The Use of Equilibrium Constants to calculcate Thermodynamic Quantities. Part II.*

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Equilibria in the gaseous systems ethyl chloride–ethylene–hydrogen chloride and *iso*propyl chloride–propene–hydrogen chloride have been examined over the temperature ranges 175—255° and 60—210°, respectively. From the variation of the equilibrium constants with temperature the heat and entropy changes accompanying hydrochlorination are derived. The latter changes enable the entropies of the alkyl halides to be found. By comparison with the statistical entropies, the energy barriers hindering free internal rotation in these molecules are obtained and hence the thermodynamic functions are calculated over the range 298—700° K.

A review of previous work on the ethyl chloride system shows that the present results agree most closely with those of Lane, Linnett, and Oswin, and of Gordon and Giauque.

THE published thermochemical and thermodynamic data for chlorohydrocarbons are relatively scanty, and moreover are often conflicting. This arises largely because few determinations of heats of combustion of simple chlorohydrocarbons have been made with an accuracy acceptable by modern standards. The present series of investigations attempts to provide some of this missing information. The equilibria between hydrogen chloride, *iso*butene, and *tert.*-butyl chloride were discussed in Part I.* The present communication deals with the equilibria resulting from the decomposition of ethyl and *iso*propyl chlorides. From the variation of these equilibrium constants with temperature the heat and entropy changes accompanying dehydrochlorination are directly obtained.

* Part I, *J.*, 1951, 1409.

The only previous work on the hydrogen chloride–propene–*iso*propyl chloride system is that briefly mentioned by Wibaut, Diekmann, and Rutgers (*Rec. Trav. chim.*, 1928, **47**, 477) concerning the reaction products. Ethyl chloride has, however, attracted periodic attention, with various results. Wibaut, Diekmann, and Rutgers (*loc. cit.*) obtained an 84·4% yield of ethyl chloride by synthesis from hydrogen chloride and ethylene over bismuth chloride on asbestos at 200° and 1 atm., whilst Tilman (Thesis, Amsterdam, 1928) reported 4% decomposition of ethyl chloride at 120°. Rudkowskii, Trifel, and Frost (*Ukrain. Chem. J.*, 1935, **10**, 277) measured equilibrium constants in this system over bismuth chloride supported on silica gel at 170°, 200°, and 230° (all ± 2°). Their results may be summarised as $\log_{10} K_p = (13,400/4·575\,T) - 4·96$. (All such equations are quoted here in atm. units, the alkyl halide being considered to be the product.) It was, however, pointed out by Linnett (*Trans. Faraday Soc.*, 1940, **36**, 527) that this equation implies an impossible value for the entropy of ethyl chloride, and in a recent paper Lane, Linnett, and Oswin (*Proc. Roy. Soc.*, 1953, **216**, *A*, 361) have described more accurate determinations in the range 176—218° carried out by a flow method over a supported ferric chloride catalyst (cf. Roush and Morell, U.S.P. 2,110,141). By comparing their results with that of the accurate determination of the entropy of ethyl chloride by Gordon and Giauque (*J. Amer. Chem. Soc.*, 1948, **70**, 1506), Lane, Linnett, and Oswin considered the equilibrium constants to be best expressed as $\log_{10} K_p = (17,320/4·575\,T) - 6·922$.

The heat of formation of ethyl chloride can be estimated in various ways from earlier work. Thus, based on Thomsen's (rather than Berthelot's or Kharasch's) value for the heat of combustion of ethyl chloride, Bichowsky and Rossini ("Thermochemistry of Chemical Substances," Reinhold, New York, 1936) consider $\Delta H_f°_{298}$ for ethyl chloride to be 25·7 kcal./mole. Hence, by using a modern value for $\Delta H_f°$ for ethylene, the heat of hydrochlorination is calculated to be 16·2 kcal./mole. More recently Casey and Fordham (*J.*, 1951, 2513) have suggested the value 13 ± 2·5 kcal./mole for the heat of hydrochlorination. The heat of reaction may also be estimated from bond-strength determinations. For example, by using Stevenson's table of bond strengths (*J. Amer. Chem. Soc.*, 1943, **65**, 209) obtained by the electron-impact method, the heat of hydrochlorination is calculated to be 16·5 kcal./mole, but this result is dependent upon thermochemical data given by Bichowsky and Rossini (*loc. cit.*). Finally, by use of the approximate method suggested by Conn, Kistiakowsky, and Smith (*J. Amer. Chem. Soc.*, 1938, **60**, 2764), viz., that the heat of hydrochlorination (corrected for $\Delta H_f°$ for hydrogen chloride) should be the mean of the heats of hydrogenation and chlorination, the value of 15·9 kcal./mole is found.

