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Laser Pulse Photolysis and Transient Infrared Investigation into the Effect of Solvent or Substituents (X) on the Reactivity of Photogenerated (η^6-$C_6H_{6-y}X_y$)Cr(CO)$_2$ Intermediates

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Time-resolved infrared spectroscopy identified the first observable species following nanosecond laser photolysis of (benzene)Cr(CO)$_3$ in alkane solution as (benzene)Cr(CO)$_2$(alkane). UV/vis-monitored laser flash photolysis was used to observe the reaction of this species with CO. The reactivity toward CO of the primary photoproducts derived from related arene complexes (arene = C_6H_5Cl, C_5H_5Me, *p*-ClC_6H_4Me, C_6H_5Et, $C_6H_5Bu^t$, *o*- and *p*-$C_6H_4Me_2$, $C_6H_3Me_3$, C_6Me_6, C_6Et_6) were also determined by this technique. The rate of reaction with CO was found to depend on the alkane solvent and on the nature and degree of substitution of the arene ligand. The enthalpies of activation for all reactions were constant (24 ± 2 kJ mol^{-1}), while the entropy of activation increased upon methyl substitution of the arene and upon a change in the solvent from cyclohexane to a linear alkane.

Introduction

In comparison to the enormous interest in the photochemistry of Cr(CO)$_6$ in both the gas[2] and condensed phases,[3] there have been few investigations into the photochemistry of (η^6-benzene)Cr(CO)$_3$ or its derivatives.[4] Of these, only three reports describe the nature of transient species formed by photolysis in alkane solution. This is somewhat surprising, given the dramatic difference between the thermal and photochemical reactions of this compound.[5] Early work using conventional flash photolysis identified (η^6-benzene)Cr(CO)$_2$(s) (s = alkane solvent) as the primary photoproduct on the basis of kinetic rather than spectroscopic data (reaction 1).[4b] The arene exchange process was also observed following photolysis (reaction 2), and the ability of CO to quench this process implies the intermediacy of (η^6-benzene)Cr(CO)$_2$ in this reaction.[4b]

$$(\eta^6\text{-arene})\mathrm{Cr(CO)}_3 \xrightarrow{h\nu} (\eta^6\text{-arene})\mathrm{Cr(CO)}_2 + \mathrm{CO} \quad (1)$$

$$(\eta^6\text{-arene})\mathrm{Cr(CO)}_3 + \text{arene}' \xrightarrow{h\nu} (\eta^6\text{-arene}')\mathrm{Cr(CO)}_3 + \text{arene} \quad (2)$$

We now report a study of the primary photochemistry of a range of (η^6-arene)Cr(CO)$_3$ complexes in alkane solution at ambient temperature. This forms part of an investigation into the photochemistry of "half-sandwich" compounds.[6] The goal is to characterize the primary photoproducts and to obtain kinetic data for their reactions with CO and other potential ligands. We have used both laser pulse photolysis and time-resolved infrared spectroscopy (TRIR) in this investigation. A range of alkyl- and halogen-substituted arene compounds was synthesized, and the effect of the substituent on the reactivity of the primary photoproducts toward CO was measured. These results were compared to those obtained for the isoelectronic (η^5-C_5R_5)Mn(CO)$_3$ system (R = H, Me, Et). Here the reactivity of the dicarbonyl photoproduct toward CO was found to increase with the size rather than the electronic nature of the substituents on the cyclopentadienyl ring.[7] The equivalent reactions of the photoproducts, Cr(CO)$_5$(s)[8] and (η^5-C_5H_5)Mn(CO)$_2$(s),[6,9] are affected by the nature of the alkane solvent, reactions in linear alkanes being approximately twice as fast as those in cyclic alkanes. Consequently, we have also investigated the effect of altering the nature of the solvent on the reactivity of (η^6-arene)Cr(CO)$_2$(s) toward CO.

