

c. The Co(II) acts as a catalyst at low concentration but inhibits the reaction at high concentration. The catalytic effect is clearly seen from (R<sub>1</sub>) and (R<sub>2</sub>). At high Co(II), however, the radicals produced can not build up sufficiently to initiate the propagation of the reaction through (R<sub>3</sub>) and (R<sub>4</sub>), because they are quickly consumed by (R<sub>5</sub>). This is in agreement with the velocity-decreasing effect of [Co(II)] and with earlier results.<sup>11-14</sup> In accordance with the opposing effects, we have found that the "bulk" reaction taking place in the capillary tube without initiation is too fast for waves to be measured at [Co(Ac)<sub>2</sub>] < 0.004 M; i.e., the reaction is complete soon after mixing the components. Therefore, we could not carry out experiments at sufficiently low Co(II) concentration to illustrate the catalytic effect. At the same time, no wave could be initiated at all at [Co(Ac)<sub>2</sub>] > 0.04 M under our experimental condition, because the inhibitory effect prevents the wave propagation. At low Co(II) concentration the wave accelerates because of the bulk reaction, as seen in Figure 1. (The diffusion of the perbenzoic acid used to initiate the reaction may influence the velocity within the first 10-15 mm; thus the initial parts of the curves are not shown.)

d. According to the skeleton mechanism, an increase in [Co(II)] increases the rate of the bulk reaction. This is in agreement with our observation that at high Co(II) concentration ([Co(Ac)<sub>2</sub>] > 0.02) the pink color of the solution before the front slowly changes to apple-green, causing the disappearance of the sharp boundary

within 1-2 h. (This does not necessarily mean that the perbenzoic acid front comes to an end, only that the front cannot be observed visually any further.)

e. At intermediate Co(II) concentration a "second" front following the first one can be observed, where the green Co(III) color changes back to pink Co(II). This phenomenon also limits the observable time interval to about 1-2 h.

f. The velocity of the front propagation as a function of the percentage oxygen content of the O<sub>2</sub>-N<sub>2</sub> mixture used to saturate the solution is seen in Figure 4. No visual observation of the front was possible with O<sub>2</sub> < 40%. Figure 4 suggests that there is a threshold in O<sub>2</sub> concentration below which no wave can be initiated. The reason is that below this limit the dissolved O<sub>2</sub> is completely consumed by Co(II), and no excess is available to produce perbenzoic acid, which is responsible for the propagation of the wave.

### Conclusion

The present paper is the first report on the phenomenon of propagating reaction fronts in the autoxidation process and in a nonaqueous solution. Since most autoxidation processes of organic compounds follow a similar mechanism, the discovery of many other waves can be anticipated. The mechanistic details of these type of reactions are well known. Thus the extension of experimental studies in this field is a promising venture and may be of a great value in understanding nonlinear phenomena in chemical kinetics.

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**Registry No.** PhCHO, 100-52-7; Co(Ac)<sub>2</sub>·4H<sub>2</sub>O, 6147-53-1; O<sub>2</sub>, 7782-44-7.

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## Partial Molar Volumes of Sulfur Dioxide in Organic Solvents: Formation of Charge-Transfer Complexes

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**Abstract:** New apparatus for measuring the apparent molar volumes of gases in liquids is described. The apparatus has been used to obtain the limiting partial molar volume of sulfur dioxide in 17 organic solvents. The limiting partial molar volume of sulfur dioxide is found to be significantly smaller in electron-donating solvents than in non-electron-donating solvents, with this difference being interpreted in terms of charge-transfer complex formation. We propose two methods for estimating the standard volume change of the complexation reaction and illustrate the use of these methods by application to the sulfur dioxide + benzene system.

Many investigators have shown that sulfur dioxide forms charge-transfer complexes with electron donors. Evidence has been reported for complex formation between sulfur dioxide and aromatic hydrocarbons, olefinic hydrocarbons, and hydrocarbons containing a heteroatom. Accounts of some representative studies can be found in ref 2-10.

Since the formation of charge-transfer complexes will lead to enhanced solubility of sulfur dioxide in electron-donating solvents, such solvents may have industrial importance as good absorbents for removing sulfur dioxide from gaseous effluents.<sup>11</sup> Further investigation of this possibility requires knowledge of the solubility of sulfur dioxide in electron-donating solvents.

