[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

# The Equilibrium $(CH_3)_3CI \rightleftarrows (CH_3)_2C{=}CH_2 + HI$

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

In carrying out the program previously outlined[1] by Jones and Ogg, *e. g.*, the study of the kinetics of the thermal decomposition of the lower alkyl iodides, the results of the investigation of *t*-butyl iodide are presented here. The experimental results obtained for the series of compounds *n*-propyl, isopropyl, *n*-butyl and *t*-butyl iodides strikingly illustrate the differences in the molecular structure of the molecules. Gaseous *t*-butyl iodide decomposes into isobutylene and hydrogen iodide. Under suitable experimental conditions, equilibrium is established between the alkyl iodide and its reaction products.

$$(CH_3)_3CI \rightleftarrows (CH_3)_2C{=}CH_2 + HI \qquad (1)$$

The reaction is not homogeneous, showing definite surface effects in a Pyrex system. However, the equilibrium has been studied and the data obtained enable one to calculate some useful thermodynamic constants of *t*-butyl iodide.

## Experimental Section

**Preparation of *t*-Butyl Iodide.**—The *t*-butyl iodide was prepared as in the case of the previous iodides, according to the procedure of Bogart and Slocum.[2] Because of the decomposition of the iodide at the normal boiling point, the reacting mixture of alcohol and red phosphorus was vacuum distilled in an atmosphere of nitrogen to yield a yellow crude product. The crude product was washed with 0.1 *N* sodium thiosulfate and dried over calcium chloride. It was fractionally distilled through two evacuated cooling traps attached in series to the iodide reservoir of the apparatus. A water white product was obtained. It was decomposed easily by light and was kept in a dark container.

The isobutylene was a portion of a sample used by Todd and Parks[3] in their determination of its heat capacity. The sample was quite pure and was used as obtained from them.

**Homogeneity of the Thermal Decomposition.**—The same technique and apparatus was employed in measuring the decomposition of *t*-butyl iodide as for the previously described *n*-propyl, isopropyl and *n*-butyl iodides. Heterogeneity tests indicated that the reaction is appreciably heterogeneous. In view of the facts which appeared later it was not necessary to study the heterogeneity further. This type of reaction was not surprising in view of the similar results obtained by Brearley, Kistiakowsky and Stauffer[4] for the unimolecular decomposition of *t*-butyl chloride and *t*-amyl chloride. They found that it was necessary to treat their reaction flask several times with decomposition products at high temperature, depositing a carbonaceous layer, in order to obtain reproducible results. Kistiakowsky and Stauffer[5] reported that even more similar treatments were necessary in order to obtain reproducible results in the case of the unimolecular decomposition of *t*-butyl bromide into isobutylene and hydrogen bromide.

## Experimental Results

**Nature of the Over-all Reaction.**—As the reaction cell was equipped for visual observation, it soon became evident that the reaction which occurred did not involve formation of iodine in most experiments. The nature of the final to initial pressure ratio for experiments at the same temperature indicated that equilibrium constants could be calculated for reaction (1).

Hydrogen iodide was detected qualitatively by its reaction with sodium iodate solution. Iodine was formed in the experiments at the highest temperature 175°, if the initial pressure was greater than 150 mm., no doubt due to the reduction of the butyl iodide by hydrogen iodide. Such a bimolecular reaction was sufficiently slow at the lower concentrations as to be negligible. The absence of side reactions at the lower pressures was corroborated by the agreement of the equilibrium constants below this pressure. The formation of iodine was also observed at 150° for pressures of 150 mm. or greater. Agreement between the equilibrium constants obtained for experiments in which isobutylene was added initially to the iodide and equilibrium constants for experiments without added isobutylene showed that isobutylene was a product of the decomposition of the *t*-butyl iodide.

It was interesting to note that the experimental pressure went through a maximum for the experiments with initial pressure of about 190 mm. or more, when the temperature was 150° or greater. This was not investigated extensively, but it seems probable that this pressure maximum was due to the polymerization of the isobutylene formed in the primary reaction. Supporting this is the experimental fact that the final pressure never fell below the initial iodide pressure,

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

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

[3] Todd and Parks, *ibid.*, **58**, 134 (1936).

