Silica Gel Mediated Photoreactivity of (η⁶-Arene)tricarbonylchromium(0) Complexes

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The electronic spectra and photoreactivity of slurries of several (arene)tricarbonylchromium(0) complexes (arene = benzene, acetophenone, acenaphthene), prepared by adsorbing the complexes onto wet silica gel and suspending the support in cyclohexane, have been investigated. Shifts in the IR carbonyl stretching bands and electronic Cr → arene charge-transfer (MLCT) bands of the complexes that accompany adsorption are indicative of weak chemisorptive interactions. The magnitude of the electronic spectral shifts is ~1000 cm⁻¹ with the band red-shifting for the acetophenone complex and blue-shifting for the acenaphthene complex. Photodecomposition of the complexes with excitation into or near their Cr → arene CT bands has been examined in cyclohexane solution as well as with slurries employing both regular- and large-pore silica gels. The different gels provide evidence for steric effects in slurry photoreactivity: despite the identical electronic spectra observed with the two gels, the large-pore support gives larger measured quantum yields for disappearance of the complex (ϕ_d), presumably reflecting less competitive recombination of photodissociated CO. Electronic effects also appear to contribute to the photoreactivity of the slurries and are interpreted in terms of a state-switching model that has been applied to several low-spin d⁶ systems: as an MLCT band, representing an excited state believed to be inert toward substitution, is tuned to below a ligand field state, whose population is thought to lead to substitution, ϕ_d decreases. This trend in slurry ϕ_d values, spanning roughly 2 orders of magnitude, parallels that observed for solutions of the complexes. Modest variations in ϕ_d observed for the complexes in passing from solution to slurry environments are discussed.

Environment is increasingly being exploited as a tool for controlling excited-state processes of molecular systems. Organometallic species, with their rich diversity of steric and electronic properties, are excellent candidates for these studies. Much of the work reported to date has explored the effects of solvent, temperature, and, more recently, adduct formation on the excited-state properties of organometallic compounds in homogeneous solution.[1,2]

In contrast, the photochemistry of adsorbed organometallic species has received little attention, despite the novel molecular neighborhoods afforded by such supports as alumina or silica gel.[3] For the physisorbed metal carbonyl complexes whose photochemistry has been investigated, Fe(CO)₅ on silica[4] and the group 6 hexacarbonyls on porous Vycor glass,[5] neither the electronic structures nor primary photoprocesses of the adsorbates appear to have been perturbed by the supports; yet, the supports did influence the observed net photochemistry. That electronic structure and primary photoprocesses can be altered by adsorption is, of course, well established for organic species, particularly through the use of silica as a support.[6] Results with retinal provide a particularly compelling illustration of the effects of adsorption and of environment in general: electronic spectra and photoisomerization patterns found with polar solvents, nonpolar solvents, adduct formation, and silica gel adsorption are all different.[7]

In searching for organometallic systems that might permit comparisons of the effects of adduct formation and adsorption on electronic structure and excited-state properties, our attention was drawn to (η⁶-arene)tricarbonylchromium(0) (ATCr) complexes for two reasons. First, the arene ligand might be expected to adsorb strongly onto a silica gel support based on the affinity of aromatic molecules for the adsorbent.[8] Second, studies of ATCr complexes reveal their photoreactivity to be very sensitive to electronic structure and environment, owing to the existence of two energetically proximate excited states.[2] Evidence was presented that excited-state reordering with a concomitant change in photoreactivity could be accomplished by derivatizing the arene ring and, for the acetophenone complex, by adduct formation employing Eu(fod)₃ (fod is 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate) as a Lewis acid.

In this paper, we describe the excited-state properties of a family of weakly chemisorbed organometallic molecules. Specifically, we demonstrate that adsorption of several ATCr complexes onto silica gel can significantly perturb both the electronic structure of these complexes and the quantum efficiencies with which they undergo photodecomposition. Moreover, evidence is provided that both steric and electronic factors contribute to the silica gel mediated photoreactivity of ATCr complexes.

Results and Discussion

In characterizing ATCr/silica gel systems, we have employed the benzene, acetophenone, and acenaphthene complexes in conjunction with both large- and regular-pore silica gel. From manufacturers' data, the large-pore sup-

(1) For examples of solvent and temperature effects, see: Geoffroy, G. L.; Wrighton, M. S. "Organometallic Photochemistry"; Academic Press: New York, 1979.

(2) Adduct effects are discussed in: Schreiner, R.; Ellis, A. B. *J. Am. Chem. Soc.* **1982**, *104*, 3374.

(3) Initial studies of the photolysis of adsorbed organometallic species were conducted with metal–alkyl compounds: Ehrlich, D. J.; Osgood, R. M., Jr. *Chem. Phys. Lett.* **1981**, *79*, 381. Systems based on adsorption are distinguished here from those involving complexes confined to surfaces by chemical derivatization of the support. Photochemical studies of metal carbonyl complexes covalently attached to silica have been reported. See, for example: (a) Kinney, J. B.; Staley, R. H.; Reichel, C. L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1981**, *103*, 4273. (b) Liu, D. K.; Wrighton, M. S. *Ibid.* **1982**, *104*, 898.

