geneous reactions at low pressures. One of these is undoubtedly $H + OH + M \longrightarrow H_2O + M$. The water-forming reaction between hydrogen atoms and oxygen may involve the formation of hydrogen peroxide as an intermediate but the failure to obtain any evidence of the formation of hydrogen peroxide in the gaseous phase is rather surprising.

The heterogeneous reaction of hydroxyl appears to result in the formation of hydrogen and oxygen. No evidence was obtained for a homogeneous reaction between hydroxyls.

There is no indication that the HO_2 molecule is anything more than a "collision complex" of very short life.

URBANA, ILLINOIS

RECEIVED JULY 2, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

The Kinetics of the Pyrolysis of *n*-Propyl Iodide and *n*-Butyl Iodide

BY J. L. JONES AND R. A. OGG, JR.

In this paper are presented the results of the kinetic studies on the thermal decompositions of gaseous *n*-propyl and *n*-butyl iodides. The *n*-propyl iodide was studied in the temperature range of 584 to 627°K. and the *n*-butyl iodide in the temperature range of 590 to 624°K. The two compounds decomposed somewhat similarly, but the *n*-butyl iodide could not be treated quantitatively, for reasons which will be given later.

Two other papers will treat respectively the kinetics of the decomposition of isopropyl iodide and the equilibrium established between *t*-butyl iodide and its pyrolytic products, *e. g.*, isobutylene and hydrogen iodide. These three papers in conjunction with the two papers mentioned below constitute a more or less coherent series of studies on the thermal decomposition of the alkyl iodides which should facilitate a better understanding of the free radicals involved in such reactions and of the strength of the bonds affected by the pyrolysis.

The thermal decomposition of *s*-butyl iodide was investigated by Ogg[1] in the temperature range 238–276°. He found that the results were best fitted as a combination of a unimolecular reaction plus an iodine catalyzed decomposition of the iodide.

$$-\frac{d(C_4H_9I)}{dt} = k_1(C_4H_9I) + k_2(C_4H_9I)(I_2)^{1/2} \quad (1)$$

The activation energies for the two reactions were 39,420 and 35,220 cal., respectively. If the iodine catalyzed reaction was considered to occur between an iodine atom and a butyl iodide molecule, the activation energy of the reaction became 35,220 cal. minus one-half the heat of dissociation of an iodine molecule (*e. g.*, 18,400 cal.), or 16,820 cal.

The gas phase reaction between hydrogen iodide and methyl, ethyl and *n*-propyl iodides, respectively, was investigated by Ogg[2] in the temperature range 250–300°. The reaction proceeded exclusively by the over-all reaction

$$RI + HI \longrightarrow I_2 + RH$$

His kinetic studies indicated that the reactions proceeded by a common mechanism, which was the sum of a simple bimolecular metathesis, as above, and a complex rate expression, being given by

$$\frac{d(I_2)}{dt} = k_1(RI)(HI) + k_2\frac{(RI)(HI)}{(I_2) + (HI)} \quad (2)$$

k_2 has the dimensions of a unimolecular rate constant, *e. g.*, seconds^{-1}. The bimolecular reaction has an activation energy of 33,000, 29,800 and 29,200 cal. for the methyl, ethyl and *n*-propyl iodides, respectively, while the unimolecular reaction has an activation energy of 43,000 cal. for all three iodides. Much evidence[2] indicates that the dissociation energy of the C–I linkage is approximately equal to the activation energy of the above unimolecular reaction, *e. g.*, 43,000 cal.

Experimental Section

Preparation of Alkyl Iodides.—The *n*-propyl and *n*-butyl iodides were prepared by the method of Bogart and Slocum,[3] *e. g.*, by the action of red phosphorus and iodine on the *n*-alcohol. The dry *n*-propyl iodide employed boiled over the range of 102.5 to 102.8°. The *n*-butyl iodide had a boiling range of 128.0 to 128.2°.

Apparatus and Procedure.—The Pyrex reaction flask (about 800-cc. capacity) was contained in an electrically heated air thermostat provided with an efficient stirrer.

---

(1) Ogg, *Trans. Faraday Soc.*, **31** 482 (1934).

(2) Ogg, THIS JOURNAL, **56**, 532 (1934).

(3) Bogart and Slocum, *ibid.*, **46**, 764 (1924).

A de Khotinsky thermoregulator controlled the temperature to ±0.1° up to about 250°, above which temperature it was necessary to supplement the thermoregulator with hand control, thus providing control to within ±0.2° at least and in most cases to within ±0.1°. The temperature of the thermostat was determined by direct reading of a calibrated 360° mercury thermometer which could be read to 0.1° by a low-power magnifying eyepiece. A quartz spiral manometer[2] was used as a null point instrument in conjunction with a mercury manometer to measure the reaction vessel gas pressure.

A Bodenstein type glass greaseless valve was used to close off the reaction vessel from the high vacuum line. This valve was modified and made stronger by replacing the glass membrane expansion bellows with a brass sylphon bellows sealed to the glass through a copper–glass joint. The valve was very strong and had the advantage that the bellows was removed easily (heating soft soldered copper–brass joint) to replace the silver chloride seat of the needle point. A small side-arm was placed in the line between the greaseless valve and the reaction vessel, just outside of the thermostat. The capillary tubing connecting the valve and the reaction vessel was heated to 115° by electrical resistance wire and the side-arm covered by a removable auxiliary heater. The high vacuum line used in the experiments was quite typical of the construction in this field.

