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Probing the Solvation Properties of Liquid versus Supercritical Fluids with Laser Flash Photolysis of W(CO)₆ in the Presence of 2,2′-Bipyridine

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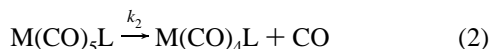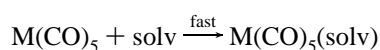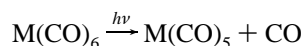*Department of Chemistry, University of Utah, Salt Lake City, Utah 84112*

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The ring-closure reaction of M(CO)₅L−L (M = W, L−L = bipyridine) to produce M(CO)₄(L−L) in nonpolar supercritical (sc) CO₂/benzene mixtures was selected to investigate the repulsive (or intrinsic) part of the activation volume associated with this reaction. The activation volumes over the range between 7.5 and 24 MPa at different temperatures were higher than those in liquid benzene and liquid CO₂/benzene, but much lower than those in pure sc CO₂. The UV/vis spectral studies of this reaction showed that the addition of small amounts of cosolvent can increase the solubility of the ring-closure species. The kinetic traces recorded for the reaction also demonstrated this solubility enhancement.

Introduction

Over the past few years, we have developed an interest in the importance of solvent effects in photoinduced ligand substitution reactions of hexacarbonyl group 6 metal complexes.[1−10] In these studies we have systematically varied the nature of the metal (Cr, Mo, W), the entering ligand (mono- versus bidentate), and the solvent. It is especially the coordination ability and solvation properties of the solvent that affect the observed CO displacement reactions and the nature of the underlying reaction mechanism. We have therefore found these systems to be especially suitable for analyzing these solvent effects in more detail.

The selected chemical system basically consists of the reactions shown below, in which flash photolysis of dissolved M(CO)₆ (M = W in the present study) with ultraviolet light results in the loss of CO and the rapid formation of M(CO)₅-(solvent). In the presence of a strong nucleophile L (L = 2,2′-bipyridine in this study), the coordinated solvent molecule is displaced to produce M(CO)₅L in reaction 1. When L is a bidentate ligand, M(CO)₅L will undergo a subsequent thermal ring-closure reaction to produce the ring-closed M(CO)₄L species shown in reaction 2.

$$M(CO)_6 \xrightarrow{h\nu} M(CO)_5 + CO$$

$$M(CO)_5 + \text{solv} \xrightarrow{\text{fast}} M(CO)_5(\text{solv})$$

$$M(CO)_5(\text{solv}) + L \xrightarrow{k_1} M(CO)_5L + \text{solv} \qquad (1)$$

$$M(CO)_5L \xrightarrow{k_2} M(CO)_4L + CO \qquad (2)$$

Both reaction steps 1 and 2 have been studied in considerable detail in order to investigate the influence of the selected solvents.[10] Reaction 2 depends strongly on the nature of the bidentate ligand, it is very sensitive to the influence of steric hindrance, and the values of k_2 can vary over many orders of magnitude for different ligands L.

Our work has shown that the application of high-pressure techniques can yield detailed mechanistic insight into both

reactions 1 and 2. The volume of activation for these reactions, estimated from the effect of high pressure on k_1 and k_2, is a very sensitive parameter in the absence of any significant changes in electrostriction (neutral complexes and neutral L) and gives direct information regarding the extent of bond formation/bond breakage in the transition states of reactions 1 and 2. These data and their mechanistic interpretation have been discussed in detail in the literature.[1−10]

In our previous study,[11] we used the W(CO)₆/1,10-phenanthroline system to investigate the above-outlined reactions in supercritical CO₂ and ethane. Activation volumes as high as +7000 cm³ mol⁻¹ were found just above the critical point in each of these fluids for the ring-closure reaction 2. By way of comparison, this number drops to +36 cm³ mol⁻¹ in liquid CO₂ at 30 °C. These experimental results were interpreted in terms of the strong dependence of the isothermal compressibility, k_T, of the medium on the selected conditions (liquid versus supercritical) since the volume of activation is magnified by k_T. The data demonstrate the huge repulsive contribution to the activation volume in these two supercritical fluids associated with the thermal ring-closure reaction of W(CO)₅(phen).[11] We have now extended this study to the ring-closure reaction of W(CO)₅(bpy), bpy = 2,2′-bipyridine. This latter reaction is several orders of magnitude slower than in the case of the phenanthroline complex and therefore enables us to study solvation effects of liquid and supercritical fluids on a totally different time scale. Laser flash photolysis techniques were employed to initiate the reaction as before. The detailed kinetic analysis of the process turned out to be significantly more complicated than in our previous study due to the interference of different perturbations in the supercritical fluid on a longer time scale.