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Experimental Section

Apparatus. The laser pulse photolysis apparatus consists of a Spectron Laser Systems SL801 Nd YAG laser capable of generating both the third (λ = 355 nm; 30 mJ) and fourth (λ = 266 nm; 40 mJ) harmonic of the fundamental wavelength (pulse duration 11 ns). The monitoring system, arranged in a cross-beam configuration, consisted of a 275-W Xe-arc lamp, an F/3.4 monochromator (containing a grating blazed at 300 nm), and a five-stage photomultiplier supplied by Applied Photophysics. The signals were captured by either a Philips PM3311 or a Hewlett-Packard 54510A digitizing oscilloscope, and the data reduction was performed on a 286/287-based computer system using software developed in house. Solutions for analysis were placed in a fluorescence cuvette (*d* = 10 mm) attached to a degassing bulb. The solutions were degassed by three cycles of freeze–pump–thaw to 10^{-3} Torr, followed by a substantial liquid pump to remove traces of water and carbon dioxide which were not removed in the degassing procedure (*vide infra*). The UV/vis spectrum of each sample solution was monitored throughout the experiments to ensure the sample stability. The absorbance of each solution was adjusted to between 0.2 and 1.6 AU at the excitation wavelength 355 or 266 nm ([(η^6-arene)Cr(CO)$_3$] typically 10^{-5}–10^{-4} M). The concentration of CO was determined by the pressure of CO admitted to the reaction cell after the degassing process.[10] For experiments in which the temperature was varied, it was assumed that the concentration of CO remained constant. Although data to verify this assumption are scarce, it does appear to be valid for cyclohexane.[11] The solubilities of CO in *n*-pentane, *n*-heptane, *n*-decane, *n*-dodecane, and cyclohexane were taken to be 1.6×10^{-2}, 1.2×10^{-2}, 8.5×10^{-3}, 6.8×10^{-3}, and 9.0×10^{-3} M, respectively, under 1 atm of CO.[12]

A typical concentration of (η^6-arene)Cr(CO)$_3$ used for the TRIR experiments would be in the range 5×10^{-4} to 5×10^{-3} M. The TRIR apparatus has been described elsewhere.[13] Briefly, it consists of a pulsed excimer laser (Lumonics Hyper EX-440; λ = 308 nm) as the excitation source and a CW CO laser to monitor the changes in absorption at a particular fixed infrared frequency. The CO laser is line-tunable in steps of ca. 4 cm^{-1} between 2000 and 1550 cm^{-1}. Time-resolved infrared spectra are built up point by point by recording absorption traces over a range of monitoring frequencies.

Reagents. All arenes were obtained from BDH Ltd. and were used without further purification. Cyclohexane, *n*-pentane, *n*-heptane, *n*-decane, and *n*-dodecane were of spectroscopic grade obtained from Aldrich Chemical Co. and were dried over molecular sieves before use.

Preparation of (η^6-arene)Cr(CO)$_3$ Compounds. The arene complexes were synthesized by heating a solution of Cr(CO)$_6$ in the appropriate aromatic solvent to reflux temperature under an argon atmosphere for 24 h.[14] A small quantity of tetrahydrofuran was also added. The crude materials were recrystallized from either *n*-hexane or diethyl ether. Compound purity was verified as satisfactory by microanalyses (University College Dublin, Microanalysis Laboratory) and infrared spectroscopy (Table I). All compounds were air-stable crystalline materials.

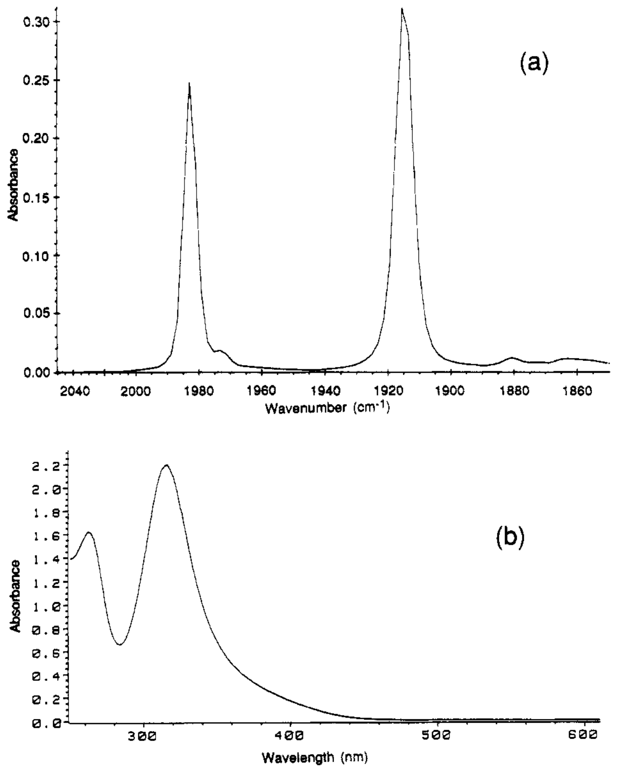

Figure 1. (a) Infrared spectrum in the ν_{CO} region of (η^6-benzene)Cr(CO)$_3$ in cyclohexane at 4 cm^{-1} resolution. (b) UV/vis spectrum of (η^6-benzene)Cr(CO)$_3$ in cyclohexane (concentration 1.9×10^{-4} M).