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At low pressures of sulfur dioxide, the solubility can be calculated from the appropriate values of the Henry's law constant and the equilibrium constant of complex formation.<sup>12</sup> At higher pressures, the dependences of both the equilibrium constant and the Henry's law constant on pressure are needed for calculation of the solubility. The first of these is related to the standard volume change of the complexation reaction. The second is given by the Krichevsky-Kasarnovsky equation:<sup>13-15</sup>

$$\ln k_H^P = \ln k_H^\circ + \bar{V}_2^\circ(P - p_1)/RT \quad (1)$$

Here  $k_H^P$  and  $k_H^\circ$  represent the Henry's law constant at pressure  $P$  and at the saturation pressure of the solvent, respectively;  $\bar{V}_2^\circ$  represents the partial molar volume of the gas at infinite dilution;  $P$  and  $p_1$  represent the total pressure and the partial pressure of the solvent, respectively;  $R$  and  $T$  have their usual meanings. The only assumptions required in deriving eq 1 are that the partial molar volume of dissolved gas is independent of pressure and that the solution is dilute enough that Henry's law holds. One aim of the present work was to obtain values of  $\bar{V}_2^\circ$  for sulfur dioxide in various electron-donating solvents for use in predicting solubilities of sulfur dioxide at elevated pressures by way of eq 1.

Summaries of experimental methods for obtaining partial molar volumes of dissolved gases have been given by Battino and Clever<sup>16</sup> and Clever and Battino.<sup>17</sup> Although several investigations have led to accurate and reliable values of the desired limiting partial molar volumes of several gases in several liquids, the experimental methods that have been used are unattractively complicated and time-consuming. For this reason, we have developed a less complicated method for obtaining the desired quantities based on measurements of apparent molar volume ( $V_{\phi,2}$ ):

$$\bar{V}_2^\circ = \lim [V_{\phi,2} + n_2(\partial V_{\phi,2}/\partial n_2)_{n_1,T,P}] \quad (2)$$

We have designed and built a new dilatometer that is inexpensive and relatively easy to operate and that allows speedy measurement of apparent molar volumes of dissolved gases to 1% precision. For very dilute solutions and especially in the case where the apparent molar volume does not vary much with composition, eq 2 shows that  $V_{\phi,2}$  is an excellent approximation to  $\bar{V}_2^\circ$ . With our new dilatometer, we have measured the apparent molar volumes and thence obtained values for the limiting partial molar volumes of sulfur dioxide in 11 electron-donating solvents: 7 unsaturated hydrocarbons and 4 organic compounds containing oxygen.

A second aim of the present work was to determine the effect of the formation of a charge-transfer complex on the limiting partial molar volume of sulfur dioxide. This effect should be apparent in differences in the  $\bar{V}_2^\circ$  of sulfur dioxide in electron-donating solvents as compared to non-electron-donating solvents, and these differences should in turn contain information about the volume change due to complex formation. This latter property ( $\Delta V^\theta$ ) may be used to calculate the pressure dependence of the equilibrium constant of the complexation reaction by way of the thermodynamic relationship,  $(\partial \ln K/\partial P)_T = -\Delta V^\theta/RT$ . We have therefore measured apparent molar volumes of sulfur dioxide in six saturated hydrocarbons. Two methods for estimating the  $\Delta V^\theta$  of the reaction between sulfur dioxide and an electron donor are presented.

### Design and Operation of the Dilatometer

**Apparatus.** The dilatometer consists of a Pyrex glass bulb, capacity 68 cm<sup>3</sup>, wall thickness 1.5–2.0 mm, fitted with a straight capillary tube 100 mm long and 3 mm in bore. As a reference

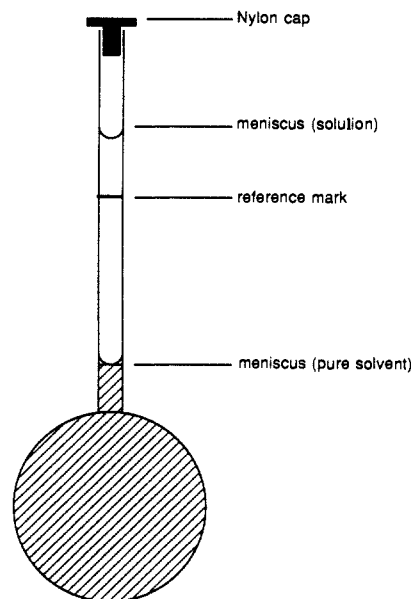


Figure 1. Diagram of the dilatometer for measuring apparent molar volumes of dissolved gases.

mark, a thin copper wire was attached halfway up the capillary tube. The open end of the capillary tube can be closed with a loose fitting Nylon cap. A diagram of the dilatometer is presented in Figure 1.