(4) (a) Jackson, R. L.; Trusheim, M. R. *J. Am. Chem. Soc.* **1982**, *104*, 6590. (b) Trusheim, M. R.; Jackson, R. L. *J. Phys. Chem.* **1983**, *87*, 1910.

(5) Simon, R.; Gafney, H. D.; Morse, D. L. *Inorg. Chem.* **1983**, *22*, 573.

(6) See: Bauer, R. K.; Borenstein, R.; de Mayo, P.; Okada, K.; Rafalska, M.; Ware, W. R.; Wu, K. C. *J. Am. Chem. Soc.* **1982**, *104*, 4635 and references therein.

(7) (a) Denny, M.; Liu, R. S. H. *J. Am. Chem. Soc.* **1977**, *99*, 4865. (b) Waddell, W. H.; Hopkins, D. L. *Ibid.* **1977**, *99*, 6457. (c) Tsukida, K.; Kodama, A.; Ito, M. *J. Chromatogr.* **1977**, *134*, 331. (d) Ellis, A. B.; Schreiner, R.; Ulkus, R. A. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 3993. (e) Zawadzki, M. E.; Ellis, A. B. *J. Org. Chem.* **1983**, *48*, 3156.

(8) Nicholls, C. H.; Leermakers, P. A. *Adv. Photochem.* **1971**, *8*, 315 and references therein.

Table I. Electronic Spectral Features of
(Arene)Cr(CO)$_3$ Complexes in Different Environments[a]

arene	medium [b]	λ_{max}, nm ($10^{-3}\epsilon$, M^{-1} cm^{-1})[c]	ΔE,[d] cm^{-1}
benzene	cyclohexane	322[f] (10.6)	
	slurry	315[f] (6.0)	-690
acetophenone	cyclohexane	325 (10.4)	
	slurry	322 (6.0)	-300
	cyclohexane	407 (2.5)	
	slurry	423 (2.5)	$+930$
acenaphthene[e]	cyclohexane	352 (8.1)	
	slurry	335 (3.2)	-1400
	cyclohexane	437 (1.9)	
	slurry	417 (1.2)	-1100

[a] Electronic spectral features obtained by using N$_2$-saturated solvents at 295 K. [b] Entries labeled "cyclohexane" correspond to spectral features in that solvent and entries labeled "slurry" represent data obtained for cyclohexane slurries of the ATCr complex adsorbed onto silica gel (($\sim$2–5) × 10^{-6} mol of ATCr complex/g of silica gel), prepared as described in the Experimental Section. Large- and regular-pore silica gel gave the same data. [c] Wavelength of maximum absorption with absorptivity given parenthetically. [d] Spectral shift resulting from adsorption relative to the λ_{max} value in cyclohexane solution; negative and positive numbers correspond to shifts to higher and lower energies, respectively. [e] Acenaphthene is

[f] A poorly-defined shoulder is observed in this band.

port has a surface area of $\sim$300 m^2/g and a pore volume of 1.6 mL/g (average pore radius of $\sim$100 Å); a surface area of $\sim$340 m^2/g and pore volume of 1.2 mL/g (average pore radius of $\sim$50 Å) characterize the regular-pore silica gel. Both gels have a surface density of $\sim$5–7 SiOH groups/nm^2. In sections below we describe the electronic spectra and photochemistry of ATCr complexes adsorbed onto wet silica gel to form a slurry in cyclohexane.

Electronic Spectra. Light scattering in slurry spectra is minimized by the similar refractive indices of cyclohexane and silica gels.[8] The concentrations employed (($\sim$2–5) × 10^{-6} mol of ATCr complex/g of silica gel) were such that the complexes were completely adsorbed, as indicated by the absence of their absorption bands in the electronic spectra of the supernatant liquids. Figure 1 displays spectra for the three ATCr complexes taken both in cyclohexane solution and as slurries with regular-pore silica; no significant spectral differences were found for slurries prepared with the large-pore silica gel. Prominent spectral features are summarized in Table I.

The key result that emerges from the table and figure is that adsorption onto silica gel perturbs the electronic structure of all three ATCr complexes. This observation, the need to use relatively polar solvents such as CH$_2$Cl$_2$ to desorb the ATCr complexes, and evidence that adsorption involves particular sites on the silica gel (vide infra) suggest that the species be described as weakly chemisorbed. In contrast, we found that slurry spectra of complexes possessing exclusively terminal carbonyl ligands such as Cr(CO)$_6$ and Mn$_2$(CO)$_{10}$ were essentially identical with cyclohexane solution spectra; spectra of the supernatant liquid of the slurries showed that negligible adsorption had occurred. These results are in accord with previous studies of Fe(CO)$_5$ and the group 6 hexacarbonyls which indicated the species to be physisorbed onto silica surfaces under conditions analogous to those employed here.[4,5,9]
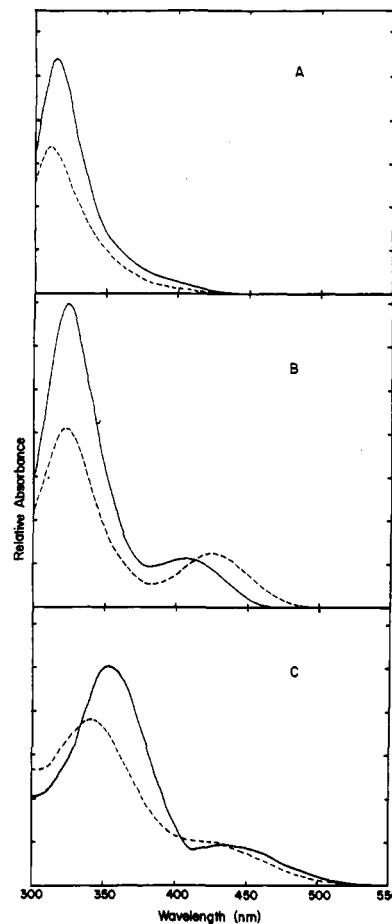