Table I. Spectroscopic Data for the Range of (η^6-arene)Cr(CO)$_3$ Compounds Investigated in Cyclohexane Solution

arene	ν_{CO},[a] cm^{-1}	λ_{max},[b] nm	ϵ(355 nm),[c] 10^{-3}M^{-1} cm^{-1}
chlorobenzene	1989 1926	322	3.87
p-chlorotoluene	1986 1918	320	4.00
benzene	1983 1915	314	3.06
ethylbenzene	1979 1910	318	3.27
p-xylene	1978 1909	320	3.40
o-xylene	1973 1905	320	4.12
1,3,5-mesitylene	1972 1904	316	3.22
hexamethylbenzene	1970 1885	324	4.05
hexaethylbenzene	1953 1881	326	3.35

[a] ±2 cm^{-1}. [b] ±2 nm. [c] ±2%.

Results

The IR and UV/vis spectra of (η^6-benzene)Cr(CO)$_3$ are given in parts a and b of Figure 1, respectively. The spectra of the other compounds are similar to these, and relevant spectroscopic data are presented in Table I. Series of experiments were performed with an excitation wavelength of 266 nm. However, the results obtained were essentially the same as those obtained following excitation at 355 nm. Consequently, the longer wavelength was used for all UV/vis flash photolysis experiments reported here.

The time-resolved infrared spectrum following photolysis of (η^6-benzene)Cr(CO)$_3$ in *n*-heptane is given in Figure 2a. In this spectrum the negative peaks represent the depletion of the parent bands. The two positive peaks correspond to the photoproduct assigned to (η^6-benzene)Cr(CO)$_2$(s) (s = *n*-heptane) by comparison of the band positions to those obtained in a CH$_4$ matrix at 12

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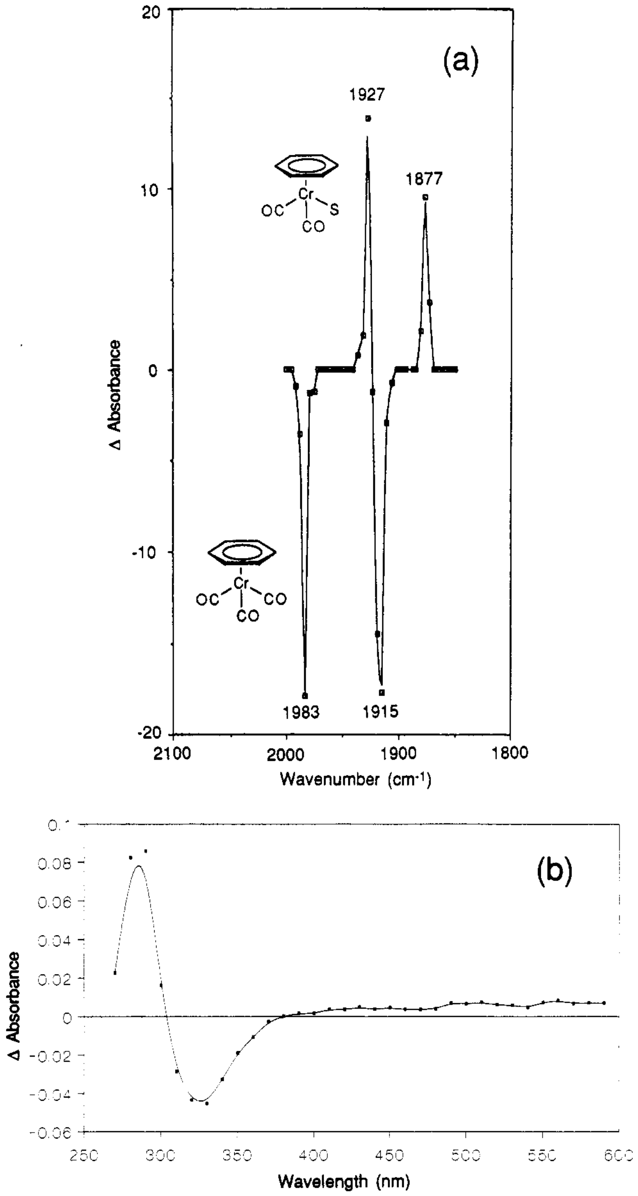