**Operation.** The solvent is degassed with a vacuum pump for 3–5 min and then loaded into the dilatometer through a 100-cm<sup>3</sup> hypodermic syringe fitted with a 200-mm needle. Solvent is loaded into the dilatometer until the solvent meniscus is about 10 mm up the capillary tube. The dilatometer is then closed with the Nylon stopper and allowed to equilibrate in a constant temperature bath. When equilibrium has been achieved, the height of the meniscus relative to the reference mark is measured with a cathetometer to  $\pm 0.2$  mm, and the loaded dilatometer is then removed from the water bath, carefully dried, and weighed to  $\pm 0.0002$  g.

The solute gas is introduced to the dilatometer under hydrostatic pressure very slightly above atmospheric pressure by connecting the top of the capillary tube to a gas cylinder with Tygon tubing. The bulb is then placed in ice-water, causing the solvent to contract and a gas space of approximately 1 cm<sup>3</sup> to be formed. This space is large enough that easy solution of the solute gas is achieved by gentle rocking and shaking of the dilatometer. The intention is not to reach saturation but merely to dissolve a sufficient mass of gas for suitable determination of the solute concentration by direct weighing.

The dilatometer is disconnected from the Tygon tubing, closed with the Nylon stopper, returned to the water bath, and left to equilibrate for 20–30 min. The final level of the meniscus relative to the reference mark and the final mass of the loaded dilatometer are then measured.

The difference between the initial and final values of the height of the meniscus is combined with a previously determined value (see section on calibration) for the cross-sectional area of the capillary tube to obtain the volume expansion on solution. Division of this volume expansion by the number of moles of gas in solution (found from the difference in mass of the dilatometer before and after addition of the solute gas) yields the apparent molar volume of the solute gas in the solvent.

Temperature control to 0.005 K and pressure control to 10 kPa are sufficient to make all temperature, dilatation, and compressibility corrections negligible. We found that at 25 °C, even with the dilatometer uncapped, toluene (one of our more volatile solvents) was lost at a rate less than 1 mg/h, indicating that no corrections need be made for solvent losses due to diffusion of solvent up the capillary.

Provided that the amount of solute taken up by the solvent results in a rise of the meniscus of at least 40 mm and a gain in

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**Table I.** Limiting Partial Molar Volumes of Sulfur Dioxide in Organic Solvents at 25 °C

solvent	limiting partial molar vol <sup>a,b</sup>
Unsaturated Hydrocarbons	
benzene	47.8
toluene	46.1
<i>m</i> -xylene	46.2
mesitylene	46.1
cyclohexene	48.7
1-methylnaphthalene	44.6
tetralin	44.3
Saturated Hydrocarbons	
cyclohexane	55.4
methylcyclohexane	54.7
1,3-dimethylcyclohexane	55.0
decalin	52.6
octane	56.2
hexadecane	53.5
Organic Compounds Containing Oxygen	
2-nonanone	45.8
diphenyl ether	45.4
dimethyl phthalate	43.1
1-octanol	44.1

<sup>a</sup>Units: cm<sup>3</sup> mol<sup>-1</sup>. <sup>b</sup>Maximum uncertainty is less than 2%.

mass of about 0.5 g, the precision and accuracy of this technique are of the order of 1%. A complete experiment requires only 1.5–2 h.

**Calibration.** The capillary tube can be calibrated conveniently by weight by loading the dilatometer first to the bottom and then to the top of the capillary with a fluid of known density.

### Experimental Section

Using our new dilatometer, we have measured the apparent molar volume of sulfur dioxide at 25 °C in seven unsaturated hydrocarbons [benzene, methylbenzene (toluene), 1,3-dimethylbenzene (*m*-xylene), 1,3,5-trimethylbenzene (mesitylene), cyclohexene, 1-methylnaphthalene, and 1,2,3,4-tetrahydronaphthalene (tetralin)], six saturated hydrocarbons [cyclohexane, methylcyclohexane, 1,3-dimethylcyclohexane, decahydronaphthalene (decalin), octane, and cetane (hexadecane)], and four organic compounds containing oxygen (2-nonanone, diphenyl ether, dimethyl phthalate, and 1-octanol). For the purpose of comparing our results with those of others, we have also measured the apparent molar volume of ethane in octane. For all measurements, the rise of the meniscus was greater than 20 mm, corresponding to a precision of better than 2%.

The temperature of the water bath was controlled to ±0.005 K with a Thermomix 1460 temperature controller.

Sulfur dioxide (Matheson), benzene (Anachemia), toluene (Anachemia), *m*-xylene (BDH), mesitylene (Fluka), cyclohexene (MCB), tetralin (Anachemia), cyclohexane (Caledon), decalin (Fisher), 1-methylnaphthalene (J. T. Baker), octane (Fisher), 2-nonanone (Fisher), hexadecane (Alfa Products), 1,3-dimethylcyclohexane (Fisher), diphenyl ether (Fisher), dimethyl phthalate (BDH), and 1-octanol (Fisher) were used without further purification. Dimethyl phthalate, 1-methylnaphthalene, and tetralin had purities of 97% or higher. All other chemicals were reagent grade.