The typical procedure of measuring a reaction rate was as follows. The reaction vessel was evacuated to a maximum pressure of 10^{-4} mm. and then a stopcock was closed, shutting off the iodide reservoir and the reaction vessel from the vacuum line. A small Dewar vessel containing liquid air was placed on the side-arm of the reaction vessel and the stopcock of the iodide reservoir was opened. From one to six minutes were required for condensation of sufficient iodide in the side-arm to give the desired initial pressure. At this time the iodide reservoir was closed off and the connection to the vacuum line opened. With the liquid air still on the side-arm, the reaction vessel was evacuated for several minutes to remove any iodide or decomposition products. The greaseless valve was closed, the liquid air removed and the iodide rapidly vaporized out of the side-arm by means of a small flame. The auxiliary heater was quickly placed on the side-arm and the first pressure measurement taken as quickly as possible. The stop watch was started near the end of the vaporization process, which required about three to five seconds, and usually thirty seconds elapsed before the first pressure reading was made.

If iodine was desired for a run, it was necessary to condense the products of the previous run with liquid air on the side-arm and then to evacuate the reaction vessel while the side-arm warmed to room temperature. In this manner all of the products were removed from the system except iodine which, due to its low vapor pressure, remained condensed in the side-arm. The pressure of iodine was then measured, the iodine recondensed, and the alkyl iodide collected upon it. The two were vaporized together and the initial pressure of the iodide was determined by extrapolation. The zero-point correction for the quartz spiral manometer was determined separately for nearly every experiment.

Homogeneity of the Thermal Decomposition.—Because of the compact arrangement of the apparatus in the thermostat and the delicate nature of the quartz spiral manometer, it was not convenient to test the homogeneity of the reactions by changing the surface–volume ratio of the reaction vessel. Instead, two 150-cc. Pyrex glass bulbs were used, attached to the vacuum line by ground glass joints. One bulb had a surface–volume ratio of 0.89 cm.$^{-1}$, while the other bulb was filled with bits of 4-mm. Pyrex tubing to give a surface–volume ratio of 8.3 cm.$^{-1}$. A measured amount of *n*-propyl iodide was allowed to decompose for fifty minutes. The iodine formed was titrated with sodium thiosulfate and indicated the same percentage decomposition in both bulbs. A second set of bulbs heated at 315° for thirty-three minutes checked this result.

As will be shown later, the rate determining step in the decomposition of *n*-propyl iodide was of the one-half order with respect to iodine, hence the comparatively close agreement of the iodine formed in each bulb to the volume ratio of the bulbs indicated the absence of appreciable wall reaction.

The same bulbs filled with *n*-butyl iodide at 76 mm. pressure were treated similarly for twenty minutes at 315°. The ratio of the iodine formed in both bulbs indicated that the reaction was homogeneous. Again the catalysis of this reaction by iodine imposes stringent conditions on this simple test.

Experimental Results

Nature of the Over-all Reactions. *n*-Propyl Iodide.—Glass and Hinshelwood[4] made two runs on the decomposition of isopropyl iodide and analyzed the products of complete reaction. They found that the reaction proceeded in accordance with the equation

$$2C_3H_7I = C_3H_8 + C_3H_6 + I_2$$

This was proved by a determination of the iodine formed in the reaction and an analysis of the permanent gases. The ratio of final to initial pressure was 1.54 at 351° and 1.45 at 301°.

An average of all determinations of the ratio of final to initial pressure, P_∞/P_0, for this work gave a value of 1.55, with no trend of the ratio when iodine was present initially. No gases were formed in the reaction which were not condensable in liquid air, thus eliminating the possibility of appreciable amounts of methane and hydrogen as products. The amount of iodine formed on complete decomposition was determined by two methods which checked well with the above equation. The first method was the direct titration of the iodine formed, while the second method involved the condensation of all the products in the side-arm of the reaction vessel by liquid air, then allowing the side-arm to warm

---

[4] Glass and Hinshelwood, *J. Chem. Soc.*, 1817 (1929).

to room temperature during evacuation of the reaction vessel. Thus the propane and propylene, together with similar gases, were removed from the vessel, but the iodine, due to its low vapor pressure, remained condensed in the sidearm. The greaseless valve was closed and the iodine vaporized into the reaction vessel for pressure measurement. No hydrogen iodide was detected in the two samples used to determine the homogeneity of the reaction.

All evidence points to the same over-all reaction for the *n*-propyl iodide as for the isopropyl iodide. This is quite remarkable in view of the experimental fact that the rate determining step in each case is quite different.

Normal Butyl Iodide.—A summary of the experimentally determined final to initial pressure ratios, P_∞/P_0, for normal butyl iodide is given in Table I. The average value of the ratio was 1.62, excluding those experiments in which iodine was added initially. When iodine was added initially (pressure P_i) in comparatively large amounts, the value of P_∞/P_0 was greatly increased, as shown in Table I. The value of the ratio was apparently independent of the rates in the range studied.

TABLE I

Run	Temp., °K.	P_0, mm.	P_∞/P_0	P_i, mm.	$t_{1/2}$ sec.	$t_{3/4}$ sec.	$t_{1/2}/t_{3/4}$
1	590.4	47.6			1907		
6	606.2	105.5			522		
4	606.4	44.5	1.62		693	1210	1.75
7	606.5	49.5	1.86	27.1	470	1034	2.20
5	607.6	110.8			463		
2	607.9	17.4	1.59		810		
3	608.6	40.4	1.63		624	1080	1.73
11	616.5	118.7			246	430	1.75
16	617.3	33.8	2.11	34.1	204	535	2.62
17	617.5	98.8	1.66		264	555	2.10
12	617.6	59.1		12.3	218	417	1.91
10	617.7	45.8			310	548	1.77
15	617.8	103.2	1.63	16.8	187	372	1.99
8	617.9	78.8	1.63		263	517	1.97
9	617.9	74.1			254	452	1.78
13	618.0	60.6	1.59		258	439	1.70
19	618.7	57.4	1.60		250	434	1.74
14	618.7	64.6	1.64	8.7	254	501	1.98
18	619.0	71.2	1.60		248	447	1.80
20	620.7	48.0	1.58		262	459	1.75
21	621.9	91.1	1.64		212	376	1.77

No positive tests for hydrogen iodide were obtained in the reaction products of the homogeneity experiments. Traces of hydrogen iodide were detected in experiments 5 and 6. The amount of iodine formed on complete reaction was in agreement with the assumption of complete existence of the element as iodine, except for a trace of hydrogen iodide.

