Ground-State Benzene–Oxygen Complex

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The Drago-Rose/Benesi-Hildebrand spectrophotometric method has been used to quantify ground-state complex formation between benzene and oxygen in the gas phase at 295 K. Absorption to the benzene-oxygen charge-transfer state was the experimental parameter monitored. Assuming a 1:1 reaction stoichiometry, the data yield a free energy for complex formation (ΔG_{295K}) of -1.2 ± 0.3 kcal/mol and a complex extinction coefficient of 14 ± 4 cm⁻¹ M⁻¹ at 218 nm. Independent experiments based on Dalton's law of partial pressures, however, indicate that the Drago-Rose/Benesi-Hildebrand results most likely overestimate the stability of the benzene-oxygen complex and that a more accurate ΔG value is ~ -0.8 kcal/mol. In an analogous experiment, the methanol-oxygen charge-transfer absorption was quantified in a series of aqueous solutions at 295 K. In this case, the data do not indicate the presence of a weakly bound complex but rather are more consistent with Mulliken's definition of a "contact" complex.

Introduction

It has been known for many years that when oxygen is dissolved in an organic solvent, the absorption onset of the solution shifts to longer wavelengths.¹ On the basis of the pioneering work of Tsubomura and Mulliken² and Evans,³ among others, this change in absorbance was assigned to a transition from a ground-state oxygen-organic molecule complex (M-O₂) to the oxygen-organic molecule charge-transfer (CT) state. A great deal of evidence indicates that the ground-state M-O₂ complex is weakly bound at best and is perhaps better characterized as a "contact" complex.^{1,4} In defining the latter, Mulliken notes that, even in the absence of a stable ground-state complex, absorption to the CT state can still occur when the overlap integral between the ground-state donor-acceptor orbitals is appreciable.⁴ Fully aware of the problems inherent in studying weak complexes,¹ we set out to quantify equilibrium constants for M-O2 complex formation by using the Benesi-Hildebrand⁵/Drago-Rose⁶ approach. Specifically, we felt it would be possible to distinguish a true $M-O_2$ contact complex from a complex that is weakly bound. We report here our results on the benzene-oxygen complex in the gas phase and the methanol-oxygen complex in the liquid phase.

Experimental Section

Absorption spectra were recorded on Beckman Model DU-40 and Cary 17 spectrophotometers. All experiments were performed at 295 K.

A. Gas-Phase Study. The sample cell (9.0 cm path length) had fused silica windows and an appendage that could be immersed in liquid N_2 and was equipped for attachment to a vacuum manifold. Gas pressures were quantified with a capacitance manometer (MKS Baratron; range 1000 Torr). The delivery of oxygen and nitrogen gas was controlled by needle valves attached to the vacuum manifold. Spectrophotometric or HPLC grade benzene (Aldrich) was degassed by three freeze-pump-thaw cycles and purified by bulb-to-bulb distillation. In a typical experiment, the vacuum manifold and sample cell were evacuated and then loaded with a specific pressure of benzene (P_M) . The benzene was subsequently condensed into the sample cell, which was then isolated from the manifold. The manifold was then loaded with a specific pressure of oxygen which, in turn, was allowed to expand into the sample cell with the frozen benzene. The final oxygen pressure in the sample cell was measured by noting the decrease in the oxygen pressure in the isolated manifold. The final 295 K benzene pressure in the sample cell was determined by normalizing $P_{\rm M}$ by the ratio of sample cell volume to total system volume. By using this technique, we were assured of complete mixing between benzene and oxygen. In this experiment, the

variable in the Benesi-Hildebrand/Drago-Rose treatment was the oxygen partial pressure (vide infra).

B. Liquid-Phase Study. A 1 cm path length, fused silica cuvette was used. Mixtures of methanol (Aldrich, spectrophotometric or HPLC grade) and distilled water were prepared such that the methanol mole fraction ranged from 0.1 to 1.0. Changes in volume due to mixing were taken into consideration. (In this case, the Benesi-Hildebrand/Drago-Rose variable was methanol concentration.) Each sample was bubbled with oxygen gas for 5 min prior to recording of the absorption spectrum. The oxygen concentration in a specific CH₃OH/H₂O mixture was determined from data compiled by Battino⁷ and normalized for the atmospheric pressure in Albuquerque (~ 630 Torr at an elevation of \sim 1609 m). The lack of similar, accurate data for other solvent mixtures precluded liquid-phase studies with molecules other than methanol and water.

