[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HOWARD UNIVERSITY]

Kinetics of the Pyrolysis of Isobutyl Iodide

BY J. LESLIE JONES

This work concerns the kinetics of the thermal decomposition of gaseous isobutyl iodide in the temperature range of 550 to 600°K. Jones and Ogg[1] investigated the pyrolysis of *n*-propyl iodide and *n*-butyl iodide in the temperature range of 584 to 627°K. They found that the rate-determining step could be represented in the case of *n*-propyl iodide by the equation

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

The kinetics of the decomposition of the *n*-butyl iodide was qualitatively the same but could not be treated quantitatively. The same authors[2] found that the rate of disappearance of isopropyl iodide was governed by a unimolecular rate expression

$$-\frac{d(C_3H_7I)}{dt} = k(C_3H_7I) \qquad (2)$$

Ogg[3] studied the thermal decomposition of gaseous *s*-butyl iodide in the temperature range 511 to 549°K. He found that the results were best fitted as a combination of a unimolecular reaction plus an iodine catalyzed decomposition of the iodide

$$-\frac{d(C_4H_9I)}{dt} = k_1(C_4H_9I) + k_2(C_4H_9I)(I_2)^{1/2} \quad (3)$$

In view of the varying rate determining equations found for the various homologs, it seemed profitable to investigate additional members of the series with the view of correlating the possible mechanisms involved in the several decompositions. The possibility of certain reactions of free radicals has been strengthened by this generalization of mechanisms. Much evidence indicates that the dissociation energy of the C–I linkage is approximately equal to the activation energy of the above unimolecular reaction,[4] *e. g.*, 43,000 cal.

Experimental Section

The isobutyl iodide employed was an Eastman product. It was dried over calcium chloride and phosphorus pentoxide, then distilled *in vacuo*. The product remained colorless.

The apparatus and procedure employed were described in a previous publication.[1] A slight change was made in this apparatus, substituting a small bore greased stopcock for the Bodenstein greaseless valve. The capillary tubing leading out of the thermostat to the stopcock was heated electrically to prevent condensation of iodine. There was apparently no effect on the rate of decomposition of the alkyl iodide due to this change in apparatus.

Homogeneity of the Thermal Decomposition.—In order to test the homogeneity of the reaction the surface–volume ratio of the system was changed. The major number of experiments were carried out in a 500-cc. Pyrex bulb. Two sets of rate measurements were made in a 280-cc. Pyrex bulb packed with Pyrex glass tubing. The bulbs had surface–volume ratios of 0.63 cm.$^{-1}$ and 8.8 cm.$^{-1}$, respectively. No increase in the rate of reaction was found for the experiments carried out in the packed bulb. As will be shown later, the rate-determining step in the decomposition is of the one-half order with respect to iodine; therefore the agreement of the rate constants for the packed bulb with those in the unpacked bulb indicates the absence of appreciable wall reaction. This result is in agreement with the investigations previously cited for the homologous alkyl iodides.[1,3]

Experimental Results

Nature of the Over-all Reaction.—Glass and Hinshelwood[5] 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

$$2\,C_3H_7I \longrightarrow C_3H_8 + C_3H_6 + I_2 \qquad (4)$$

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, P_∞/P_0, was 1.54 at 351° and 1.45 at 301°. The ratio of P_∞/P_0 was 1.47 for *s*-butyl iodide, 1.55 for *n*-propyl iodide and 1.49 for isopropyl iodide. The present work yielded 1.55 as the value of P_∞/P_0 for isobutyl iodide. There was no apparent trend of the ratio with temperature, although it was difficult to determine accurately the values of P_0 at the highest temperatures employed.

No gases were formed 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 with the above equation. The first method was the direct titration of the

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

[2] Jones and Ogg, *ibid.*, **59**, 1939 (1937).

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

[4] See also Ogg, THIS JOURNAL, **56**, 532 (1934).

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

iodine formed while the second involved the condensation of all products in the side-arm of the reaction vessel by liquid air, then allowing the side-arm to warm to room temperature during evacuation of the reaction vessel. Thus the butylenes and butanes were removed from the vessel, but the iodine, due to its low vapor pressure, remained condensed in the side-arm. The stopcock was closed and the iodine vaporized. Various experiments were frozen out before completion and tested for hydrogen iodide. In most cases none was found, but a few per cent. at most. If the reaction mixtures were allowed to stand for several hours after practical completion, hydrogen iodide formed to the extent of 5 to 10% of the iodine.