Preliminary measurements showed that  $V_{\phi,2}$  for dilute solutions is nearly independent of the concentration of sulfur dioxide; in all of our experiments, the mole fraction of sulfur dioxide was less than 0.03. Under these conditions, as stated in the Introduction, the measured apparent molar volume is an excellent estimate of the desired partial molar volume at infinite dilution, and we therefore take the two to be equivalent.

### Results

The limiting partial molar volumes of sulfur dioxide in the 17 solvents that we investigated are listed in Table I. The reliability of the values obtained with our new dilatometer is demonstrated by comparisons with values published by others. Handa et al.<sup>18</sup> found the limiting partial molar volume of ethane in octane to be 66.6 cm<sup>3</sup> mol<sup>-1</sup>, and Horiuti<sup>19</sup> reported 46.8 cm<sup>3</sup> mol<sup>-1</sup> for the limiting partial molar volume of sulfur dioxide in benzene. Our values for ethane in octane (65.8 cm<sup>3</sup> mol<sup>-1</sup>) and for sulfur dioxide

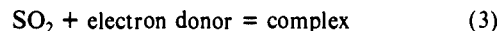
in benzene (47.8 cm<sup>3</sup> mol<sup>-1</sup>) agree with these reported values within the stated uncertainties of the measurements.

Table I shows that there is only a small variation in the limiting partial molar volumes of sulfur dioxide within each group of solvents and that the limiting partial molar volumes of sulfur dioxide in electron-donating solvents (unsaturated hydrocarbons and organic compounds containing oxygen) are significantly smaller than those in non-electron-donating solvents (saturated hydrocarbons).

### Discussion

The relatively smaller limiting partial molar volumes of sulfur dioxide in electron-donating solvents as compared to non-electron-donating solvents (Table I) is consistent with the formation of charge-transfer complexes of sulfur dioxide with the electron donors, as has been suggested by others.<sup>2–10</sup> A reduction in partial molar volume upon complex formation is due to a reduction in the equilibrium distance between solute and solvent molecules.

Our limiting partial molar volumes (Table I) can be used in eq 1 to calculate the pressure dependence of the Henry's law constant for each of the sulfur dioxide + solvent systems that we have investigated. However, as noted in the Introduction, in order to predict the solubility of sulfur dioxide in electron-donating solvents as a function of pressure, we also need to know the pressure dependence of the equilibrium constant,  $K$ , for the complexation reaction



Here "electron donor" refers to the electron-donating solvent in the pure liquid state. SO<sub>2</sub> refers to uncomplexed sulfur dioxide in solution, and complex (also in solution) refers to the charge-transfer complex formed between sulfur dioxide and the electron donor.

A further complication is that the stoichiometry of reaction 3 may vary with the electron donor, with the concomitant need to consider more than one complexation equilibrium. For example, there is evidence<sup>6</sup> that benzene and mesitylene form 1:1 compounds with sulfur dioxide in the solid state, while toluene and *m*-xylene form 2:1 compounds. The existence of a 1:1 benzene-sulfur dioxide complex in the liquid state is supported by UV absorption spectra.<sup>3</sup> Additionally, the authors of ref 3 have found only 1:1 complexes for a variety of other electron donors, including one for which a 2:1 solid is known, indicating that the 2:1 complex may not persist in the liquid. Although further investigation is needed to identify the stoichiometry of electron donor-sulfur dioxide complexes in many of the systems listed in Table I, we illustrate the use of our data by application to the benzene-sulfur dioxide system, where there is only a 1:1 complex.

It has been shown previously<sup>20–22</sup> that the standard volume change for a complexation reaction can be calculated from measured excess volumes, using the ideal associated solution model. However, since no published measurements of excess volumes for SO<sub>2</sub> + electron donor systems are available, approximate methods must be used to obtain values of  $\Delta V^\theta$  for reactions represented by eq 3. In this connection, we have developed two methods.

