zation furnished adrenosterone **13**, identical in all respects with the natural material.

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Flash Photolysis of Chromium Hexacarbonyl in Perfluorocarbon Solvents. Observation of a Highly Reactive Chromium Pentacarbonyl

Sir:

While the important role of coordinatively unsaturated coordination compounds in reactions catalyzed by organometallic compounds is widely accepted, direct observation of these intermediates in thermally induced reactions is usually difficult. It has, however, been amply demonstrated in recent years that complexes of this type can be generated by flash photolysis of metal carbonyls.[1] For example, in cyclohexane, chromium pentacarbonyl is formed by flash photolysis of $Cr(CO)_6$, and its reactivity with various nucleophiles has been studied.[1b] Detailed spectroscopic and structural information about metal carbonyl fragments has also been gained from photolytic decomposition of metal carbonyls in low-temperature matrices.[2] Perutz and Turner have observed that the position of maximum absorption of the visible band of the chromium pentacarbonyl species, formed from $Cr(CO)_6$, depends markedly on the matrix in which it is formed (e.g., Ne, 624; CF_4, 547; Ar, 533; Xe, 492; CH_4, 489 nm), and they have interpreted this blue shift in terms of an increasing interaction of electrons of the matrix material with the vacant coordination site on the metal.[2] One might conclude from these observations that $Cr(CO)_5$ in solution should be more weakly bonded, and therefore more reactive, in perfluorocarbon solvents than in hydrocarbon solvents. In this communication we report preliminary results from a study of the laser flash photolysis of $Cr(CO)_6$ in perfluoromethylcyclohexane, which confirm the above interpretation and reveal that in C_7F_{14} chromium pentacarbonyl is extremely reactive, combining with carbon monoxide, nitrogen, cyclohexane, and $Cr(CO)_6$ with rate constants approaching those of diffusion control.

Excitation of $Cr(CO)_6$ (2.5×10^{-3} to 1.5×10^{-2} M) in argon-flushed perfluoromethylcyclohexane at room temperature using the third harmonic of a Quantel neodymium laser (353 nm; pulse duration 5 ns) produces a transient species absorbing in the visible, exhibiting a broad maximum at 620 ± 10 nm (Figure 1a). The rate of decay of this species depends upon the concentration of $Cr(CO)_6$ (Figure 2a). Concurrent with the disappearance of the 620-nm species is the appearance of a product possessing maximum absorption at ~485 nm (Figure 1b).[3] These observations may be explained most simply by the following reactions:

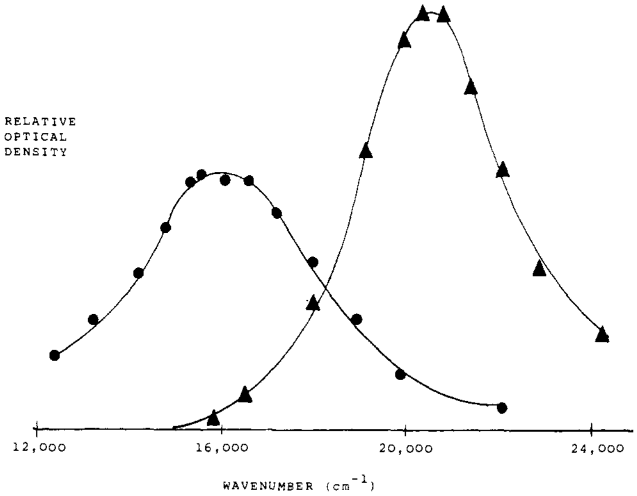

Figure 1. Transient absorption spectra recorded after laser flash photolysis of $Cr(CO)_6$ in perfluoromethylcyclohexane: (a) $Cr(CO)_5$ (●); recorded 10 ns after photolysis of 2.4×10^{-3} M $Cr(CO)_6$; (b) $Cr_2(CO)_{11}$ (▲), recorded 200 ns after photolysis of 1.2×10^{-2} M $Cr(CO)_6$.