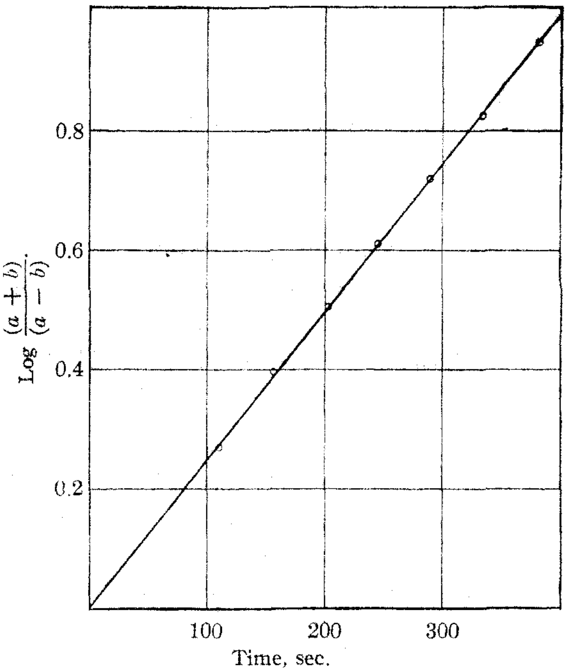

Fig. 1.—Run 24, P_0 = 42.0 mm. T = 319.5°.

All evidence points to the same over-all reaction for the decomposition of *n*-propyl iodide, isopropyl iodide, *n*-butyl iodide, *s*-butyl iodide and isobutyl iodide. This is quite remarkable in view of the fact that the rate determining step varies from case to case.

The Rate-Determining Step of the Thermal Decomposition of Isobutyl 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

$$-\frac{d(C_4H_9I)}{dt} = k(C_4H_9I)(I_2)^{1/2} \qquad (5)$$

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

$$(C_4H_9I) = \frac{1.55\,P_0 - P_t}{0.55} \qquad (6)$$

and in the absence of initial iodine concentration

$$(I_2) = \left(\frac{0.50}{0.55}\right)(P_t - P_0) \qquad (7)$$

if it was assumed that all iodine was present as butyl iodide or free iodine. On integration and evaluation of the integration constant, the rate constant k was given by

$$k = \frac{1}{0.953(0.55)P_0^{1/2}t} \ln \left\{\frac{(0.55P_0)^{1/2} + (P_t - P_0)^{1/2}}{(0.55P_0)^{1/2} - (P_t - P_0)^{1/2}}\right\} \qquad (8)$$

The rate constants were determined by plotting the value of the logarithmic factor of equation (8) against the time. However, the slope of the line was not constant initially, generally being greater over the first 10%. A typical example is given in Fig. 1, where a well-fitting straight line was obtained after the first 10% decomposition. It was noted that the slope of the initial section of the curves fell off more rapidly with increasing temperature and in the majority of experiments well fitting straight lines were obtained after not

TABLE I

Run	Temp., °K.	P_0, mm.	$k \times 10^4$ mm.$^{-1/2}$ sec.$^{-1}$	k(mole/cc.)$^{-1/2}$ sec.$^{-1}$	Log k
20	548.5	23.4	1.43	0.834	−0.0788
23	550.2	34.8	1.09	.639	− .195
22	550.2	54.9	1.18	.692	− .160
28[a]	556.7	28.5	1.19	.702	− .154
29[a]	556.7	100.0	1.09	.642	− .193
14	560.1	102.3	1.75	1.03	.0128
17	560.7	89.8	1.74	1.03	.0128
19	561.1	96.0	2.37	1.40	.146
13	563.1	62.5	2.19	1.30	.114
18	563.1	63.7	2.65	1.57	.196
15	564.4	27.5	3.51	2.08	.318
16	564.6	63.3	2.27	1.35	.130
5	577.0	53.7	4.99	3.01	.479
6	577.0	110.0	5.07	3.06	.486
4	577.3	74.8	6.10	3.68	.566
3	579.8	28.4	6.65	4.01	.603
2	579.8	58.0	6.57	3.97	.599
10	580.2	93.4	6.88	4.14	.617
7	581.3	40.1	7.82	4.71	.673
11	582.4	79.4	6.57	3.96	.598
12	583.3	77.7	7.22	4.36	.640
9	584.3	136.0	6.49	3.92	.593
8	585.9	82.3	7.92	4.79	.680
24	592.6	42.0	12.4	7.54	.877
26	592.8	25.5	13.2	8.03	.905
25	593.6	33.8	13.1	7.96	.901
27	594.4	132.0	12.0	7.31	.864