EXPERIMENTAL

Apparatus.—The apparatus was similar to that described in Part I. For the decomposition of *tert.*-butyl chloride, glass wool was found to be an effective catalyst, as it is for *tert.*-butyl bromide (Howlett, unpublished work), but glass wool is an inefficient catalyst for inducing decomposition in *iso*propyl chloride and ethyl chloride. A considerable search was made for a suitable catalyst; the static method of measurement imposed some limitation upon its nature. Thus bismuth chloride on silica gel (cf. Rudkowskii, Trifel, and Frost, *loc. cit.*) was found to be far too efficient as an adsorbent. For this reason also, carbon (cf. Lane, Linnett, and Oswin, *loc. cit.*) was avoided and glass wool was finally used as the support. Bismuth and ferric chlorides were tried, but rejected for inefficiency and volatility, respectively.

After considering Cremer's results (*Experientia*, 1948, **4**, 349) on the rates of heterogeneous pyrolysis of ethyl chloride over various metallic chlorides, namely, that the metallic chloride had a marked effect upon both the activation energy and non-exponential term, those materials inducing a reaction of low activation energy and fast rate were investigated. The catalyst eventually employed for both ethyl and *iso*propyl chlorides was a mixture of nickel, cobalt, and a little cadmium chlorides, which was sprayed on to the support in concentrated hydrochloric acid solution, dried *in vacuo* at room temperature, treated with hydrogen chloride, and thereafter maintained *in vacuo* except when in use. This enabled equilibria to be reached in a few hours under all conditions tried, and no appreciable drift in pressure was observed after equilibrium had been established.

Materials.—Commercial *iso*propyl chloride was purified by Barton and Head's method (*Trans. Faraday Soc.*, 1950, **46**, 114). The accepted material had b. p. 34·8° (corr.), n_D^{20} 1·3779.

Commercial ethyl chloride was volatilised in a stream of dry, carbon dioxide-free nitrogen and passed through soda lime and concentrated sulphuric acid traps. The first and last 15% of the distillate were rejected and the middle fraction condensed at $-80°$. This material was outgassed and its vapour pressure was measured from $0°$ to $15°$. The results, corrected to $0°$ and standard gravity (980·665 cm. sec.$^{-2}$) by assuming g in this laboratory to be 981·19 cm. sec.$^{-2}$, are given in Table 1. These vapour pressures are closely similar to those obtained in this range by Gordon and Giauque (*loc. cit.*).

TABLE 1.

T	0·30°	2·92°	3·45°	5·90°	8·55°	10·25°	10·47°	11·68°	12·20°	12·35°	12·70°	14·56°
V. p. (mm.)	474·9	527·3	540·0	597·8	661·2	702·5	710·2	740·0	756·6	760·3	770·0	824·2

Results.—The equilibria were approached by decomposition only. Concentrations at equilibrium were measured both by pressure measurements and (particularly for runs in which only small increases in pressure occurred) by condensation of the products at $-190°$ and subsequent titration of the hydrogen chloride. Table 3 shows that these two methods gave similar results. The reaction involving *iso*propyl chloride was studied at total pressures of 50—300 mm. and from $60°$ to $210°$. With ethyl chloride the corresponding figures were 45—140 mm. and $175°$ to $255°$. No variation of equilibrium constant with pressure was observed. This is illustrated in Table 2.

TABLE 2.

	Ethyl chloride at 175·0°					*iso*Propyl chloride at 161·7°			
p_0 (mm.)	29·7	35·7	37·8	53·4	57·7	52·6	70·4	126·7	172·0
K_p	41·5	42·3	40·4	42·8	42·0	18·1	16·7	17·0	17·6

