THERMODYNAMICS OF THE HYDROCHLORINATION REACTION OF PROPYLENE

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Abstract

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S. G. ENTELIS and N. M. CHIRKOV

THERMODYNAMICS OF THE HYDROCHLORINATION REACTION OF PROPYLENE

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The hydrochlorination reaction of propylene

$$C_3H_6 + HCl \rightleftarrows u\text{-}C_3H_7Cl$$

is reversible, but direct measurements of the equilibrium constants and of the heat of the process are lacking.

We assume, in accordance with tabulated data, that the heats of formation $\Delta H^0_{f\,298.2}$ of propylene, hydrogen chloride, and isopropyl chloride are, respectively: +4879 cal/mole (1); −22063 cal/mole (2) and −31000 cal/mole (3), and that the entropies $S^0_{298.2}$ are, respectively: +63.8 cal/mole · deg (1); 44.62 cal/mole · deg (2) and 72.4 cal/mole · deg (3). Hence the changes in heat content and entropy in the reaction will be $\Delta H_R = -13816$ cal/mole, $\Delta S_R = -36.02$ cal/mole · deg. Consequently:

$$2.3RK_p = 13816/T - 36.02. \tag{1}$$

Table 1

Values of α_d and α_{an} in experiments on the hydrochlorination of propylene on H_3PO_4 with 72% P_2O_5

T, °C	$p_{C_3H_60}$, mm Hg	p_{HCl0}, mm Hg	α_d	α_{an}
70	50	50	0.380	0.380
70	100	100	0.322	0.350
70	200	200	0.512	0.523
70	300	300	0.788	0.787
100	200	200	0.326	0.322
160	200	200	0.475	0.480
180	200	200	0.456	0.441

Experimentally, the heat of reaction was measured by Thomsen (4):

$$\Delta H_R = -11960 \text{ cal/mole.}$$

In our experiments the equilibrium was studied by pressure in a static apparatus (we used the same apparatus as in work (^{5})) at temperatures of 100, 120, 140, 160, and 180°C; the catalyst was orthophosphoric acid with 72% P_2O_5. Equilibrium was reached both from the side of HCl and C_3H_6 and from the side of u-C_3H_7Cl. Attainment of equilibrium by the system was determined from the complete cessation of pressure change. In those cases where it was not possible to observe a complete cessation of the reaction, the equilibrium pressure was found by extrapolation to zero rate on a pressure—reaction-rate graph. The corrections usually introduced were very small.

Before the measurements were carried out, it was found that u-C_3H_7Cl is, under our conditions, the only reaction product. For this purpose, in a flow apparatus in the presence of the catalyst—phosphoric acid on porous glass—at $T = 100$°C, an amount of the reaction product between HCl and C_3H_6 sufficient for distillation was obtained. Distillation of the dry product on a column with an efficiency of 16 theoretical plates showed,

that the entire product distills in the range 33.3-34.5° C and has $n_D^{15}1.3810$ (literature data: $n_D^{15}1.3811$ and b.p. 34.8° C).

Since observations of the course of the reaction were made by the change in pressure in the system, Δp, it was first necessary to establish that there was a correspondence between the value of Δp and the extent of reaction α. A series of experiments was carried out in which, in addition to Δp, the change in the amount of HCl (ΔN) in the system was analyzed acidimetrically. Table 1 gives the values $\alpha_{\text{p}} = \Delta p/p_0$ and $\alpha_{\text{an}} = \Delta N/N_0$, where p_0 and N_0 are, respectively, the initial pressure and the initial amount of HCl in the system.

As can be seen from Table 1, in all the cases cited there is satisfactory agreement between α_{p} and α_{an}.

In order to show that the equilibrium studied is a true one and is not associated with the presence of kinetic limiting phenomena, it must be reached both from the side of synthesis and from the side of decomposition of the product.

In Fig. 1 are shown the kinetic curves of the synthesis (1) and decomposition (2) of isopropyl chloride at 160° C in coordinates: pressure of u-C_3H_7Cl in the reaction mixture—time. For convenience in comparing curves 1 and 2, the pressure is expressed in relative units; the initial pressure of u-C_3H_7Cl in the decomposition reaction was taken as unity.

Fig. 1. Kinetic curves of the synthesis (1) and decomposition (2) of isopropyl chloride on orthophosphoric acid (72% P_2O_5). Amount of acid 1.2 g (calculated as 100% H_3PO_4); reactor volume 404.2 cm^3.

Table 2

Equilibrium constants K_p of the reaction

$$C_3H_6 + HCl = u\text{-}C_3H_7Cl$$

T, °C	K_p, atm^{-1}	Mean value K_p	T, °C	K_p, atm^{-1}	Mean value K_p
100	151.0	151.0	160	14.6	
120	57.0	58.8		13.8	
120	60.5	58.8		6.5	
140	25.4	25.8		13.5	12.6
140	27.4	25.8		14.3	12.6
140	24.4	25.8		13.8*	12.6
180	6.1	5.9		10.7	12.6
180	5.6	5.9		13.5*	12.6
				13.1	12.6
				12.6	12.6

* Equilibrium was reached from the side of decomposition.