[a] Runs in packed flask.

more than 10% decomposition. The ordinate intercepts tended toward zero with increasing temperature, indicating that the initial rate determining step has a lower activation energy than the slow reaction predominating after 10% decomposition. Those experiments at the higher temperatures and pressures had zero intercepts. There was no definite trend to the values of k with increasing initial pressure. The experimental values of k are listed in Table I. All results have been included with the exception of the first experiment.

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 37,800 cal./mole with an estimated accuracy of ±2000 cal./mole.

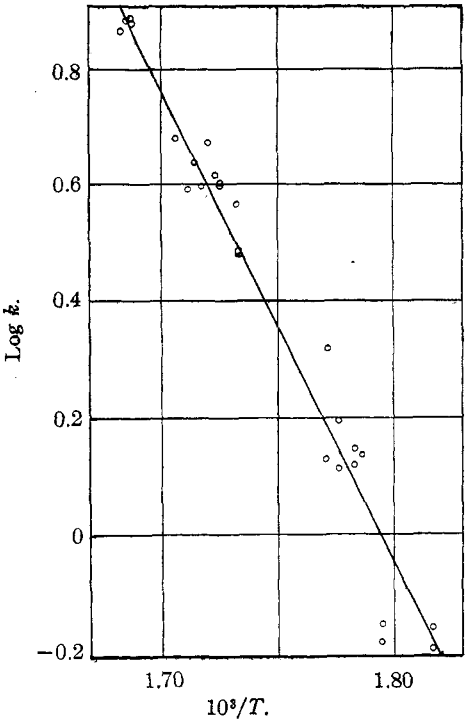

Fig. 2.

Discussion

As in the case of n-propyl iodide the rate-determining expression (5) may be written as

$$-\frac{d(C_4H_9I)}{dt} = k_1K_{I_2}^{1/2}(C_4H_9I)(I) \tag{9}$$

where K_{I_2} is the equilibrium constant for the dissociation of iodine. Two probable mechanisms based upon equation (9) can be rejected as contradictory to experimental facts. The mechanisms are

MECHANISM (a)

$C_4H_9I + I \longrightarrow C_4H_8I + HI$ (slow) (a-1)
$C_4H_8I \longrightarrow C_4H_8 + I$ (a-2)
$C_4H_9I + HI \longrightarrow C_4H_{10} + I_2$ (a-3)
$2I + M \longrightarrow I_2 + M$ (a-4)

MECHANISM (b)

$C_4H_9I + I \longrightarrow C_4H_9 + I_2$ (b-1)
$C_4H_9 + I_2 \longrightarrow C_4H_8 + HI + I$ (b-2)
$HI + C_4H_9I \longrightarrow C_4H_{10} + I_2$ (b-3)
$2I + M \longrightarrow I_2 + M$ (b-4)

In each case these mechanisms are intended to represent the main reaction occurring after about 10% decomposition of the alkyl iodide. In each mechanism reactions (a-1) and (b-1) are the slow rate-determining steps, accounting for the dependence of the experimental rate upon the square root of the iodine concentration.

