324. *The Use of Equilibrium Constants to calculate Thermodynamic Quantities. Part I. Equilibria in the System* tert.*-Butyl Chloride,* iso*Butene, Hydrogen Chloride.*

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Equilibria in the gaseous system *tert.*-butyl chloride–*iso*butene–hydrogen chloride have been measured in the temperature range 61—175°. When hydrogen chloride and *iso*butene are considered as the reactants, the results may be expressed by the formula $\log_{10}K_p = (17{,}700/4{\cdot}575T) - 8{\cdot}27$ (K_p being in atmosphere units). By combining this result with other thermochemical and thermodynamic data, the heat of formation and entropy of *tert.*-butyl chloride are deduced. Comparison of the " experimental " and statistical entropies indicates that the potential barrier to internal rotation is 4·8 kcals./g.-mol. for each methyl group in *tert.*-butyl chloride.

Equilibria in the gaseous system *tert.*-butyl chloride–*iso*butene–hydrogen chloride were studied by Kistiakowsky and Stauffer (*J. Amer. Chem. Soc.*, 1937, **59**, 165) and their results may be summarised by the equation $\log_{10}K_p = (17{,}100/4{\cdot}58T) - 7{\cdot}89$, where K_p is in atmosphere units. However, although nominally these measurements were carried out over the temperature range 90—240°, the above result is derived from only 11 experiments, more than half of which lie in a 20° range. For this and other reasons which will appear later, it has seemed desirable to repeat this work.

EXPERIMENTAL.

Material.—Commercial *tert.*-butyl chloride was purified by distillation, the main fraction of b. p. 50·3—50·5° being taken. This product was fractionally crystallised six times. For the last three crystallisations, the f. p. was constant at $-25{\cdot}4° \pm 0{\cdot}1°$ until almost the whole bulk was frozen. The accepted material was dried over calcium chloride plus a little calcium oxide and had the following physical properties : b. p. 50·4°/760 mm., f. p. $-25{\cdot}4°$, n_D^{20} 1·3852 ($dn_D/dT = -0{\cdot}00057$).

The vapour pressure of *tert.*-butyl chloride, measured over the range 0—50° with an isoteniscope, may be expressed by the equation

$$\log_{10} p = 32{\cdot}256 - (2596{\cdot}6/T) - 8{\cdot}5055 \log_{10} T$$

whence the Trouton constant is 19·81. (The best recorded values for the principal physical constants have recently been summarised by Barton and Onyon, *Trans. Faraday Soc.*, 1949, **45**, 725.)

Apparatus.—The apparatus is shown diagrammatically in Fig. 1. The Pyrex-glass reactor, which was loosely packed with glass wool [cf. Kistiakowsky and Stauffer, *loc. cit.*, and Rudkowskii and Trifel, *Org. Chem. Ind.* (*U.S.S.R.*), 1936, **2**, 203; *Chem. Abs.*, 1937, **31**, 1004], had a volume of approx. 200 ml., the unheated parts having an estimated volume of 1—2 ml. It was surrounded by a vapour jacket, and was kept at various temperatures by refluxing purified liquids under atmospheric pressure from flask *A*. Determinations of the temperatures with standard thermometers inserted at *B* showed no significant difference at any time from the b. p.s calculated under the prevailing atmospheric conditions. The Bourdon gauge was used as a null-point instrument.

Results.—The equilibria determined have been approached from one side only, namely, by the decomposition of *tert.*-butyl chloride. Equilibrium conditions were indicated by the cessation of pressure changes (cf. Kistiakowsky and Stauffer, *loc. cit.*). Attempts were also made to determine the hydrogen chloride concentration at the completion of reaction, by condensing out the products in a liquid-air trap directly connected to the reactor. The condensate was allowed to warm to room temperature in a current of nitrogen and swept into a Dreschel bottle containing water, as detailed by Barton and Howlett (*J.*, 1949, 155, 165) for ethylene or vinyl chloride–hydrogen chloride mixtures. Subsequent titration of the hydrogen chloride with alkali, however, gave variable results for the *tert.*-butyl chloride decompositions, always considerably less than the concentration indicated by pressure measurements. This is not surprising in view of the findings by Kharasch, Kleiger, and Mayo (*J. Org. Chem.*, 1939, **4**, 428) that the rate of the liquid-phase addition of hydrogen chloride to *iso*butene is appreciable at −80° and that it is many times faster than the corresponding addition to vinyl chloride at room temperature.