Results and Discussion

A. Gas-Phase Benzene-Oxygen Complex. The effect of oxygen on the absorption spectrum of benzene has been examined by a host of investigators.¹ Of particular interest are the works of Lim and Kowalski⁸ and Birks et al.,⁹ where absorption spectra for the benzene-O₂ complex were recorded in the liquid and gas phases, respectively. Although we initially intended to use the Benesi-Hildebrand/Drago-Rose technique to quantify the equilibrium constant for the formation of this complex in the liquid phase, the lack of oxygen solubility data (e.g., Henry's law constants, Bunsen coefficients, etc.) for mixtures of benzene and a solvent "inert" to complexation (vide infra) required us to perform these experiments in the gas phase.

Absorption spectra of benzene (55 Torr) recorded in the absence and presence of 825 Torr of oxygen are shown in Figure 1. It is clear that, at wavelengths between ~ 210 and 234 nm, the admission of oxygen results in an absorbance increase; 800 Torr of neat oxygen does not absorb in this region of the spectrum, and changes in the benzene spectrum were not observed upon the addition of N_2 , He, or Ar. This absorbance change can thus be assigned to the $M-O_2$ transition forming the CT state.^{1,2,8,9} In

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Figure 1. Absorption spectra of benzene (55 Torr) in the absence (---) and presence (---) of 825 Torr of oxygen.

a neat liquid, where the concentration of benzene (~11 M) greatly exceeds that of oxygen (~10⁻² M in an oxygen-saturated solution), the CT transition is manifested as a red shift of the benzene absorption onset at ~300 nm.^{2,10} Taking the difference between the spectra shown in Figure 1 yields a broad, structureless absorption band ($\lambda_{max} \sim 214-215$ nm) that is consistent with a loosely bound complex.⁹ We were not able to detect an isosbestic point in the data over this wavelength range.

In using the Benesi-Hildebrand/Drago-Rose approach to quantify complex formation,^{5,6,11} we assumed a 1:1 stoichiometry.

$$M + O_2 \stackrel{k}{\longleftrightarrow} M - O_2 \tag{1}$$

The Drago-Rose treatment for this system yields⁶

$$K^{-1} = \frac{(A - A^{0})}{l(\epsilon_{MO_{2}} - \epsilon_{M})} - [M]_{0} - [O_{2}]_{0} + \frac{[M]_{0}[O_{2}]_{0}l(\epsilon_{MO_{2}} - \epsilon_{M})}{(A - A^{0})}$$
(2)

The component in excess was chosen to be oxygen, which was varied over the range $\sim 70-825$ Torr. $[O_2]_0$ and $[M]_0$ are the total concentrations (complexed plus free) of oxygen and benzene in the system, respectively. The latter was held constant for each data set recorded. K is the equilibrium constant for complex formation, l is the sample cell path length, and ϵ_{MO_2} and ϵ_M are the molar extinction coefficients for the complex and benzene, respectively, at the measurement wavelength. A^0 is the benzene absorbance in the presence of oxygen, again at a specific wavelength.

Equation 2 has two unknowns, K and ϵ_{MO_2} for which we must solve. The Benesi-Hildebrand expression⁵ is a less general form of eq 2 that is not suited to our system for a number of reasons. Specifically, in solving for K and ϵ_{MO_2} , Benesi-Hildebrand data reduction requires a linear plot in which both the slope and intercept are used. The latter is often indistinguishable from zero and is certainly subject to large errors. In the Drago-Rose treatment,⁶ however, for each $(\mathcal{A}, [O_2]_0)$ data point (e.g., Figure 2), K^{-1} is calculated for a range of ϵ_{MO_2} by using eq 2. Values of K^{-1} and ϵ_{MO_2} that are common to different $(\mathcal{A}, [O_2]_0)$ data points represent meaningful solutions to eq 2. This approach is less sensitive to error and artifacts.

Plots of K^{-1} vs ϵ_{MO_2} , according to eq 2, are linear except when $\epsilon_{MO_2} = \epsilon_M$, where a singularity occurs (Figure 3). In cases where the expected value of ϵ_{MO_2} is close to ϵ_M , it is important to determine the slope and intercept of the K^{-1} vs ϵ_{MO_2} plot from data points that either (1) are distant from the value of ϵ_M or (2) bracket the singularity at $\epsilon_{MO_2} = \epsilon_M$ (Figure 3). Slopes and intercepts thus obtained can then be used to solve for meaningful K and ϵ_{MO_2} values; i.e., the intersections of K^{-1} vs ϵ_{MO_2} lines calculated for



Figure 2. Absorption spectra of benzene-oxygen mixtures over the range 212-237 nm. Data are presented for oxygen pressures of 803, 650, 464, 226, and 0 Torr. The benzene pressure is 40 Torr in each case.