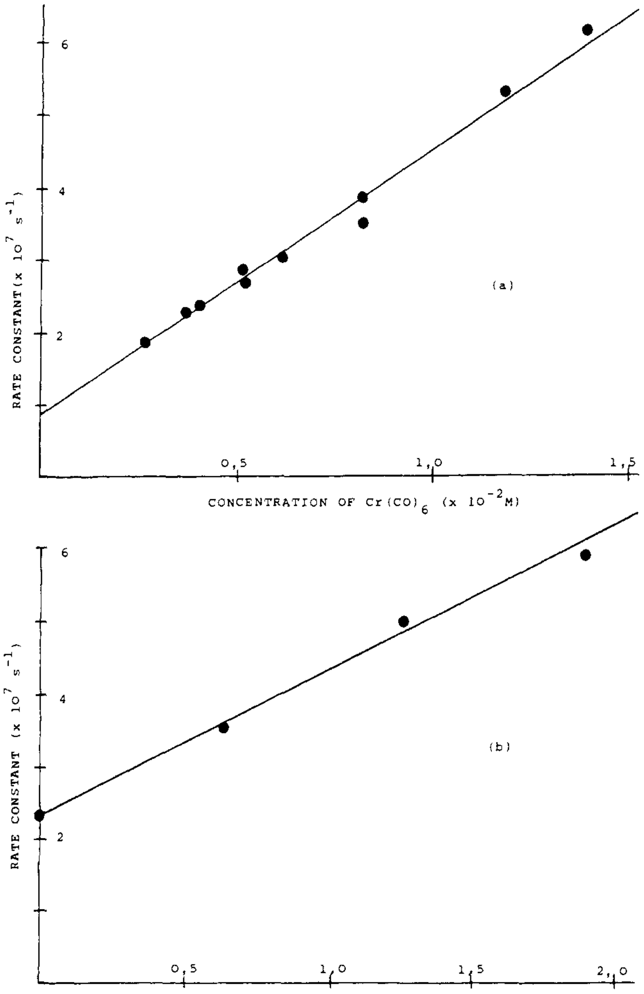

Figure 2. Dependence of the pseudo-first-order rate constant for decay (measured at λ 640 nm) of $Cr(CO)_5$ in perfluoromethylcyclohexane on (a) the concentration of $Cr(CO)_6$, (b) the concentration of cyclohexane; $[Cr(CO)_6] = 3.7 \times 10^{-3}$ M.

$$Cr(CO)_6 \xrightarrow[-CO]{h\nu\ (353\ nm)} Cr(CO)_5 \xrightarrow[k\,=\,4\,\pm\,1\,\times\,10^9\ dm^3\ mol^{-1}\ s^{-1}]{+\,Cr(CO)_6} Cr_2(CO)_{11} \qquad (1)$$

The reactivity of the pentacarbonyl suggests that it is at best only weakly coordinated to the perfluoro solvent. Indeed it is noteworthy that its wavelength of maximum absorption (620 ± 10 nm) is close to that (624 nm) reported for neon matrices,[2] where presumably it is "naked". In $Cr_2(CO)_{11}$, the coordination of the pentacarbonyl to the hexacarbonyl is presumably through a carbonyl oxygen of the latter compound.

The rate of decay of $Cr(CO)_5$ is accelerated by flushing the solution with carbon monoxide. Thus the half-life of the pentacarbonyl formed by irradiating a 2.6×10^{-3} M solution of $Cr(CO)_6$ is 13 ns when flushed with carbon monoxide compared with a half-life of 38 ns for an argon-flushed solution. Assuming that the concentration of carbon monoxide under these conditions is 1.2×10^{-2} M,[4] we may derive a rate constant of $3 \pm 1 \times 10^9$ dm^3 mol^{-1} s^{-1} for

$$Cr(CO)_5 + CO \rightarrow Cr(CO)_6 \qquad (2)$$

This rate constant is a thousand times larger than that reported for chromium pentacarbonyl in cyclohexane.[1a] The rate of decay of $Cr(CO)_5$ is also enhanced in the presence of nitrogen, presumably owing to the formation of the complex $Cr(CO)_5(N_2)$.

