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Note

ENTHALPIES OF FORMATION OF DEUTERIUM BROMIDE AND BENZENE-d_1

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Very few thermochemical data have been reported for deuterated compounds. Rabinovich and Tsvetkov [1] determined the enthalpies of combustion of perdeuterated cyclohexane, benzene, naphthalene, and biphenyl. From the results they calculated $\delta \Delta H^0_{\mathrm{atom}}$, the difference in heat of atomization between the deuterium and the hydrogen compounds. For comparison they calculated the theoretical value of $\delta \Delta H^0_{\mathrm{atom}}$ from IR spectroscopic data as a sum of zero point energies. The calorimetric and the theoretical values were both found to be 2.0 ± 0.1 kcal mole^{-1} hydrogen atom. In 1936 Erlenmeyer and Epprecht [2] published the heat of combustion of benzoic acid-d_5; their figure corresponds to $\delta \Delta H^0_{\mathrm{atom}} = 3.9$ kcal mole^{-1} hydrogen atom. In the present investigation the enthalpies of formation of deuterium bromide and benzene-d_1 have been measured and the bond dissociation energy of C—D in benzene-d_1 has been calculated.

EXPERIMENTAL

Materials

Hydrogen bromide was obtained in a steel cylinder (Gerling Holtz & Co., Hamburg). Deuterium bromide was prepared from deuterium oxide (99.8% D) and phosphorus tribromide. The gas was passed through a cold trap at —60°C and collected in a steel cylinder at —78°C. Phenylmagnesium bromide in diethyl ether was prepared as described [3].

Calorimeter

The steady state heat flow calorimeter arrangement has been described previously [3,4].

Procedure

The hydrogen and deuterium bromide cylinders were kept in a water thermostat at 15°C. By means of glass capillaries fitted to the outlets, constant streams of approximately 18 μm s^{-1} were obtained and checked by titration to be within ±0.1%. The temperature in the calorimeter was read to ±0.001°C by means of a Beckmann thermometer. The electrical effect of the manganin heating coil was obtained from current (Fluke 832A) and voltage (Keithley 177 DMM) readings.

RESULTS AND DISCUSSION

The following reactions were studied

$$HBr(g) + KOH(280\ H_2O) \rightarrow KBr(280\ H_2O) + H_2O(l) \quad (1)$$

$$DBr(g) + KOH(280\ H_2O) \rightarrow KBr(280\ H_2O) + DOH(l) \quad (2)$$

$$C_6H_5MgBr(\text{soln. in ether}) + HBr(g) \rightarrow C_6H_5\text{-}H(l) + MgBr_2(\text{soln. in ether}) \quad (3)$$

$$C_6H_5MgBr(\text{soln. in ether}) + DBr(g) \rightarrow C_6H_5\text{-}D(l) + MgBr_2(\text{soln. in ether}) \quad (4)$$

The results are presented in Table 1.
From reactions (1) and (2) it follows

$$\Delta H_f[HBr](g) - \Delta H_f[DBr](g) = \Delta H_r(2) - \Delta H_r(1) + \Delta H_f[H_2O](l) - \Delta H_f[DOH](l)$$

and from reactions (3) and (4)

$$\Delta H_f[C_6H_5H](l) - \Delta H_f[C_6H_5D](l) = \Delta H_r(4) - \Delta H_r(3) + \Delta H_f[DBr](g) - \Delta H_f[HBr](g)$$

Inserting the experimental results and known data [5] it is found that deuterium bromide and benzene-d_1 have enthalpies of formation which are 0.3 and 1.2 kcal $mole^{-1}$, respectively, more negative than the protium analogs, and therefore $\Delta H_f^0[DBr](g) = -8.9 \pm 0.1$ kcal $mole^{-1}$ and $\Delta H_f^0[C_6H_5D](l) = +10.5 \pm 0.2$ kcal $mole^{-1}$. For the processes

$$C_6H_5\text{—}H(g) \rightarrow C_6H_5^{\cdot} + H^{\cdot}$$

$$C_6H_5\text{—}D(g) \rightarrow C_6H_5^{\cdot} + H^{\cdot}$$

TABLE 1

Enthalpies of reaction (kcal $mole^{-1}$) obtained for reactions (1)—(4)

$\Delta H_r(1)$	−33.57	−33.67		−33.6 ± 0.1
$\Delta H_r(2)$	−34.36			−34.4 ± 0.1
$\Delta H_r(3)$	−62.53	−62.95	−62.90	−62.8 ± 0.1
$\Delta H_r(4)$	−63.65	−63.75	−63.75	−63.7 ± 0.1

is found

$$D(C_6H_5{-}D) - D(C_6H_5{-}H) = \Delta H_f[D^\bullet] - \Delta H_f[H^\bullet] - \Delta H_f[C_6H_5{-}D] + \Delta H_f[C_6H_5{-}H]$$

Assuming identical values for the heat of vaporization of benzene and benzene-d_1 and inserting known values [5] for the enthalpy of formation of atomic hydrogen and deuterium, the difference in the bond dissociation energy is found to be 2.1 ± 0.2 kcal mole^{-1}.

The results seem to support the data obtained by the Russian group, while the value published for the heat of combustion of benzoic acid-d_5 appears dubious.

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