The decomposition products of the iodide were completely condensable in liquid air, but required a comparatively longer time to condense than in the case of the propyl iodide. This may indicate the presence of small amounts of hydrogen or methane in the products, which dissolved in the condensate.

Since the kinetic study of the reaction proved unsatisfactory, it was not thought advisable to analyze the products further. The over-all reaction is probably the formation of iodine, butane, and butylene, in the main, but the hydrocarbon products evidently vary considerably from this scheme. This variation may be due either to the decomposition of the free butyl radical or the pyrolysis of some hydrocarbon. It is difficult to understand why normal butane or isobutylene should behave so differently from propane and propylene. The remarkable increase in the value of the ratio P_∞/P_0 on the initial addition of iodine is inexplicable, for it follows that the iodine exerts a special influence on some intermediate stage of the reaction. This has not been observed in any previous studies of the iodides.

The Rate-Determining Step of the Thermal Decomposition of *n*-Propyl Iodide.—A rate expression fitting the data was obtained by testing various empirical equations which seemed likely. The data obtained fitted most closely the simple expression

$$-\frac{\mathrm{d}(\mathrm{C_3H_2I})}{\mathrm{d}t} = k(\mathrm{C_3H_7I})(\mathrm{I_2})^{1/2} \tag{3}$$

The pressure of propyl iodide at any time t was given by

$$(\mathrm{C_3H_7I}) = \frac{1.55\,P_0 - P_t}{0.55} \tag{4}$$

and in the absence of initial iodine concentration

$$(\mathrm{I_2}) = \left(\frac{0.50}{0.55}\right)(P_t - P_0) \tag{5}$$

if it was assumed that all iodine was present as propyl iodide or as iodine. Such an assumption should not cause any great error. Placing equations (4) and (5) in the rate expression

$$\frac{\mathrm{d}P_t}{\mathrm{d}t} = 0.953\,k\,(1.55P_0 - P_t)\,(P_t - P_0) \tag{6}$$

which on integration and evaluation of the integration constant became

$$0.953kt = \frac{1}{(0.55P_0)^{1/2}} \ln \left\{ \frac{(0.55P_0)^{1/2} + (P_t - P_0)^{1/2}}{(0.55P_0)^{1/2} - (P_t - P_0)^{1/2}} \right\} \tag{7}$$

If iodine was present initially in the reaction, then its concentration at any time t was given by $(P_t - P_0 - P_i)$ to a first approximation. The effect of the 1.55 ratio on the concentration of iodine may be neglected due to the large initial concentration of iodine and since the iodine appeared in the rate expression to the one-half power. The integrated rate equation then became

$$k = \frac{1}{(0.55P_0 + P_i)^{1/2}\,(t_2 - t_1)} \ln \left\{ \frac{\left[\dfrac{(P_t - P_0 + P_i)^{1/2} + (0.55P_0 + P_i)^{1/2}}{(P_t - P_0 + P_i)^{1/2} - (0.55P_0 + P_i)^{1/2}}\right]_{t_2}}{\left[\dfrac{(P_t - P_0 + P_i)^{1/2} + (0.55P_0 + P_i)^{1/2}}{(P_t - P_0 + P_i)^{1/2} - (0.55P_0 + P_i)^{1/2}}\right]_{t_1}} \right\} \quad (8)$$

The rate constants for the reactions without initial iodine concentration were determined by plotting the logarithmic factor of equation (7) against the time. However, the slope of the line was not constant initially, being greater over about the first 15–20%. A typical example is given in Fig. 1, where a well-fitting straight line was obtained after the first 20% decomposition.

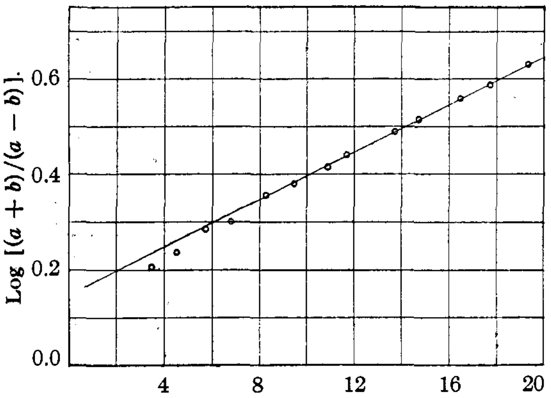

Fig. 1.—Kinetics of thermal decomp. of *n*-propyl iodide.

In those runs where iodine was added initially the rate constants were calculated by the interval method according to equation (8). In order to secure fair average values of the rate constant, the time intervals were taken for periods of about 10% decomposition, each run being calculated to about 70% completion, and the value of k averaged for the experiment. There was no definite trend to the interval values of k for a given run. Table II gives the complete calculated values of the rate constants for the thermal decomposition of *n*-propyl iodide.

To obtain the activation energy for the rate determining step, the term (log k) was plotted against $(1/T)$ and the best fitting straight line drawn through the experimental points (Fig. 2). The activation energy was 37,900 cal./mole with an estimated accuracy of ±1000 cal./mole.

