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1958

SovietRxiv

Abstract

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ON THE THERMODYNAMICS OF THE HYDROCHLORINATION REACTION OF ISOBUTYLENE

The hydrochlorination reactions of unsaturated hydrocarbons are equilibrium reactions, and their thermodynamic calculation is of not only theoretical but also substantial practical interest for choosing the optimal process parameters. In particular, the thermodynamic calculation of the hydrochlorination reaction of isobutylene deserves attention. The equilibrium of this reaction was first studied experimentally by Kistiakowsky and Stauffer [(1)], who, on the basis of the equilibrium composition of the gases, calculated the equilibrium constants and the changes in the free energy of the reaction for a narrow temperature interval. They proposed a linear equation for ΔF_T^0, extrapolation of which to wide temperature intervals without verification by a more rigorous calculation may prove risky.

Later B. A. Krentsel and N. A. Pokotilo [(2)] studied the catalytic hydrochlorination of butenes on solid catalysts. In their work the main attention was directed toward the experimental determination of the optimal reaction conditions. Recently S. G. Entelis [(3)] investigated the kinetic regularities of the hydrochlorination reaction of isobutylene on film acid catalysts. He also proposed an approximate linear equation for determining the equilibrium constant of the reaction.

At present we have the possibility of carrying out a more rigorous thermodynamic calculation of the hydrochlorination reaction of isobutylene, using molecular and spectral data for tertiary butyl chloride.

The molecule of tertiary butyl chloride has symmetry of class C_{3v}. It may be regarded as a C–Cl frame to which three symmetric tops–CH_3–are attached. For calculating the functions due to translational motion, external rotation, and torsional vibrations, the following data were used: C–H distances = 1.09 Å, C–C distances = 1.54 Å, Cl–C–C angles = 111°, and H–C–H angles tetrahedral. Since rotation of the methyl groups does not change the principal moments of inertia of the molecules, for simplicity of calculation a "staggered" model of the molecule was chosen, i.e., one C–H bond of each methyl group was regarded as lying in the same plane as the C–C bond. With the selected angles and interatomic distances, the atomic coordinates have the values given in Table 1; the z axis coincides with the direction of the C–C bond. These data give the following values of the principal moments of inertia of the whole molecule: $I_x = I_y = 26.77 \cdot 10^{-39}$ g · cm^2, $I_z = 18.65 \cdot 10^{-39}$ g · cm^2. The product of the principal moments of inertia $I_x I_y I_z = 1.400 \cdot 10^{-113}$.

Table 1

Atomic coordinates (in Å)

Atom	x	y	z
Cl	0	0	+1.334
C_6	0	0	−0.436
C_1	+1.466	0	−0.910
H_{11}	+2.126	0	−0.043
H_{12}	+1.653	+0.890	−1.510
H_{13}	+1.653	−0.890	−1.510
C_2	−0.733	+1.271	−0.910
H_{21}	−1.063	+1.841	−0.043
H_{22}	−1.597	+0.987	−1.510
H_{23}	−0.056	+1.877	−1.510
C_3	−0.733	−1.271	−0.910
H_{31}	−1.063	−1.841	−0.043
H_{32}	−1.597	−0.987	−1.510
H_{33}	−0.057	−1.877	−1.510

The value of the molecular weight (92.569) and the product of the principal moments of inertia make it possible to calculate the corresponding terms of the entropy, free energy, and other thermodynamic functions of one mole of the given gas as a function of temperature. For the entropy and free energy the following formulas were obtained:

$$S_T^0(\text{trans.} + \text{ext. rot.}) = 25.1663 \lg T + 19.094, \tag{1}$$

$$-\frac{F_T^0 - E^0}{T} = 25.1663 \lg T - 1.164. \tag{2}$$

For tert-butyl chloride, an assignment of frequencies has already been made in the literature ([4]). The missing vibration frequency of the methyl group (A_2) is here taken as equal to 960 cm^{-1}, by analogy with other compounds. Thus, in the present work the following frequencies were used: 304(2), 570, 372, 406(2), 812, 925(2) 160, 1026(2), 1147, 1234(2), 1361(3), 1445(6), 2950(9). On the basis of these and of formulas (1) and (2), the values of the thermodynamic functions due to translational, all rotational (including the CH_3 rotors), and vibrational motions of the molecules were calculated.

Table 3

T, °K	ΔF°_T	$\lg K$	K	ΔF°_T (Kistyakovsky)	ΔF°_T (Y = 3000 cal/mol)
298.0	−6400	4.675	$4.7 \cdot 10^4$	−6.334	−6.000
300	−6300	4.61	$4.08 \cdot 10^4$		
350	−4500	2.86	730		−4100
400	−2700	1.47	29.7	−2660	−2200
450	−900	0.45	2.78		−400
500	+800	−0.48	0.33	+950	+1440

The results are given in Table 2. To calculate the corrections due to hindrance of rotation of the methyl groups (the reduced moment of the model group in this case is equal to $5.19 \cdot 10^{-40}$ g · cm^2), a restricting potential of height 3000 cal/mol was first chosen. However, comparison of the calculation results with the experimental data of Kistyakovsky ([1]) for the hydrochlorination of isobutylene showed that the best agreement is obtained with a potential height of 2000 cal/mol. This value is closer to Eucken' s data ([5]) for the potential in ethyl chloride (Y = 2700 cal/mol) than to the data of American authors ([6]) (Y = 4700 cal/mol). The lowering of the potential height in comparison with isobutane may be explained by the decrease in the repulsive forces of the hydrogen atoms both as a result of the absence of a tertiary hydrogen atom and as a result of an increase in the angle between the