different $(\mathcal{A}, [O_2]_0)$ data points reflect K^{-1} and ϵ_{MO_2} values common to the different data sets. Drago-Rose plots for two independent experiments are shown in Figure 4. Data from these and other experiments yield

$$K = 7.5 \pm 2.5 \text{ M}^{-1}$$

$$K = (4.1 \pm 1.4) \times 10^{-4} \text{ Torr}^{-1}$$

$$\Delta G_{295K} = -1.2 \pm 0.3 \text{ kcal/mol}$$

$$\epsilon(218 \text{ nm}) = 14 \pm 4 \text{ M}^{-1} \text{ cm}^{-1}$$

It has been emphasized by many scientists that caution must be exercised in the determination and interpretation of Benesi-Hildebrand/Drago-Rose data for weak complexes. Our K^{-1} vs ϵ_{MO_2} plots (Figure 4) are indeed consistent with those expected by Drago for a small K.¹² In Drago's analysis, as applied to our experiments, we would need to work at higher oxygen pressures to obtain more accurate values of K and ϵ_{MO_2} . This is consistent with qualifying stipulations set forth by Deranleau.¹³ In our case, the saturation fraction S of the dilute component exceeds the minimum quantity desired by Deranleau (~ 0.2) only at oxygen pressures in excess of ~600 Torr ($S = [M-O_2]/[M]_0 = K[O_2]/(1$ + $K[O_2]$). A less stringent requirement was set forth by Person¹⁴ in which, for our case, the oxygen concentration should exceed $\sim 0.1/K$. At oxygen pressures in excess of ~ 250 Torr, we indeed meet the Person criterion for meaningful results. Although it would be reasonably straightforward to carry out our experiments at oxygen pressures that exceed our present upper limit of ~ 825 Torr, we are hesitant to do so for fear that the data may reflect the unique high-pressure benzene-O₂ phenomenon reported by Kasha.15

In an attempt to support our spectrophotometric results, an independent series of experiments based on Dalton's law of partial pressures was performed. In this case, a known volume element (V_1) on our vacuum manifold was filled with a known partial pressure of benzene (P_M) . Similarly, a separate volume element (V_2) was filled with oxygen (P_{O_2}) . A value separating the two chambers was then opened, the gases were allowed to mix, and the total pressure (P) was measured for the new volume $(V_T = V_1 + V_2)$. On the basis of Dalton's law, the total pressure of the system is given by eq 3 and the quantity XP_{MO_2} can be determined by simple subtraction.

$$P = (P_{\rm M}V_1/V_{\rm T}) + (P_{\rm O_2}V_2/V_{\rm T}) - XP_{\rm MO_2}$$
(3)

$$K = P_{\rm MO_2} / (P_{\rm M} - P_{\rm MO_2}) (P_{\rm O_2} - P_{\rm MO_2})$$
(4)

 P_{MO_2} is the partial pressure due to the M-O₂ complex, and X represents an integer. If X = 0, no complex is formed and the

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Figure 3. Plot of K^{-1} vs ϵ_{MO_2} (eq 2) for one $(\mathcal{A}, [O_2]_0)$ data point showing the singularity at $\epsilon_{MO_2} = \epsilon_M$. The slope and intercept of the solid line were used in the Drago-Rose treatment.



Figure 4. Drago-Rose plots for two independent benzene-oxygen experiments. (A) The system absorbance was monitored at 218 nm for oxygen pressures of 226, 384, 513, and 723 Torr. The benzene partial pressure was 40 Torr. (B) The system absorbance was monitored at 217 nm for oxygen pressures of 74, 286, 376, 464, and 629 Torr. The benzene partial pressure was 50 Torr.

total system pressure is simply the sum of P_M and P_{O_2} normalized by the change in volume. If benzene combines with oxygen in a 1:1 ratio to form a complex, then X = 1. If either benzene or oxygen combines with each other in a 2:1 ratio, then X = 2 and so forth.

Under the conditions described above and within the accuracy of our gas handling and measurement system ($\sim 0.5-1\%$ error), we were unable to see a difference in total pressure between benzene-O₂ and benzene-N₂ mixtures. This observation indicates



Figure 5. Absorption spectra of neat liquid methanol in the absence (---) and presence (---) of 8.3×10^{-3} M oxygen.

that K cannot be larger than $\sim 3-5.8 \text{ M}^{-1}$ and ΔG_{295K} cannot be more exergonic than $\sim 0.6-1.0 \text{ kcal/mol}$. Thus, it appears that our Drago-Rose/Benesi-Hildebrand results overestimate the stability of the benzene-oxygen complex by approximately 0.4 kcal/mol and that a more accurate value for ΔG_{295K} is $\sim -0.8 \text{ kcal/mol}$.