The Rate-Determining Step of the Thermal Decomposition of *n*-Butyl Iodide.—Since the initial presence of comparatively large amounts of iodine changes the final to initial pressure ratio, P_∞/P_0, (*vide supra*) one cannot safely use the rate of pressure change as a measure of the alkyl iodide concentration. Indeed, all efforts to write a satisfactory rate-determining equation were unsuccessful. A survey of the experimentally determined data in Table I for the pyrolysis of *n*-butyl iodide indicated that it decomposed in a manner very similar to *n*-propyl iodide. The facts are as follows: (1) the reaction is catalyzed by iodine; (2) the half-life of a reaction decreases with increasing initial pressure; (3) the ratio, $t_{3/4}/t_{1/2}$, is increased markedly by the initial addition of iodine; and (4) the reaction rate in the same temperature range is of the same magnitude as the thermal decomposition of *n*-propyl iodide; however, the

TABLE II

THERMAL DECOMPOSITION OF NORMAL PROPYL IODIDE

un[a]	Temp., °K.	$10^3/T$	$k \times 10^4$, mm.$^{-1/2}$ sec.$^{-1}$	k (mol./cm.^{3})$^{-1/2}$ sec.$^{-1}$	(log k)
5	595.9	1.678	1.40	0.854	0.0685
4	596.3	1.677	1.68	1.01	.0043
2	596.8	1.676	1.66	1.01	.0043
7	598.8	1.670	1.47	0.899	.0462
17	611.3	1.636	3.17	1.96	.2923
19	614.7	1.627	4.06	2.51	.3997
42	584.4	1.711	0.717	0.433	.3635
41	584.4	1.711	0.777	.469	.3288
43	585.8	1.707	0.859	.519	.2845
44	595.6	1.679	1.20	.732	.1355
33	597.7	1.673	1.54	.941	.0264
38	598.0	1.672	1.47	.898	.0467
39	598.2	1.672	1.64	.938	.0280
36	603.4	1.657	2.02	1.24	.0934
35	604.4	1.654	2.38	1.46	.1644
34	604.5	1.654	2.34	1.44	.1584
33	606.5	1.649	2.47	1.52	.1818
32	608.7	1.643	2.69	1.66	.2201
31	610.8	1.639	3.26	2.01	.3032
20	615.2	1.625	4.71	2.85	.4548
18	616.5	1.622	4.20	2.61	.416
24	622.9	1.605	5.60	3.49	.5428
25	623.7	1.603	5.89	3.67	.5647
23	624.8	1.601	5.84	3.65	.5623
30	625.7	1.598	6.34	3.96	.5977
29	625.7	1.598	6.66	4.16	.6191
27	625.8	1.598	5.68	3.55	.5502
28	627.2	1.594	7.13	4.46	.6493

[a] All runs up to No. 19 were made without added iodine.

decomposition of *n*-propyl iodide appears to be more strongly catalyzed by iodine than in the case of *n*-butyl iodide.

If the value of the ratio, P_∞/P_0, is defined as A, then the concentration of the *n*-butyl iodide at any time during an experiment is given by $(AP_0 - P_t)/(A - 1)$. In order to calculate the rate constant for the rate determining step, the expression

$$\left(\frac{dP}{dt}\right)\Big/\left(\frac{AP_0 - P_t}{A - 1}\right) \qquad (9)$$

was calculated for a number of values of P_t within each of several experiments. The above expression is equal to the product of the rate constant of a unimolecular reaction and the factor $(A-1)$. If the rate determining step is unimolecular, the above expression would be constant. If the rate expression was similar to the one found for *n*-propyl iodide, then a plot of the above expression against $(I_2)^{1/2}$ would be a straight line whose slope is the rate constant and whose intercept would be zero. If the rate determining step were of higher order than the first with respect to alkyl iodide, then the above expression would decrease during a given run. It was found that (9) passed through a maximum value during experiments numbered 5, 7, 8, 9, 11 and 14 (random experiments chosen for calculation). Such a result can be explained if one assumes that the true rate expression which obtains is the same as for the *n*-propyl iodide and if the value A, of the ratio P_∞/P_0, is actually increasing during a given experiment from its theoretical value of 1.50. Then the numerator of the expression $(AP_0-P_t)/(A-1)$ would be expected to increase faster than the denominator and hence the expression (9) would pass through a maximum under some conditions. Because of the above occurrence, no values of the rate constants for the reaction can be determined accurately. It seems probable that the rate determining reaction is similar to the one found for the decomposition of *n*-propyl iodide, but some complicating side reaction is involved in the mechanism.

Discussion

The Mechanism of the Pyrolysis of *n*-Propyl Iodide.—It is seen readily that the rate expression given by equation (3) may be written as

$$-\frac{d(C_3H_7I)}{dt} = k_1K_{I_2}{}^{1/2}\,(C_3H_7I)\,(I) \qquad (10)$$

where K_{I_2} is the equilibrium constant for the dissociation of iodine and k_1 is given by the relation $k/K_{I_2}{}^{1/2}$. Several mechanisms will be presented, based upon equation (10), and the reasons given for their rejection as implausible.

Mechanism (a)

$$C_3H_7I + I \longrightarrow C_3H_6I + HI \qquad (a\text{-}1)$$
$$C_3H_6I \longrightarrow C_3H_6 + I \qquad (a\text{-}2)$$
$$C_3H_7I + HI \longrightarrow C_3H_8 + I_2 \qquad (a\text{-}3)$$
$$2I + M \longrightarrow I_2 + M \qquad (a\text{-}4)$$

Reaction (a-1) is assumed to be the slow rate-determining step, accounting for the dependence of the experimental rate upon the square root of the iodine concentration. Equation (a-2) is very similar to an intermediate step in the decomposition of diiodoethane (compare Arnold and Kistiakowsky[5] and Ogg[6]).

