

Note

ENTHALPIES OF FORMATION OF DEUTERIUM BROMIDE AND BENZENE- d_1

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(Received 20 December 1980)

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 $\delta\Delta H_{\text{atom}}^0$, the difference in heat of atomization between the deuterium and the hydrogen compounds. For comparison they calculated the theoretical value of $\delta\Delta H_{\text{atom}}^0$ 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 $\delta\Delta H_{\text{atom}}^0 = 3.9$ 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].

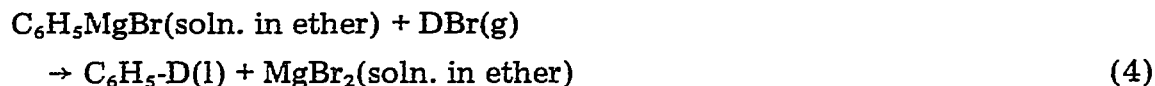
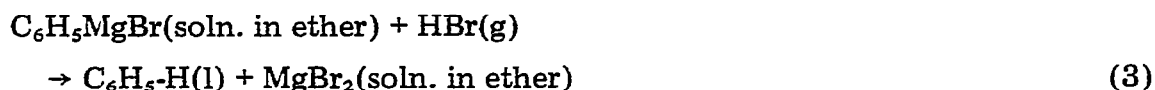
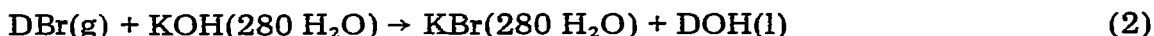
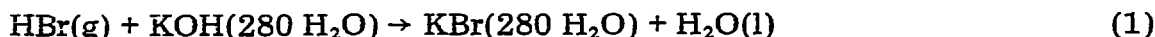
Procedure

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 $18 \mu\text{m s}^{-1}$ were obtained and checked by titration to be within $\pm 0.1\%$. The temperature in the calorimeter was read to $\pm 0.001^\circ\text{C}$ 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



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

$$\begin{aligned} \Delta H_f[\text{HBr}](\text{g}) - \Delta H_f[\text{DBr}](\text{g}) = \Delta H_r(2) - \Delta H_r(1) + \Delta H_f[\text{H}_2\text{O}](\text{l}) \\ - \Delta H_f[\text{DOH}](\text{l}) \end{aligned}$$

and from reactions (3) and (4)

$$\begin{aligned} \Delta H_f[\text{C}_6\text{H}_5\text{H}](\text{l}) - \Delta H_f[\text{C}_6\text{H}_5\text{D}](\text{l}) = \Delta H_r(4) - \Delta H_r(3) + \Delta H_f[\text{DBr}](\text{g}) \\ - \Delta H_f[\text{HBr}](\text{g}) \end{aligned}$$

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 $\Delta H_f^0[\text{DBr}](\text{g}) = -8.9 \pm 0.1$ kcal mole $^{-1}$ and $\Delta H_f^0[\text{C}_6\text{H}_5\text{D}](\text{l}) = +10.5 \pm 0.2$ kcal mole $^{-1}$. For the processes

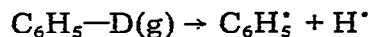
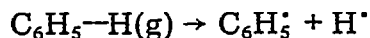


TABLE 1

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

$$D(\text{C}_6\text{H}_5\text{-D}) - D(\text{C}_6\text{H}_5\text{-H}) = \Delta H_f[\text{D}^{\cdot}] - \Delta H_f[\text{H}^{\cdot}] - \Delta H_f[\text{C}_6\text{H}_5\text{-D}] \\ + \Delta H_f[\text{C}_6\text{H}_5\text{-H}]$$

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.

REFERENCES

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