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The Ethane Equilibrium

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Storch and Kassel[1] have suggested that the experimental data on the position of equilibrium in the reaction

$$C_2H_4 + H_2 \rightleftarrows C_2H_6$$

are in error because of the occurrence of side-reactions in general, and particularly because the alleged presence of propylene has interfered with the analytical determination of ethylene. As to the latter, a correction would decrease the calculated ethylene concentration, and increase the value obtained for the equilibrium constant. This would lead to better agreement with quantum-statistical calculations in which free rotation about the C–C band in ethane is assumed.

As a matter of fact, Travers and Hockin[2] state explicitly that no C_3 hydrocarbons are found on fractionation of the products. Nevertheless, in view of the interest attaching to the question of free rotation in ethane, an additional test seemed desirable. We have, therefore, carried out a series of experiments in which ethane–ethylene–hydrogen mixtures were circulated through a reaction tube at 600°, and the mixture subsequently fractionated in a modified Podbielniak still.

The net result was that in no case was a fraction obtained condensing between −88° and room temperature which contained more than 10% of the total olefin. Moreover, since the paraffin hydrocarbon accompanying this was shown by combustion analysis to be ethane, it is more than likely that at least a part of this residuum was ethylene. We therefore feel safe in saying that considerably more than 90% of the total olefin is certainly ethylene. Similarly we can say that no appreciable amount of volatile paraffin higher than ethane is present. This holds equally for starting material consisting of either ethane alone, or ethylene plus hydrogen, or of a near-equilibrium mixture of all three.

Although we were not especially interested in adding to the already numerous data on the equilibrium constant, the results that were obtained may be reported. These appear in Table I. Our final runs were made at 600° (with close temperature control and measurement). There is one run starting with pure ethane, one run with a 50% ethylene–hydrogen mixture and four runs with near-equilibrium mixtures. The times given are the total times of circulation. We are not prepared to convert these to actual heating times, since the method of circulation consisted of "thermal siphoning" (flow due to difference in density between hot and cold gas) and the constants of the apparatus were not accurately determined. Judging from other equilibrium data, our longest time (one hundred and eighty minutes) is equivalent to something less than thirty minutes of actual heating. About 400 cc. of gas was used in each experiment.

TABLE I

EQUILIBRIUM MEASUREMENTS AT 600°

Time, min.	Final press., atm.	Composition, % C_2H_6	C_2H_4[a]	H_2	CH_4	N_2	"K_P," atm.
		Ethane side					
180	0.602	67.9	15.3	14.4	1.0	1.4	51.2
		Ethylene–hydrogen side					
180	0.734	28.5	20.6	43.9	6.4	0.6	4.3
		Near-equilibrium mixtures (C_2H_4–H_2 side)					
30	0.858	58.2	19.5	20.6	0.7	1.0	16.9
60	.968	60.2	16.8	16.5	5.4	1.0	22.4
120	.902	64.8	15.2	17.3	2.1	0.6	27.3
180	.952	63.2	13.8	16.1	5.1	1.7	29.9

[a] "C_2H_4" = total olefin.

The results for the "near-equilibrium" mixture indicate a value somewhat greater than 30 for the equilibrium constant at 600°. This is in good agreement with previous determinations (see below).

It is perhaps not generally appreciated that the experimental data for the equilibrium constant of this reaction are in excellent agreement not only among themselves, but also with Third Law calculations based on thermal data alone (except for the entropy of hydrogen). Kemp and Pitzer[3] have, to be sure, emphasized the latter point by a calculation of the entropy of ethane based on a single value of the equilibrium constant. However, the concordance goes far beyond this.

We may calculate the equilibrium constant from thermal data as follows. For ΔH°_{298}, Kistiakowsky finds −32,575 cal. by direct measure-

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(1) Storch and Kassel, THIS JOURNAL, **59**, 1240 (1937).

(2) Travers and Hockin, *Proc. Roy. Soc.* (London), **136A**, 1 (1932).

(3) Kemp and Pitzer, THIS JOURNAL, **59**, 276 (1937).

ment,[4] whereas Rossini obtains −32,783 cal. from heats of combustion.[5] We take $\Delta H^\circ_{298} = -32{,}675 \pm 100$ cal. as the average value. Heat capacities of the three gases between 250 and 400° A.[6] are in agreement with the equation

$$\Delta C_P = \Delta\Gamma_0 + \Delta\Gamma_1 T$$
$$= -6.77 + 0.00747T$$

The "conventional" value of ΔH°_0 is then −30,986 cal.