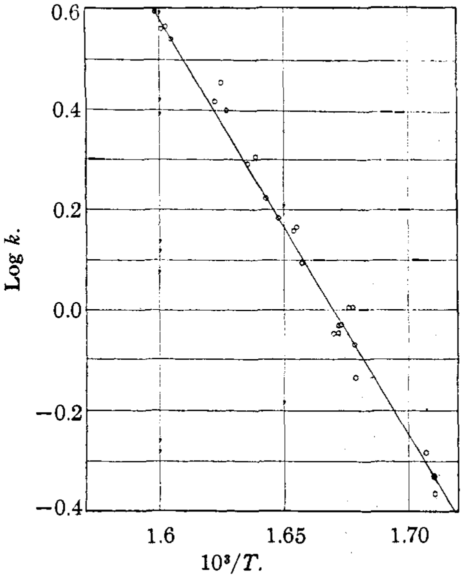

Fig. 2.—Kinetics of thermal decomp. of *n*-propyl iodide.

One may arrive at some conclusions as to the validity of this reaction by calculating the rate of reaction (a-3) in the experimental range. Ogg[2] has studied this reaction and determined the rate constant. If his results are extrapolated 15° above the highest experimental temperature, the rate constant for reaction (a-3) is 1.99×10^{-3} (mol./cc.)$^{-1}$ sec.$^{-1}$ at 585°K. It should be pointed out at this time that the true bimolecular constants of Ogg (his K_1 values) are too large by a factor of 10, the error arising in the conversion of the concentration units from mm. to (mol./cc.). However, using the corrected value of the rate

---

[5] Arnold and Kistiakowsky, *J. Chem. Phys.*, **1**, 166 (1933).

[6] Ogg, THIS JOURNAL, **58**, 607 (1936).

constant and a concentration of 40 mm. of propyl iodide and 5 mm. of hydrogen iodide, the absolute rate of disappearance of *n*-propyl iodide is 3×10^{-11} (mol./cc.)/sec. Using the experimentally determined rate constant for expression (3) of 0.469 $(\text{mol./cc.})^{-1/2}\ \text{sec.}^{-1}$, the absolute rate of disappearance of the *n*-propyl iodide is 1.91×10^{-10} (mol./cc.)/sec. at the same temperature and alkyl iodide concentration and 5-mm. concentration of iodine. Since the iodine concentration appears as its square root in the rate expression, assumption of 20 mm. of iodine doubles the rate. The discrepancy between the rates would be even larger at the higher experimental temperatures, as the pyrolytic reaction has the smaller activation energy. Also the hydrogen iodide concentration used above is greater than the maximum amount found in any experiment. Since reaction (a-3) is slower than the experimentally determined rate of disappearance of *n*-propyl iodide, this mechanism must be discarded. Under these conditions a large concentration of hydrogen iodide would be built up, but experiments have shown that it does not exceed 3% of the total iodine from the alkyl iodide.

There is evidence[1] to indicate that the reverse of reaction (a-1) requires an activation energy of about 14 kcal. If the energy required to break the carbon–iodine bond is taken as 43 kcal., and the heat of dissociation of hydrogen iodide is 70.7 kcal., then the energy required to break the carbon–hydrogen bond in the forward reaction (a-1) is 74.7 kcal. This value is quite low in comparison with the value of 94.5 kcal. calculated by Kistiakowsky and Gershinowitz[7] from the dissociation of cyanogen into cyanide radicals. While it is very probable that the heat of dissociation of the carbon–hydrogen linkage decreases progressively from primary, secondary to tertiary carbon atoms, such a low value of the carbon–hydrogen bond does not seem plausible. This is a second serious objection to the above mechanism.

Mechanism (b)

$$\mathrm{C_3H_7I + I \longrightarrow C_3H_7 + I_2} \qquad \text{(b-1)}$$
$$\mathrm{C_3H_7 + I_2 \longrightarrow C_3H_6 + HI + I} \qquad \text{(slow) (b-2)}$$
$$\mathrm{HI + C_3H_7I \longrightarrow C_3H_8 + I_2} \qquad \text{(rapid) (b-3)}$$
$$\mathrm{M + 2I \longrightarrow I_2 + M} \qquad \text{(b-4)}$$

The study of the kinetics of the thermal decomposition *s*-butyl iodide indicates that (b-1) occurs in the forward direction and the reverse reaction has been shown to occur in the reaction of hydrogen iodide with *n*-propyl iodide; therefore, such a mechanism is not impossible. However, the objection to reaction (b-3) which was given for mechanism (a) is still valid here and hence this mechanism must be rejected.

Mechanism (c)

$$\mathrm{C_3H_7I + I \longrightarrow C_3H_7 + I_2} \qquad \text{(c-1)}$$
$$\mathrm{C_3H_7 + C_3H_7I \longrightarrow C_3H_8 + C_3H_6I} \qquad \text{(c-2)}$$
$$\mathrm{C_3H_6I \longrightarrow C_3H_6 + I} \qquad \text{(c-3)}$$
$$\mathrm{M + 2I \longrightarrow I_2 + M} \qquad \text{(c-4)}$$

It is known from the mechanism of the reaction between hydrogen iodide and *n*-propyl iodide, that the reaction between free propyl radical and iodine molecule is more rapid than reaction (c-2); therefore, the above mechanism is not valid. The simple unimolecular decomposition of the *n*-propyl iodide, $\mathrm{C_3H_7I \longrightarrow C_3H_7 + I}$, is too rapid at the experimental temperature and hence would produce an absolute rate of disappearance of alkyl iodide in excess of the experimental rate. The calculated value of the unimolecular rate expression at 585°K. is 2.39×10^{-3} sec. $^{-1}$. At an alkyl iodide concentration of 40 mm., the absolute rate of the reaction is 2.64×10^{-9} (mol./cc.)/sec. Compare this with the experimentally determined rate of disappearance of alkyl iodide at the same concentration and 20 mm. concentration of iodine, *e. g.*, 3.82×10^{-10} (mol./cc.)/second. Hence this mechanism must be rejected.