It was previously reported that the species assigned as chromium pentacarbonyl in cyclohexane solution (λ_{max} 503 ± 5 nm) was formed within 50 ns of the excitation of the hexacarbonyl.[1a] The present study confirms this observation and shows that in cyclohexane the pentacarbonyl complex is formed within the 5-ns excitation pulse. Further we have been able to measure the rate constant of addition of cyclohexane to $Cr(CO)_5$ in perfluoromethylcyclohexane. Thus on excitation of a solution of $Cr(CO)_6$ in C_7F_{14} containing $\sim 10^{-2}$ M cyclohexane, a rapid decay of the 620-nm species is accompanied by the formation of a species with a broad band centered at 510 ± 10 nm, a spectrum similar to that reported for $Cr(CO)_5$ in cyclohexane.[1a,b] The observed reaction appears to be the production of a cyclohexane complex of $Cr(CO)_5$:

$$Cr(CO)_5 + c\text{-}C_6H_{12} \rightarrow Cr(CO)_5(c\text{-}C_6H_{12}) \qquad (3)$$

From the dependence of the rate of decay of $Cr(CO)_5$ on the cyclohexane concentration (Figure 2b), a rate constant of $2.0 \pm 0.5 \times 10^9$ dm^3 mol^{-1} s^{-1} has been derived. The formation of this complex is presumably the reason for the appreciably slower reaction of $Cr(CO)_5$ with carbon monoxide in cyclohexane solution compared with that in C_7F_{14} and for the lack of observation of the formation of $Cr_2(CO)_{11}$ in hydrocarbon solvents. It is also probable that formation of similar hydrocarbon complexes affects the rate of reaction of catalytically important coordinatively unsaturated species.

Short-lived transients are also observed with $W(CO)_6$ and $Mo(CO)_6$, and we are currently investigating these systems, as well as determining the stability constants for $Cr_2(CO)_{11}$ and $Cr(CO)_5(C_6H_{12})$ in perfluoromethylcyclohexane.

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A Novel ^{18}O Kinetic Isotope Effect in an α-Chymotrypsin Catalyzed Transesterification

Sir:

The ability of serine proteases to catalyze the transesterification of esters and amides is well known.[1] In studying the α-chymotrypsin catalyzed ethanolysis of *p*-nitrophenyl 2-(5-*n*-propyl)furoate we have observed a novel [^{18}O]ethanol kinetic isotope effect (KIE). Shortly after initiation of the reaction the KIE is normal ($k^{16}_{app} > k^{18}_{app}$), then decreases with time to become inverse ($k^{16}_{app} < k^{18}_{app}$), and levels off at a magnitude greater than any ^{18}O KIE reported heretofore.

Reactions were started by injecting the nitrophenyl ester into a stoppered vial immersed in a constant-temperature bath, and containing a mixture of [^{16}O]- plus [^{18}O]ethanol, α-chymotrypsin, and buffer. (See legend to Figure 1 for typical concentrations. Enzyme was purchased from Worthington Biochemical Corp. and used with no further purification; [^{18}O]-ethanol was synthesized by the procedure of Sawyer[2] and the ^{18}O enrichment determined as described below; substrate ester was synthesized as described previously.[3]) As the reaction proceeded, samples were withdrawn through the rubber cap into a Hamilton syringe, and injected promptly into a Hewlett-Packard Model 5840 gas chromatograph (GC) connected to a MP5985 quadrupole mass spectrometer (MS) controlled by an MP 21 MXE data acquisition and processing system. The GC was equipped with a 6-ft glass column packed with 10% AT-1000 on 80–100 mesh Chromosorb W/AW (Johns-Manville Co.). The MS was operated to scan a small number of preselected *m/e* ratios repetitively throughout the chromatographic separation. The intensities from individual ions were then displayed as a function of time to yield chromatographic peaks at specific *m/e*, usually chosen as 46 and 48 for the parent molecular ions of [^{16}O]- and [^{18}O]ethanol and as 182 and 184 for the corresponding ions of the reaction product ethyl 2-(5-*n*-propyl)furoate. Relative ^{18}O enrichments were computed from the ratios of the peak areas, and the apparent KIE then calculated from the ratio of enrichments in alcohol and ester.

Results obtained at 4 °C are presented in Figure 1. The first point after starting the reaction shows a normal KIE. Because of the very small amount of product formed at this time, the S/N is low, and the magnitude of the KIE is uncertain; however, a normal KIE shortly after reaction initiation has been observed in more than a dozen experiments conducted at various temperatures. The KIE then decreases to a plateau value, which in this experiment was 0.85, before the reaction stops. The values of the plateau KIE were ≤0.90 for all MS-GC experiments, while the estimated standard deviations varied from 0.01 to 0.06.