Consideration of reaction (a-3) or (b-3) indicates that both of these mechanisms are probably invalid. Ogg[4] studied the reaction for the case of methyl, ethyl and n-propyl iodides. He found that the rate of reaction decreased in going from the ethyl iodide to the n-propyl iodide, hence the rate of reaction in the case of isobutyl iodide would be slower. If Ogg's value of the bimolecular constant (his k value) is corrected by a factor of 10^{-1}, the error arising in conversion of the concentration units from mm. to (mole/cc.), the value of the absolute rate of the reaction (a-3) or (b-3) may be calculated. Since the rate of the reaction for the case of ethyl iodide is approximately 0.43 that of n-propyl iodide, it will be assumed that the rate of the corresponding reaction for isobutyl iodide is 0.43 the rate of the reaction for n-propyl iodide. At 550°K. the rate constant for n-propyl iodide is 37.6 (mole/cc.)$^{-1}$ sec.$^{-1}$. Assuming an alkyl iodide concentration of 40 mm. and a hydrogen iodide pressure of 10 mm., the absolute rate of n-propyl iodide disappearance is 1.28×10^{-11} mole/cc./sec. At 550°K. the value of k for isobutyl iodide is 0.637 (mole/cc.)$^{-1/2}$ sec.$^{-1}$. Assuming an alkyl iodide concentration of 40 mm. and an iodine concentration of 10 mm., the absolute rate of disappearance of isobutyl iodide is 3.95×10^{-10} mole/cc./sec. Hence one may consider the experimental rate of disappearance of isobutyl iodide as 72 times the rates of disappearance as calculated for reaction (a-3) or (b-3). Assuming the same concentration values at 585°K., the absolute rate of reaction (a-3) for n-propyl iodide is 5.18×10^{-11} mole/cc./sec. and the experimental rate of disappearance of isobutyl iodide is 2.86×10^{-9} mole/cc./sec. Therefore, at 585°K. the experimental rate of disappearance of isobutyl iodide is 127 times the rate of disappearance as calculated for the reaction (a-3) or (b-3).

Evidence[2,4] indicates that the energy required to break the C–I linkage is 43 kcal., and the heat of dissociation of hydrogen iodide is 70.7 kcal. The reverse of reaction (a-1) (for *n*-propyl iodide) is thought to possess an activation energy[3] of 14 kcal. These data yield a value of the carbon–hydrogen linkage of 74.7 kcal. This value is quite low in comparison with the value of 94.5 kcal. calculated by Kistiakowsky and Gershinowitz[6] from the dissociation of cyanogen into cyanide radicals. Such a low value for the C–H bond does not seem plausible even in the possible case of a secondary hydrogen linkage. This constitutes a second serious objection to mechanism (a).

Mechanism (c)

$$C_4H_9I + I \longrightarrow C_4H_9 + I_2 \tag{c-1}$$
$$C_4H_9 + C_4H_9I \longrightarrow C_4H_{10} + C_4H_8I \tag{c-2}$$
$$C_4H_8I \longrightarrow C_4H_8 + I \tag{c-3}$$
$$2I + M \longrightarrow I_2 + M \tag{c-4}$$

This mechanism is quite probably the one which prevails in the decomposition of *s*-butyl iodide (with the addition of a simple unimolecular rate determining step). The absolute rate of the iodine atom catalyzed reaction for *s*-butyl iodide at 549°*K*. and the previous concentration units is 1.86×10^{-10} mole/cc./sec. Compare this with the experimental absolute rate of disappearance of isobutyl iodide, *e. g.*, 3.95×10^{-10} mole/cc./sec. at 550°K. The structure of isobutyl iodide with regard to the carbon–iodine bond is similar to the normal alkyl iodide. In the case of *n*-propyl iodide[4] the reaction between free propyl radical and iodine molecule is more rapid than reaction (c-2). Hence, on the basis of the similar rate-determining steps one can rule out this mechanism as it is also improbable for *n*-propyl iodide.

Mechanism (d).—A mechanism was presented in the paper on *n*-propyl iodide which adequately described the decomposition. This mechanism may be generalized to account for the pyrolysis of isobutyl iodide.

The reaction rate constant is comparatively high for the first 10% decomposition, decreasing meanwhile to give a constant value over the remainder of the pyrolysis. Comparison of the unimolecular rate data for *s*-butyl iodide and *n*-propyl iodide yields some interesting results. At 550°K. and the given concentration units, the absolute rate of disappearance of *s*-butyl iodide is 2.42×10^{-10} mole/cc./sec. and for *n*-propyl iodide 2.62×10^{-10} mole/cc./sec. On this basis one can account for the rate of the initial decomposition of isobutyl iodide by the mechanism proposed for *n*-propyl iodide, *e. g.*

$$C_4H_9I \longrightarrow C_4H_9 + I \tag{d-1}$$
$$C_4H_9 + C_4H_9I \longrightarrow C_4H_{10} + C_4H_8 + I \tag{d-2}$$

Reaction (d-2) is a comparatively slow reaction, the rate constant of the reaction of the free radical with iodine molecule probably being larger.