Figure 1. Electronic spectra of ATCr complexes at 295 K. Panels A, B, and C correspond to the benzene, acetophenone, and acenaphthene complexes, respectively. Solid curves are spectra of $\sim$1 mM cyclohexane solutions of the complexes. Dashed curves are spectra of the complexes adsorbed onto regular-pore silica gel (($\sim$2–5) × 10^{-6} mol of ATCr complex/g of silica gel) which was subsequently suspended in cyclohexane to form a slurry. For each complex, the quantity of ATCr complex adsorbed was adjusted to give an absorbance comparable to that shown in the corresponding solid curve. A 0.10-cm path length cell was employed for all spectra.

Interpretation of the effect of silica gel on spectral features of the ATCr complexes rests on both the physicochemical properties of the environment and the nature of the electronic transitions. With regard to physicochemical properties, the observed spectra reflect interactions of the adsorbates with the water and silanol and siloxane functionalities present in the support. Of these interactions, those with the silanol functionalities appear most significant: adsorption of the ATCr complexes did not occur after dehydroxylation of the silica gels with (CH$_3$)$_2$SiCl$_2$ but did occur after dehydration (110 °C at 10^{-5} torr for $\gtrsim$3 h).

For the adsorbates, IR data suggest that the support interacts principally with the arene ligands. Particularly revealing in this regard are experiments with Cr(CO)$_6$ and Mn$_2$(CO)$_{10}$: besides exhibiting congruent slurry and solution electronic spectra, neither complex displays a shift in carbonyl stretching frequencies, ν_{CO}, following deposition onto silica gel by solvent evaporation. In contrast, the fluorolube mull IR spectra of Figures 2 and 3 demonstrate

(9) (a) Hughes, F.; Bassett, J. M.; Ben Taarit, Y.; Choplin, A.; Peimet, M.; Rojas, D.; Smith, A. K. *J. Am. Chem. Soc.* **1982**, *104*, 7020. (b) Brenner, A.; Hucul, D. A.; Hardwick, S. J. *Inorg. Chem.* **1979**, *18*, 1478. (c) Bailey, D. C.; Langer, S. H. *Chem. Rev.* **1981**, *81*, 144 and references therein.
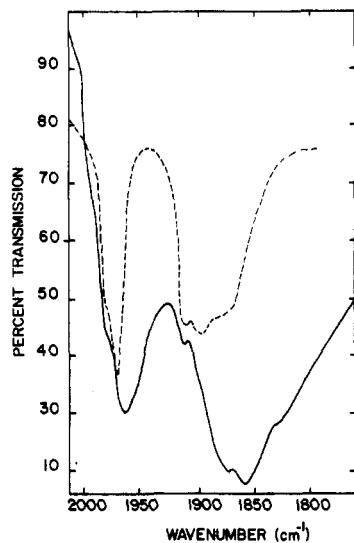
Figure 2. Fluorolube mull IR spectra of $(\eta^6\text{-benzene})Cr(CO)_3$ (solid curve) and of the complex adsorbed onto regular-pore silica gel (dashed curve).
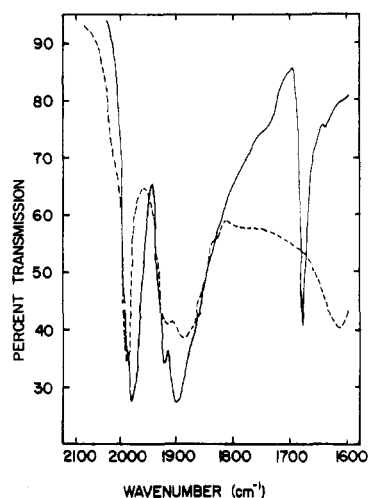

Figure 3. Fluorolube mull IR spectra of $(\eta^6\text{-acetophenone})Cr(CO)_3$ (solid curve) and of the complex adsorbed onto regular-pore silica gel (dashed curve).

that these bands are significantly affected in ATCr complexes. The shift of the highest energy band (symmetric A stretching mode) to higher energy by ~10–20 cm^{-1} in the benzene and acetophenone complexes (Figures 2 and 3) is consistent with an enhanced ability of the arene ligand to withdraw electron density through its interaction with the support: as more electron density is shifted toward the arene ligand, less electron density is placed in the $\pi^*(CO)$ orbitals, thereby increasing ν_{CO}. The acenaphthene complex exhibits a comparable shift in ν_{CO} for the same band.

