

in toluene; however, quenching by two alkylated pyridinium acceptors¹⁷ in acetonitrile reveals a sharp decrease in the quenching rate in the region around -1.8 V. Quenching by α,β -unsaturated keto and aldehyde esters in acetonitrile confirms the diminished quenching rate in the region where the reduction potential of the acceptor is below -1.8 V. The functional dependence of the quenching rates upon the reduction potential of the quencher indicates that quenching is due to outer-sphere electron transfer from the excited complex to the quenching agent.¹⁸ These quencher/solvent combinations do not constitute a homologous series;¹⁸ however, the rather sharp break in quenching rates of the alkylated pyridinium acceptors suggests a rough estimate of -1.8 V vs. SCE for the reduction potential of the oxidized ground-state/excited-state couple, $\text{Ir}(\text{ppy})_3^+/*\text{Ir}(\text{ppy})_3$. This value agrees well with an estimate based upon the excited-state energy taken from emission measurements (2.5 V) and the $E_{1/2}$ value of $+0.7$ V vs. SCE for $\text{Ir}(\text{ppy})_3^+/\text{Ir}(\text{ppy})_3$ in cyclic voltammetric measurements in acetonitrile.¹⁹ The contrast of the strong reducing power of $*\text{Ir}(\text{ppy})_3$ compared to the strong oxidizing power of $*\text{Ir}(\text{bpy})_3^{3+}$ ($E^\circ(*\text{Ir}(\text{bpy})_3^{3+}/\text{Ir}(\text{bpy})_3^{2+}) > 2$ V)²⁰ illustrates the large effects of Ir-C bonding in altering the electron-transfer properties in ortho-metalated species relative to those in N-chelated complexes.

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Gas-Phase Photofragmentation of $\text{Cr}(\text{CO})_6$: Time-Resolved Infrared Spectrum and Decay Kinetics of "Naked" $\text{Cr}(\text{CO})_5$

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The photochemistry of transition-metal carbonyl complexes continues to be an area of active research with $\text{Cr}(\text{CO})_6$ receiving particularly heavy investigation.¹ In condensed media, photolysis of $\text{Cr}(\text{CO})_6$ leads to formation of $\text{Cr}(\text{CO})_5$ which weakly interacts with a matrix atom (20 K)² or solvent molecule (293 K).³⁻⁵ However, surprisingly few details are known regarding the gas-phase photofragmentation of $\text{Cr}(\text{CO})_6$. The nature of the photoproducts may in fact be sensitive to photolysis wavelengths.⁶⁻⁸

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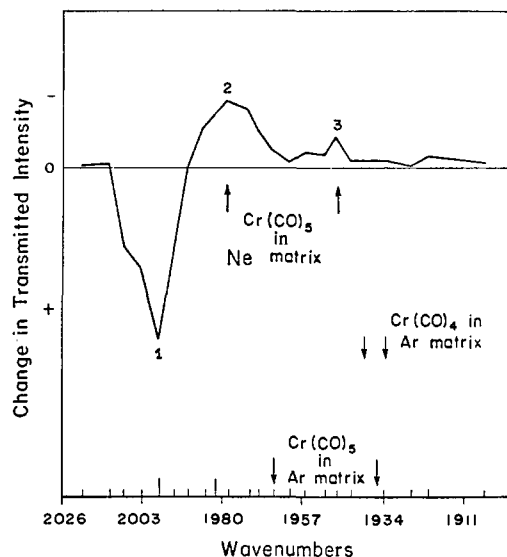


Figure 1. Time-resolved IR spectrum obtained 500 ns after XeF laser excitation ($\lambda = 351$ nm) of a mixture of ~ 30 mtorr of $\text{Cr}(\text{CO})_6$ with 0.3 torr of CO and 5 torr of Ar buffer at 20 °C. The + and - on the ordinate correspond to increased and decreased transmitted light, respectively. Feature 1 corresponds to photolyzed $\text{Cr}(\text{CO})_6$ (increase in transmitted light intensity). Features 2 and 3 are assigned to photogenerated $\text{Cr}(\text{CO})_5$ (decrease in transmitted light intensity). Absorptions of matrix-isolated $\text{Cr}(\text{CO})_5$ and $\text{Cr}(\text{CO})_4$ are displayed for comparison (see text). The tick marks on the abscissa show the CO laser lines used to construct the spectrum. The two large tick marks are the frequencies at which the kinetic measurements, displayed in Figure 2, were performed.

Recent advances in fast monitoring of photochemical reactions via infrared (IR) probes have yielded valuable information concerning the structure and kinetics of transient metal carbonyl species.^{5,8-11} Indeed, the square pyramidal structure of $\text{Cr}(\text{CO})_5$ in solution has recently been verified by fast IR spectroscopy.⁵ We wish to report here that XeF laser (351 nm) photolysis of $\text{Cr}(\text{CO})_6$ in the gas phase leads to predominant formation of "naked" $\text{Cr}(\text{CO})_5$. We also report on the structure of $\text{Cr}(\text{CO})_5$ and the rate of its reaction with CO.

The time-resolved IR apparatus used for monitoring photochemically generated metal carbonyl transients in the gas phase has been previously described.¹⁰ In this study a Questek excimer laser was used as the photolysis source and a line-tunable liquid nitrogen cooled CO laser as the IR probe. Changes in intensity of transmitted IR light were detected via a high-speed InSb detector. The output of the detector was fed to appropriate amplifiers and was subsequently signal averaged. Spectral data were obtained from the transient absorption signals for each CO laser line of interest by having a computer join points corresponding to the amplitude of the transient signal at these frequencies for a given time delay following the photolysis pulse. Kinetic data for CO recombination were obtained from transients at a given probe laser wavelength.