Recent experimental measurements of the entropies of ethylene[7] and ethane,[8] together with the statistical value for hydrogen,[9] give

$$C_2H_4\text{: } S^\circ_{298} = 52.48 \pm 0.10 \text{ e. u.}$$
$$H_2\text{: } S^\circ_{298} = 31.23 \pm 0.01 \text{ e. u.}$$
$$C_2H_6\text{: } S^\circ_{298} = 54.85 \pm 0.20 \text{ e. u.}$$
$$\Delta S^\circ_{298} = -28.86 \pm 0.20 \text{ e. u.}$$

Then

$$\Delta F^\circ_{298} = -24{,}072 \text{ cal.}$$

The estimated error in this quantity is ± 150 cal.

For the integration constant, I, in the equation

$$\Delta F^\circ = \Delta H^\circ_0 - \Delta\Gamma_0 T \ln_e T - {}^1/_2\, \Delta\Gamma_1 T^2 + I\,T$$

one then obtains

$$I = -14.274$$

Thus

$$\Delta F^\circ = -30986 + 6.77T \ln_e T - 0.0037T^2 - 14.274T$$

and

$$\log_{10} K = +\frac{6774}{T} - 3.408 \log_{10} T + 0.000809T + 3.120$$

Experimental equilibrium data have been obtained by Frey and Huppke[10] at 400, 450 and 500° using a chromium oxide catalyst; by Videnski and Vinikova[11] at 500°, also using a chromium oxide catalyst; by Travers and Pearce[12] between 550 and 620°; and by Pease and Durgan[13] at 600, 650 and 700°.

These data represent altogether about 150 individual measurements over a 300° temperature range, and a range of pressures from about 0.5 to 2 atm. Among the experiments are some in which equilibrium was approached from either side, and also with varying ratios of ethylene to hydrogen. As already mentioned, it cannot be maintained that the analytical measurements are in serious error. There is admittedly the possibility that all measured equilibria are displaced by the side-reactions yielding methane and liquid products. However, it would be extraordinary if under all the conditions studied (especially in the work of Travers and Pearce), the displacement should have been of the same magnitude. All things considered, therefore, it is difficult to see how the experimental determinations can be seriously in error.

The comparison of experimental and theoretical values is given in Table II. The agreement is very satisfactory. A somewhat better fit would be obtained by decreasing slightly the integration constant of the free energy equation. However, any such change would fall well within the estimated uncertainty of ± 150 cal. in ΔF^0_{298}.

TABLE II

EXPERIMENTAL AND CALCULATED VALUES OF THE EQUILIBRIUM CONSTANT

$$K_P = \frac{x_{C_2H_6}}{x_{C_2H_4} x_{H_2}} \frac{1}{P_{\text{atm.}}}$$

Temp.		K_P		
°C.	°Abs.	Exptl.	Calcd.	Observer
400	673	12000	12530	F
450	723	1800	2162	F
500	773	420	465	F
		320	465	V
550	823	135	121	T
570	843	65.4	73.8	T
590	863	41.0	45.7	T
600	873	32.2	36.6	P
610	883	27.9	29.2	T
620	893	22.4	23.5	T
650	923	12.2	12.6	P
700	973	5.0	4.8	P

(F = Frey; V = Videnski; T = Travers; P = Pease)

It may be recalled that the entropy data on which the free energy equation is based favor a high potential barrier against internal rotation in ethane.[8] The assumption of a low barrier (or free rotation) leads to values of K_P at 600° which are two to three times larger than the experimental.[14] As already indicated, there is no obvious reason why the experimental data should be in error by anything like this amount.

The question as to whether some gross error has been made in the assignment of the seventeen normal modes of vibration and the corresponding

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(4) Kistiakowsky, *et al.*, THIS JOURNAL, **57**, 65 (1935).

(5) Rossini, *J. Research Natl. Bur. Standards*, **17**, 629 (1936).

(6) H_2: Davis and Johnston, THIS JOURNAL, **56**, 1045 (1934). C_2H_4 and C_2H_6: Eucken and Parts, *Z. physik. Chem.*, **20B**, 184 (1933).

(7) Egan and Kemp, THIS JOURNAL, **59**, 1264 (1937).

(8) Witt and Kemp, *ibid.*, **59**, 273 (1937).

(9) Giauque, *ibid.*, **52**, 4816 (1930).