Figure 2. (a) TRIR spectrum obtained 1 μs after photolysis of (η^6-benzene)$Cr(CO)_3$ in *n*-heptane. (b) Differential UV/vis absorption spectrum obtained 2 μs after photolysis in cyclohexane solution.

K.[15] The lifetime of (η^6-benzene)$Cr(CO)_2$(s) was dependent on the concentration of CO, affording an estimate of the second-order rate constant for reaction 3 of 3.0×10^7 M^{-1} s^{-1} at 300 K.

$$(\eta^6\text{-benzene})Cr(CO)_2(s) + CO \xrightarrow{k_3} (\eta^6\text{-benzene})Cr(CO)_3 + s \quad (3)$$

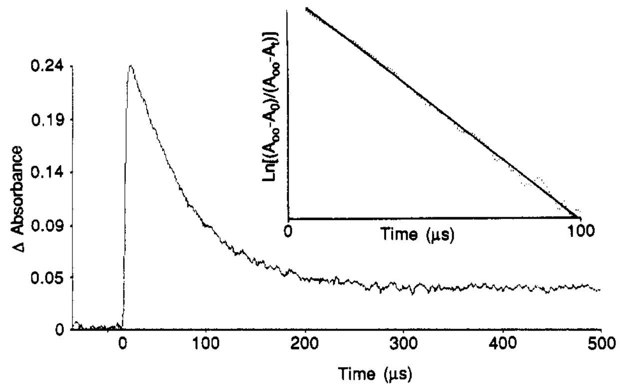

Figure 3. Typical transient signal obtained following photolysis of (η^6-benzene)$Cr(CO)_3$ in *n*-heptane monitored at 280 nm (for details of inset see text).

Table II. Activation Parameters Measured over the Temperature Range 290–320 K and Rate Constant Data at 298 K, Obtained by UV/vis Flash Photolysis, for the Reactions of (η^6-arene)$Cr(CO)_2$(s) with CO

arene	$\Delta H^{\ddagger}$ [a]	$\Delta S^{\ddagger}$ [b]	$10^{-6}k_3$ [c]	solvent(s)
chlorobenzene	23	−38	5.7	cyclohexane
p-chlorotoluene	25	−34	4.0	cyclohexane
benzene	22	−37	9.8	cyclohexane
	24	−18	13	*n*-pentane
	26	−16	23	*n*-heptane
	26	−12	28	*n*-decane
	26	−10	34	*n*-dodecane
toluene	23	−35	9.4	cyclohexane
ethylbenzene	24	−31	6.6	cyclohexane
p-xylene	24	−28	8.3	cyclohexane
o-xylene	25	−28	6.8	cyclohexane
1,3,5-mesitylene	24	−27	13	cyclohexane
hexamethylbenzene	25	−26	15	cyclohexane
hexaethylbenzene	22	−23	59	cyclohexane
	23	−12	110	*n*-heptane

[a] ±2 kJ mol^{-1}. [b] ±10 J mol^{-1} K^{-1}. [c] M^{-1} s^{-1}, ±10%.

The UV/vis difference spectrum obtained in cyclohexane 1 μs after the laser pulse is given in Figure 2b. The strong differential absorption at 280 nm contrasts with the weakness of the bands in the visible region and occurs in the valley of the absorption profile of the parent compound (Figure 1b). A typical transient signal (average of three shots) obtained in *n*-heptane at 280 nm from (η^6-benzene)$Cr(CO)_3$ (2.87×10^{-4} M) in the presence of CO (1.2×10^{-2} M) is presented in Figure 3. The inset represents a plot of $\ln[(A_\infty - A_0)/(A_\infty - A_t)]$ versus time for the decay of this absorption, showing that the process follows pseudo-first-order kinetics. However, under these conditions the process is not fully reversible on this time scale, as exemplified by the residual absorption. The second-order rate constant derived from this experiment (2.3×10^7 M^{-1} s^{-1} at 298 K) is similar to that obtained with TRIR (*vide supra*). Depletion of the parent absorption at 340 nm (Figure 2b) provides an estimate of the conversion of the parent species to photoproduct, and this was typically <10% (this assumes that the photoproduct does not absorb strongly at this wavelength). The lifetime of (η^6-benzene)$Cr(CO)_2$(s) depends on the concentration of CO, and these data provide the second-order rate constant (k_3) for the reaction of (η^6-benzene)$Cr(CO)_2$(s) with CO (reaction 3; Table II). The plots of observed rate constant versus [CO] were linear with negligible intercepts, which indicates that, under these conditions, no other reactions contribute significantly to the decay of the dicarbonyl species.