FIG. 1.

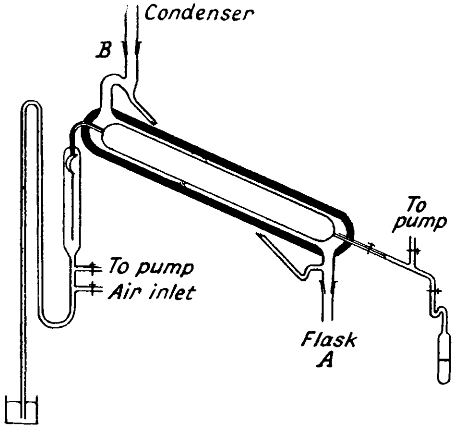
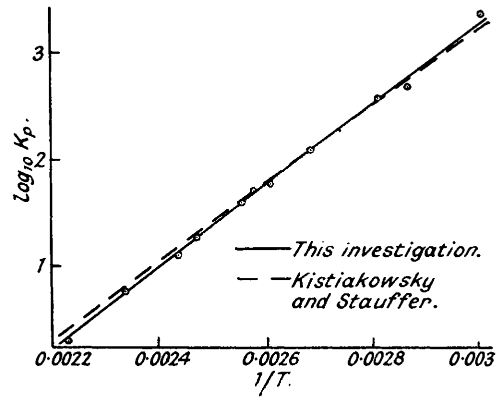


FIG. 2.



The reaction was studied at total pressures of between 70 and 200 mm. over the temperature range 61—175°.

It is pertinent to enquire whether pressure gives an accurate measure of concentrations under the stated experimental conditions. The fugacities of hydrogen chloride, *iso*butene, and *tert.*-butyl chloride were therefore calculated from the respective van der Waals constants (see following table, where *a* and *b* are quoted in litre-atmosphere units).

Substance.	*a*.	*b*.	Source.
HCl	3·67	0·0408	Partington, " Advanced Treatise on Physical Chemistry," Vol. I., p. 667.
iso-C_4H_8	12·6	0·109	Calc. from critical data of Beattie, Ingersoll, and Stockmayer, *J. Amer. Chem. Soc.*, 1942, **64**, 546.
tert.-C_4H_9Cl	21·3	0·152	Est. from constants for *iso*butane.

For all these gases up to 1 atmosphere total pressure and over the temperature range covered in these experiments, the fugacities may be expressed as $P - f = xP^2$, where x is a constant for each substance dependent only on the temperature. With P in atmospheres, values of x are as listed below. From these

Temp., ° K.	HCl.	*iso*-C_4H_8.	*tert.*-C_4H_9Cl.	Temp., ° K.	HCl.	*iso*-C_4H_8.	*tert.*-C_4H_9Cl.
323	0·0036	0·0098	0·0187	423	0·0019	0·0041	0·0086
373	0·0027	0·0062	0·0129	473	0·0014	0·0026	0·0064

it is found that the corrections to be applied to pressure measurements are negligible except at the lowest temperatures, where they are of the order of the experimental accuracy (0·1—0·2 mm.). Where necessary, the corrections were applied, and the equilibrium constants obtained are shown below. To facilitate comparison with the earlier work of Kistiakowsky and Stauffer, K_p is calculated by considering the reaction to be the addition of hydrogen chloride to *iso*butene to give *tert.*-butyl chloride as product.