[4] Brearley, Kistiakowsky and Stauffer, *ibid.*, **58**, 43 (1936).

[5] Kistiakowsky and Stauffer, *ibid.*, **59**, 168 (1937).

and in several cases dropped to just that value after a sufficient time interval.

**Determination of the Equilibrium Constants.**—Since the equilibrium measured is given by (1), the equilibrium constant for the reaction as written is

$$K = (C_4H_8)(HI)/(C_4H_9I) \qquad (2)$$

If no isobutylene is added initially, the concentration of hydrogen iodide and isobutylene is given by

$$(C_4H_8) = (HI) = (P_\infty - P_0)$$

and the concentration of *t*-butyl iodide by

$$(C_4H_9I) = (2P_0 - P_\infty)$$

$P_0$ is the initial pressure of alkyl iodide and $P_\infty$ represents the final pressure of the system. If an initial concentration, $P_i$, of isobutylene is added then the equilibrium concentration of isobutylene is

$$(C_4H_8) = (P_i + P_\infty - P_0)$$

where the initial and the final experimental pressures must be corrected by subtracting $P_i$, and the concentration of hydrogen iodide and *t*-butyl iodide are given as above.

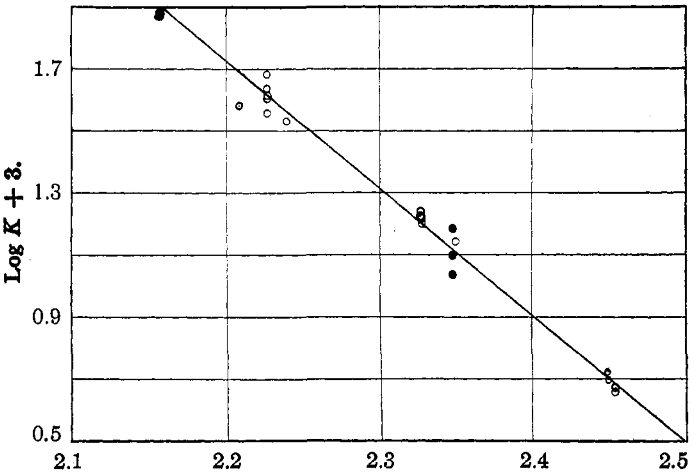

Fig. 1.—○, no isobutylene added initially; ●, isobutylene added initially.

All of the experimentally determined equilibrium constants are given in Table I, the values of $K$ being expressed in atmospheres. Figure 1 is a plot of the values of log $K$ against $(1/T)$ and the heat of the reaction in the experimental temperature range is determined by the slope of the best line drawn through the points. The value of $\Delta H^0$ is 19,150±1000 cal.