One of the biggest challenges for kinetic studies in supercritical fluids is the poor solubility of the reactants and products, especially in the region near the critical point. As mentioned above, the isothermal compressibility in the critical region is several orders of magnitude greater than that of liquids, and the density changes dramatically with a small change in pressure near the critical point. All the density-dependent properties, such as solubility parameter, dielectric constant, etc., vary strongly with respect to pressure and temperature in the critical region. Previous studies[12−14] had demonstrated that the solubility of certain chemicals varies exponentially with the density of a nonpolar supercritical solvent such as carbon dioxide or

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ethane. Finally, addition of a cosolvent usually increases the density of a SCF solution.[15] Since solubility increases exponentially with density, a cosolvent can have a significant effect on solubility in a SCF solution. Many studies[16-20] have demonstrated that the addition of small amounts of liquid cosolvent to a supercritical fluid can increase the solubilities and selectivities of certain substances. In this study, benzene and methanol were used to improve the solubility of the ring-closure reaction species with considerable success.

Experimental Section

Tungsten hexacarbonyl (Aldrich, 98%) was vacuum-sublimed before use. The 2,2′-bipyridine (Aldrich, >99%) was used as received. SFC grade carbon dioxide (>99.9%) was purchased from Scott Specialty Gases (Longmont, CO). Research grade ethane was purchased from AGA Gas, Inc. (Maumee, OH). Spectral grade liquid benzene and methanol (Aldrich, >99.9%) were refluxed under a nitrogen atmosphere and were distilled before use.

Small amounts of reactants (1 mg of $W(CO)_6$ and 1 mg of 2,2′-bipyridine) and liquid solvent (100-200 μL) were transferred into the quartz cuvette inside the high-pressure cell; the supercritical fluids were then introduced into the cell to flush out the remaining air in the cell, while the temperature of the cell was kept at 0 °C to minimize evaporation of the cosolvent. A Quanta Ray DCR-2 Nd:YAG laser sends a 6 ns duration laser pulse (about 100 mJ/pulse) with a wavelength of 355 nm through the sapphire window of a homemade high-pressure cell at 90° to the path of the transient absorption probe beam. The detection system could be either a UV−vis spectrometer (HP8452A) or a photomultiplier tube (PMT) assembly.[11] The latter consisted of an Oriel 75 W xenon lamp, a Durrum monochromator, and a Hamamatsu 1P28 PMT. The voltage signal from the PMT is sent to a LeCroy 9400 oscilloscope interfaced (GPIB) to a 386-based computer (ARCHE DX-40). Data are analyzed by KINFIT software from OLIS (Bogart, GA). The temperature is controlled to within ±0.1 °C by a temperature probe (Omega CF-000-RTD-4-60-2). The pressure is adjusted with a 200 cm³ syringe pump and is measured to within 10 psi by a pressure transducer (SETRA 280E) with a DATUM pressure meter (DATUM 2000). The experimental methods in this study, including the design of the apparatus, are described elsewhere.[11]

Results and Discussion

In the present study we selected bipyridine as the entering ligand since it is known from ambient pressure studies in conventional organic solvents such as benzene[4,21] that the ring-closure rate of photoproduced $W(CO)_5$bpy is 0.04 s^{-1} at 20 °C as compared to 210 s^{-1} for the corresponding $W(CO)_5$phen complex. The 5×10^3 slower reaction in the case of $W(CO)_5$-bpy permits a detailed investigation of solvent effects in liquid and supercritical fluids over a more extended time scale. A potential difficulty for such studies in supercritical CO_2 and ethane, as mentioned above, is the low solubility of many substances. Unfortunately, in the present studies, the ring-closure product $W(CO)_4$bpy is not soluble in the near-critical region of SFC CO_2 and ethane, not even in the supercritical region well above the critical point. The UV−vis spectra show a steady absorbance increase of the base line, which clearly indicates the slow formation of the insoluble species. The addition of small amounts of a cosolvent (7-15 vol %) can improve selectively the solubility of substances in such media.[16-20,22-24] Preliminary experiments clearly demonstrated that solubility of $W(CO)_6$ and bpy was a serious problem, and
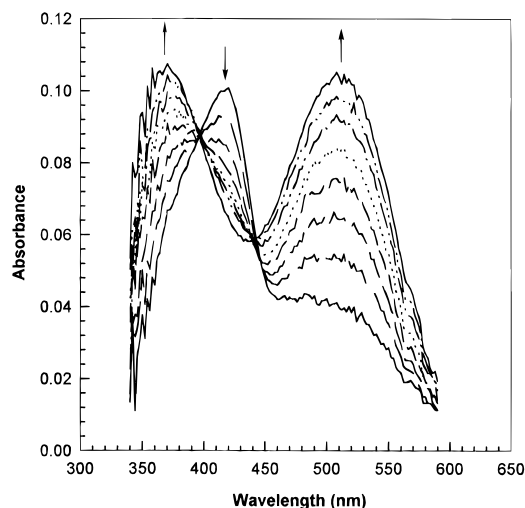
Figure 1. Typical kinetic UV−vis spectra for the ring-closure reaction of $W(CO)_5$bpy in supercritical CO_2 with 7% methanol recorded at 70 °C, 13.5 MPa, and $\Delta t = 15$ s.

