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Thermochemistry of Gas-Phase Molecular Complexes of Fluorobenzene and Toluene with Oxygen

Juan J. Casero and Jeffrey A. Joens*

Department Of Chemistry, Florida International University, Miami, Florida 33199

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The enthalpy of reaction for the formation of the gas-phase complexes fluorobenzene−O_2 and toluene−O_2 has been determined using a spectroscopic method previously applied to the benzene + O_2 system. The results are $\Delta H_{rxn} = -5.4 \pm 2.1$ kJ/mol for the fluorobenzene−O_2 complex and $\Delta H_{rxn} = +1.1 \pm 0.9$ kJ/mol for the toluene−O_2 complex. Attempts to observe complexes of oxygen with chlorobenzene and the three xylene compounds were unsuccessful, most likely due to the low vapor pressure of the donor molecules and small value for the equilibrium constant for complex formation. Results are compared to those previously obtained for other aromatic−O_2 complexes.

Introduction

Molecular complexes formed by noncovalent interactions between donor and acceptor molecules have been extensively studied for over 50 years.[1,2] Thermochemical data on such complexes can be used to predict chemical reactivity and in developing methods for representing the acid−base properties of chemical species. There have also been several recent experiments on the dissociation dynamics of weakly bound complexes on a femtosecond time scale.[3−10]

In an earlier publication,[11] we showed how a method developed in our laboratory[12] for determining thermochemical data on weakly bound molecular complexes in condensed phase could be applied to the study of gas-phase molecular complexes. The method was used to determine the enthalpy of reaction for the process forming a 1:1 complex between benzene and molecular oxygen. On the basis of the experimental results we were able to resolve inconsistencies in previous measurements[13,14] of the enthalpy of reaction for benzene−oxygen complex formation.

In the present paper, we report reaction enthalpies for the formation of gas-phase complexes between molecular oxygen and two benzene derivatives, toluene and fluorobenzene. Results are compared to those previously found for other aromatic−O_2 gas-phase complexes. Unsuccessful attempts to determine thermodynamic information for other complexes between aromatic donor molecules and oxygen are also discussed.

Experimental Section

The apparatus and experimental methods used in the present study have been discussed previously[11,15] and are summarized as follows. Absorption measurements were carried out on a home-built apparatus consisting 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 were controlled by a PC via a Keithley 500A measurement and control system. Calibration of the monochromator was carried out by use of a mercury−xenon atomic lamp. Preliminary experiments were performed to determine the precision and accuracy of the apparatus in measuring absorption. Sample temperature in the absorption cell was controlled by circulating water from a refrigerated circulating bath (Fisher Isotemp 9100) through a tubing coil surrounding the cell. Temperature gradients and fluctuations in the cell were less than ±0.5 °C.

Gas samples for measurements were prepared on a gas handling manifold with inlets for gas and vapor samples and connections to the absorption cell, a 12 L mixing bulb, and a capacitance manometer. The mixing bulb was fitted with a Teflon stirrer for rapid mixing of samples. Gas pressures were measured using an MKS Baratron capacitance manometer calibrated against a mercury manometer. Toluene, fluorobenzene, chlorobenzene, *o*-xylene, *m*-xylene, and *p*-xylene (Aldrich, 99+% or 99.9% purity) were degassed prior to use by several freeze−pump−thaw cycles to remove dissolved air. Argon (Air Products, 99.998%) and oxygen (Air Products, 99.996%) were used as received.

Experiments were carried out by introducing a gas sample of known composition and total pressure into the absorption cell at room temperature. The cell was closed off from the rest of the system and then cooled to the first temperature. Measurements were carried out at three temperatures, 17.3, 32.5, and 47.6 °C. As shown in the previous study of the benzene−oxygen molecular complex,[11] this temperature range is sufficient for determining the reaction enthalpy for complex formation.

