	21·80	0·57	37·3	42·95	3·95	—	1·24
55·3	99·0	9·10	—	0·86	35·8	26·10	2·70	1·60	1·41
67·1	72·9	8·75	5·40	0·92	32·3	27·35	2·05	1·80	1·42
35·9	194·4	13·70	12·30	0·93	25·0	41·80	1·70	—	1·52
38·1	101·4	12·65	7·30	1·03	13·6	101·10	3·20	1·86	1·53

$$C_3H_6 + HI \longrightarrow C_3H_7I \quad \text{. . . . .} \quad (-2)$$

$$C_3H_7I + HI \longrightarrow C_3H_8 + I_2 \quad \text{. . . . .} \quad (1)$$

with reaction (−2) as the rate-determining step.

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[17] Mrs. M. Back, personal communication.