Due to the reaction between *n*-propyl radicals and iodine molecules the equilibrium (d-3) is established quite rapidly. On this basis the main mechanism is

$$i\text{-}C_4H_9I \rightleftarrows i\text{-}C_4H_9 + {}^1/_2\, I_2(\text{equil.}) \tag{d-4}$$
$$i\text{-}C_4H_4 + I_2 \longrightarrow \underline{\underline{C_4H_9I}} + I(\text{slow}) \tag{d-5}$$
$$i\text{-}C_4H_9 + \underline{\underline{C_4H_9I}} \longrightarrow C_4H_{10} + C_4H_8 + I(\text{rapid}) \tag{d-6}$$
$$2I + M \longrightarrow I_2 + M$$

The formula $\underline{\underline{C_4H_9I}}$ represents an activated molecule whose spatial configuration is not necessarily that of isobutyl iodide. This activated molecule reacts with an isobutyl radical, simultaneously losing a hydrogen atom and an iodine atom to form butene. Calculations below indicate that reaction (d-4) has a steric factor of about 10^{-4}. This factor can represent the infrequent occurrence of the proper internal phase conditions necessary for the formation of the activated molecule which has the opportunity of colliding with an isobutyl radical. In the case of *n*-propyl iodide it was considered[1] that the slow step (d-4) resulted in the formation of isopropyl iodide whose rate of decomposition is known[2] to be faster than that of *n*-propyl iodide. Calculations which are presented above indicate that the absolute rate of decomposition of *s*-butyl iodide is less than that of isobutyl iodide; hence, *s*-butyl iodide could not be a possible isomerization product of isobutyl iodide. In addition the isomerization would involve a shift of a carbon atom, a process requiring high activation energy. Isomerization to *t*-butyl iodide would require only the shift of a hydrogen atom; however, *t*-butyl iodide decomposes[7] to form isobutylene and hydrogen iodide and the hydrogen iodide would accumulate in concentrations greater than the experimental values.

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(6) Kistiakowsky and Gershinowitz, *J. Chem. Phys.*, **1**, 432 (1933).

(7) Jones and Ogg, THIS JOURNAL, **59**, 1942 (1937).

Some interesting calculations can be made concerning the rate of reaction (d-5). Since the equilibrium constant K for (d-4) is

$$\frac{(I_2)^{1/2}(i\text{-}C_4H_9)}{(i\text{-}C_4H_9I)} = K$$

then

$$-\frac{d(i\text{-}C_4H_9I)}{dt} = k_5(i\text{-}C_4H_9)(I_2) = k_5K(i\text{-}C_4H_9I)(I_2)^{1/2}$$

The experimental value k is equal to k_5K. As the equilibrium constant K is given by $K = e^{\Delta S^0/R}$ $e^{-Q/RT}$, where ΔS^0 is the standard entropy change for reaction (d-4), the rate constant k_5 can be calculated if the entropies of the compounds involved in the reaction are known.

The value of ΔS^0 is calculated at 570°K. The entropy of the iodine molecule at 570°K. (62.53 e. u.) is calculated from the spectroscopic data of Murphy[8] and the Sackur–Tetrode equation. As an approximation, the entropy of the isobutyl radical is taken to be that of isobutane, the data of Pitzer[9] being used to calculate the translational plus rotational entropy of the molecule. The value is 65.64 e. u. at 570°K. Since the calculation of ΔS^0 is primarily concerned with the breaking of the carbon–iodine bond, it will be assumed that the remaining vibrational entropy of isobutyl iodide and isobutyl radical will cancel in the reaction. Hence, only the vibrational entropy ascribed to the carbon–iodine bond is calculated,[10] using 503 and 260 cm.$^{-1}$ (doubly degenerate) as the proper frequencies. The total value of the vibrational entropy ascribed to the bond is 4.41 e. u. The rotational and translational entropy of isobutyl iodide is calculated as 74.01 e. u. where the moments of inertia are taken as 9.0×10^{-39}, 61.0×10^{-38} and 61.0×10^{-38} g. cm.^{2}.