we were forced to introduce a cosolvent. We selected MeOH and benzene, both solvents that improve the solubility of the investigated species. Typical UV−vis spectra recorded following flash photolysis of $W(CO)_6$/bpy mixtures in sc CO_2 in the presence of 7% (v/v) MeOH are reported in Figure 1. For both solvent additions spectra clearly show the initial formation of $W(CO)_5$bpy, characterized by a band around 400 nm, which then decreases in a subsequent thermal reaction to produce a new band around 510 nm, ascribed to the formation of the ring-closed $W(CO)_4$bpy species. The bands in sc CO_2/MeOH at 410 and 510 nm are indeed in close agreement with those reported for the same reaction in liquid benzene as solvent, viz. 406 and 524 nm, respectively.[21] Kinetic traces for the ring-closure reaction were in general recorded at 510 nm over a much longer time scale of 200 s in the mixture of CO_2 and methanol compared to 100 s in the mixture of CO_2 and benzene. These traces turned out to be significantly more reproducible in the case of benzene as cosolvent. General difficulties in recording kinetic traces over such a long time scale in a supercritical medium are the inhomogeneity of the medium and the inhomogeneous distribution of product species. These effects in some cases, depending on the selected cosolvent and experimental conditions (temperature and pressure that control the density of the medium), cause erratic kinetic traces that clearly indicate that diffusion of species is occurring over such a long time scale. In general, this was not a problem for the ring-closure reaction of the $W(CO)_5$phen system studied earlier[11] since these reactions are ca. 10^4 times faster[11,21] and occur in a time frame where medium effects play a minor role. The observed chemistry is then restricted to a more defined sample cell region in which the reactive species are produced photochemically. In some experiments, we introduced a magnetic stirring bar into the optical cell and stirred the fluids slowly in order to homogenize the medium for reactions occurring over a long time scale. This technique did help in some cases to improve the quality of the kinetic traces.

A typical kinetic trace recorded at ca. 510 nm for the ring-closure reaction 2 in sc CO_2/benzene (7% v/v) is shown in Figure 2. The kinetic traces show a significant dependence on the selected temperature and pressure and, in general, are very reproducible. The kinetic traces can all be fitted by a single exponential. Typical plots of ln k_{obs} versus pressure as a function of temperature are shown in Figures 3 and 4. The corresponding volumes of activation, $\Delta V^{\ddagger} = -(\partial \ln k_{obs}/\partial P)_T$, are summarized in Table 1. The values of $\Delta V^{\ddagger}$ are all positive,

Laser Flash Photolysis of W(CO)₆/bpy

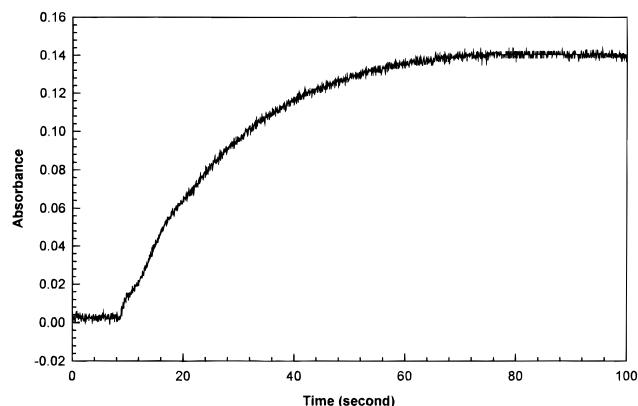*J. Phys. Chem. A, Vol. 101, No. 3, 1997* **245**