If we assume that the entropy loss upon complexation in the benzene-oxygen system is similar to that in the benzene-iodine system, then data reported by Lang and Strong¹⁶ can be used in conjunction with our approximate ΔG value to calculate the enthalpy for benzene-oxygen association.

$$\Delta G_{295K} \sim -0.8 \text{ kcal/mol}$$
$$\Delta H \sim -1.9 \text{ kcal/mol}$$
$$\Delta S = -3.7 \text{ eu}^{16}$$

The ΔH value thus obtained is similar to those reported by Lang and Strong¹⁶ and Duerksen and Tamres¹⁷ for the benzene-I₂ complex, $\Delta H = -2.0 \pm 0.1$ and -1.8 kcal/mol, respectively. When viewed as a limit for the exothermicity of complex formation, our data are also consistent with results from a molecular beam experiment in which the dissociation energy of the benzene-O₂ complex was determined by measuring its ionization potential.¹⁸ In this case, data obtained at 5 K yield a dissociation energy of 0.9 ± 0.3 kcal/mol when normalized to 298 K (i.e., ΔH (complexation) = -0.9 ± 0.3 kcal/mol).

Our data indicate that the expected negative entropy for benzene- O_2 complex formation is unable to offset an appreciably exothermic enthalpy term of ~1.9 kcal/mol, yielding a free energy (ΔG) for complex formation that is negative. We conclude that benzene, which has a polarizable π electron system and a reasonably low ionization potential (9.24 eV), indeed forms a discrete, weakly bound complex with oxygen. We suggest that the negative enthalpy for complex formation is due in part to configuration interaction in which the bound CT state (M*+O₂+) is the principal contributor.^{19,20}

B. Liquid-Phase Methanol-Oxygen Complex. In a liquid-phase Benesi-Hildebrand/Drago-Rose treatment for oxygen complexation, the organic molecule M is the component in excess and its concentration is varied in a solvent that is inert to oxygen complexation. To perform an accurate analysis in this case, it is essential to have available oxygen solubility data for mixtures of the inert solvent and the molecule to be complexed. Furthermore, oxygen solubility may not be linear in mixtures of two liquids over the mole fraction range 0-1.0, and thus extrapolations from oxygen

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Figure 6. Absorption spectra of oxygenated methanol-water mixtues used in the Drago-Rose/Benesi-Hildebrand analysis. Data are presented for χ_{CH_3OH} of 1.0, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, and 0.3.

solubilities in neat liquids are insufficient (the deviation from ideality may be positive or negative). One system for which accurate oxygen solubility data are known is $CH_3OH/H_2O.^7$

Neat liquid methanol has a pronounced $M-O_2$ absorption band that is manifested as a red shift in the onset of methanol absorption upon the introduction of oxygen (Figure 5). This transition is also well to the red of any water absorption band. Furthermore, since water's ionization potential (12.6 eV) is higher than that of methanol (10.8 eV), we assume that the H_2O-O_2 CT state will be sufficiently high in energy so as not to impart a stabilizing influence on the ground-state complex. Thus, when compared to methanol, oxygen complexation with water may be minimal, and we propose that water may indeed be an appropriate inert solvent.²¹

(21) If water is not a completely inert solvent, in addition to the desired equilibrium $% \left(\frac{1}{2} \right) = 0$

$$CH_3OH + O_2 \rightleftharpoons CH_3OH \cdot O_2$$

we could also be studying a displacement reaction.

$$H_2O \cdot O_2 + CH_3OH \rightleftharpoons H_2O + CH_3OH \cdot O_2$$

In this circumstance, it is possible that our results could underestimate the stability of the $CH_3OH \cdot O_2$ complex. A reviewer of the manuscript indicated that, on the basis of Drago's ECT values,²² this latter circumstance may indeed exist.

For these experiments, a variety of CH₃OH/H₂O solutions were prepared ($\chi_{CH_3OH} = 0.1-1.0$) and saturated with oxygen. For the solvent mixtures used, the oxygen concentration ranged from 1.6 $\times 10^{-3}$ to 8.3×10^{-3} M.⁷ Sample absorbances were determined at three different wavelengths (222, 225, 230 nm; Figure 6). Both Drago-Rose and Benesi-Hildebrand treatments indicate that, in this case K is sufficiently small (<1.0 M⁻¹; $\Delta G > 0$ kcal/mol) that it cannot be accurately determined. It thus appears that, unlike benzene, the methanol-oxygen interaction is indeed an example of a Mulliken contact complex and that the pronounced CT absorption band is due to fleeting overlap between donor and acceptor orbitals. The methanol data are consistent with an M-O₂ CT state that is less able to impart a stabilizing influence on the ground-state complex through configuration interaction.

Conclusions

We have quantified the weak interaction between benzene and oxygen. Our data indicate that the electronic transition to the benzene– O_2 CT state originates from a discrete, weakly bound ground-state benzene-oxygen complex. The corresponding transition to the methanol-oxygen CT state, however, appears to originate from a true ground-state contact complex in which there is only fleeting overlap between donor and acceptor orbitals. Our data are consistent with an M- O_2 ground-state potential surface defined, in part, by state mixing with the higher energy and bound CT (M^{*+} O_2^{*-}) state.²³

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