Our first method is based on a direct comparison of the limiting partial molar volume of sulfur dioxide in benzene with that in a solvent that is not an electron donor. The volume of a solution of sulfur dioxide in benzene,  $V_{\text{soln}}$ , can be written as

$$V_{\text{soln}} = x(\text{C}_6\text{H}_6)V^*(\text{C}_6\text{H}_6) + x(\text{SO}_2)V^\circ(\text{SO}_2)_u + V^E \quad (4)$$

where  $V^*(\text{C}_6\text{H}_6)$  and  $V^\circ(\text{SO}_2)_u$  represent the molar volume of pure benzene and the limiting partial molar volume of uncomplexed sulfur dioxide, respectively,  $x(i)$  represents the stoichiometric mole fraction of substances  $i$ , and  $V^E$  represents the excess

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volume. If the solution were an ideal mixture, then there would be no excess volume ( $V^E = 0$ ). Since we anticipate a chemical interaction between sulfur dioxide and benzene, we expect that  $V^E$  in eq 4 will be nonzero. Furthermore, if the dominant contribution to the excess volume arises from this chemical interaction, then the excess volume may be related to the standard volume change of the complexation reaction<sup>20-22</sup> by

$$V^E = r\Delta V^\theta \quad (5)$$

where  $r$  represents the extent of the complexation reaction. Combining eq 4 and 5 gives

$$V_{\text{soln}} = x(\text{C}_6\text{H}_6)V^*(\text{C}_6\text{H}_6) + x(\text{SO}_2)\bar{V}^\circ(\text{SO}_2)_u + r\Delta V^\theta \quad (6)$$

Another way of expressing the volume of a dilute solution of sulfur dioxide in benzene is

$$V_{\text{soln}} = x(\text{C}_6\text{H}_6)V^*(\text{C}_6\text{H}_6) + x(\text{SO}_2)\bar{V}^\circ(\text{SO}_2/\text{C}_6\text{H}_6) \quad (7)$$

where  $\bar{V}^\circ(\text{SO}_2/\text{C}_6\text{H}_6)$  represents the limiting partial molar volume of sulfur dioxide in benzene. Equating the right-hand sides of eq 6 and 7 and rearranging gives

$$r\Delta V^\theta = x(\text{SO}_2)[\bar{V}^\circ(\text{SO}_2/\text{C}_6\text{H}_6) - \bar{V}^\circ(\text{SO}_2)_u] \quad (8)$$

The extent of reaction,  $r$ , is related to the equilibrium composition of the solution by<sup>23</sup>

$$r = n_{\text{cx}}/[N(\text{C}_6\text{H}_6) + N(\text{SO}_2) - n_{\text{cx}}] \quad (9)$$

where  $n_{\text{cx}}$  represents the equilibrium amount of complex and  $N(\text{C}_6\text{H}_6)$  and  $N(\text{SO}_2)$  represent the stoichiometric amounts of benzene and sulfur dioxide, respectively. Since the solutions are very dilute in sulfur dioxide,  $n_{\text{cx}}$  is much smaller than the total stoichiometric number of moles of solution, and therefore  $r$  may be approximated by

$$r \sim n_{\text{cx}}/[N(\text{C}_6\text{H}_6) + N(\text{SO}_2)] \quad (10)$$

Combination of eq 10 with eq 8 and the definition of mole fraction yields

$$\Delta V^\theta = [N(\text{SO}_2)/n_{\text{cx}}][\bar{V}^\circ(\text{SO}_2/\text{C}_6\text{H}_6) - \bar{V}^\circ(\text{SO}_2)_u] \quad (11)$$

Matsui et al.<sup>24</sup> have shown that for a dilute ideal associated solution (i.e., a solution in which the excess thermodynamic properties arise solely from the redistribution of the stoichiometric components due to a complexation reaction) the ratio,  $N(\text{SO}_2)/n_{\text{cx}}$ , is related to the equilibrium constant for the complexation reaction,  $K$ , by the expression

$$N(\text{SO}_2)/n_{\text{cx}} = (K + 1)/K \quad (12)$$

Substituting eq 12 into eq 11 yields

$$\Delta V^\theta = [(K + 1)/K][\bar{V}^\circ(\text{SO}_2/\text{C}_6\text{H}_6) - \bar{V}^\circ(\text{SO}_2)_u] \quad (13)$$

which expresses  $\Delta V^\theta$  in terms of three constants:  $K$ ,  $\bar{V}^\circ(\text{SO}_2/\text{C}_6\text{H}_6)$ , and  $\bar{V}^\circ(\text{SO}_2)_u$ . The value of the equilibrium constant for the formation of the sulfur dioxide-benzene complex ( $K = 0.47$ ) has been determined spectroscopically by Andrews and Keefer.<sup>3</sup> The limiting partial molar volume of sulfur dioxide in benzene is reported in this work,  $\bar{V}^\circ(\text{SO}_2/\text{C}_6\text{H}_6) = 47.8 \text{ cm}^3 \text{ mol}^{-1}$ . The only other quantity needed for application of eq 13 to the evaluation of  $\Delta V^\theta$  for the sulfur dioxide + benzene complexation reaction is the limiting partial molar volume of uncomplexed sulfur dioxide,  $\bar{V}^\circ(\text{SO}_2)_u$ .