To examine how the reactivity of the photoproducts is affected by substituents on the arene ligand, experiments were conducted with a range of arene derivatives as outlined in Table II. The second-order rate constant for the reaction of (η^6-arene)$Cr(CO)_2$(s) with CO shows a general increase with increasing number of alkyl substituents for the more highly substituted derivatives. The (C_6Et_6)$Cr(CO)_2$(s) species is the most reactive toward CO.

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Table II also includes activation parameters obtained from Eyring plots over the temperature range 290–320 K. The reactivities of (η^6-arene)$Cr(CO)_2$(s) toward CO in linear alkanes were also measured, and the results are in Table II.

The photochemistry of these compounds has been studied in Ar-saturated cyclohexane solution. Under these conditions a long-lived transient species was observed. For (η^6-benzene)$Cr(CO)_3$, the rate of formation of this species was linearly dependent on the concentration of the parent tricarbonyl, and this is consistent with the formation of a dimeric product by the reaction of the intermediate (η^6-benzene)$Cr(CO)_2$(s) with the parent (η^6-benzene)$Cr(CO)_3$, as shown in reaction 4. The slope of this plot yields the second-order rate constant of $4.8 \times 10^7\ M^{-1}\ s^{-1}$ for this reaction. The formation of a dinuclear compound was observed in a Nujol matrix at 77 K.[16,17]

$$(\eta^6\text{-benzene})Cr(CO)_2(s) + (\eta^6\text{-benzene})Cr(CO)_3 \xrightarrow{k_4} (\eta^6\text{-benzene})Cr(CO)_2(\mu\text{-}CO)Cr(CO)_2(\eta^6\text{-benzene}) + s \quad (4)$$

Discussion

Spectroscopic Characterization and Reactions of (η^6-arene)$Cr(CO)_2$(s). The spectroscopic data obtained by TRIR measurements allow a direct comparison with data obtained using low-temperature matrix isolation methods. The ν_{CO} band positions for the first observable species of 1927 and 1877 cm^{-1}, derived from these TRIR experiments, are close to those previously observed and assigned to (η^6-benzene)$Cr(CO)_2$ in a methane matrix at 12 K (1937 and 1885 cm^{-1})[15] and confirm for the first time that (η^6-benzene)$Cr(CO)_2$(s) is indeed the primary photoproduct in alkane solution at room temperature (Figure 2a). As with $Cr(CO)_5$, it is likely that the vacant coordination site in this intermediate is occupied by a molecule of solvent (s) as a "token" ligand.[18] The relative intensities of the symmetric and antisymmetric bands suggest that the angle between the carbonyl groups in the dicarbonyl intermediate is approximately 80°. Thus, the structure of the intermediate resembles that of the parent tricarbonyl compound, in which one of the carbonyl ligands is replaced by a molecule of the solvent.

The kinetic data obtained by TRIR allow a correlation between the signals derived from the TRIR experiments and those obtained from conventional flash photolysis. This permits the unambiguous assignment of the strong transient absorbance at 280 nm to the dicarbonyl species. Spectroscopic monitoring of (η^6-benzene)$Cr(CO)_2$(s) in the visible region is difficult because of both the weakness and the featureless nature of its absorbance spectrum in this region.[4b]

For all compounds in this investigation, the difference spectra of the corresponding primary photoproducts exhibit a maximum at approximately 280 nm. A depletion of the tricarbonyl absorption between 330 and 350 nm was also observed, and by analogy, we have assigned this primary photoproduct to the appropriate (η^6-arene)$Cr(CO)_2$(s) species. As with the benzene compound, the dicarbonyl species reacted with added CO, providing the rate constants presented in Table II.[19] We have exclusively used UV/vis-monitored flash photolysis to determine the kinetic behavior of these photoproducts.

