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Thermochemistry of the Gas Phase Molecular Complex of Benzene with Oxygen

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A method previously developed to study the thermochemistry of weakly bound molecular complexes in condensed phase has been used to investigate the gas phase molecular complex that forms between benzene and oxygen. Observed changes in absorbance in benzene−oxygen mixtures with temperature are attributed to changes in complex concentration. Based on this, ΔH_{rxn}, the enthalpy change for complex formation, is found to be −4.3 ± 1.0 kJ/mol, indicating that the complex is a "contact charge transfer" complex. The result from the present study is compared to two previous determinations of ΔH_{rxn} for the benzene−oxygen complex and is used to resolve the discrepancies in the previous results.

Introduction

Weakly bound molecular complexes have been the focus of experimental study for 50 years. Thermochemical information on molecular complexes can be used to predict chemical reactivity and to develop general methods for representing the acid−base properties of molecules. Recently, weakly bound complexes have also been used as model systems for femtosecond photodissociation dynamics studies.

There have been several previous investigations of molecular complexes of benzene with oxygen in condensed phase[1−7] and in the gas phase.[8−10] Two recent studies have reported conflicting thermodynamic information on the gas phase benzene−oxygen complex. Using the Rose−Drago spectrophotometric method and independent experiments based on Dalton's law of partial pressures, Gooding and co-workers[9] found $\Delta G_{298} = -3.3$ kJ/mol for the benzene−oxygen complex. By assuming that ΔS_{298} for this complex is the same as for the benzene−iodine complex they obtained $\Delta H_{298} = -7.9$ kJ/mol for the reaction enthalpy for complex formation. In contrast to this result, Grover and co-workers,[10,11] on the basis of molecular beam photoionization studies, reported that $\Delta H_{298} = -4.0 \pm 1.5$ kJ/mol for the benzene−oxygen complex.

The purpose of the present paper is to present the results of measurements of the enthalpy of reaction for the formation of the gas phase complex of benzene with molecular oxygen. The experimental technique is one previously developed and used for obtaining thermodynamic information on weakly bound condensed phase molecular complexes.[12−18] The results of the present study are compared to those previously found.

Experimental Section

The apparatus used in the present experiments is a home-built system previously used in absorption cross-section measurements.[19] The apparatus consists of a deuterium light source, 50 cm path length gas absorption cell, 0.35 m grating monochromator, and PMT light detector. The monochromator and light detector are interfaced to a PC through a Keithly 500A measurement and control system for wavelength selection and data acquisition. Sample temperature in the absorption cell is controlled by circulating water from a refrigerated circulating bath (Fisher Isotemp 9100) through a coil of tubing surrounding the cell. Temperature gradients in the absorption cell and fluctuations in cell temperature are both less than ±0.5 °C. Additional information on the apparatus including details on wavelength calibration and tests on the precision and accuracy with which absorption measurements can be made on the system have been previously presented.[19]

Gas samples were prepared on a gas handling manifold with connections to a 12 L mixing bulb, capacitance manometer (either Omega Engineering or MKS Baratron, calibrated against a mercury manometer), inlets for introduction of gas and vapor samples, and the absorption cell. The mixing bulb was fitted with a Teflon stirrer for rapid mixing of samples. Benzene (Aldrich, 99.9+%) was degassed by several freeze−pump−thaw cycles before use to remove dissolved air. Argon (Air Products, 99.998%) and oxygen (Air Products, 99.996%) were used as received.

To begin an experiment, a gas sample of known composition and total pressure was introduced into the absorption cell at room temperature. The cell was closed off from the gas handling manifold and then cooled to the first temperature. Absorbance measurements were carried out at three temperatures (17.3, 32.5, and 47.6 °C) under conditions of constant volume. Over the range of temperatures used in the experiments, absorbance due to the complex was observed to decrease by approximately 25%, a change sufficient to obtain a reaction enthalpy for complex formation.

Results and Discussion

Figure 1 gives the absorption spectrum for a benzene−argon and benzene−oxygen gas mixture between 208 and 230 nm at $T = 17.3$ °C. The gas mixtures contain the same partial pressure of benzene and approximately the same total pressure. The absorption spectrum for neat benzene at the same pressure (not shown in the figure) is the same to within experimental error as that found for the benzene−argon mixture. The increase in absorption in the benzene−oxygen mixture relative to that observed for neat benzene or for a benzene−argon mixture is due to the presence of benzene−O_2 complexes and has been previously observed.[8,9] The present results are consistent with previous experiments, which place the peak of the complex absorption spectrum at approximately 215 nm.[8,9]

The enthalpy of reaction for the process

$$\mathrm{B} + \mathrm{O_2} \leftrightarrow \mathrm{B{-}O_2};\quad K_{\mathrm{p}} = P_{\mathrm{B-O_2}}/P_{\mathrm{B}}P_{\mathrm{O_2}} \qquad (1)$$

(where B is benzene, B−O_2 is the complex, and K_{p} is the equilibrium constant for complex formation) is found using a

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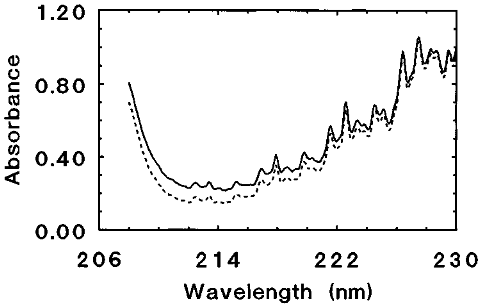

Figure 1. Absorbance vs wavelength for (- - -) 25.7 Torr of benzene + 320 Torr of Ar; (—) 25.7 Torr of benzene + 318 Torr of O_2. Data are at $T = 17.3$ °C.

modification of a procedure previously developed for obtaining thermochemical data for weakly bound complexes in solution.[12,18] The absorbance due to the complex is found for a particular gas mixture at each experimental temperature. Since absorption from benzene overlaps the complex absorption band, separate experiments on neat benzene and benzene−Ar mixtures are used to obtain benzene absorption cross sections. These cross sections are used to remove the contribution from uncomplexed benzene molecules in the absorption of benzene−oxygen mixtures.