On the basis that cyclohexane, for example, is not an electron donor and hence not likely to form complexes with sulfur dioxide, we take the limiting partial molar volume of sulfur dioxide in cyclohexane to be a reasonable estimate of the limiting partial molar volume of uncomplexed sulfur dioxide:  $\bar{V}^\circ(\text{SO}_2)_u =$

**Table II.** Molecular Diameters ( $\sigma$ ) of  $\text{SO}_2$ ,  $\text{C}_6\text{H}_6$ , and  $\text{C}_6\text{H}_{12}$ , Molar Volumes ( $V$ ) and Isothermal Compressibilities ( $\beta$ ) at 298.15 K of  $\text{C}_6\text{H}_6$  and  $\text{C}_6\text{H}_{12}$ , and Molecular Polarizabilities ( $\alpha$ ) of  $\text{C}_6\text{H}_6$  and  $\text{C}_6\text{H}_{12}$

	$\sigma/\text{nm}$	$10^4\beta/\text{MPa}^{-1}$	$V/\text{cm}^3 \text{ mol}^{-1}$	$10^{24}\alpha/\text{cm}^3 \text{ molec}^{-1}$
$\text{C}_6\text{H}_6$	0.5455 <sup>a</sup>	9.66 <sup>b</sup>	89.408 <sup>b</sup>	10.32 <sup>c</sup>
$\text{C}_6\text{H}_{12}$	0.5771 <sup>a</sup>	11.20 <sup>b</sup>	108.755 <sup>b</sup>	10.78 <sup>c</sup>
$\text{SO}_2$	0.4102 <sup>a</sup>			

<sup>a</sup> Reference 27. <sup>b</sup> Reference 28. <sup>c</sup> Reference 26.

$\bar{V}^\circ(\text{SO}_2/\text{C}_6\text{H}_{12}) = 55.4 \text{ cm}^3 \text{ mol}^{-1}$  (Table I).

Substituting our values of  $K = 0.47$ ,  $\bar{V}^\circ(\text{SO}_2)_u = 55.4 \text{ cm}^3 \text{ mol}^{-1}$ , and  $\bar{V}^\circ(\text{SO}_2/\text{C}_6\text{H}_6) = 47.8 \text{ cm}^3 \text{ mol}^{-1}$  in eq 13, we obtain  $\Delta V^\theta = -23.8 \text{ cm}^3 \text{ mol}^{-1}$  for the standard volume change for the sulfur dioxide + benzene complexation reaction.

Our second method for estimating  $\Delta V^\theta$  for reaction 3 is based on scaled particle theory,<sup>25,26</sup> which gives an expression for the reversible work of forming in the solvent a cavity of size sufficient to contain the solute molecule. That is, the theory allows calculation of the free energy,  $G_{\text{cav}}$ , of transferring a noninteracting hard sphere (same diameter as a solute molecule) from an ideal gas phase to infinite dilution in the solvent. The derivative of  $G_{\text{cav}}$  with respect to pressure yields the scaled particle theory expression for the hard-sphere contribution,  $V_{\text{cav}}$ , to the limiting partial molar volume:

$$V_{\text{cav}} = \beta RT[(1 - y)^2 + 3(1 - y)(\sigma_2/\sigma_1) + 3(1 + 2y)(\sigma_2/\sigma_1)^2]/(1 - y) + (N\pi\sigma_2^3)/6 \quad (14)$$

In eq 14,  $\beta$  represents the isothermal compressibility of the pure solvent,  $\sigma_1$  and  $\sigma_2$  represent the hard-sphere diameters of solvent and solute molecules, respectively,  $N$  represents Avogadro's constant, and  $y$  represents the reduced number density

$$y = (N\pi\sigma_1^3)/(6V_1) \quad (15)$$

where  $V_1$  represents the molar volume of the pure solvent.