The apparent preference of silica gel for the arene ligand prompts comparisons with the properties and forces involved in the interactions of aromatic molecules with the support. Such systems have been extensively studied and described in terms of dispersion forces, electrostatic interactions, and hydrogen bonding.[6] Benzene, in particular, has been shown to adsorb in a "flat-on" manner, and its interaction with the support attributed to dispersion forces.[8] A similar interaction seems reasonable for the benzene and acenaphthene complexes. For aromatic molecules possessing heteroatoms, hydrogen bonding has often been identified as the principal cohesive force.[8] The acetophenone complex does exhibit a shift in its ketonic

CO stretching frequency consistent with hydrogen bonding; the band red-shifts on adsorption from 1678 to 1626 cm^{-1} (Figure 3).

In describing the interactions characterizing the ATCr/silica gel systems, it is worth emphasizing their complexity. For example, although we have focused on hydrogen bonding in discussing the acetophenone complex, interactions of the aromatic ring with the support are likely also important. Moreover, the great variety of sites that exist on the support provide the basis for a broad range of interactions for each system. If the adsorbates can migrate,[6] these interactions may also be time dependent.

The effects of adsorbate–silica gel interactions on the electronic spectra of the ATCr complexes (Figure 1) are manifested in intense transitions ($\epsilon \approx 10^3$–10^4 M^{-1} cm^{-1}) which are believed to be predominantly metal-to-ligand charge-transfer (MLCT) in character.[2,10] Solution studies reveal that, with the exception of the acenaphthene complex, the ATCr complexes examined have electronic spectra consisting of a low-energy band whose position is arene dependent and a higher energy band whose energy is relatively arene independent. Shifts in the low-energy band with arene substituents are consistent with an assignment of Cr $\rightarrow$ arene CT. The assignment of the higher energy band is not well established in the literature, although its independence of arene substituent suggests it to be predominantly Cr $\rightarrow$ $\pi^*(CO)$ CT in character; intraligand (IL) π,π^* transitions may also contribute to this band, particularly in its high-energy tail. Ligand field (LF) transitions represent other contributions to the spectra of Figure 1, but they are relatively weak and should show little change with adsorption, since the donor atoms directly coordinated to Cr are unaffected by this process. In contrast, MLCT bands can be very sensitive to environment; in many systems, for example, a strong dependence on solvent polarity is observed.[1]

For the systems at hand, bands having Cr $\rightarrow$ arene CT and Cr $\rightarrow$ $\pi^*(CO)$ CT character would be expected to red- and blue-shift, respectively, as electron density is withdrawn from the arene ring by adsorption. Evaluating these predictions with the benzene complex is difficult, owing to substantial overlap of the two bands; in solution, the low-energy band appears as a shoulder on the band with λ_{max} at 322 nm. Figure 1 and Table I reveal that adsorption results in a modest blue shift in λ_{max} for the benzene complex (~690 cm^{-1}), but from what combination of band movements the shift derives is difficult to say.

For the acetophenone complex, the two bands are more clearly separated and, in fact, adsorption produces a color change from yellow-orange to orange-red. As expected for a transition having predominantly Cr $\rightarrow$ arene CT character, the lower energy band does red-shift upon adsorption of the complex. The shift, nearly 1000 cm^{-1}, is reminiscent of the red-shift induced in homogeneous solution by adduct formation with Eu(fod)$_3$.[2] The β-diketonate complex produced a larger shift (~2100 cm^{-1}), perhaps reflecting a more localized and uniform interaction. In contrast to the large red-shift of the lower energy band, the higher energy band of the acetophenone complex exhibited only a slight blue shift upon adsorption.

The last member of the trio of ATCr complexes, the acenaphthene compound, was previously identified as being anomalous in the sense that both its electronic and IR bands are substantially displaced from those of the other ATCr complexes examined. Adsorption effects reinforce this notion. Figure 1 and Table I reveal that both

(10) Reference 1, p 59.
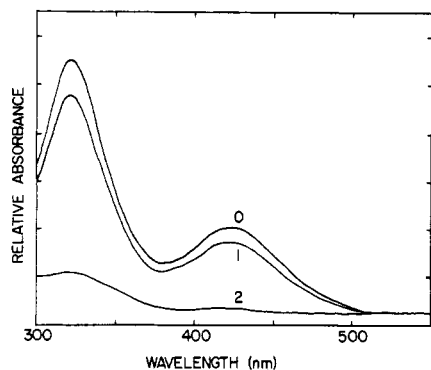
(11) Reference 1, pp 78–81.

Figure 4. Electronic spectral changes accompanying the 488-nm photolysis of a cyclohexane slurry of (η^6-acetophenone)Cr(CO)$_3$ adsorbed onto silica gel (~2 × 10^{-6} mol of complex/g of silica gel; 0.10-cm path length cell). Curve 0 is the initial spectrum, and curves 1 and 2 are spectra after total photolysis times of 40 and 240 s. The entire solution (~1.5-cm² cell window area) was irradiated with 80 mW of power.