TABLE I

THE THERMAL EQUILIBRIUM $(CH_3)_3CI \rightleftharpoons C_4H_8 + HI$

| Run | Temp., °K. | $10^3/T$ | $P_0$, mm. | $P_\infty$, mm. | $P_i$, mm. | $K$, atm. | log $K$ + 3 |
|---|---|---|---|---|---|---|---|
| 21 | 407.5 | 2.454 | 79.4 | 94.3 | | 0.00453 | 0.6561 |
| 23 | 407.5 | 2.454 | 89.9 | 106.1 | | .00469 | .6712 |
| 17 | 408.1 | 2.449 | 53.9 | 66.7 | | .00525 | .7202 |
| 18 | 408.1 | 2.449 | 129.9 | 150.2 | | .00495 | .6946 |
| 24 | 425.6 | 2.350 | 111.3 | 140.6 | | .01377 | 1.1389 |
| 28 | 425.7 | 2.349 | 32.1 | 133.7 | 99.3 | .01085 | 1.0354 |
| 27 | 425.7 | 2.349 | 45.3 | 140.7 | 90.5 | .01523 | 1.1827 |
| 26 | 425.7 | 2.349 | 50.2 | 149.1 | 94.5 | .01250 | 1.0969 |
| 11 | 429.6 | 2.328 | 93.0 | 121.5 | | .01657 | 1.2193 |
| 12 | 429.6 | 2.328 | 26.7 | 39.6 | | .01587 | 1.2006 |
| 14 | 429.8 | 2.327 | 116.2 | 148.8 | | .01673 | 1.2235 |
| 16 | 429.8 | 2.327 | 56.5 | 78.0 | | .01737 | 1.2400 |
| 22 | 446.5 | 2.240 | 115.1 | 158.2 | | .0340 | 1.5315 |
| 8 | 449.0 | 2.227 | 22.7 | 37.5 | | .0365 | 1.5623 |
| 9 | 449.0 | 2.227 | 67.2 | 101.8 | | .0483 | 1.6839 |
| 7 | 449.0 | 2.227 | 115.4 | 161.5 | | .0404 | 1.6064 |
| 5 | 449.1 | 2.227 | 26.8 | 44.3 | | .0433 | 1.6365 |
| 4 | 449.1 | 2.227 | 53.8 | 82.1 | | .0413 | 1.6160 |
| 1 | 449.1 | 2.227 | 103.2 | 146.2 | | .0404 | 1.6064 |
| 31 | 452.7 | 2.209 | 32.8 | 53.1 | | .0382 | 1.5820 |
| 35 | 463.5 | 2.157 | 22.0 | 122.9 | 93.0 | .0744 | 1.8716 |
| 34 | 463.5 | 2.157 | 35.4 | 137.7 | 90.7 | .0765 | 1.8837 |

**Calculations.**—Utilizing the equation for free energy, the temperature dependence of $\Delta F^0$ is determined as

$$\Delta F^0 = 19{,}150 - 36.4T$$

and the standard free energy of the reaction

$$(CH_3)_3CI\ (g) \rightleftharpoons C_4H_8\ (g) + HI\ (g)$$

is $\Delta F^0_{298} = 8300$ cal. Todd and Parks[3] give the free energy of formation of gaseous isobutylene as $\Delta F^0_{298} = 14{,}240$ cal. and the value for gaseous hydrogen iodide is taken[6] as $\Delta F^0_{298} = 315$ cal. From these data the standard free energy of formation of *t*-butyl iodide at 298.1°K. is 6260 cal. From the third law of thermodynamics, the value of $\Delta S^0_{298}$ for reaction (1) is 36.4 ± 3.3 e. u. Taking $S^0_{298} = 69.0$ e. u. for isobutylene and $S^0_{298} = 49.4$ e. u. for gaseous hydrogen iodide,[6] the entropy of gaseous *t*-butyl iodide becomes $S^0_{298} = 82.0 \pm 3.3$ e. u. In order to determine the entropy of liquid *t*-butyl iodide it is necessary to know the entropy of vaporization of the liquid at 298.1°K. Since there is no work in the literature from which this can be calculated, one must use the vapor pressure equation[7] of isopropyl iodide. The heat of vaporization of *t*-butyl iodide is taken as 7900 cal. in the temperature range 0 to 30° and the vapor pressure at 298°K. is assumed to be 71 mm. Hence the entropy of liquid *t*-butyl iodide is $S^0_{298} = 60.2 \pm$

(6) Giauque and Wiebe, THIS JOURNAL, **51**, 1441 (1929).

(7) "International Critical Tables," Vol. III, McGraw-Hill Book Co., 1928, p. 216.

3.3 e. u. Parks and Huffman[8] predict a value of 55.8 e. u.

## Summary

The thermal decomposition of *t*-butyl iodide was found to be heterogeneous; however, a successful study was made of the equilibrium involved, *e. g.*

$$(CH_3)_3CI \rightleftarrows (CH_3)_2C{=}CH_2 + HI$$

The heat of the reaction in the temperature range of 408 to 464°K. was found to be 19,150 ± 1000 cal. endothermic. The standard entropy of the liquid iodide was calculated as $S^0_{298} = 60.2 \pm 3.3$ e.u. and the free energy of formation of the gaseous iodide as $\Delta F^0_{298} = 6260$ cal.