It is well established that equilibria in the ethyl chloride system involve only hydrogen chloride, ethylene, and ethyl chloride, but it was felt desirable to examine the products from *iso*propyl chloride. Accordingly the products from about 50 runs, which had been allowed to reach equilibrium at $161°$, were condensed at liquid-air temperature, and combined. The material was slowly warmed to room temperature, the gaseous products were allowed to escape, and the liquid was dried (CaCl$_2$). 9 c.c. of this were refluxed for a few min. and then fractionally distilled. The whole distillate boiled at 34—34·5°, and three fractions of about 3 c.c. each were collected, together with 0·4 c.c. of residue. These fractions had n_D^{17} 1·3796, 1·3797, 1·3800, and 1·3828 respectively. Freshly distilled *iso*propyl chloride has n_D^{17} 1·3796, whilst *n*-propyl chloride (b. p. 46°) has n_D^{17} 1·3900, so this suggests that *n*-propyl chloride is absent from the equilibrium mixture, and furthermore if all the discrepancy in the refractive index of the still residue were due to *n*-propyl chloride, this would constitute 1% of the alkyl chloride present at equilibrium. This possibility has been ignored. The measured equilibrium constants, in atmosphere units, are set out in Table 3. The results may be summarised (by the least-squares method) by the equations :

$$\text{Ethyl chloride : } \log_{10} K_p = (17{,}440/4{\cdot}575\,T) - 6{\cdot}88_5$$

$$\textit{iso}\text{Propyl chloride : } \log_{10} K_p = (17{,}540/4{\cdot}575\,T) - 7{\cdot}56_3$$

compared with the result from Part I :

$$\textit{tert.}\text{-Butyl chloride : } \log_{10} K_p = (17{,}700/4{\cdot}575\,T) - 8{\cdot}27$$

TABLE 3.

*iso*Propyl chloride

$T°$	61·1	61·8^t	79·8^t	79·8^p	99·9^p	111·3^{p,t}	131·9^p	161·7^p	211·3^p
No. of expts.	2	1	5	9	6	14	11	4	2
Mean K_p	8595	8290	2040	1950	470	237	81·6	17·35	2·125

Ethyl chloride

$T°$	175·0^p	210·4^p	255·8^p
No. of expts.	7	6	3
Mean K_p	41·8	9·88	2·12

t, by titration; *p*, by pressure measurement.

DISCUSSION

The equilibrium constants found for the three hydrochlorination reactions so far studied may be combined with the known rate constants for unimolecular decomposition of the appropriate alkyl chlorides (Barton and Howlett, *J.*, 1949, 165; Barton and Onyon, *Trans. Faraday Soc.*, 1949, **45**, 725; Barton and Head, *loc. cit.*) to obtain the rate constants for

the bimolecular additions of hydrogen chloride to the olefins. Thus, if the decomposition rate constant equations are applicable at 200°, the rate constants of the bimolecular additions of hydrogen chloride to ethylene, propene, and *iso*butene are $10^{9\cdot8}$ exp ($-44,000/RT$), $10^{9\cdot0}$ exp ($-34,000/RT$), and $10^{6\cdot1}$ exp($-25,000/RT$) l. mole^{-1} sec.$^{-1}$ respectively.

Although, under normal experimental conditions, one might expect that these mechanistically bimolecular reactions would be swamped by alternative faster ionic reactions, these rate constants are interesting theoretically. The non-exponential terms fall, as expected, with increase in complexity of the olefin. The activation energies, however, invite theoretical justification. Howlett (Thesis, London, 1948) estimated the first of these activation energies to be 48—50 kcal./mole by the semi-empirical method. Such an estimate of these activation energies cannot, however, account for the variation from one reaction to another because the bond dissociation energies involved do not vary significantly from ethyl chloride to *tert.*-butyl chloride.

The equilibrium constant expressions indicate that all three alkyl halides were examined kinetically under conditions where the equilibrium constants were less than 0·1. Thus even at the lowest temperatures for which rate constants for pyrolysis are quoted, 100 mm. initial pressure of reactant would proceed to more than 99% decomposition, and the rate constants are not in error from this cause.