Table II. Disappearance Quantum Yields for (Arene)Cr(CO)$_3$ Complexes in Different Environments^a

arene	medium ^{b}	λ_{ex},^{c} nm	ϕ_d^{d}
benzene	cyclohexane	337	0.50
	slurry-lp	337	0.40
	slurry-rp	337	0.11
acetophenone	cyclohexane	488	0.10
	slurry-lp	488	0.032
	slurry-rp	488	0.0090
acenaphthene	cyclohexane	488	0.0010
	slurry-lp	488	0.0034
	slurry-rp	488	0.0016

^{a} Experiments were conducted with N$_2$-saturated cyclohexane at 295 K. ^{b} The entries labeled "cyclohexane" correspond to experiments conducted in that solvent at concentrations of ~1-2 mM; entries labeled "slurry-lp" and "slurry-rp" refer to data for cyclohexane slurries employing large-pore and regular-pore silica gel, respectively. ^{c} Excitation wavelength. ^{d} Quantum yield for the disappearance of the ATCr complex through decomposition. Procedures used for determining ϕ_d are described in the Experimental Section. Each value is the average of at least three separate experiments. Values are uncorrected for reflective and scattering losses; reproducibility was ±15%.

of the acenaphthene complex's absorption bands undergo substantial blue shifts of 1100 and 1400 cm^{-1} upon adsorption. The blue shift of the low-energy Cr → arene CT band was unexpected, IR data having indicated that the adsorbed complex could more easily withdraw electron density through its arene ligand. Although a detailed interpretation of this result awaits a better picture of the adsorbate/adsorbent interaction, one possible explanation might be that adsorption redistributes electron density between the two rings of the arene ligand in such a manner as to raise the energy of the transition.

Other data worth noting in Table I are the absorptivities of adsorbed ATCr species. In general, ϵ at λ_{max} declines by ~40–60% in passing from the solution to the slurry environment. Only the intensity of the Cr → arene CT band of the acetophenone complex appeared unaffected by adsorption.

Photochemistry. The diversity of adsorption-induced spectral shifts observed for ATCr complexes prompted us to examine the photochemical consequences of adsorption. The ATCr complexes are known to undergo photoinduced loss of CO, a reaction extensively exploited for the synthesis of dicarbonyl derivatives.[11] In our slurry photolyses, we have not employed an entering Lewis base but have simply carried out the decomposition of the ATCr complex.

Figure 4 presents spectral changes accompanying the 488-nm photolysis of a N$_2$-purged cyclohexane slurry of the acetophenone complex. As illustrated by the figure, the slurries bleach under irradiation. Although we have not identified the reaction products, a flocculent green material, presumably containing Cr(III) species, appears as the photolysis proceeds.[12] An IR spectrum of the photolysate (taken by desorbing the complex with CH$_2$Cl$_2$, removing the solvent, and redissolving the residue in CCl$_4$) shows no evidence for formation of new carbonyl-containing complexes.

We have used the decline in absorbance in a spectral region where the decomposition products do not absorb to determine ϕ_d, the disappearance quantum yield for the ATCr complex; the extent of decomposition was kept to ≲30% for determinations of ϕ_d, and Beer's law was verified

for the concentration range of (~0.1–1) × 10^{-6} mol/g of silica gel for the benzene and acetophenone complexes. Additionally, the changes in absorbance resulting from photolyses extrapolated linearly to zero conversion at zero time. This observation supports the assignment of the spectral changes to primary photoprocesses, although contributions from secondary photochemistry cannot be completely ruled out. In control experiments, we saw no evidence of a dark reaction and were able to recover the ATCr complexes almost quantitatively by desorption with CH$_2$Cl$_2$.

Measured values of ϕ_d for slurries have been compiled in Table II along with values obtained in N$_2$-purged cyclohexane solution. In all cases, samples have been excited at energies corresponding to roughly their lowest-energy absorption band. With regard to the accuracy of the slurry values, we should note that the thermal reversal of CO photoelimination, scattering effects, and secondary photochemistry can all lead to a reduction in ϕ_d. While we cannot quantify the effect of each of these processes, the value of 0.40 obtained for the adsorbed benzene complex suggests that the processes collectively reduce ϕ_d by at most a factor of about 2.

Inspection of Table II reveals that measured ϕ_d values vary with ATCr complex for a given medium and with medium for a given complex. We believe that the tabulated data provide evidence that the photoreactivity of the slurries reflects both steric and electronic effects.

Steric effects are most easily evaluated by comparing ϕ_d data for the large- and regular-pore silica gel slurries, since the two supports produce virtually indistinguishable spectral changes. For all three complexes, ϕ_d values which are larger by factors of ~2–4 are observed with the large-pore silica gel. This difference may reflect the relative ease with which CO can leave the silica gel: despite the N$_2$-purging employed, the silica gel's pores may act as cages, reducing ϕ_d by facilitating the re-formation of Cr–CO bonds.[13] As the pore volume increases, this back-reaction should be less competitive and ϕ_d should increase, as observed.