Since both toluene and fluorobenzene absorb in the same region where complex absorption is monitored, separate experiments with mixtures of each molecule with and without added argon were used to obtain absorption cross sections for the molecules in the absence of complex formation. These cross section values were then used to separate light absorption from uncomplexed aromatic molecules from that due to the aromatic−oxygen complex.

Results and Discussion

Figure 1 gives the absorption spectrum for a fluorobenzene + argon and fluorobenzene + oxygen gas mixture between 220 and 236 nm and at a temperature of 17.3 °C. The gas mixtures contain similar partial pressures of fluorobenzene. The absorp-

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* To whom correspondence should be addressed. Fax: (305) 348−3772. E-mail: JOENSJ@FIU.EDU.

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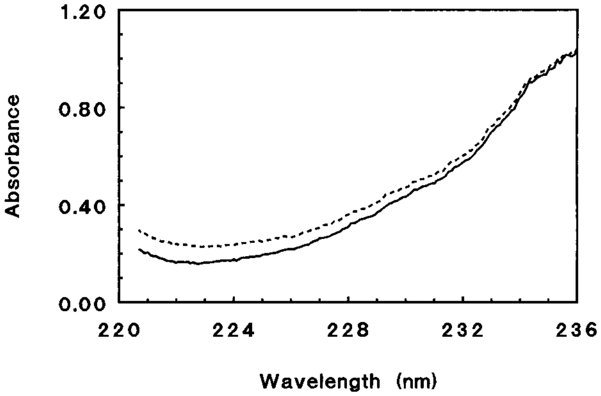

Figure 1. Absorbance vs wavelength for (—) 19.4 Torr fluorobenzene + 416 Torr Ar and (- - -) 19.2 Torr fluorobenzene + 556 Torr O_2. Data are at $T = 17.3$ °C.

tion spectrum of neat fluorobenzene at the same partial pressure (not shown in the figure) is the same as that for the fluorobenzene−argon mixture within the experimental error of the measurement. The increase in absorption in this region of the spectrum when oxygen is used in place of argon, which is also seen in toluene + oxygen gas mixtures, has previously been observed for mixtures of benzene and oxygen[11,13,16] and attributed to the formation of a weakly bound molecular complex.

Following the procedure previously used in our study of the benzene-oxygen molecular complex,[11] the enthalpy of reaction for the process

$$B + O_2 \leftrightarrow B{-}O_2; \quad K_p = P_{B-O2}/P_B P_{O2} \tag{1}$$

(where B is the benzene derivative, $B{-}O_2$ is the molecular complex, and K_p is the equilibrium constant for complex formation) is found from examination of the temperature dependence of the absorbance arising from complex formation. An apparent enthalpy of reaction, ΔH_{app}, is defined as

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

where A is the absorbance due to the complex. In the present experiments, the average absorbance of the complex between 226 and 231 nm (for fluorobenzene−O_2) or 225−230 nm (for toluene−O_2) is used in eq 2. These absorbance ranges are selected to maximize the absorbance from the molecular complex while avoiding interference from the strong electronic transition present in benzene derivatives, which in fluorobenzene and toluene begins at approximately 220 nm.

The apparent enthalpy of reaction is related to ΔH_{rxn}, the enthalpy of reaction, by the expression

$$\Delta H_{rxn} + RT = (\Delta H_{app} + RT)\,(1 + K_p(P_{O2})_0) \tag{3}$$

where $(P_{O2})_0$ is the initial partial pressure of oxygen in the system. In principle, eq 3 can be used to determine experimental values for both K_p and ΔH_{rxn}. However, no systematic change in ΔH_{app} with oxygen pressure is observed in the present experiments, indicating that the value for K_p for these complexes is small and cannot be found from the experimental data. In this case, it is a good approximation to say $\Delta H_{rxn} \cong \Delta H_{app}$.

