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Note

A thermodynamic study of H–D exchange in the hydrogen–difluoroborane system

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The hydrogen–deuterium exchange reaction between D_2 and HBF_2 is unique in certain respects due to its unusually fast reaction rate at ordinary temperatures. For this reason it has been possible to observe H–D exchange equilibria for this system and evaluate the thermodynamic properties of HBF_2 and DBF_2. In this paper we present the results of those equilibrium measurements.

EXPERIMENTAL

Mixtures of HBF_2/BF_3 were prepared by a method similar to that of Coyle et al.[1]. In a typical synthesis a mixture of BF_3 and B_2H_6 in a molar ratio of 2/1 at a total pressure of 200 torr was heated to 200°C for 0.5 h. in a 1-l stainless steel vessel. Under these reaction conditions HBF_2–BF_3 product mixtures contained 30 to 40% HBF_2 with less than 1% B_2H_6. Mixtures of DBF_2–BF_3 were prepared by reaction of HBF_2–BF_3 mixtures with deuterium gas[2]. Sample purities were checked by infrared and mass spectra.

Equilibrium reactions were carried out by heating a stainless steel vessel containing various proportions of HBF_2, DBF_2, H_2 and D_2 to approximately 110°C for 24 h, then cooling the mixture and allowing it to remain at room temperature for periods of 3 to 5 days prior to mass spectral analysis. The reaction vessel was a 5.25 × 1.125-in. O.D. sealed stainless-steel tube with 3 × 0.37 in. O.D. neck equipped with a Whitey 1KS6 valve. Reaction products were analyzed with a CEC-21-103A mass spectrometer. The pressure ratio of HBF_2/DBF_2 was obtained directly from ion intensity ratios of HBF^+/DBF^+. The composition of H_2–HD–D_2 in the product mixture was obtained from intensity measurements of the H_2^+, HD^+ D_2^+ peaks. The sensitivity of the mass spectrometer toward H_2 and D_2 was checked by analyzing standard H_2–D_2 mixtures of known composition. The H_2 used was Fisher high purity grade and D_2 was Air Products Chemical research grade. The BF_3 (Matheson) was used without further purification.

RESULTS AND DISCUSSION

Equilibrium constants were measured for the reactions

$$D_2+H^{11}BF_2 \rightleftharpoons D^{11}BF_2+HD \tag{1}$$

$$H_2+D^{11}BF_2 \rightleftharpoons H^{11}BF_2+HD \tag{2}$$

at 297.5±1.0 K. These quantities in combination give K_{eq} for the overall reaction

$$D_2+2H^{11}BF_2 \rightleftharpoons H_2+2D^{11}BF_2 \tag{3}$$

Initial reaction conditions and the resultant equilibrium constants are shown in Table 1. It was assumed that equilibrium for reaction (1) and (2) was reached when the concentrations of H_2, HD and D_2 corresponding to the hypothetical reaction*

$$H_2+D_2 \rightleftharpoons 2HD \tag{4}$$

has attained equilibrium values. The measured K_{eq} (eqn (4)) shown in Table 1 are in good agreement with previously calculated[3,4] and measured[5,6] values for this equilibrium constant.

Calculation of the entropies and enthalpies for reactions (1)–(3) required knowledge of the six fundamental vibrational frequencies of $HBF_2(DBF_2)$. Of the six only ν_5, the inplane B–H(D) bend has not been observed spectroscopically. The ratio $\nu_{5,H}/\nu_{5,D}$ for the B_1 mode is given by the Teller–Redlich product rule[7]

$$\frac{(\nu_4\nu_5)_H}{(\nu_4\nu_5)_D}=\left(\left[\frac{m_D}{m_H}\right]\left[\frac{M_H}{M_D}\right]\left[\frac{I_{z,H}}{I_{z,D}}\right]\right)^{1/2}$$