The value of ΔS^0 is 15.52 e. u. at 570°K. and the value of $e^{\Delta S^0/R}$ is 2.48×10^3. The data of Murphy give the heat of dissociation of iodine at 570°K. as 36.65 kcal./mole. The probable heat of dissociation of the primary carbon–iodine bond is 43 kcal. Hence, the value of the heat of reaction Q for the equilibrium (d-4) is 24.7 kcal. So

$$K = 2.48 \times 10^3 e^{-24{,}700/RT}\ (\text{mole/cc.})^{1/2}$$

The critical increment E_5 for the reaction (d-4) is related to the true activation energy Q_5 by the relation $E_5 = Q_5 + {}^1/_2RT$ (simple bimolecular reaction theory). As E_5 is 13.1 kcal./mole, Q_5 is 12.5 kcal./mole. The temperature dependent equation for k_5 is given by $k_5 = 3.39 \times 10^9$ $T^{1/2}e^{-12{,}500/RT}$ (mole)$^{-1}$/(cc.) sec.$^{-1}$. This equation gives an effective collision diameter of 9.1×10^{-10} cm. Assuming a "true collision diameter" of 6×10^{-8} cm., this corresponds to a steric factor of approximately 2.3×10^{-4}. This value of the steric factor is probably accurate to a factor of 10^2.

On the basis of the above experimental data the reaction

$$i\text{-}C_4H_9 + I_2 \longrightarrow i\text{-}C_4H_9I + I$$

may be considered to have the same activation energy as (d-5). Previous work indicates that the reaction

$$s\text{-}C_4H_9 + I_2 \longrightarrow s\text{-}C_4H_9I + I$$

has an activation energy of 14.2 kcal. and the reaction

$$C_2H_4I + I_2 \longrightarrow C_2H_4I_2 + I$$

has an activation energy of 11.2 kcal. On the basis of the above discussion the reaction

$$n\text{-}C_3H_7 + I_2 \longrightarrow n\text{-}C_3H_7I + I$$

has an activation energy of 12.6 kcal.

On the whole a consistent interpretation can be given to the thermal decomposition of the alkyl iodides based upon a large amount of experimental data. It is felt that the work indicates that the reactions of free radicals require appreciable activation energy, in accord with other existing experimental evidence. At the present there is no evidence which indicates that the strength of the primary carbon–iodine bond is not approximately 43 kcal.

Summary

An experimental study is presented on the kinetics of the thermal decomposition of gaseous isobutyl iodide in the temperature range of 550 to 600°K. The rate of disappearance of isobutyl iodide is expressed by

$$-\frac{d(C_4H_9I)}{dt} = k(C_4H_9I)(I_2)^{1/2}$$

Several proposed mechanisms are shown to be invalid. A mechanism consistent with the experimental data and also explaining the decomposition of n-propyl iodide is in the main

$$\begin{array}{rcll} i\text{-}C_4H_9I & \rightleftharpoons & i\text{-}C_4H_9 + {}^1/_2\, I_2(\text{equil.}) & (\text{d-4}) \\ i\text{-}C_4H_9 + I_2 & \longrightarrow & \underline{\underline{C_4H_9I}} + I(\text{slow}) & (\text{d-5}) \\ i\text{-}C_4H_9 + \underline{\underline{C_4H_9I}} & \longrightarrow & C_4H_9 + C_4H_{10} + I(\text{fast}) & (\text{d-6}) \\ 2I + M & \longrightarrow & I_2 + M & \end{array}$$

The equilibrium constant K for reaction (d-4) is

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[8] Murphy, *J. Chem. Phys.*, **4**, 344 (1936); Tolman, "Statistical Mechanics as Applied to Physics and Chemistry," Chemical Catalog Co., New York, N. Y., 1927.

[9] Pitzer, *J. Chem. Phys.*, **5**, 473 (1937).

[10] Halford, *ibid.*, **2**, 694 (1934); Mayer, Brunauer and Mayer, THIS JOURNAL, **55**, 37 (1933).

calculated from certain assumptions and spectroscopic data; the rate constant k_5 for reaction (d-5) also has been calculated.

WASHINGTON, D. C. RECEIVED APRIL 18, 1938

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

The Synthesis of Disubstituted Acetylenes

BY JOHN R. JOHNSON, A. M. SCHWARTZ AND THOMAS L. JACOBS

In pursuing an investigation of the reactions of certain acetylenic systems, a number of disubstituted propynes of the type $R—C≡C—CH_2—R'$ were required. The present paper reports a study of synthetic methods for the preparation of pure individuals of known structure.