Figure 2. Typical kinetic trace for the ring-closure reaction of $W(CO)_5bpy$ in supercritical CO_2 with 7% benzene recorded at 35 °C and 17.7 MPa.
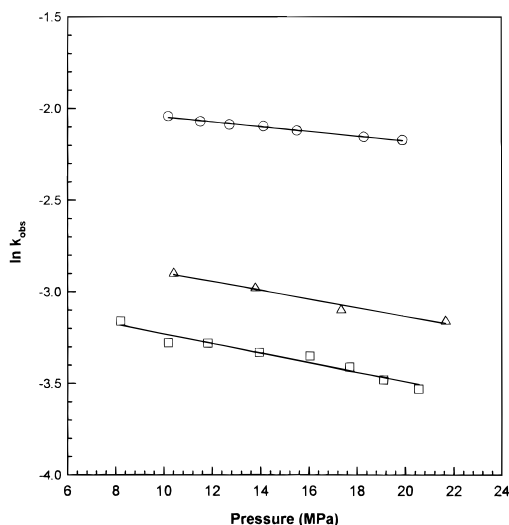

Figure 3. Plots of $\ln k_{obs}$ versus pressure for the thermal ring-closure reaction of $W(CO)_5bpy$ in supercritical CO_2 with 7% benzene at several temperatures: □, 35 °C; △, 45 °C; ○, 55 °C.
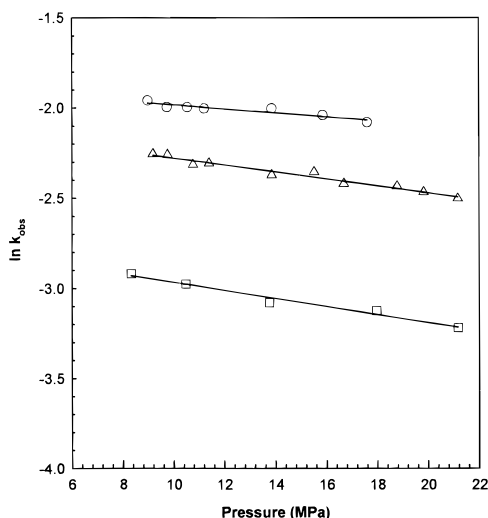

Figure 4. Plots of $\ln k_{obs}$ versus pressure for the thermal ring-closure reaction of $W(CO)_5bpy$ in supercritical CO_2 with 15% benzene at several temperatures: □, 35 °C; △, 45 °C; ○, 55 °C.

significantly smaller than those observed for the more rapid ring-closure of $W(CO)_5phen$,[11] and depend to some extent on the concentration of the cosolvent employed.

Experiments were also performed in liquid benzene and liquid CO_2/benzene mixtures (35% benzene). Plots of $\ln k_{obs}$ versus

TABLE 1: Activation Volume for the Ring-Closure Reaction of $W(CO)_5bpy$

	$\Delta V^{\ddagger}$ [a] for different solvent mixtures (cm³/mol)			
temp (°C)	CO_2 with 7% benzene	CO_2 with 14% benzene	CO_2 with 35% benzene	liquid benzene
25				+4.4
35	+66.2	+56.4		
45	+62.5	+50.7	+6.5	
55	+34.8	+29.7		

[a] The standard deviation for $\Delta V^{\ddagger}$ is within ±10%.

pressure are reported in Figures 5 and 6, respectively (both found in the Supporting Information). The resulting volumes of activation are also shown in Table 1.

The same system was also investigated in sc ethane mixtures (with 5−15% v/v of benzene, methanol, chlorobenzene, heptane, etc., as cosolvent). From the recorded UV−vis spectra, it appeared that the solubility of the ring-closed species had improved by the addition of a small amount of cosolvent, but still not enough dissolved to give reproducible kinetic data.

Many investigations[16−18,22,25−32] (including experimental, computational, and theoretical studies) demonstrated that the local environment surrounding solute molecules can be considerably different from the bulk. The local environment is characterized by large, negative solute partial molar properties, and the microstructure around the solute is characterized by a large augmentation of solvent density (or solvent−solute clustering) with respect to bulk solvent density.[3,32] In such studies, solvatochromism is most often invoked as experimental evidence for local solvent density enhancements in supercritical fluids and mixtures. The nonlinear dependence of absorption (solvent-sensitive transition) or emission (solvent-insensitive transition) energy on solvent composition is used as the "index of preferential solvation" to monitor the difference between local and bulk compositions.[22,25−28] An alternative approach is the use of charge-transfer complexes which may be very sensitive to local compositions.[33,34] From these studies, it is well established that local density enhancement does occur around the solute molecules in supercritical fluids and supercritical mixtures, especially in the region near the critical point.