The heat and entropy changes accompanying hydrochlorination of propene (17,540 cal./mole and $-34\cdot60$ e.u.) may be taken to apply to the mean temperature, 385° K. $\Delta S°_{385}$ has been used in conjunction with the values 68·13 for $S°_{385}$ of propene (Kilpatrick and Pitzer, *J. Res. Nat. Bur. Stand.*, 1946, **37**, 163) and 46·38 for $S°_{385}$ of hydrogen chloride (Linnett, *loc. cit.*) to determine the value 79·91 for $S°_{385}$ of *iso*propyl chloride. This " experimental " value for the entropy may be compared with the statistical figure calculated for the rigid molecule, to obtain an estimate of the potential barrier hindering free rotation of the two methyl groups in *iso*propyl chloride. The usual assumption that translational, rotational, and vibrational contributions may be treated separately was made to calculate the statistical entropy. By assuming the dimensions of the *iso*propyl chloride molecule to be C–H, 1·10; C–C, 1·54; C–Cl, 1·77 Å, and that all interbond angles are tetrahedral, one of the principal momental axes is calculated to be inclined at 15° 34·5′ to the C–Cl bond. The principal moments of inertia are given in Table 4. The vibrational entropy was found by using the frequencies given by Sheppard (*Trans. Faraday Soc.*, 1950, **46**, 533) grouped as follows : 2920 (7), 1461 (2), 1446 (2), 1386, 1372, 1337, 1258, 1160, 1129, 1060, 949, 935, 882, 614, 424, 337, and 326 cm.$^{-1}$ S(trans. + rot. + vib.) at 385° K is thus found to be 73·709, leaving 6·20 e.u. arising from the two internal rotations. With the appropriate reduced moment of inertia (I_m) (see Table 4), reference to Pitzer and Gwinn's tables (*J. Chem. Phys.*, 1942, **10**, 428) indicates that the hindering potential (V) is 2200 cal./mole for each methyl group. This has been used to calculate the entropy of *iso*propyl chloride over the range 298—700° K. The results are collected in Table 5, which also gives the calculated values of the heat of formation ($\Delta H_f°$) and the heat capacity ($C_p°$) over the same temperature range. In these last computations the effect upon $C_p°$ of estimating the vibrational contributions according to the approximate method suggested by Crawford and Parr (*J. Chem. Phys.*, 1948, **16**, 233), has been compared with Wilson's more exact table of $C_p°$ contributions (cf. Taylor and Glasstone, " Physical Chemistry," Macmillan, London, 1942). Crawford and Parr claimed an overall accuracy of 2% on $C_p°$ for simple molecules. This statement is substantiated in all the cases considered here.

A similar treatment has been carried through for ethyl chloride. Thus $\Delta S°$ for hydrochlorination ($-31\cdot50$) is taken to be appropriate to 473° K. $S°_{473}$ for ethylene is 58·04 (cf. Kilpatrick and Pitzer's calculations corrected by using the more recent vibrational assignment of Arnett and Crawford, *J. Chem. Phys.*, 1950, **18**, 118) whilst $S°_{473}$ for hydrogen chloride is 47·84 (Linnett, *loc. cit.*). Therefore $S°_{473}$ for ethyl chloride is 74·38.

Gordon and Giauque, and also Linnett, have calculated the rotational constants for ethyl chloride, but these have been recalculated here by using the same interatomic dimensions as for *iso*propyl chloride. The principal axis, which is not immediately obvious, is thus found to be inclined at 43° 39·6′ to the C–C bond and the newly calculated moments of inertia are given in Table 4. By using the same vibrational assignment as Gordon and

Giauque, S(trans. + rot. + vib.) at 473° K is found to be 71·227, whence the entropy due to internal rotation in ethyl chloride is 3·15 at this temperature. Pitzer and Gwinn's tables indicate in this case that V is 2900 cal./mole. This enables the thermodynamic functions to be computed for ethyl chloride, and some of the results are included in Table 5.

In Part I an arithmetical slip was made in assessing the statistical entropy of *tert.*-butyl chloride. This calculation has therefore been repeated by using Williams and Gordy's value for the larger moments of inertia of this molecule (*J. Chem. Phys.*, 1950, **18**, 994). Thus $S°_{390}$ for the rigid molecule is recalculated as 77·42 and hence the restricted rotational entropy is 7·78. From this, V is estimated to be 3600 cal./mole per methyl group. The thermodynamic functions for *tert.*-butyl chloride have been determined as for ethyl and *iso*propyl chlorides and are included in Table 5, whilst the moments of inertia are given in Table 4.

The calculated heights of the barriers hindering internal rotation in these molecules are extremely sensitive to changes in the experimental value for ΔS, and furthermore they are obtained after a long chain of argument. They are therefore subject to experimental errors and to errors arising from the assumptions made—notably that the molecular partition function may be exactly factorised into contributions from the separate motions, even including two or more internal rotations. Neglect of such coupling between the internal rotations has been discussed by Pitzer (*J. Chem. Phys.*, 1942, **10**, 605). The energy barriers reported should therefore be taken as a general indication of the consistency of the experimental results and supporting assumptions, rather than as exact indications of their heights, although they are undoubtedly of the correct order of magnitude. The result for ethyl chloride may be compared with the figure 3700 cal./mole obtained by Gordon and Giauque (*J. Amer. Chem. Soc.*, 1948, **70**, 4277).