The enthalpy of reaction for complex formation is obtained from the experimental absorbance data as follows. ΔH_{app}, the apparent enthalpy of formation, is defined as

$$\Delta H_{app} = -R[\partial \ln A/\partial(1/T) + T] \qquad (2)$$

where A is the absorbance due to the complex. In practice, A is found by summing the absorbances due to the complex over a range of wavelengths. In the present experiments, absorbance has been summed over the region from 210 to 220 nm, where the absorbance due to uncomplexed benzene is a minimum. ΔH_{app} is then found from a plot of ln A vs $1/T$.

As previously shown in the work on weakly bound condensed phase molecular complexes[12,18]

$$\partial \ln A/\partial(1/T) = (1 + K_c[O_2]_0)^{-1}\, \partial \ln K_c/\partial(1/T) \qquad (3)$$

In the above expression $[O_2]_0$ is the initial oxygen concentration and $K_c = [B-O_2]/[B][O_2]$ is the equilibrium constant for the complex expressed in concentration units. Assuming ideal gas behavior $K_c = RTK_p$. By substituting K_p for K_c in eq 3 and noting that $\partial \ln K_p/\partial(1/T) = -\Delta H_{rxn}/R$ it can be shown that ΔH_{app} is related to ΔH_{rxn} by the expression

$$\Delta H_{app} + RT = (\Delta H_{rxn} + RT)\{1 - K_p(P_{O_2})_0 + (K_p(P_{O_2})_0)^2 - ...\} \qquad (4)$$

$$= (\Delta H_{rxn} + RT)/(1 + K_p(P_{O_2})_0) \qquad (5)$$

where $(P_{O_2})_0$ is the initial oxygen pressure. Equations 4 and 5 are the gas phase analogues to the equations previously found for weakly bound molecular complexes in condensed phase.[12,18] In principle, eq 4 or 5 can be used to find values for both ΔH_{rxn} and K_p from a plot of ΔH_{app} vs $(P_{O_2})_0$. However, the data from the present experiment indicate that the equilibrium constant for formation of the benzene−oxygen complex is small ($K_p \ll 1$), so it was only possible to find ΔH_{rxn} from the data.

Data for experiments on benzene-oxygen gas mixtures are summarized in Table 1. Based on these data, the experimental value for ΔH_{rxn} is −4.3 ± 1.0 kJ/mol.

TABLE 1: Summary of Experimental Results for Benzene−Oxygen Molecular Complexes

P_B (Torr)	P_{O_2} (Torr)	ΔH_{app} (kJ/mol)
24.3	146	−3.72
33.6	199	−5.53
28.1	258	−2.69
25.7	318	−5.29
23.6	380	−2.88
21.5	450	−6.80
15.1	534	−3.39
52.3	702	−4.23
40.3	806	−4.20
		ΔH_{rxn} −4.3 ± 1.0 kJ/mol[a]

[a] Error range given for random error at 95% confidence limits.

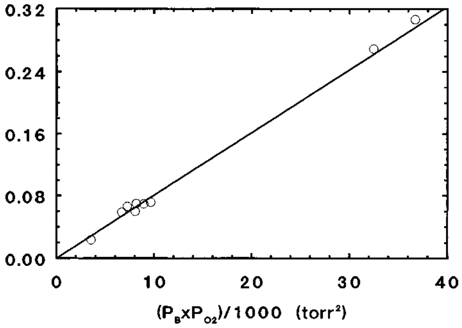

Figure 2. Average absorbance A_{ave} (between 210 and 220 nm) vs $(P_B)_0 \times (P_{O_2})_0$. Data are at $T = 17.3$ °C.

As a check on the experiments, A_{ave}, the average absorbance between 210 and 220 nm, was plotted against $(P_B)_0 \times (P_{O_2})_0$, the product of the initial benzene and oxygen pressures. Since the equilibrium constant for complex formation is small, eq 1 can be rearranged to give

$$P_{B-O_2} = K_p P_B P_{O_2} \cong K_p(P_B)_0(P_{O_2})_0 \qquad (6)$$

The average absorbance of the $B-O_2$ complex should therefore be proportional to $(P_B)_0 \times (P_{O_2})_0$. As shown in Figure 2, such behavior is in fact observed.

The value for ΔH_{rxn} obtained in the present experiment is in excellent agreement with the value $\Delta H_{rxn} = -4.0 \pm 1.5$ kJ/mol previously reported by Grover and co-workers[10,11] but disagrees with the value $\Delta H_{rxn} = -7.9$ kJ/mol found by Gooding and co-workers.[9] Given the difficulty in using the Rose−Drago method or Dalton's law of partial pressures to determine thermodynamic data on such weakly bound molecular complexes, it seems likely that the result given by Gooding and co-workers is in error, as has previously been suggested.[10]

Summary

The results from the present experiments indicate that ΔH_{rxn} for formation of the gas phase molecular complex of benzene with oxygen is close to zero. This suggests that the complex is a "contact charge transfer" complex, that is, a complex that briefly forms due to random encounters between benzene molecules and oxygen molecules.

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