The alkylation of monosubstituted acetylenes was investigated as a promising preparative method. Nef[1] reported the methylation of phenylacetylene by heating it with methyl iodide and potassium hydroxide, and Morgan[2] effected ethylation of phenylacetylene by heating the sodium derivative with ethyl iodide. Both reactions were carried out in sealed tubes at relatively high temperature (140°) and the yields were low. Preliminary studies of these methods indicated that neither would be satisfactory for preparative purposes. In attempting to employ the method of Morgan, it was found that the sodium derivatives of typical alkyl- and arylacetylenes were surprisingly inert toward alkyl halides. At temperatures sufficiently high to bring about a reaction, vigorous deep-seated decomposition occurred. The substituted acetylides are evidently much less reactive than the monosodium derivative of acetylene itself, which reacts smoothly with alkyl halides at low temperatures.[3] Attempts to effect metathetical reactions between alkyl halides and other metallic derivatives of monosubstituted acetylenes (such as the bromomagnesium, cuprous, silver, and mercuric compounds), in a variety of solvent media, were also unsuccessful.[4]

In an investigation of the action of alkyl *p*-toluenesulfonates on organomagnesium halides, Gilman and Beaber[5] reported the synthesis of β-chloroethylphenylacetylene from the bromomagnesium derivative of phenylacetylene and β-chloroethyl *p*-toluenesulfonate. We have employed their method with excellent results for the preparation of several alkyl derivatives of phenylacetylene. However, the modification of Truchet,[6] in which the sodium derivatives of the acetylenes are used, is advantageous in one respect. When the organomagnesium halide is used, two moles of the sulfonic ester is consumed in producing one equivalent of the alkylated acetylene, since one mole of the ester is converted to the corresponding alkyl bromide (reaction I);[7] but with the sodium acetylides only one equivalent of the sulfonic ester is required (reaction II).

$$R—C≡C—MgBr + 2R'—OSO_2—C_7H_7 \longrightarrow R—C≡C—R' + R'—Br + Mg(OSO_2—C_7H_7)_2 \quad \text{(I)}$$

$$R—C≡C—Na + R'—OSO_2—C_7H_7 \longrightarrow R—C≡C—R' + NaOSO_2C_7H_7 \quad \text{(II)}$$

The sodium derivatives were used with satisfactory results for the alkylation of phenylacetylene and *n*-octylacetylene, to obtain the following disubstituted acetylenes: ethyl-, *n*-butyl-, and γ-chloropropylphenylacetylene; ethyl- and γ-chloropropyl-*n*-octylacetylene. The sodium derivatives appeared to be particularly advantageous in the aliphatic series, but there are certain limitations. Attempts to effect syntheses using phenylethynylsodium and benzyl or β-chloroethyl *p*-toluenesulfonate were unsuccessful. In these instances, however, the desired compounds were obtained by the use of phenylethynylmagnesium bromide.

The structures of the disubstituted acetylenes were checked by several methods. In some instances oxidation with aqueous potassium permanganate was employed and the resulting acids

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(1) Nef, *Ann.*, **310**, 333 (1900).

(2) Morgan, *J. Chem. Soc.*, **29**, 162 (1876).

(3) Picon, *Compt. rend.*, **169**, 32 (1919).

(4) A few exceptionally active halides do react with phenylethynylmagnesium bromide to give substituted phenylacetylenes; *e. g.*, allyl bromide [Grignard and Lapayre, *ibid.*, **192**, 250 (1931)], benzohydryl bromide [Wieland and Kloss, *Ann.*, **470**, 217 (1928)], α-furfuryl chloride [Gilman, Van Ess and Burtner, THIS JOURNAL, **55**, 3461 (1933)].

(5) Gilman and Beaber, *ibid.*, **45**, 839 (1923).

(6) Truchet, *Compt. rend.*, **191**, 854 (1930); *Ann. chim.*, [10] **16**, 309 (1931).

(7) Marvel and Rossander, THIS JOURNAL, **50**, 1491 (1928). The correctness of this equation was confirmed in the present work by the isolation of ethylene chlorobromide and benzyl bromide from the reactions in which β-chloroethyl and benzyl *p*-toluenesulfonates were used.