Mechanism (d).—The mechanism to be presented now describes quantitatively the experimental results and hence may be accepted with some certainty as the true description of the reacting system.

When no iodine is added to the alkyl iodide initially, the reaction rate constant is comparatively high during the first 15 to 20% decomposition, decreasing meanwhile to give a rate constant which is the same as for those reactions to which iodine is added initially. In order to account for these results, the initial reaction is most probably

$$\mathrm{C_3H_7I \longrightarrow C_3H_7 + I} \qquad \text{(d-1)}$$
$$\mathrm{C_3H_7 + C_3H_7I \longrightarrow C_3H_8 + C_3H_6I} \qquad \text{(d-2)}$$
$$\mathrm{C_3H_6I \longrightarrow C_3H_6 + I} \qquad \text{(d-3)}$$

The absolute rate of the unimolecular decomposition (d-1) has been calculated and presented in the discussion of mechanism (c). As it is more rapid than the mechanism which obtains after 15

---

[7] Kistiakowsky and Gershinowitz, *J. Chem. Phys.*, **1**, 432 (1933).

to 20% decomposition (no initial iodine), it can be used to explain this rapid initial rate. Reaction (d-2) is a comparatively slow reaction and it has been shown that the reaction of the n-propyl radicals with iodine molecules is a faster reaction. The rapid reaction (d-3) already has been discussed. It probably has an activation energy of 13.4 kcal.

Due to the reaction between the n-propyl radicals and iodine molecules, one may expect that the equilibrium (d-4) will be established very rapidly if iodine is added initially to the alkyl iodide (or after 15 to 20% decomposition in case of no initial iodine concentration).

$$n\text{-}C_3H_7I \rightleftarrows n\text{-}C_3H_7 + {}^1/{}_2I_2 \quad \text{(equil.)} \qquad \text{(d-4)}$$

$$n\text{-}C_3H_7 + I_2 \longrightarrow \text{iso-}C_3H_7I + I \quad \text{(slow)} \qquad \text{(d-5)}$$

$$\text{iso-}C_3H_7I \longrightarrow {}^1/{}_2C_3H_8 + {}^1/{}_2C_3H_6 + {}^1/{}_2I_2 \quad \text{(rapid)} \qquad \text{(d-6)}$$

$$M + 2I \longrightarrow I_2 + M \qquad \text{(d-7)}$$

The rate determining step is (d-5), followed by the rapid decomposition of the isopropyl iodide as in reaction (d-6). Thus

$$\frac{(I_2)^{1/2}\,(n\text{-}C_3H_7)}{(n\text{-}C_3H_7I)} = K \qquad (11)$$

where K is an equilibrium constant, therefore

$$-\frac{d(n\text{-}C_3H_7I)}{dt} = k_5(n\text{-}C_3H_7)(I_2) = k_5K(n\text{-}C_3H_7I)(I_2)^{1/2} \qquad (12)$$

These constants are related to the experimental value of k by the expression, $k = k_5K$.

The decomposition of isopropyl iodide is faster[8] than the observed rate of pyrolysis of the n-propyl iodide as shown by a comparison of the unimolecular rate constants of the two compounds. At 600°K. the unimolecular rate constant k is 3.74×10^{-3} sec.$^{-1}$ for isopropyl iodide and the corresponding unimolecular rate constant for n-propyl iodide, calculated for 20 mm. of iodine concentration, is 3.47×10^{-4} sec.$^{-1}$. Due to the higher activation energy of the isopropyl iodide decomposition (42.9 kcal.), the rate constant of the corresponding reaction increases more rapidly with increasing temperature than for that of the n-propyl iodide. It is to be noted that the fit of the experimental results on n-propyl iodide decomposition by the given rate expression improves at higher temperatures.

It will be interesting to calculate the rate constant k_5 for reaction (d-5). In order to do that, one must calculate the equilibrium constant K, where

$$K = Be^{-Q/RT} = e^{-\Delta S^0/R}\, e^{-Q/RT} \qquad (13)$$

ΔS^0 is the standard entropy change for reaction (d-4) and it will be approximately calculated at 600°K. from the estimated values of the entropies of the compounds involved in the reaction.

The entropy of the iodine atom is calculated from the Sackur–Tetrode equation[9] and is 43.93 e. u. at 600°K. The value of the entropy of the iodine molecule at 600°K. (63.84 e. u.) is calculated from the spectroscopic data of Murphy.[10] No change of the nuclear or electronic spin was considered for this reaction.

In order to calculate the entropy of the n-propyl iodide and n-propyl radical, we shall use the concept that the total entropy of a molecule is the sum[11] of the translational, rotational and vibrational entropies. The translational entropy is calculated from the Sackur–Tetrode equation. For such complex molecules an exact calculation of the vibrational and rotational entropies is a difficult task, for the exact spectroscopic constants of these molecules are unknown. Fortunately, it is only necessary to know the entropy change of the reaction and we hope to show that this value may be calculated with some certainty. With this in mind, we shall assume that the hydrocarbon portion of the n-propyl iodide possesses the same vibrational entropy as the propyl radical and thus it will only be necessary to consider the vibrational entropy change involved in breaking the carbon–iodine linkage. From the Raman data of Kohlrausch,[12] the stretching and bending frequencies of the C–I bond may be taken as 503 and 590 cm.$^{-1}$, respectively. Therefore, the entropy decrease involved in breaking this bond is calculated by the equation[9]

$$S_{\text{vib}} = R\sum_{j=1}^{j=2}\left[\frac{h\nu_i/kT}{e^{h\nu_i/kT} - 1} - \ln\left(1 - e^{h\nu_i/kT}\right)\right] \qquad (14)$$

and is 3.20 e. u.