Since the solvent clusters around the solute, it seems reasonable to assume that the cosolvent will do so as well, especially when the cosolvent is capable of solute−solvent interaction or otherwise complexing with solute. In this kind of supercritical mixture, the solvent's density in the vicinity of the solute is considerably higher than in the bulk, even after averaging over three solvation shells. Computer simulation results show that local densities can exceed the bulk value by as much as 50%.[22] The local density enhancement gradually disappears as the pressure is increased above that of the critical point, while the bulk density gets higher and the solvent becomes gradually incompressible. Therefore, solute solubility enhancement can be achieved by adding a small amount of cosolvent due to the increased local density of the solvent mixtures, as well as the solvent−solute and solvent−solvent interaction which helps to disperse the solute into the supercritical fluid.

The density of a supercritical fluid can be adjusted from a gaslike low density (critical region) to a liquidlike high density by simply increasing the pressure, while isothermal compressibility (k_T) will decrease as the density increases. As we know, addition of the liquid cosolvent will increase the density of the fluid mixture, but it is unlikely for its density to exceed the liquid phase density. It is reasonable to assume that the density of a supercritical fluid mixture lies between that of a supercritical fluid and a liquid. The same should be true of its isothermal

compressibility. As in our previous study,[11] we consider the elementary chemical reaction

$$a\mathrm{A} + b\mathrm{B} + ... = \mathrm{M}^{\ddagger}$$
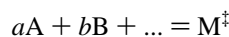
where $\mathrm{M}^{\ddagger}$ represents the transition state. Johnston and Haynes[35] explained earlier why either attractive or repulsive forces can have a large impact on $\Delta V^{\ddagger}$, the activation volume. According to van der Waals theory used in our previous study,[11] the large $\Delta V^{\ddagger}$ values in supercritical fluids are due to magnification by the isothermal compressibility:

$$\Delta V^{\ddagger} = \upsilon k_T n\{(\partial P/\partial n^{\ddagger} - \partial P/\partial n_a - \partial P/\partial n_b)^{\text{repulsive}} + \\ (\partial P/\partial n^{\ddagger} - \partial P/\partial n_a - \partial P/\partial n_b)^{\text{attractive}}\} \quad (3)$$

where P is the pressure, n is the number of moles, υ is the specific volume, and k_T is the isothermal compressibility. From the application[36] of transition state theory to kinetics at elevated pressures, we have

$$\Delta V^{\ddagger} = \bar{V}^{\ddagger} - a\bar{V}_a - b\bar{V}_b - ... \quad (4)$$

from which it follows that

$$\Delta V^{\ddagger} = \bar{V}^{\ddagger} - \bar{V}_{\text{W(CO)5bpy}} \quad (5)$$

From eqs 3 and 5, it follows that

$$\Delta V^{\ddagger} = \upsilon k_T n\{(\partial P/\partial n^{\ddagger} - \partial P/\partial n_{\text{W(CO)5bpy}})^{\text{repulsive}} + \\ (\partial P/\partial n^{\ddagger} - \partial P/\partial n_{\text{W(CO)5bpy}})^{\text{attractive}}\} \quad (6)$$

Since both benzene and CO_2 are very weakly coordinated solvents, we can assume that the attractive contribution of the activation volume is small compared to the repulsive part. Therefore, it is reasonable to assume that

$$\Delta V^{\ddagger} = \upsilon k_T n(\partial P/\partial n^{\ddagger} - \partial P/\partial n_{\text{W(CO)5bpy}})^{\text{repulsive}} \quad (7)$$

As we mentioned above, the isothermal compressibility of a supercritical mixture with cosolvent is smaller than that of the pure supercritical fluid, especially in the near-critical region, but it is still much larger than the isothermal compressibility of the liquid phase. The $\Delta V^{\ddagger}$ values found in these studies are expected to be between the large $\Delta V^{\ddagger}$ values observed in pure supercritical fluids (up to 7000 cm^3/mol) and small $\Delta V^{\ddagger}$ values observed in liquids (within the range of ± 10 cm^3/mol).