The rate constant data presented in Table II show that it is only for highly substituted arene complexes that large differences in k_3 are observed. This would suggest that the origin of any differences is steric rather than electronic. Similar conclusions were drawn from experiments on the (η^5-C_5R_5)$Mn(CO)_3$ system (R = H, Me, Et).[7]

The enthalpy of activation $\Delta H^{\ddagger}$ for the carbon monoxide recombination for all the complexes is constant at 24 ± 2 kJ mol^{-1} (s = cyclohexane; Table II). This may be compared to the reported binding energy of cyclohexane to $Cr(CO)_5$ of 52 kJ mol^{-1} from photoacoustic measurements,[20] although this may be an overestimate because similar studies on the $W(CO)_6$ system yielded binding energies somewhat greater than those obtained from equilibrium[21] or $\Delta H^{\ddagger}$ measurements.[22] To our knowledge there are no estimates in the literature for the Cr to alkane bond energy in (η^6-arene)$Cr(CO)_2$(alkane) intermediates. In other systems, including $Cr(CO)_6$, it has been shown that the reactions of the photofragment (*e.g.* $Cr(CO)_5$) with the solvent is rapid. Therefore, $\Delta H^{\ddagger}$ for the loss of solvent from the solvent adduct approximates the bond energy of the metal to solvent bond.[23] Similar assumptions may well be valid for the (η^6-arene)$Cr(CO)_3$ system studied here, although no ps studies on this system have been reported as yet. Assuming the interaction energy between $Cr(CO)_5$ and cyclohexane is similar to that of (η^6-arene)$Cr(CO)_2$ and cyclohexane, and given the fact that our data are significantly lower than those reported by Burkey,[20] it is unlikely that dissociative loss of solvent from (η^6-arene)$Cr(CO)_2$(s) is involved in the rate-determining step and that an interchange mechanism should be considered.[24]

As indicated previously, the observed rates of these reactions show a linear dependence on [CO], and the intercepts of these pseudo-first-order plots are within experimental error of the origin. This behavior is consistent with both an interchange mechanism and one involving dissociative loss of solvent from (η^6-arene)$Cr(CO)_2$(s) in a preequilibrium step, in which the reaction of (η^6-arene)$Cr(CO)_2$ with the solvent is rapid. The activation entropies $\Delta S^{\ddagger}$ are negative for the CO recombination reactions studied here. This observation, along with those of the $\Delta H^{\ddagger}$ measurements above, is more

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(16) Bitterwolf, T. E.; Lott, K. A.; Rest, A. J.; Mascetti, J. *J. Organomet. Chem.* **1991**, *419*, 113.

(17) Care must be exercised in the interpretation of these results, as reactions of the (η^6-arene)$Cr(CO)_2$(s) species with traces of impurities can dominate the chemistry in the absence of quenching ligands such as CO.

(18) Zhang, S.; Dobson, G. R. *Organometallics* **1992**, *11*, 2447 and references therein.

(19) As in the case of (benzene)$Cr(CO)_3$, the transient signals indicate the formation of a further species on long time scales, and experiments conducted with solvents of different dryness suggest that the formation of (arene)$Cr(CO)_2(H_2O)$ might be responsible for this absorption signal. Impurities in the solvent, some of which may be introduced during the degassing procedures, have been shown to have a dramatic effect on the transient signals obtained for the $Cr(CO)_6$ system in conventional and nanosecond flash photolysis. Cf.: Kelly, J. M.; Bent, D. V.; Hermann, H.; Schulte-Frohlinde, D.; Koerner von Gustorf, E. *J. Organomet. Chem.* **1974**, *69*, 259.

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consistent with an interchange mechanism for CO binding than a dissociative one, in which the $\Delta S^{\ddagger}$ values should be closer to zero or perhaps positive.[22]

It may be noted that as the number of methyl substituents on the arene increases, the activation entropy becomes less negative (Table II), whereas $\Delta H^{\ddagger}$ remains unchanged within experimental error. The presence of methyl substituents on the arene ligand increases the electron density on the metal atom, as confirmed by the regular drop in ν_{CO} in the parent tricarbonyl compounds (Table I). This would presumably have the effect of destabilizing the chromium–alkane interaction in the dicarbonyl species, but the effect on CO binding would be less significant. This may be the explanation for the lack of any marked change in $\Delta H^{\ddagger}$ upon increasing the number of methyl substituents on the arene ligand.