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

P_{arene} (Torr)	P_{O2} (Torr)	ΔH_{app} (kJ/mol)
	Fluorobenzene	
28.8	356.0	−5.14
23.5	362.0	−5.20
18.8	363.0	−1.73
19.2	556.0	−8.93
14.7	649.0	−3.50
7.8	743.0	−4.96
4.7	840.0	−8.03
	average $\Delta H_{rxn} = -\ 5.4 \pm 2.1$ kJ/mol	
	Toluene	
14.5	203.0	+1.05
11.5	351.0	+1.76
15.5	425.0	−0.31
8.7	428.0	+1.08
16.0	490.0	+2.05
15.9	557.0	+3.37
15.6	639.0	+1.02
15.7	771.0	−0.13
13.8	826.0	−0.17
	average $\Delta H_{rxn} = +\ 1.1 \pm 0.9$ kJ/mol	

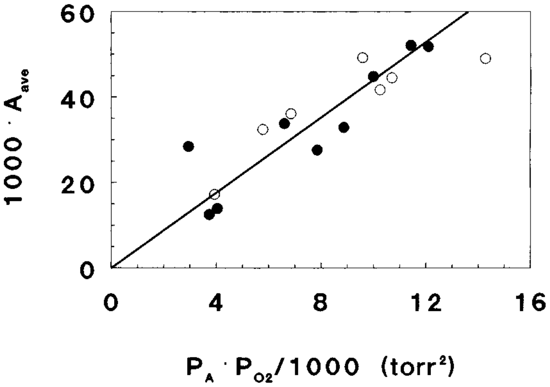

Figure 2. Average absorbance vs $(P_B)_0(P_{O2})_0$ for (○) fluorobenzene and (●) toluene. A line is included in the figure to indicate deviations from linear behavior.

Data for experiments on fluorobenzene−oxygen and toluene−oxygen gas mixtures are summarized in Table 1. On the basis of these data, $\Delta H_{rxn} = -\ 5.4 \pm 2.1$ kJ/mol for the fluorobenzene−oxygen complex and $\Delta H_{rxn} = +\ 1.1 \pm 0.9$ kJ/mol for the toluene−oxygen complex, where error limits are reported at the 95% confidence limits.

As a check on the experiments A_{ave}, the average absorbance due to complex formation, has been plotted against $(P_B)_0(P_{O2})_0$, the product of the initial pressure of the benzene derivative and that of molecular oxygen. Since the equilibrium constant for complex formation is small, it follows that

$$P_{B-O2} = K_p P_B P_{O2} \cong K_p (P_B)_0 (P_{O2})_0 \tag{4}$$

The average absorbance of the $B{-}O_2$ complex should therefore be proportional to $(P_B)_0(P_{O2})_0$. As seen in Figure 2, this behavior is observed both for the fluorobenzene−O_2 and toluene−O_2 complexes.

Results for the change in enthalpy for formation of gas-phase complexes of aromatic molecules with oxygen are summarized in Table 2. The value reported for the hexafluorobenzene−O_2 complex has been calculated from the data of Grover and coworkers[14] using the procedure given in their paper. The same set of vibrational constants for the van der Waals modes used by them to convert D_0 to D_{298} (dissociation energy for the complex at 0 and 298 K, respectively) for the benzene−O_2 complex is also used to convert D_0 to D_{298} for the hexafluorobenzene−O_2 complex. While these vibrational constants (11, 15, 24, 38, and 55 cm^{-1}) are certainly not correct for the hexafluorobenzene−O_2 complex, the conversion of D_0 to D_{298}

TABLE 2: Experimental Values for ΔH_{rxn} and D_0 for Aromatic + O_2 Complex Formation

aromatic molecule	ΔH_{rxn} (kJ/mol)	D_0 (kJ/mol)	reference
benzene	-4.3 ± 1.0	7.2	11
	-7.9	10.8	13
	-4.0 ± 1.5	6.9	14
toluene	$+1.1 \pm 0.9$	1.8	this paper
fluorobenzene	-5.4 ± 2.1	8.3	this paper
hexafluorobenzene	-5.9 ± 1.8	8.8	14[a]

[a] Calculated from data from ref 14, as discussed in the text.

is not sensitive to the exact values for the vibrational constants as long as $\omega \ll kT$. Since $kT = 207$ cm^{-1} at 298 K, this condition is satisfied for the weakly bound hexafluorobenzene$-O_2$ complex.