In order to calculate the rotational entropy of the n-propyl radical and n-propyl iodide it will be necessary to make some simplifying assumptions about their structures, as no spectroscopic data on their moments of inertia are available. All stretching of the bonds will be neglected as will internal rotation of the terminal groups. Since only the entropy change of the reaction is needed,

---

[8] Jones and Ogg, THIS JOURNAL, **59**, 1939 (1937).

[9] Tolman, "Statistical Mechanics as Applied to Physics and Chemistry," Chemical Catalog Co., N. Y., 1927.

[10] Murphy, *J. Chem. Phys.*, **4**, 344 (1936).

[11] Mayer, Brunauer and Mayer, THIS JOURNAL, **55**, 37 (1933); Halford, *J. Chem. Phys.*, **2**, 694 (1934).

[12] Kohlrausch, Dadieu and Pongratz, *Monatsh.*, **61**, 413 (1932).

it appears that these influences will be so nearly the same for the two compounds that their effects will be canceled. The *n*-propyl iodide is approximately a symmetrical top and so has two equal moments of inertia. In this model, the C–C distance is 1.53 Å., the C–I distance is 2.28 Å. and the C–H distance is 1.11 Å. The three hydrogen atoms of the terminal carbon will be taken as a mass of 3.02 at a distance 0.37 Å. from that carbon atom. The three carbon atoms are in the same plane as the iodine atom forming a zig-zig chain (tetrahederal angles are assumed). The moments of inertia are calculated for the gravitational axes instead of principal axes. The moment of inertia I_z about the longitudinal axis is 8.96×10^{-39} g. cm.^{2}. The two identical moments, I_x and I_y, have been calculated as 61.0×10^{-39} g. cm.^{2}. Using the equation of Halford,[10] the entropy of rotation of *n*-propyl iodide is 29.48 e. u. at 600°K. and the translational entropy is 44.78 e. u.

The principal moments of inertia of the *n*-propyl radical have been assumed the same as for propane. They are taken from the calculations of Kassel[13] as $I_x = 109.2 \times 10^{-40}$ g. cm.^{2}, $I_y = 92.2 \times 10^{-40}$ g. cm.^{2} and $I_2 = 22.44 \times 10^{-40}$ g. cm.^{2}. The entropy of rotation for the radical is 23.60 e. u.

The value of ΔS^0 for reaction (d-4) at 600°K. is 18.71 e. u. Hence, the value of $e^{\Delta S^0/R}$ is 1.22×10^4. From the data of Murphy the heat of dissociation of iodine molecules at 600°K. is 36.65 kcal./mole. Ogg estimates[2] the heat of dissociation of the C–I bond as 43 kcal. in *n*-propyl iodide. Therefore, the calculated heat of reaction Q for the equilibrium (d-4) is 24.7 kcal. Hence

$$K = 1.22 \times 10^4 e^{-24,700/RT} \left(\frac{\text{mole}}{\text{cc.}}\right)^{1/2}$$

On the basis of the simple theory of bimolecular reactions (*e. g.*, assuming that the activation energy is confined to the component of relative translational energy parallel to the line of centers) the critical increment E_5 for reaction (d-5) is related to the true activation energy by the expression $E_5 = Q_5 + \frac{1}{2}RT$. As $E_5 = 13.2$ kcal./mole, $Q_5 = 12.6$ kcal./mole. In the experimental temperature range k_5 may be expressed by the standard equation

$$k_5 = 1.79 \times 10^8 T^{1/2} e^{-12,600/RT} \left(\frac{\text{mole}}{\text{cc.}}\right)^{-1} \text{sec.}^{-1} \qquad (15)$$

Therefore the rate of collision between iodine atoms and *n*-propyl radicals effective in reaction (d-5) is given by

$$1.79 \times 10^8 T^{1/2} \text{ (mole/cc.)}^{-1}\text{sec.}^{-1}$$

This corresponds to an effective collision diameter of 1.98×10^{-10} cm. If the "true collision diameter" is assumed to be some 6×10^{-8} cm., this corresponds to a steric factor of approximately 10^{-5}.

Experimental evidence indicates that the reaction

$$s\text{-}C_4H_9 + I_2 \longrightarrow s\text{-}C_4H_9I + I \qquad (16)$$

requires an activation energy of about 14.2 kcal. while the reaction

$$C_2H_4I + I_2 \longrightarrow C_2H_4I_2 + I \qquad (17)$$

has an activation energy of 11.9 kcal. Hence it seems probable that the two reactions

$$n\text{-}C_3H_7 + I_2 \longrightarrow n\text{-}C_3H_7I + I \qquad (18)$$
$$n\text{-}C_3H_7 + I_2 \longrightarrow \text{iso-}C_3H_7I + I \qquad (\text{d-5})$$

have nearly the same activation energy, *e. g.*, 12.6 kcal. Due to the slowness of reaction (d-5), the equilibrium represented by (d-4) is obtained easily. The small steric factor of (d-5) is to be expected as such a reaction involves the shift of a hydrogen atom from one carbon atom to another. Hence the reaction to form *n*-propyl iodide is about 10^5 times faster. Any error in the calculation of the moments of inertia would probably result in an increase in the steric factor, but it is improbable that the error is sufficient to change the complexion of the results.

These reactions increase the evidence in favor of the conception that considerable activation energy is required for reactions of free radicals. The evidence presented here is definitely in favor of mechanism (d) and no contradictions have resulted from its application. On this basis it is probable that this mechanism is a close approximation to experiment. No mechanism has been advanced for the thermal decomposition of isopropyl iodide in this paper, but it has been shown to be faster than the experimentally determined rate of decomposition of the *n*-propyl iodide. The data on the decomposition of isopropyl iodide will be presented in a subsequent paper.