Table 4

Composition of gases at equilibrium

	Temperature, °K									
	298.16	350	400	450	500					
Pressure, atm	1	20	1	20	1	20	1	20	1	20
i-C_4H_8, %	0.46	0.1	3.56	0.82	15.3	4.0	34.0	11.7	45.4	26.6
HCl, %	0.46	0.1	3.56	0.82	15.3	4.0	34.0	11.7	46.4	26.8
tert-C_4H_9Cl, %	99.08	99.8	92.88	98.36	69.4	92.0	32.0	76.6	6.2	46.4

C–C bonds to 111°. Therefore, in Table 2 all thermodynamic functions are calculated with a potential of 2000 cal/mol. Nevertheless, corrections for hindrance at a potential of 3000 cal/mol are also given there. Combining the value $\Delta H^0_{298.16} - E^0_0$ from Table 2 for tert-butyl chloride with the heats of formation

of isobutylene and hydrogen chloride and with the heat of hydrochlorination of isobutylene (according to Kistyakovsky), $\Delta H^0_{298.16} = -17{,}1000$ cal/mol, we obtain for the given substance $\Delta H^0_{298.16} = -43206$ cal/mol and

Table 2

Values of the thermodynamic functions of tertiary isobutyl chloride

T, °K	298.16	300	400	500	600	700	800	900	1000
1. Functions of translational and rotational motions (free internal rotation)									
S°_T, cal	74.367	74.434	77.579	80.016	82.009	83.694	85.154	86.442	87.593
$-\frac{F^\circ_T - E^\circ_0}{T}$	63.437	63.504	66.649	69.086	71.073	72.654	74.224	75.512	76.663
$C_P =$ $4R$	7.949								
$\frac{U^\circ_T - E^\circ_0}{T}$	10.93								

T, °K	298.16	300	400	500	600	700	800	900	1000
2. Functions caused by vibrational motions									
S°_T, cal	7.266	7.344	11.991	17.131	22.066	27.071	31.766	36.625	41.163
$-\frac{F^\circ_T - E^\circ_0}{T}$	2.302	2.351	4.160	6.334	8.453	10.737	13.075	15.461	17.700
C_{cal}	13.072	13.218	19.407	26.056	30.367	34.420	38.128	41.344	43.992
3. Functions caused by hindered internal rotation ($Y =$ 2000 cal/mole)									
$3\left(S^\circ_f - 2.502\right)$	2.562	2.562	1.731	1.215	0.909	0.675	0.546	0.438	0.335
$-3\frac{F^\circ_T - E^\circ_0}{T}$	3.948	3.948	3.489	3.081	2.760	2.457	2.205	2.022	1.908
$3c^\circ$	6.156	6.156	5.553	4.965	4.311	4.203	3.972	3.789	3.636

T, °K	298.16	300	400	500	600	700	800	900	1000
4. Final values of the thermodynamic functions (Y = 2000 cal/mole)									
S_T°	79.1	79.2	87.8	95.9	103.2	110.1	116.4	122.7	128.4
$-\frac{F_T^\circ - E_0^\circ}{T}$	61.8	61.9	67.3	72.3	76.8	80.9	85.1	89.0	92.5
$\frac{U_T^\circ - E_0^\circ}{T}$	17.3	17.3	20.5	23.6	26.4	29.2	31.2	33.7	36.0
C_P°	27.18	27.33	32.91	38.97	42.63	46.57	50.05	53.08	55.58
$-(F_T^\circ - E_0^\circ)$	18 420	18 570	26 930	36 170	46 060	56 650	68 080	80 060	92 460
$U_T^\circ - E_0^\circ$	5160	5190	8210	11 800	15 840	19 710	25 020	30 310	36 000
F_T°	−55 580	−55 730	−64 090	−73 330	−83 220	−93 810	−105 240	−117 220	−129 620
U_T°	−32 000	−31 970	−28 950	−25 370	−21 320	−17 450	−12 140	−6840	−1250
ΔF_T°, kcal	−15.346	−15.2	+5.6	+4.3	+14.6	+24.3	+35.2	+45.9	+56.5
ΔH_T°, kcal	−43.200	−43.3	−44.8	−46.0	−47.7	−48.5	−48.7	−48.8	49.0
ΔS_T°	−93.44	−93.7	−98.0	−100.7	−102.7	−103.9	−104.9	−105.2	−105.5

T, °K	298.16	300	400	500	600	700	800	900	1000
5. Functions of hindered rotation (Y = 3000 cal/mole)									
$3\left(S_f^\circ - \frac{F_T^\circ - E_0^\circ}{T}\right)$	4.308	3.987	2.979	2.253	1.740	1.474	1.200	1.020	0.840
$-3\frac{F_T^\circ - E_0^\circ}{T}$	5.019	5.013	4.602	4.239	3.789	3.483	3.189	2.898	2.664
ΔF_T°, kcal	−14.8	−14.6	−5.0	+4.8	+15.3	+24.4	+35.9	+46.6	+57.4

$E_0^0 = 37160$ cal/mole (17,160). To check the values obtained, the free energies and equilibrium constants of the reaction

$$i\text{-}C_4H_8 + HCl \rightleftarrows \text{tert-}C_4H_9Cl.$$

were calculated.

For the choice of the height of the potential, the data of Kistiakowsky, calculated for 400° K, were taken. The results of the calculation are given in Table 3, which also gives the values of ΔF_T^0 at a potential of 3000 cal/mole for certain temperatures, calculated from Kistiakowsky' s work. As is seen from Table 3, at other temperatures as well, over a wide interval (300-1000°), the agreement is good. For a series of temperatures (300-500°), at intervals of 50°, the composition of the equilibrium mixture for i-$C_4H + HCl$ in a ratio of 1 : 1 at pressures of 1 atm and 20 atm was calculated (Table 4). The calculated data obtained agree well with the experimental results indicated above.

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