In addition to  $V_{\text{cav}}$  there are two other contributions to the limiting partial molar volume of a solute in a solvent.<sup>26</sup>

$$\bar{V}_2^\circ = V_{\text{cav}} + V_{\text{int}} + \beta RT \quad (16)$$

The term  $V_{\text{int}}$  in eq 16 represents the pressure derivative of the free energy of solute/solvent interactions and  $\beta RT$  is the kinetic contribution of the hard sphere to the partial molar volume of solute. The first and third terms on the right-hand side of eq 16 can be evaluated for any solute/solvent system for which the compressibility of the solvent and the diameters of solvent and solute molecules are known. Therefore, if the limiting partial molar volume of a gas in a solvent has been determined experimentally, the contribution of solute/solvent interactions,  $V_{\text{int}}$ , to this property can be calculated:

$$V_{\text{int}} = \bar{V}_2^\circ - V_{\text{cav}} - \beta RT \quad (17)$$

For mixtures of sulfur dioxide + benzene, both chemical and physical interactions occur between the solute and the solvent. Accordingly, we separate  $V_{\text{int}}$  into chemical and physical contributions:

$$V_{\text{int}} = V_{\text{int}}(\text{chem}) + V_{\text{int}}(\text{phys}) \quad (18)$$

Physical contributions to  $V_{\text{int}}$  arise from all interactions between solute and solvent that do not lead to the formation of the complex. We approximate  $V_{\text{int}}(\text{phys})$  for sulfur dioxide + benzene by  $V_{\text{int}}(\text{phys})$  for sulfur dioxide + a non-electron-donating "model of benzene", such as cyclohexane. Cyclohexane is similar to benzene in size and polarizability (see Table II) and, like benzene, has no permanent dipole moment. This similarity suggests that  $V_{\text{int}}(\text{phys})$  for sulfur dioxide + cyclohexane is approximately equal to  $V_{\text{int}}(\text{phys})$  for sulfur dioxide + benzene. Since cyclohexane is not an electron donor,  $V_{\text{int}}(\text{chem}) = 0$  for sulfur dioxide + cyclohexane. On this basis, we interpret the difference between  $V_{\text{int}}$

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for sulfur dioxide + benzene and  $V_{\text{int}}$  for sulfur dioxide + cyclohexane as being entirely due to chemical interactions between sulfur dioxide and benzene. That is to say, the volume change per stoichiometric mole of sulfur dioxide [ $N(\text{SO}_2)$ ] is given by

$$\Delta V = V_{\text{int}}(\text{SO}_2/\text{C}_6\text{H}_6) - V_{\text{int}}(\text{SO}_2/\text{C}_6\text{H}_{12}) \quad (19)$$

$\Delta V^\theta$ , the standard volume change of the complexation reaction per mole of complex formed ( $n_{\text{cx}}$ ), is thus

$$\Delta V^\theta = \Delta V[N(\text{SO}_2)/n_{\text{cx}}] \quad (20)$$

Combination of eq 12, 19, and 20 gives

$$\Delta V^\theta = [V_{\text{int}}(\text{SO}_2/\text{C}_6\text{H}_6) - V_{\text{int}}(\text{SO}_2/\text{C}_6\text{H}_{12})](K + 1)/K \quad (21)$$

Recommended "best" values of the molecular diameters of sulfur dioxide, benzene, and cyclohexane were taken from a critical compilation<sup>27</sup> and are listed in Table II. This table also lists the molar volumes and isothermal compressibilities of benzene and cyclohexane. Inserting these values into eq 14, we calculate  $V_{\text{cav}}(\text{SO}_2/\text{C}_6\text{H}_6)$  and  $V_{\text{cav}}(\text{SO}_2/\text{C}_6\text{H}_{12})$ . Combining these values of  $V_{\text{cav}}$  with our values of  $V^\circ(\text{SO}_2/\text{C}_6\text{H}_6)$  and  $V^\circ(\text{SO}_2/\text{C}_6\text{H}_{12})$  in eq 17 leads to  $V_{\text{int}}(\text{SO}_2/\text{C}_6\text{H}_6) = -60.0 \text{ cm}^3 \text{ mol}^{-1}$  and  $V_{\text{int}}(\text{SO}_2/\text{C}_6\text{H}_{12}) = -46.7 \text{ cm}^3 \text{ mol}^{-1}$ . From eq 21 ( $K = 0.47$ ),<sup>3</sup> we then calculate a value of  $\Delta V^\theta = -41.6 \text{ cm}^3 \text{ mol}^{-1}$  for the standard volume change of the benzene + sulfur dioxide complexation reaction.

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Scaled particle theory might be used also to estimate  $\Delta V^\theta$  for other  $\text{SO}_2$  + electron donor systems, provided that a non-electron-donating model compound with physical properties (molecular diameter, dipole moment, and polarizability) similar to those of the electron donor of interest exists.

Both of the methods we have proposed for estimating  $\Delta V^\theta$  for reaction 3 introduce the idea of a non-electron-donating "model" of the electron-donating solvent of interest. Our results show that  $\Delta V^\theta$  for the formation of the sulfur dioxide-benzene complex is large (for chemical interactions of this type) and negative. The sign of  $\Delta V^\theta$  indicates that the average sulfur dioxide molecule is closer to a benzene molecule than it would be in an ideal solution. This is as we would expect if sulfur dioxide and benzene are interacting chemically to form a complex.