Summary

An experimental study was made of the kinetics of the thermal decomposition of gaseous *n*-propyl iodide in the temperature range 584 to 627°K. and the rate expressed by the relation

$$-\frac{d(C_3H_7I)}{dt} = k(C_3H_7I)(I_2)^{1/2}$$

---

[13] Kassel, *J. Chem. Phys.*, **4**, 276 (1936).

Several mechanisms were proposed and the reasons presented for rejecting them. A satisfactory mechanism was presented which was in agreement with all experimental facts. The main mechanism was represented by the reactions

$$n\text{-C}_3\text{H}_7\text{I} \rightleftarrows n\text{-C}_3\text{H}_7 + {}^1/{}_2\text{I}_2 \qquad \text{(equil.) (d-4)}$$
$$n\text{-C}_3\text{H}_7 + \text{I}_2 \longrightarrow \text{iso-C}_3\text{H}_7\text{I} + \text{I} \qquad \text{(slow) (d-5)}$$
$$\text{iso-C}_3\text{H}_7\text{I} \longrightarrow {}^1/{}_2\text{C}_3\text{H}_8 + {}^1/{}_2\text{C}_3\text{H}_6 + {}^1/{}_2\text{I}_2 \text{ (rapid) (d-6)}$$

The equilibrium for reaction (d-4) was calculated from the strength of the bonds involved and the entropies of the reactants. It is expressed by the equation

$$K = 1.22 \times 10^4\, e^{-24{,}700/RT} \left(\frac{\text{mole}}{\text{cc.}}\right)^{1/2}$$

The rate constant k_5 for reaction (d-5) was calculated as

$$k_5 = 1.79 \times 10^8 T^{1/2}\, e^{-12{,}600/RT} \left(\frac{\text{mole}}{\text{cc.}}\right)^{-1} \text{sec.}^{-1}$$

The study of the pyrolysis of *n*-butyl iodide in the temperature range of 590 to 622°K. showed that the reaction rate is similar to the decomposition of *n*-propyl iodide, exhibiting catalysis by iodine. However, no exact calculations of the rate could be made because the ratio of final to initial pressure of the decomposing gases varied when iodine was added to the *n*-butyl iodide initially. Thus the time-pressure measurements were not an accurate measure of the rate of disappearance of *n*-butyl iodide.

STANFORD UNIV., CALIF. RECEIVED JULY 7, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

Kinetics of the Thermal Decomposition of Isopropyl Iodide

BY J. L. JONES AND R. A. OGG, JR.

In a previous paper the kinetics of the thermal decomposition of *n*-propyl iodide and *n*-butyl iodide were discussed.[1] It was shown that the rate determining step for *n*-propyl iodide was given by the expression

$$\frac{-\text{d}(\text{C}_3\text{H}_7\text{I})}{\text{d}t} = k(\text{C}_3\text{H}_7\text{I})(\text{I}_2)^{1/2} \qquad (1)$$

The decomposition of *n*-butyl iodide resembled qualitatively that for *n*-propyl iodide, but it was not treated quantitatively due to a variation in the product composition with the amount of free iodine in the system. It was shown that the pyrolysis of *n*-propyl iodide could be explained by the mechanism

$$n\text{-C}_3\text{H}_7\text{I} \rightleftarrows {}^1/{}_2\text{I}_2 + n\text{-C}_3\text{H}_7\text{(equil.)} \qquad (2)$$
$$n\text{-C}_3\text{H}_7 + \text{I} \longrightarrow iso\text{-C}_3\text{H}_7\text{I(slow)} \qquad (3)$$
$$iso\text{-C}_3\text{H}_7\text{I} \longrightarrow \text{C}_3\text{H}_8 + \text{C}_3\text{H}_6 + {}^1/{}_2\text{I}_2\text{(rapid)} \qquad (4)$$
$$\text{M} + 2\text{I} \longrightarrow \text{I}_2 + \text{M} \qquad (5)$$

Reaction (3) is a slow reaction having an activation energy of 12.6 kcal./mole and a steric factor of 10^{-5}. This small steric factor is not surprising in view of the requirement of this reaction, *e. g.*, the transfer of a hydrogen atom from one carbon atom to another. The activation energy for this reaction is also in line with previous work.

Experimental Section

The isopropyl iodide was prepared according to the procedure of Bogart and Slocum[2] and the fraction boiling at 89.6° was used.

Homogeneity of the Thermal Decomposition.—Since the decomposition of *n*-propyl iodide and *n*-butyl iodide was proved to be homogeneous, it was not thought necessary to test this reaction for homogeneity. Ogg[3] likewise showed that the thermal decomposition of *s*-butyl iodide was homogeneous.

Apparatus and Procedure.—The apparatus and procedure have been described in a previous article.[1]

Experimental Results

Nature of Over-all Reaction.—As previously stated Glass and Hinshelwood[4] determined that the products of the reaction are propylene, propane and iodine in the proper ratio for the over-all reaction

$$2\text{C}_3\text{H}_7\text{I} \longrightarrow \text{C}_3\text{H}_8 + \text{C}_3\text{H}_7 + \text{I}_2 \qquad (6)$$

The average value of the ratio of final to initial pressure, P_∞/P_0, for this work was 1.49 and there was no trend of the ratio with the temperature of the reaction.

---

[1] Jones and Ogg, THIS JOURNAL, **59**, 1931 (1937).

[2] Bogart and Slocum, *ibid.*, **46**, 764 (1924).

[3] Ogg, *Trans. Faraday Soc.*, **31**, 482 (1934).

[4] Glass and Hinshelwood, *J. Chem. Soc.*, 1817 (1929).