The increase in $\Delta S^{\ddagger}$ in this series is consistent with the greater steric interactions in the substituted arene complexes. In particular, a pronounced steric hindrance of the internal motions of both the alkane and the arene's alkyl substituents in (η^6-arene)$Cr(CO)_2$(s) is expected. This will be eased as the Cr–alkane distance increases on passage to the transition state. The increase in freedom of motion (e.g. the rotation of the alkyl substituents on the arene) will be especially marked for the more substituted arenes.

A further insight into these phenomena was obtained by varying the nature of the alkane solvent and examining the effect this has on the kinetic behavior of (η^6-arene)$Cr(CO)_2$(s) species. The second-order rate constants for the recombination of (η^6-benzene)$Cr(CO)_2$(s) with CO in *n*-heptane and *n*-dodecane are approximately 2 and 6 times that in cyclohexane, respectively (Table II). Time-resolved photoacoustic calorimetric studies have shown that *n*-heptane and cyclohexane bind to the coordinatively unsaturated $Cr(CO)_5$ fragment with an interaction energy of 40 and 52 kJ mol^{-1}, respectively.[20] Previously, this observation was used to explain the differences in the reactivity of the photofragments in cyclic as opposed to linear alkanes. However, gas-phase studies on $W(CO)_5$(s) indicate a binding enthalpy of 44 and 48 kJ mol^{-1} for s = *n*-pentane and cyclohexane, respectively.[22] Moreover, our results indicate that it is not a variation in the enthalpy term but, rather, the entropy term in the free energy of activation that alters the rate of the reaction of (η^6-arene)$Cr(CO)_2$(s) species with CO in solution. The rate constant for the reaction of (η^6-C_6Et_6)$Cr(CO)_2$(s) with CO is almost 4 times that of the hexamethylbenzene compound. This is consistent with the results obtained for the (η^5-C_5Me_5)$Mn(CO)_2$(s) and (η^5-C_5Et_5)$Mn(CO)_2$(s) systems.[7] A comparison of the results obtained in cyclohexane, *n*-heptane, *n*-decane, and *n*-dodecane (Table II) would suggest that it is the increased freedom of the alkane fragment that dominates the entropy term rather than any molecular motion associated with the arene ligand (*vide supra*). Indeed, there appears to be a linear relationship between the $\Delta S^{\ddagger}$ term and the carbon chain length for linear alkanes.

Reaction of (η^6-arene)$Cr(CO)_2$(s) with (η^6-arene)$Cr(CO)_3$. Under conditions of low CO concentration (*i.e.* in experiments conducted under an argon atmosphere), (η^6-benzene)$Cr(CO)_2$(s) reacts with the parent tricarbonyl to form the dinuclear species (η^6-benzene)$_2Cr_2(CO)_5$ with a rate constant of 4.8 × 10^7 L mol^{-1} s^{-1} at 298 K (k_4). The formation of dinuclear species is not uncommon and has been reported in the $Cr(CO)_6$,[3e] (η^5-C_5H_5)$Co(CO)_2$,[25] and (η^5-C_5H_5)$Mn(CO)_3$[6] systems. It is also worth noting that the rate constant for the reaction of (η^6-benzene)$Cr(CO)_2$(s) with CO is smaller than for the formation of (η^6-benzene)$_2Cr_2(CO)_5$. Similar behavior was observed for the (η^5-C_5H_5)$Mn(CO)_3$ and (η^5-C_5H_5)$V(CO)_4$ systems.[6,26]

Concluding Remarks. We have systematically varied the alkyl substituents on the arene ligand in compounds of the type (η^6-arene)$Cr(CO)_3$ and examined their photochemistry. This work indicates that the variation in reactivity of the (η^6-arene)$Cr(CO)_2$(s) photoproducts, as exemplified by the rate constant for the reaction of the dicarbonyl photoproduct with CO, can be explained by changes to the entropy of activation in the free energy expression and not by variations in the interaction energy between the coordinatively unsaturated photofragment and the solvent. Further work is underway to determine if similar effects are observed with other systems such as $Cr(CO)_6$.

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