For the synthesis reaction, 200 mm Hg of u-C_3H_7Cl was taken; for the synthesis reaction, HCl and C_3H_6 in a 1:1 ratio were taken at a total pressure of 400 mm Hg. Obviously, when true thermodynamic equilibrium is attained, in both cases the composition of the equilibrium mixture must be the same. As can be seen from Fig. 1, both curves reach equilibrium at one and the same composition of the mixture HCl—C_3H_6—u-C_3H_7Cl.

The equilibrium constants of the reaction obtained in the experiments represented by curves 1 and 2 in Fig. 1 are close in magnitude and are equal, respectively, to 13.1 and 13.5 atm^{-1}. Table 2 gives the values found for the equilibrium constants

$$K_p = \frac{p_{u-C_3H_7Cl}}{p_{HCl}\, p_{C_3H_6}}.$$

In Fig. 2 the data of Table 2 are presented in coordinates $\lg K_p$—$1/T$. From the slope of the straight line, the heat of reaction was found to be

$$\Delta H_R = -13800 \pm 300 \text{ cal/mol}.$$

Knowing ΔH_R and K_p, one can find the change in entropy at

reaction: $\Delta S_R = -27.0 \pm 0.7$ cal/mol • deg, whence for the equilibrium constant in the temperature interval 100–180°C we obtain the expression

Fig. 2. Temperature dependence of the equilibrium constant K_p atm^{-1} for the reaction $C_3H_6 + HCl \rightleftarrows$ u-C_3H_7Cl.

Figure 1: Fig. 2. Temperature dependence of the equilibrium constant K_p atm^{-1} for the reaction $C_3H_6 + HCl \rightleftarrows$ u-C_3H_7Cl.

$$2.3R\lg K_p^* = 13800/T - 27.0. \tag{2}$$

As can be seen, the heat of reaction found by us agrees well with the value $\Delta H_{R\,298.2} = -13816$ cal/mol, calculated from tabulated data; however, ΔS_R differs markedly from the calculated $\Delta S_{R\,298.2} = -36.02$ cal/mol · deg. The difference in temperatures cannot explain the discrepancy in ΔS_R of 9 entropy units. Although the values of c_p for the substances participating in the reaction of interest to us are unknown, the order of the change in entropy with temperature can be seen from the example of the hydrochlorination reaction of ethylene. The change in heat capacity in the course of the reaction is

$$\Delta c_p = c_{p\,C_2H_5Cl} - c_{p\,C_2H_4} - c_{p\,HCl} =$$

$$= -2.37 \text{ cal/mol} \cdot \text{deg}$$

(calculated from the data of (^{2})), whence, according to the known formula

$$\Delta S_{RT} = \Delta S_{R\,298.2} - 2.3 \cdot 2.37 \cdot \lg\frac{T}{298.2}.$$

As can be seen from the formula, a change in temperature from 298.2 to 453 °K will cause a change in ΔS_R of only 0.98 cal/mol · deg.

Fig. 2. Temperature dependence of the equilibrium constant K_p atm^{-1} for the reaction $C_3H_6 + HCl \rightleftarrows$ u-C_3H_7Cl.

For clarity we have given in Table 3 the values of the maximum depths of conversion $\alpha_\infty = \Delta p_\infty / p_0$, where Δp_∞ is the maximum change of pressure in the reaction in mm Hg, and p_0 is the initial partial pressure of one of the components in a mixture of composition 1:1 in mm Hg. The values α_∞ were calculated by the formula:

$$\alpha_\infty = \left(1 + \frac{A}{2}\right) - \sqrt{\left(1 + \frac{A}{2}\right)^2 - 1}, \quad \text{where} \quad A = \frac{760}{K_p p_0}.$$

Table 3

Values of α_∞ for the hydrochlorination reaction of propylene

	$T=70$°C, $K_p=775$ atm^{-1*}	$T=70$°C, $K_p=775$ atm^{-1*}	$T=70$°C, $K_p=775$ atm^{-1*}	$T=70$°C, $K_p=775$ atm^{-1*}	$T=100$°C, $K_p=151$ atm^{-1}	$T=100$°C, $K_p=151$ atm^{-1}	$T=100$°C, $K_p=151$ atm^{-1}	$T=100$°C, $K_p=151$ atm^{-1}	$T=120$°C, $K_p=59.5$ atm^{-1}	$T=120$°C, $K_p=59.5$ atm^{-1}	$T=120$°C, $K_p=59.5$ atm^{-1}	$T=120$°C, $K_p=59.5$ atm^{-1}
p_0, mm	50	100	200	250	50	100	200	500	50	100	200	500
α_∞	0.88	0.94	0.93	0.94	0.63	0.80	0.84	0.90	0.61	0.70	0.77	0.84

From Table 3 it is seen that reversibility begins to have an appreciable effect only at 120°C; at 100°C, and still more at 70°C, reversibility is small.

Institute of Chemical Physics
Academy of Sciences of the USSR

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* The value of K_p for 70°C was calculated from equation (2).

Note: Figure translations are in progress. See original paper for figures.