Relationships between photoreactivity and electronic structure have been investigated for ATCr complexes in

(12) There is precedence for the photochemical oxidative decarbonylation of ATCr complexes in solution studies. Photolysis of ATCr complexes in dry methanol resulted in formation of Cr(OMe)$_3$: Brown, D. A.; Cunningham, D.; Glass, W. K. *J. Chem. Soc., Chem. Commun.* **1966**, 306. Analogous reactions involving silanol groups may be occurring in the ATCr/silica gel systems.

(13) Leermakers, P. A.; Thomas, H. T.; Weis, D. L.; James, F. C. *J. Am. Chem. Soc.* **1966**, *88*, 5075.

solution[2] and are found to exhibit characteristics common to a number of low-spin d[6] systems.[14] Evidence has accrued that photoinduced loss of CO occurs from LF states that are often spectroscopically masked by an MLCT band corresponding to a photoinert excited state. As the MLCT excited state is tuned to below the LF state by ligand substituents or adduct formation ("state-switching"), ϕ_d diminishes. Solution data for the ATCr complexes highlight this trend: in passing from the benzene to the acetophenone to the acenaphthene complex, the band which is presumably Cr $\rightarrow$ arene CT in nature red-shifts and ϕ_d drops from $\sim$0.5 to 0.1 to 0.001, respectively. Energies of LF states are assumed to be relatively independent of the arene ligand, since the donor atoms are invariant. Results obtained with slurries are also consistent with the "state-switching" model. Table II reveals that with either large- or regular-pore silica gel, red shifts in the onsets of Cr $\rightarrow$ arene CT bands (Figure 1) are accompanied by reductions in ϕ_d spanning roughly 2 orders of magnitude.

More modest are the changes in ϕ_d observed in passing from solution to slurry environments for the individual ATCr complexes. On the basis of the adsorption-induced spectral shifts and the state-switching model, we anticipated little change in ϕ_d for the benzene complex, a decrease for the acetophenone complex, and an increase for the acenaphthene complex. Table II demonstrates that these expectations are fulfilled by using the large-pore silica gel data for which steric effects are presumably minimized. Although this correlation is gratifying, the variations in ϕ_d values are relatively small and need to be qualified by the uncertainties characterizing ϕ_d measurements. Thus, if thermal reversal of CO photoelimination, scattering, and secondary photochemistry serve to reduce ϕ_d values, this will blur the adsorption-induced trends described above for the benzene and acetophenone complexes. For the acenaphthene complex, the observed slurry-induced enhancement in ϕ_d is a more secure trend, since the aforementioned corrections would amplify the effect.

One other interesting comparison involves the adduct formed from the acetophenone complex and Eu(fod)$_3$. Although the Cr $\rightarrow$ arene CT band maximum of the adduct is at lower energy than the slurry band maximum, both systems exhibit ϕ_d values of $\sim$10^{-2}. Thus, despite the different forms of steric and electronic perturbation introduced by adsorption and adduct formation, their overall effect on photoreactivity is similar.

Conclusion

The studies described above demonstrate considerable variation in the perturbations of electronic structure and photoreactivity induced in ATCr complexes by adsorption onto silica gel. Photoreactivity of the adsorbates appears to reflect both the steric constraint and perturbed electronic structure introduced by the support. Given the myriad of complexes known to exhibit color changes when adsorbed onto silica gel, we anticipate that the susceptibility of electronic structure and photoreactivity to perturbation by adsorption will be a characteristic of many organometallic species.

Experimental Section

Materials. Both Cr(CO)$_6$ and Mn$_2$(CO)$_{10}$ were obtained from Pressure Chemical Co. and were sublimed under vacuum prior to use. (Benzene)Cr(CO)$_3$ was purchased from Strem Chemical

Co. and was sublimed prior to use. (Acetophenone)Cr(CO)$_3$ was synthesized as previously described,[2] and (acenaphthene)Cr(CO)$_3$, a gift of Professor P. M. Treichel and R. Fronko was recrystallized from isooctane. Cyclohexane, Aldrich spectrophotometric grade, was dried over 4A molecular sieves and purged with N$_2$. The regular-pore (Fisher S-704; $\sim$75-250-μm particle size) and large-pore (Alfa #89384; 70-μm particle size) silica gels were used as received. Dimethyldichlorosilane (Petrarch) was also used as received.

Spectra. Infrared spectra were recorded on a Beckman 4230 spectrophotometer. All samples were prepared as fluorolube mulls on NaCl plates with a film of fluorolube between NaCl plates serving as a reference. For preparation of the samples having the complexes in contact with silica gel, about 2 mL of a 0.5-1 mM solution of the complex in cyclohexane was stirred with 0.6 g of silica gel. A stream of N$_2$ was used to evaporate the solvent, and the powder was subsequently ground into a mull with a few drops of fluorolube.