The values of  $\Delta V^\theta$  for the sulfur dioxide + benzene complexation reaction obtained from the two methods differ by a factor of 2. This difference arises principally from the different way in which the contribution of uncomplexed sulfur dioxide to the total volume of the solution is taken into account. At this time, we cannot judge which of the two methods is more likely to give an accurate result.

We recommend further investigations of both the excess volumes of solutions of sulfur dioxide in benzene and the variation of the complexation equilibrium constant with pressure to provide accurate estimates of  $\Delta V^\theta$ . Until such information becomes available, the methods presented in this section afford reasonable estimates of the sign and magnitude of  $\Delta V^\theta$ .

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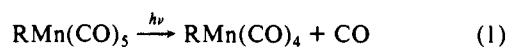
## Photochemistry of $(\eta^1\text{-C}_5\text{Cl}_5)\text{Mn}(\text{CO})_5$ and $(\eta^1\text{-C}_6\text{H}_5\text{CH}_2)\text{Mn}(\text{CO})_5$ : Competitive Formation of 16- and 17e Intermediates

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**Abstract:** Irradiation of  $\text{RMn}(\text{CO})_5$  ( $\text{R} = \eta^1\text{-C}_5\text{Cl}_5$ ,  $\eta^1\text{-C}_6\text{H}_5\text{CH}_2$ ) in alkane glasses at 95 K leads to CO loss as the only detectable photoprocess: the ring-slipped  $(\eta^3\text{-C}_5\text{Cl}_5)\text{Mn}(\text{CO})_4$  and  $(\eta^3\text{-C}_5\text{Cl}_5)\text{Mn}(\text{CO})_3$  or  $(\eta^3\text{-C}_6\text{H}_5\text{CH}_2)\text{Mn}(\text{CO})_4$  are formed, respectively. The identities of the  $\eta^3$  intermediates from  $(\eta^1\text{-C}_5\text{Cl}_5)\text{Mn}(\text{CO})_5$  and  $(\eta^1\text{-C}_6\text{H}_5\text{CH}_2)\text{Mn}(\text{CO})_5$  have been established by spectroscopic means and by chemical-trapping experiments. Room-temperature irradiation of  $\text{RMn}(\text{CO})_5$  yields both CO loss and Mn-R bond cleavage, giving  $\text{Mn}(\text{CO})_5$  and R radicals. The relative importance of these two competitive primary photoprocesses is wavelength dependent. The quantum yield for Mn-R bond homolysis is largely independent of wavelength, 436-254 nm,  $\phi \cong 0.05$ , whereas the CO-loss quantum yield for  $(\eta^1\text{-C}_5\text{Cl}_5)\text{Mn}(\text{CO})_5$  increases from  $\sim 0.03$  at 436 nm to  $\sim 0.30$  at 254 nm. The relative importance of net photoproducts is also dependent on the presence of CO, which suppresses CO-loss products. From the wavelength dependence and effects of added CO on product distribution, it is concluded that axial or equatorial CO loss from  $(\eta^1\text{-C}_5\text{Cl}_5)\text{Mn}(\text{CO})_5$  can be observed from populations of  $d_{z^2}$  or  $d_{x^2-y^2}$  orbitals, respectively, with higher energy excitation favoring equatorial CO loss.

We report a quantitative study of the primary photoprocesses in  $\text{RMn}(\text{CO})_5$  ( $\text{R} = \eta^1\text{-C}_5\text{Cl}_5$ ,  $\eta^1\text{-C}_6\text{H}_5\text{CH}_2$ ). The principal aim of our work has been to establish the relative importance of CO loss and Mn-R homolysis (eq 1 and 2). In connection with CO loss (eq 1), there is also the possibility of equatorial versus axial labilization following photoexcitation.



The photochemistry of  $\text{RMn}(\text{CO})_5$  ( $\text{R} = \text{alkyl, aryl, benzyl}$ ) has been studied both in solution<sup>1-4</sup> and at low temperature under

matrix isolation conditions.<sup>5,6</sup> Lappert has shown that irradiation of  $\text{RMn}(\text{CO})_5$  ( $\text{R} = \text{CH}_3$ ,  $\text{CH}_2\text{SiMe}_3$ ,  $\text{CH}_2\text{C}_6\text{H}_5$ ) in solution leads to the formation of  $\text{Mn}(\text{CO})_5$  and R radicals.<sup>2,7</sup> Other studies

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