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[8] Parks and Huffman, "Free Energy of Some Organic Compounds," Chemical Catalog Co., N. Y., 1932, p. 210.

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# β-Vinylpyridine and β-Vinylpiperidine

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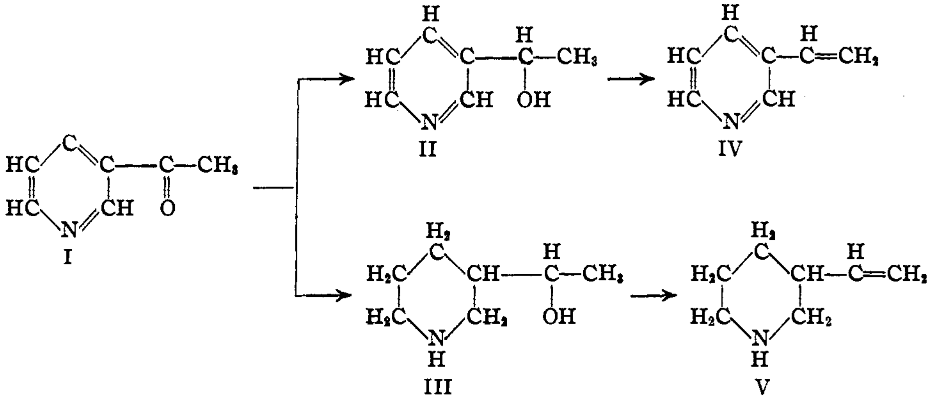
β-Vinylpyridine and β-vinylpiperidine are of interest because of the structural relationship of the latter to the meroquinine structure and to that of the normal cinchona alkaloids.[1] Previously α-vinylpyridine,[2,3] γ-vinylpyridine,[4] α-vinylpiperidine[2] and β-vinylpiperidine[5] have been prepared.

In this study β-vinylpyridine has been prepared and characterized and β-vinylpiperidine has been prepared by a different synthesis and further characterized.

β-Acetylpyridine (I), prepared by the sequence of reactions developed by Strong and McElvain,[6] was reduced with hydrogen and Adams platinum oxide catalyst to β-pyridylmethylcarbinol (II).[6] In separate runs, after the addition of one molecular equivalent of hydrogen, hydrochloric acid was added, and the reduction continued further, producing both β-ethylpiperidine and β-piperidylmethylcarbinol (III).[6] These products were separated by fractional distillation. The secondary carbinols were dehydrated successfully to yield the corresponding vinyl derivatives (IV and V) which were characterized by the formation of solid salts. The properties of the β-vinylpiperidine prepared by the dehydration of the secondary alcohol (III) agreed with those recorded in a previous preparation of the compound[5] from the primary alcohol, 2-β-piperidylethanol-1.



## Experimental

**β-Acetylpyridine.**—β-Acetylpyridine hydrochloride prepared according to the directions of Strong and McElvain,[6] was dissolved in water and treated with an excess of a saturated solution of sodium carbonate solution. The free base was recovered as an oily layer and by ether extraction. After drying and removal of ether, the free base was distilled at 100–110° (10–15 mm.). The average yield was 95–96%.

β-Pyridylmethylcarbinol, b. p. 135–140° (10–15 mm.), was prepared as described by Strong and McElvain[6] with an average yield of 75–90%.

β-Piperidylmethylcarbinol, distilling at 130–135° (10–15 mm.), was produced with an average yield of

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[1] Henry, Solomon and Gibbs, *J. Chem. Soc.*, 593 (1937).

[2] Ladenburg, *Ber.*, **22**, 2585 (1889).

[3] Einhorn, *Ann.*, **265**, 229 (1891).

[4] Meisenheimer, *ibid.*, **420**, 208 (1919).

[5] Merchant and Marvel, THIS JOURNAL, **50**, 1197 (1928).

[6] Strong and McElvain, *ibid.*, **55**, 816 (1933).