Electronic spectra were recorded on a Cary 17D spectrophotometer. All samples were prepared in a N$_2$-filled glovebag. Spectra of 0.5-1 mM cyclohexane solutions of the complexes were obtained in quartz cells with a 0.10-cm optical path and a 0.4-mL volume. To obtain spectra of the adsorbed complexes, a slurry consisting of 4.0 mL of the 0.5-1 mM cyclohexane solution of the complex and 1.17 g of silica gel was prepared. After the solvent was evaporated under a stream of N$_2$, 0.12 g of the silica gel was poured into a 0.10-cm path length cell, nearly filling it. The cell was shaken for several minutes and combined with 0.4 mL of cyclohexane to again form a slurry; a cell filled with the same quantity of untreated silica gel in cyclohexane served as a reference. The procedure employed was designed to place the same number of molecules in the optical path in both solution and slurry experiments. In similar experiments conducted in a large cuvette, the addition of more solvent to the slurry optical cell provided supernatant liquid that was used to evaluate the completeness of adsorption. For the benzene and acetophenone complexes, Beer's law was verified over a concentration range of ($\sim$0.1-1) $\times$ 10^{-6} mol/g of silica gel. Spectra were also obtained of slurries prepared from silica gel which had been dehydrated[15] by heating at 110 °C for at least 3 h under vacuum (10^{-5} torr) and dehydroxylated[16] by exposure to (CH$_3$)$_2$SiCl$_2$ vapor for 14 h.

Optical Sources. Excitation at 488.0 nm was provided by a Coherent Radiation CR-12 Ar$^+$ laser. The 2-3-mm diameter laser beam was passed sequentially through an Oriel interference filter to eliminate laser plasma background and a 10X beam expander. Laser power, measured with a Scientech 362 power meter, was maintained at $\sim$40 mW during photolyses. An NRG 0.7-5-200 pulsed N$_2$ laser provided about 20 mW of 337-nm excitation.

Photolyses. All photolysis experiments were conducted in a single cell, similar in design to one previously reported.[17] The bottom portion of the cell has roughly an "H" shape, with one leg a test tube and the other a 0.10-cm path length cuvette; solvent or slurry can be transferred between the two legs by tipping the cell. The test tube is fused at its top to a Teflon stopcock which provides two openings to the cell, both of which are covered with a septum. The sample is irradiated in the test tube portion of the cell and is stirred and purged during irradiation with cyclohexane-saturated N$_2$ brought into the test tube by a cannula; a cannula placed through the other septum serves as a vent for the cell.

For the solution experiments, 5 mL of a 1.0-1.5 mM cyclohexane solution of the ATCr complex was irradiated for short periods of time with a maximum conversion of 30%. The N$_2$ purge was disconnected after each photolysis period, and a portion of the photolysate was poured into the cuvette portion of the cell. Disappearance of the complex was monitored at 350 nm, after any flocculent material was allowed to settle. The solution in the cuvette was then returned to the test tube portion of the cell prior to the next photolysis period.

Techniques for the determination of quantum yields of adsorbed molecules have been documented.[18] Similar to the pro-

(14) (a) Malouf, G.; Ford, P. C. *J. Am. Chem. Soc.* **1974**, *96*, 601. (b) *Ibid.* **1977**, *99*, 7213. (c) Wrighton, M. S.; Abrahamson, H. B.; Morse, D. L. *Ibid.* **1976**, *98*, 4105. (d) Abrahamson, H. B.; Wrighton, M. S. *Inorg. Chem.* **1978**, *17*, 3385. (e) Giordano, P. J.; Wrighton, M. S. *Ibid.* **1977**, *16*, 160. (f) Figard, J. E.; Petersen, J. D. *Ibid.* **1978**, *17*, 1059.

(15) Young, G. J. *J. Colloid Sci.* **1958**, *13*, p. 73.
(16) Bobbitt, J. M.; Schwarting, A. E.; Gritter, R. J. "Introduction to Chromatography"; Van Nostrand: New York, 1968; p. 104.
(17) Schlesener, C. J.; Ellis, A. B. *Organometallics* **1983**, *2*, 529.

cedure used to obtain electronic spectra, 5 mL of a 1.0–1.5 mM solution of the ATCr complex was stirred with 1.46 g of silica gel to form a slurry; the solvent was then evaporated under a stream of N_2. This sample was transferred to the test tube portion of the cell, and 7 mL of cyclohexane was added to it. The slurry was then placed in the path of the laser beam for short intervals of time with a maximum conversion of 15%. A fresh slurry was used for each photolysis period. The optically dense slurries were stirred by a cyclohexane-saturated N_2 purge as described above. After each photolysis period, the purge was disconnected and a portion of the slurry was poured into the cuvette portion of the cell. The cell was gently shaken for several minutes to ensure dense, reproducible packing of the silica gel in the optical path. Disappearance of the complex was monitored at 350 nm.

For both solutions and slurries, disappearance quantum yields, ϕ_d, were calculated by using a computer program.[2] Good linearity

in the data were found including extrapolation to zero conversion at zero time. Values of ϕ_d are based on at least three complete sets of data with five data points per set. The quantum yields are uncorrected for reflective and scattering losses; reproducibility was ±15%.

(18) Fassler, D.; Gade, R.; Guenther, W. *J. Photochem.* 1980, *13*, 49 and references therein.