The results in Table 2 suggest that there may be a small increase in the magnitude of ΔH°_{rxn} with increasing substitution of fluorine atoms for hydrogen atoms on the benzene ring. While the values for the reaction enthalpy for benzene, fluorobenzene, and hexafluorobenzene are the same within the stated experimental error, indirect evidence from the experiments of Grover and co-workers[14] suggests that D_0(fluorobenzene$-O_2$) > D_0(benzene$-O_2$), as does the increased solubility of oxygen in liquid hexafluorobenzene relative to that observed for benzene.[17] Formation of the toluene$-O_2$ complex is slightly endothermic according to the present results.

The trends noted above for the change in ΔH°_{rxn} with substitution of fluorine or a methyl group on the benzene ring, if correct, are the opposite of those seen for the gas-phase complexes of aromatic molecules with I_2 or other halogen or mixed halogen acceptor molecules.[1] The difference may be due to the fact that for I_2 charge transfer occurs to the unoccupied σ^* molecular orbital, while for O_2 it will be to the half-filled π^* molecular orbitals. Because of this, electron-donating groups such as the methyl group, by providing more π-electron density to the aromatic ring, may, due to interaction with the σ^* electrons of oxygen, lead to destabilization of the resulting complex, rather than stabilization, as is observed for aromatic$-I_2$ complexes.

Several theoretical calculations for the dissociation energy of aromatic$-O_2$ molecular complexes have been reported which can be compared to the experimental results given in Table 2. Granucci and Persico[18] obtained a value of $D_0 = 5.36$ kJ/mol for the benzene$-O_2$ complex using an SCF/MP2 calculation, corrected to account for the difference between the computed and experimental polarizabilities of benzene and oxygen. This is about 2 kJ/mol smaller than the value for D_0 obtained from the experimental results of Casero and Joens[11] and reported by Grover and co-workers.[14] Wesolowski and co-workers[19,20] have calculated values for D_0 for the benzene$-O_2$ complex using density functional theory with a variety of commonly used functionals. Since the purpose of their work was to compare various approximation methods within the Kohn$-$Sham framework, and not to obtain a highly accurate value for D_0 for the benzene$-O_2$ complex, the results that they report do not provide a good test of the quality of the experimental results. Finally, Grover and co-workers,[14] using the program CHARMM with both electrostatic and van der Waals contributions, found $D_0 = 5.6$ kJ/mol for the benzene$-O_2$ complex and $D_0 = 9.6$ kJ/mol for the hexafluorobenzene$-O_2$ complex, in good agreement with the experimental values they report for these two complexes. Their calculations are consistent with the weak trend of increasing D_0 with increasing substitution seen in the experimental data on fluorobenzene$-O_2$ complexes.

Attempts were also made to determine reaction enthalpies for several additional aromatic$-O_2$ complexes, including chlorobenzene$-O_2$ and the three xylene$-O_2$ complexes. However, no complex absorption was observed for these donor molecules. This is probably due to a combination of small value for K_p for complex formation and the low vapor pressure for these donor molecules (at 20 °C, the vapor pressures (in Torr) are chlorobenzene (9), *o*-xylene (5), *m*-xylene (6), *p*-xylene (6), benzene (58), fluorobenzene (56), and toluene (21)). To determine reaction enthalpies for complex formation for these donor molecules by the present method will require use of a much longer path length, as can be obtained in a multipass cell.

In summary, the relatively small values for ΔH_{rxn} for the formation of the fluorobenzene$-O_2$ and toluene$-O_2$ complexes suggest that these complexes fall into the category of "contact charge-transfer" complexes. In light of the present results and those previously found for complexes of benzene and substituted benzene derivatives with oxygen, it is expected that the reaction enthalpy for formation of all of these complexes will be small.

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