when m_H and m_D are masses of H and D atoms respectively; M_H and M_D are the molecular weights of $H^{11}BF_2$ and $D^{11}BF_2$; I_z is the moment of inertia taken about an axis perpendicular to the plane of the molecule; and $\nu_{4,H}$ (1401.5 cm^{-1})[8] and $\nu_{4,D}$ (1392.5 cm^{-1})[8] are the BF asymmetric stretching modes of $H^{11}BF_2$ and $D^{11}BF_2$, respectively. Using the I_z values of Kasuya et al.[9] we calculate $\nu_{5,H}/\nu_{5,D}=1.357$. The other equation needed to calculate $\nu_{5,H}$ and $\nu_{5,D}$ was obtained as follows. The entropies of $H^{11}BF_2$ and $D^{11}BF_2$ were calculated by the usual statistical thermodynamic procedure[10]. Vibrational partition functions were calculated using the five frequencies given by Porter and Wason[8] and estimated values for $\nu_{5,H}$ and $\nu_{5,D}$ (ref. 11). The entropies of $H^{11}BF_2$ and $D^{11}BF_2$ were combined with the tabulated entropies of H_2, HD, and D_2[5] to obtain $\Delta S^\circ_{298.15}$ (eqns (1)–(3). These entropies were used in combination with the K_{eq} from Table 1 to obtain $\Delta H^\circ_{298.15}$ (eqns (1)–(3). The $\Delta H^\circ_{298.15}$ were corrected to ΔH°_0 (refs. 4 and 10) and these values compared to the zero point energies of reactions (1)–(3) (E°_0 (eqns (1)–(3) calculated without the use of $\nu_{5,H}$ and $\nu_{5,D}$. The resulting energy difference was attributed to $E^\circ_0(\nu_{5,H})-E^\circ_0(\nu_{5,D})$. Substitution of eqn (5) allowed calculation of new $\nu_{5,H}$ and $\nu_{5,D}$

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*This reaction is too slow for observation at room temperature.

TABLE 1

EQUILIBRIUM CONSTANTS AT 297.5±1 FOR REACTIONS (1)–(4)

Initial composition ($H_2/D_2/HBF_2/DBF_2/BF_3$)	P_{total} *(torr)*	K_{eq} *(eqn (1))*	K_{eq} *(eqn (2))*	K_{eq} *(eqn (3))*	K_{eq} *(eqn (4))*
1/0.36/0/0.100/0.16	288	4.22	0.78	5.42	3.28
1/0.89/0.42/0.35/1.15	171	4.43	0.73	6.05	3.25
1/1/1.3/1.0/3.6	150	4.54	0.73	6.20	3.32
1/0.89/0.59/0.42/1.25	110	4.49	0.73	6.13	3.28
1/1/0.38/0.31/1.11	76	4.48	0.76	5.90	3.39
Averages[a]	—	4.49±0.05[b]	0.74±0.02	6.07±0.13	3.31±0.06

[a] First run discounted in average. [b] Error limits represent one std. dev.

TABLE 2

THERMOCHEMICAL DATA FOR REACTIONS (1)–(3) AT 298 K

Reaction	$\Delta G°$ *(kcal mol⁻¹)*	$\Delta S°$ *(e.u.)*	$\Delta H°$ *(kcal mol⁻¹)*	ν_3 $(H^{11}BF_2)$ cm^{-1}	ν_3 $(D^{11}BF_2)$ cm^{-1}
$D_2 + H^{11}BF_2 = D^{11}BF_2 + HD$	−0.89±0.01[a]	0.31±0.05[b]	−0.80±0.06[b]	1610±125[b]	1185±100
$H_2 + D^{11}BF_2 = H^{11}BF_2 + HD$	0.18±0.02	2.55±0.05	0.94±0.07	1575±175	1160±135
$D_2 + 2H^{11}BF_2 = 2D^{11}BF_2 + H_2$	−1.07±0.02	−2.23±0.05	−1.73±0.07	1590±100	1170±75

[a] Error limits = 1 std. dev. [b] Estimated error limits.

values which were then substituted into the appropriate vibrational partition functions and the process repeated. The resultant values for the various thermodynamic quantities are shown in Table 2. The thermodynamic quantities listed are calculated using harmonic oscillator and rigid rotator assumptions for $H^{11}BF_2$ and $D^{11}BF_2$. The ν_{5H} and ν_{5D} frequencies listed in Table 2 are some-what higher than those calculated by Lynds and Bass[11] (1348 and 992 cm^{-1}, respectively) using Greens functions and matrix partitioning techniques, but comparable to the B–H (1604 cm^{-1}) and B–D (1184 cm^{-1}) in plane deformation frequencies of BH_3 and BD_3 observed by Kaldor and Porter[12]. The present method of calculation yields ν_{5H} and ν_{5D} frequencies which are quite sensitive to small changes in $\Delta H^\circ_{298.15}$ (eqns (1)–(3). Changes of 100–200 cm^{-1} in the ν_{5H} and ν_{5D} frequencies do not substantially affect the values for the thermodynamic quantities listed in Table 2.

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