Temp., ° K. ...	334·1	349·9	356·6	373·2	384·0	388·7	392·3	404·8	410·6	428·3	448·2
No. of expts.	2	3	5	5	4	1	1	2	3	7	1
Mean K_p	2590	506	397	127	60·4	54·2	40·8	19·1	12·9	5·97	2·10

These results are shown graphically in Fig. 2, where $\log_{10} K_p$ is plotted against the reciprocal of the absolute temperature. The graph obtained by Kistiakowsky and Stauffer is also shown. It will be observed that, though at the lower temperatures the two investigations yield results which are identical within the limits of experimental error, yet at the higher temperatures there is a divergence. Kistiakowsky and Stauffer measured temperatures by means of a thermocouple, whereas in this investigation temperatures have been both calculated from the b. p. of the refluxing liquid at the prevailing atmospheric pressure and observed by the use of standard mercury-in-glass thermometers.

The results of the present investigation may be summarised (by the least-squares method) by the equation

$$\log_{10} K_p = (17{,}700/4{\cdot}575T) - 8{\cdot}27$$

whence $\Delta G^\circ = 17{,}700 + 37{\cdot}8T$, compared with $17{,}100 + 36{\cdot}1T$ obtained by Kistiakowsky and Stauffer.

DISCUSSION.

The heat change derived above, for the dehydrochlorination of *tert.*-butyl chloride, may be combined with other thermochemical data for the heats of formation of *iso*butene and hydrogen chloride, to give the heat of formation of *tert.*-butyl chloride. Thus

$$\Delta Hf^\circ_{390} \text{ for HCl} = -22{\cdot}1 \text{ kcals./g.-mol.}$$

$$\text{and } \Delta Hf^\circ_{390} \text{ for } iso\text{-C}_4\text{H}_8 = -4{\cdot}6 \text{ kcals./g.-mol.}$$

(Kilpatrick, Prosen, Pitzer, and Rossini, *J. Res. Nat. Bur. Stand.*, 1946, **36**, 559), whence, if the calculated heat change is taken to refer to the mid-point of the temperature range studied (*viz.*, 390° K.),

$$\Delta Hf^\circ_{390} \text{ for } tert.\text{-C}_4\text{H}_9\text{Cl} = -44{\cdot}4 \text{ kcals./g.-mol.}$$

This is of particular interest in that the result may be used to obtain a figure for the bond dissociation energy of the carbon–chlorine bond, $D_{\text{CMe}_3\text{–Cl}}$, in *tert.*-butyl chloride. From ΔHf°_{298} for *tert.*-C_4H_9 = 3·2 (Roberts and Skinner, *Trans. Faraday Soc.*, 1949, **45**, 339), ΔHf°_{390} for *tert.*-C_4H_9 is estimated to be 1·7 kcals./g.-mol., whence

$$D_{(tert.\text{-C}_4\text{H}_9\text{–Cl})} = 75{\cdot}0 \text{ kcals./g.-mol.}$$

This bond dissociation energy may also be calculated by the method suggested by Evans and Polanyi (*Trans. Faraday Soc.*, 1938, **34**, 11) from the corresponding known bond dissociation energy in methyl chloride and the energies of activation for the reactions of sodium atoms with the two halides. Thus, by assuming that $D_{\text{CH}_3\text{–Cl}}$ = 80·7 kcals./g.-mol. (Stevenson, *J. Amer. Chem. Soc.*, 1943, **65**, 209), and that the collision yields for the reactions of sodium with methyl chloride and *tert.*-butyl chloride are respectively 1/7100 at 260° (Heller and Polanyi, *Trans. Faraday Soc.*, 1936, **32**, 633) and 1/1065 at 275° (recalculated from Hartel, Meer, and Polanyi, *Z. physikal. Chem.*, 1932, **19**, *B*, 139), $D_{\text{CMe}_3\text{–Cl}}$ is calculated from the formula

$$\Delta E_{\text{A}} \text{ for Na} + \text{RCl} = 0{\cdot}27\Delta D_{\text{C–Cl}}$$

to be 74·0 kcals./g.-mol., in good agreement with the figure derived above.