Cleavage of Acylcobalt Carbonyl with Hydridocobalt Tetracarbonyl

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The reaction $CH_3(CH_2)_4COCo(CO)_4 + HCo(CO)_4 \rightarrow CH_3(CH_2)_4CHO + Co_2(CO)_8$ proceeds with second-order kinetics (first order in each reactant), $k_2 = 1 \times 10^{-2}$ M^{-1} s^{-1} at 23 °C. Contrary to earlier reports we find that the rate is independent of the partial pressure of CO. Less viscous solvents give somewhat faster rates. The kinetic isotope effect, $k[HCo(CO)_4]/k[DCo(CO)_4]$, is equal to 3.6. Although no direct evidence has been secured, our results suggest that the mechanism of the reaction involves fast reversible homolysis of the acyl compound followed by hydrogen abstraction from HCo(CO)$_4$ in the rate-controlling step. The reaction of HCo(CO)$_4$ with RCOCo(CO)$_4$ is slower than its reaction with Ph$_2$C=CH$_2$ but faster than its reaction with 1-pentene. The kinetic data strongly suggest that the slow step in stoichiometric hydroformylation is very likely the initial π complexation of olefin with HCo(CO)$_3$ rather than the final cleavage step of the acyl complex to aldehyde.
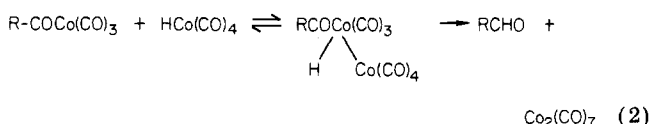
Introduction

The mechanism of the cleavage of acylcobalt carbonyls with HCo(CO)$_4$ (eq 1) remains unresolved despite more

$$RCOCo(CO)_n + HCo(CO)_4 \rightarrow$$
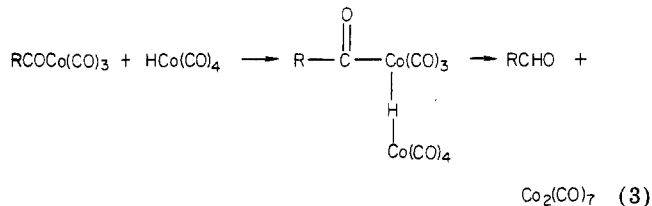$$RCHO + Co_2(CO)_{4+n} \quad (n = 3 \text{ or } 4) \quad (1)$$
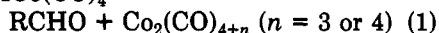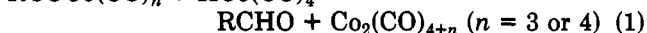
than 40 years of investigations of the oxo process in which this reaction is assumed to play a major role. Equation 1 is crucially important in the stoichiometric reaction[1] and is thought to also play a role in the catalytic process.[2]

The usual proposal for the mechanism of reaction 1 involves oxidative addition followed by reductive elimination. Because acylcobalt tetracarbonyl and hydridocobalt tetracarbonyl are both coordinatively saturated, it is assumed that in the cleavage reaction one of them is a tricarbonyl species and that the most likely candidate is the acyl compound. The reaction has thus been written as in eq 2[3] or a somewhat similar formulation in which the

$$R\text{-}COCo(CO)_3 + HCo(CO)_4 \rightleftharpoons RCOCo(CO)_3 \longrightarrow RCHO +$$
$$/ \backslash$$
$$H \quad Co(CO)_4$$
$$Co_2(CO)_7 \quad (2)$$

hydrogen is not completely transferred to the acyl complex in the transition state.[4a,b] More recently the generalized process of which eq 2 is an example has been called a binuclear reductive elimination.[5] The process has also been visualized as occurring by hydrogen transfer from the metal hydride to the coordinatively unsaturated second metal center, without metal–metal bond assistance, followed by reductive elimination.[5] In the example under discussion this would be represented by eq 3 without specifying

$$RCOCo(CO)_3 + HCo(CO)_4 \longrightarrow R\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}Co(CO)_3 \longrightarrow RCHO +$$
$$|$$
$$H$$
$$|$$
$$Co(CO)_4$$
$$Co_2(CO)_7 \quad (3)$$

whether the binuclear species is an intermediate or a transition state.

The principal support for the oxidative addition–reductive elimination proposal in the cobalt case is the

(1) Roos, L.; Orchin, M. *J. Org. Chem.* 1966, *31*, 3015.
(2) Alemdaroglu, N. H.; Penninger, J. L. M.; Oltay, E. *Monatsh. Chem.* 1976, *107*, 1153.

(3) Heck, R. F. *Adv. Organomet. Chem.* 1966, *4*, 243.
(4) (a) Norton, J. *Acc. Chem. Res.* 1979, *Prog.* 139 (b) Humphries, A. P., Kaesz, H. D. *Prog. Inorg. Chem.* 1979, *25*, 145. (c) Kappa, M. J.; Santi, R.; Drefenbach, S. P.; Halpern, J. *J. Am. Chem. Soc.* 1982, *104*, 619.
(5) Jones, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* 1979, *101*, 5447.