The data in Table 1 show a larger difference in $\Delta V^{\ddagger}$ found for a supercritical fluid versus a liquid medium. This is mainly due to $\Delta V^{\ddagger}$ being magnified by the isothermal compressibility (k_T) in supercritical fluids. $\Delta V^{\ddagger}$ shows no significant pressure dependence; i.e., plots of ln k_{obs} versus pressure are all very linear. This is in contrast to what we found for the W(CO)5phen system.[11] However, $\Delta V^{\ddagger}$ data in Table 1 show a decrease with increasing temperature, which is due to the change in k_T with temperature. $\Delta V^{\ddagger}$ should be normalized by dividing through by k_T, which will then compensate for the decrease in k_T with increasing temperature.

$$\Delta V^{\ddagger}/\upsilon k_T = n(\partial P/\partial n^{\ddagger} - \partial P/\partial n_{\text{W(CO)5L}})^{\text{repulsive}} \quad (8)$$

The addition of more cosolvent (benzene) causes a slight shift to lower $\Delta V^{\ddagger}$ values, presumably due to a slightly more dense medium on increasing the cosolvent concentration.

Rather surprising is our finding that $\Delta V^{\ddagger}$ for the ring closure of W(CO)5bpy is almost 2 orders of magnitude smaller than for the ring closure of W(CO)5phen[11] when both are measured close to the critical point. The bpy complex ring closes ca. 10^3 times slower than the phen complex. In the case of the rigid phen complex, it has been suggested that there is a strong preassociation of the second nitrogen lone pair with the metal center and that release of CO causes the large repulsive contribution that accounts for the very positive $\Delta V^{\ddagger}$ value. In the case of the bpy complex, however, the uncoordinated pyridine ligand is free to rotate and is not expected to be involved in a preassociation with the metal center. The ring-closure reaction will therefore have more of an interchange character, i.e., bond formation accompanied by release of CO, which will result in a significantly less positive volume of activation. The dissociation of CO during ring closure of W(CO)5bpy does not cause such a large repulsion as in the case of the much faster ring-closure reaction on W(CO)5phen. The longer time scale for W(CO)5bpy allows more solvent reorganization and a less drastic medium effect. This is also consistent with the observed pressure independence of $\Delta V^{\ddagger}$. This means that for the ring closure of W(CO)5bpy we are dealing with a less compressible transition state, which could be related to the interaction of the dangling bipyridine arm with the surrounding medium. Solvent dynamics on the time scale of the reaction cause a more homogenized system, coupled with a much less positive $\Delta V^{\ddagger}$ and no significant decrease in $\Delta V^{\ddagger}$ with increasing pressure.

The volume increase associated with the release of CO is partially compensated for by the volume decrease associated with the ring-closure reaction. A similar result is seen in liquid benzene and liquid CO_2/benzene mixtures. The reported $\Delta V^{\ddagger}$ is a small positive number typical for an interchange type of ligand substitution mechanism, observed for such reactions in many other systems.[7-10] The values of $\Delta V^{\ddagger}$ found here for the bpy system are once again significantly smaller than those reported[11] for the phenanthroline system in liquid CO_2. This could once again be due to the different time scale of the investigated reaction, the influence of the less rigid bipyridine ligand, and the addition of the cosolvent. Evidence accumulates[37,38] for the formation of solute–solvent clusters in supercritical fluids due to the addition of cosolvents, resulting in local solvent density augmentation around solute molecules. While the addition of the cosolvent enhances the solute solubility,[22] isothermal compressibility decreases with the increasing of the solvent density. Therefore, the activation volumes in supercritical mixtures, which are magnified by the medium isothermal compressibility, will lie between the $\Delta V^{\ddagger}$ in the supercritical fluids and the liquid. The experimentai data in this study agree nicely with this assumption, further demonstrating the significant repulsive contribution[35] to the activation volume in supercritical mixtures (van der Waals model[11]).

Conclusion

In this study, the van der Waals model was used to interpret the enhancement of the repulsive part of the activation volume, which demonstrated a direct link between the activation volume and the compressibility of the reaction medium. This study also demonstrated the solubility enhancement of the reaction species by adding small amounts of cosolvent.

Supporting Information Available: Figure 5, presenting a plot of ln k_{obs} versus pressure for the thermal ring-closure

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reaction of W(CO)$_5$bpy in liquid benzene at 25 °C; Figure 6, depicting a plot of ln k_{obs} versus pressure for the thermal ring-closure reaction of W(CO)$_5$bpy in liquid CO$_2$/benzene mixture at 45 °C (2 pages). Ordering information is given on any current masthead page.

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