Similarly, knowledge of the entropy change accompanying the reaction allows the calculation of the entropy of *tert.*-butyl chloride. From the experimental equilibrium constant equation, $\Delta S^\circ_{390} = 37{\cdot}82$, and if S°_{390} for HCl = 46·47 (Linnett, *Trans. Faraday Soc.*, 1940, **36**, 527) and S°_{390} for *iso*-C_4H_8 = 76·55 (Kilpatrick and Pitzer, *J. Res. Nat. Bur. Stand.*, 1946, **37**, 163), then S°_{390} for *tert.*-C_4H_9Cl = 85·2.

It is also possible to calculate the statistical entropy of *tert.*-butyl chloride, except for the entropy arising from internal rotations in the molecule. Sheppard (*Trans. Faraday Soc.*, 1950, **46**, 527) has recently given an assignment of the vibrational spectra for the *tert.*-butyl halides. The assigned 33 out of the 36 possible vibrational frequencies of *tert.*-butyl chloride have been grouped for calculation purposes as follows : 304 (2), 372, 406 (2), 570, 811, 917 (2), 950, 1028 (2), 1156, 1237 (2), 1361, 1370 (2), 1450 (6), 2900 (9) cm.$^{-1}$. From these $S^\circ_{v,390} = 11{\cdot}52$. In order to calculate the moment of inertia of the rigid molecule, all interbond angles were assumed to be tetrahedral and the following dimensions were used: C–C = 1·54 A., C–H = 1·093 A., C–Cl = 1·76 A. Williams and Gordy (*J. Chem. Physics*, 1950, **18**, 994) have shown that the microwave-absorption spectrum is in accord with these assumptions. By using the equation $S_{t+r} = (3\boldsymbol{R}/2)\log_e M + 4\boldsymbol{R}\log_e T + (\boldsymbol{R}/2)\log_e ABC + 265{\cdot}289 - \boldsymbol{R}\log_e 3$, where A, B, and C are the principal moments of inertia of *tert.*-butyl chloride and where the last term arises because the rigid molecule has a three-fold axis of symmetry, the sum of the translational and rotational entropies at 390° K. is found to be 66·95. There is therefore a discrepancy of $6{\cdot}7_3$ E.U. at 390° K. between the " experimental " and statistical entropies, which may be ascribed to that arising from the three internal rotations in the molecule. The tables published by Pitzer and Gwinn (*J. Chem. Physics*, 1942, **10**, 430) indicate that the potential barrier restricting rotation of each methyl group is 4·8 kcals./g.-mol. In this evaluation the partition function for free internal rotation was calculated by employing formula 1(*b*) given by Pitzer and Gwinn, in order to take account of the fact that the molecule possesses three tops. If the entropy change in the reaction studied experimentally were as deduced by Kistiakowsky and Stauffer (*loc. cit.*), then the height of the barrier would be 3·0 kcals./g.-mol. Gordon and Giauque (*J. Amer. Chem. Soc.*, 1948, **70**, 1506) have shown by a comparison of statistical and thermal entropies that the barrier restricting the single internal rotation in ethyl chloride is 4·7 kcals./g.-mol. This result is seen to be in better agreement with the entropy found for *tert.*-butyl chloride in the present investigation than that found by Kistiakowsky and Stauffer, since the barrier to rotation per methyl group in *tert.*-butyl chloride would be expected to be at least as high as in ethyl chloride (cf. the values quoted by Pitzer, *J. Amer. Chem. Soc.*, 1948, **70**, 2140, for ethane, propane, and *neo*-pentane).

From the value of S°_{390} and the evaluation of the potential barriers to internal rotation, the standard entropies of gaseous *tert.*-butyl chloride at 25° and at the b. p. are calculated to be 76·06 and 78·35 E.U. respectively.

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