(10) Frey and Huppke, *Ind. Eng. Chem.*, **25**, 54 (1933).

(11) Videnski and Vinikova, *J. Gen. Chem.* (*Moscow*), **4**, 120 (1934).

(12) Travers and Pearce, *J. Soc. Chem. Ind.*, **53T**, 321 (1932). See also Travers and Hockin, *Proc. Roy. Soc.* (London), **136A**, 1 (1932).

(13) Pease and Durgan, THIS JOURNAL, **50**, 2715 (1928).

(14) Smith and Vaughan, *J. Chem. Phys.*, **3**, 341 (1935); Teller and Topley, *J. Chem. Soc.*, 876 (1935).

frequencies for the ethane molecule is one which the authors are not prepared to discuss. If such an error has not been made, there would seem to be a flat contradiction between the thermodynamic data (including heat capacity measurements for gaseous ethane[15]) on the one hand, and on the other, the spectroscopic data as analyzed by Bartholomè and Karweil.[16] In addition, there is the difficulty in accounting theoretically for the high potential barrier apparently demanded by the thermodynamic data.[17]

However this contradiction may be resolved, the authors wish to emphasize that in dealing with the problem the experimental data on the ethane equilibrium cannot be ignored.

Summary

Additional experiments on the ethane–ethylene–hydrogen equilibrium have been carried out to determine whether the presence of volatile hydrocarbons higher than ethylene and ethane could have invalidated previous analytical work, as suggested by Kassel and Storch.[1] The evidence is that the error is certainly less than 10%, confirming the conclusion of Travers and Hockin.[2]

A comparison of all experimental values with values based on the Nernst Heat Theorem (and the Third Law) emphasizes the internal consistency of the data.

It is concluded that there is no good ground for ignoring the experimental data on the ethane equilibrium in dealing with the question of free rotation in the ethane molecule.

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(15) Kistiakowsky, *et al.*, *J. Chem. Phys.*, **6**, 407 (1938). See, however, Hunsman, *Z. physik. Chem.*, **39B**, 23 (1938).

(16) Bartholomè and Karweil, *ibid.*, **39B**, 1 (1938).

(17) Eyring, THIS JOURNAL, **54**, 3191 (1932).

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Fluorinated Derivatives of Propane. II

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Three chlorinated derivatives of propane (C_3Cl_8, $CHCl_2CCl_2CCl_3$ and $CCl_3CHClCCl_3$) have been synthesized and subjected to fluorination. Three monofluorides, three difluorides and two trifluorides have thus been made. These new compounds are described, their structural formulas established and the course of the fluorination thereby demonstrated.

Extending to the propane series the investigations which have covered methane and ethane compounds is not a mere expansion, because the propane molecule offers a new position on its center carbon atom, and because the increased distance between its ends affects the course of the fluorination. As the ultimate purpose is the synthesis of fluorinated derivatives of much greater length, it is essential to learn the effect that the position and the distance of the fluorinated groups exert upon the molecule as a whole.

Synthesis.—The heptachloropropanes were synthesized by condensing chloroform with tetrachloroethylene, or carbon tetrachloride with trichloroethylene, in the presence of aluminum chloride. From asymmetrical heptachloropropane, a treatment with potassium hydroxide gave hexachloropropylene, and the latter combined with chlorine to yield octachloropropane. This method, originated by Prins,[1] has been improved, as described in the experimental part, but it cannot be extended to the condensation of fluorinated molecules of methane and ethylene, for the reasons previously reported.[2]

The chlorinated propanes were thoroughly purified before subjecting them to fluorination. This precaution was taken because fluorination gives only one of the possible isomers at each stage, and the isolation of the fluorinated compounds in a pure state is much facilitated by starting from well-defined material. The fluorination was performed as indicated in the experimental part, but the isolation, purification, analysis and description of the new compounds followed the methods of preceding papers[3] and the results have been tabulated.

The reason for describing the fluorination procedures in detail is that chlorinated propanes may split into one molecule of chlorinated methane and one of chlorinated ethylene, which is merely the reverse of the condensation reaction by means of

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(1) Prins, *J. prakt. Chem.*, [2], **89**, 416 (1914).

(2) I, Henne and Newman, THIS JOURNAL, **60**, 1697 (1938).

(3) *Ibid.*, **56**, 1726 (1934); **58**, 402, 404, 882, 884, 887, 889 (1936); **59**, 1200, 1400, 2434 (1937).