TABLE 4.

Principal moments of inertia (10⁻⁴⁰ g.cm.²)

Substance	I_A	I_B	I_C	I_m	V (cal./mole)
Ethyl chloride	27·63	151·2	168·1	4·704	2900
*iso*Propyl chloride	103·6	185·2	261·3	5·154	2200
tert.-Butyl chloride	185·0	279·7	279·7	5·221	3600

TABLE 5.

Entropies, specific heats, and heats of formation in the gas phase.

T °K =	298·16	400	500	600	700
Ethyl chloride					
$S°$	66·21	71·10	75·54	79·67	83·54
$C_p°$	15·01	18·40	21·41	23·98	26·15
$C_p°$ *	15·30	18·47	21·22	23·70	25·91
$\Delta H_f°$ (kcal.)	−26·66	−27·69	−28·47	−29·07	−29·52
***iso*Propyl chloride**					
$S°$	74·10	80·89	87·03	92·76	98·10
$C_p°$	20·93	25·48	29·59	33·19	36·33
$C_p°$ *	21·33	25·58	29·34	32·81	36·01
$\Delta H_f°$ (kcal.)	−34·56	−35·89	−36·93	−37·71	−38·30
***tert.*-Butyl chloride**					
$S°$	77·04	86·04	94·26	101·9	109·0
$C_p°$	27·30	34·01	39·60	44·23	48·11
$C_p°$ *	27·85	34·05	39·21	43·68	47·65
$\Delta H_f°$ (kcal.)	−42·99	−44·53	−45·62	−46·38	−46·90

* Calculated by using Crawford and Parr's equations.

As more measurements appear upon the heights of internal potential barriers it becomes clearer that V is relatively insensitive to variation in the nature of the passing groups, *i.e.*, whether these are hydrogen, chlorine, or fluorine atoms or methyl groups. Thus V is 2·8 kcal./mole for ethane (Kistiakowsky, Lacher, and Stitt, *J. Chem. Phys.*, 1938, **6**, 407), 3·9 for *iso*butane (Aston, Kennedy, and Schumann, *J. Amer. Chem. Soc.*, 1940, **62**, 2059), 2·7 for 1 : 1 : 1-trichloroethane (Rubin, Levedahl, and Yost, *ibid.*, 1944, **66**, 279), 3·4 for 1 : 1 : 1-trifluoroethane (Russell, Golding, and Yost, *ibid.*, p. 16) and it is only in cases such

as hexachloroethane that appreciably higher results are found (cf. Morino and Iwasaki, *J. Chem. Phys.*, 1949, **17**, 216). It appears therefore that the origin of these barriers cannot lie in dipole interactions, and hence steric effects and/or quadrupole interactions (Lassettre and Dean, *ibid.*, 1948, **16**, 157; Oosterhoff, *Discuss. Faraday Soc.*, 1951, **10**, 79) are the only effects which seem capable of giving such barrier heights.

The heats of reaction found from the temperature dependence of the equilibrium constants may be used to determine the C–Cl bond dissociation energies in the alkyl halides. Unfortunately there are some discrepancies in the published estimates of the heats of formation of the ethyl, *iso*propyl, and *tert.*-butyl radicals, upon which such bond strength estimates must rest. Thus the earlier results obtained by the Polanyi school are some 3 kcal. lower than the figures recommended by Stevenson (*Discuss. Faraday Soc.*, 1951, **10**, 35). For consistency, the electron-impact results have been used throughout this paper. Stevenson (*J. Amer. Chem. Soc.*, 1943, **65**, 209) considers that these values refer to 298° K and by combining them with Rossini's thermochemical figures for hydrocarbons (*Chem. Rev.*, 1940, **27**, 1) and the heats of formation of atoms recommended by Cottrell ("The Strengths of Chemical Bonds," Butterworths, London, 1954) the C–Cl bond dissociation energies in ethyl, *iso*propyl, and *tert.*-butyl chlorides are found to be respectively 80·1, 80·5, and 78·0 kcal./mole at 298° K. These may be compared with the figures given by Lane, Linnett, and Oswin (*loc. cit.*). It may be noted that the alternative use of Eckstein, Scheraga, and Van Artsdalen's determination of $D(C_4H_9^t–H)$ (*J. Chem. Phys.*, 1954, **22**, 28) would raise $D(C_4H_9^t–Cl)$ by 1·6 kcal./mole.