Figure 1 shows the IR spectrum obtained 500 ns after photolysis of a mixture of ~ 30 mtorr of $\text{Cr}(\text{CO})_6$ with 0.3 torr of CO and 5 torr of Ar buffer at 21 °C. Depletion (increase in transmitted light intensity) of $\text{Cr}(\text{CO})_6$ is evident at ca. 2000 cm^{-1} (feature 1), illustrating that net photolysis has occurred. The positive absorptions (decrease in transmitted light intensity) at ca. 1980

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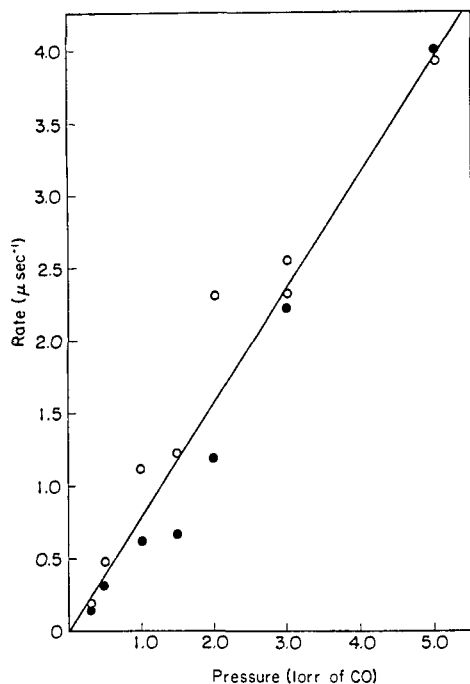


Figure 2. Plot of the rate of reaction of $\text{Cr}(\text{CO})_5$ (●) and the rate of reformation of $\text{Cr}(\text{CO})_6$ (○) as a function of added CO. Parent pressure and buffer gas pressure were the same as in Figure 1. Both give the same rate within experimental error, and thus the slope of the data points is indicated as a single line.

and 1948 cm^{-1} (features 2 and 3), which grow in to a near maximum amplitude 500 ns after excitation, are assigned to the e and low-frequency a_1 vibrations of $\text{Cr}(\text{CO})_5$. The remaining high-frequency CO stretching vibration is not within the range of our probe laser. The existence of two $\text{Cr}(\text{CO})_5$ absorptions, their approximate relative intensity ratio, and their correlation within experimental error to absorptions observed for $\text{Cr}(\text{CO})_5$ in a neon matrix, where a significant matrix shift vs. the gas phase is not expected, imply that $\text{Cr}(\text{CO})_5$ in the gas phase has the same square-pyramidal C_{4v} geometry as assigned to matrix isolated $\text{Cr}(\text{CO})_5$.

It is evident from Figure 1 that the intensity of the 1980-cm^{-1} absorption (feature 2) is approximately $2/3$ that of the 2000-cm^{-1} band (feature 1). This is in accord with expectations based on simple intensity arguments, with the implicit assumption that the major product of $\text{Cr}(\text{CO})_6$ photolysis is $\text{Cr}(\text{CO})_5$. The large relative yield of $\text{Cr}(\text{CO})_5$ at this photolysis wavelength is consistent with the observations of Breckenridge and Sinai.⁶ The weaker features in Figure 1 (not labeled) can most likely be assigned to small amounts of $\text{Cr}(\text{CO})_4$. The features attributed to the gas-phase absorptions of both $\text{Cr}(\text{CO})_5$ and $\text{Cr}(\text{CO})_4$ are, as expected, blue-shifted by similar amounts relative to their position in an argon matrix.^{12,13}

Existing data imply that the energy of a 351-nm photon (82 kcal mol^{-1}) is just sufficient to remove two CO groups.¹⁴ This could account for the low yield of products other than $\text{Cr}(\text{CO})_5$ at this wavelength. Experiments, currently under way, show that fragments other than $\text{Cr}(\text{CO})_5$ can be generated by increasing the energy of the incident photon.¹⁵ This is consistent with chemical trapping studies.⁷

The identification of $\text{Cr}(\text{CO})_5$ was confirmed by correlating its rate of decay (features 2 and 3) with the rate of reappearance of $\text{Cr}(\text{CO})_6$ (feature 1) as a function of added CO. Figure 2 shows that the rate for both processes is concurrent within experimental error. From the slopes of the lines the rate constant for reaction

of $\text{Cr}(\text{CO})_5$ with CO was determined as $(1.5 \pm 0.3) \times 10^{13}\text{ cm}^3\text{ mol}^{-1}\text{ s}^{-1}$ ($800 \pm 150\text{ ms}^{-1}\text{ torr}^{-1}$). (The error brackets represent the 95% confidence values.) Moreover, the same rate constant was obtained under a variety of conditions, i.e., with and without added He or Ar, both in a flow cell and in a static cell. This implies that any complex formation with added rare gas is minimal and certainly does not affect the recombination kinetics.

In solution $\text{Cr}(\text{CO})_5$ is known to be highly reactive.³⁻⁵ We note that in the gas phase the rate constant for reaction of $\text{Cr}(\text{CO})_5$ with CO is more than 2 orders of magnitude higher than the corresponding rate for reaction of $\text{Fe}(\text{CO})_4$ with CO ($(3.5 \pm 0.9) \times 10^{10}\text{ cm}^3\text{ mol}^{-1}\text{ s}^{-1}$).¹⁰ This difference can be, at least in part, rationalized in terms of $\text{Fe}(\text{CO})_4$ having a triplet ground state,¹⁶ whereas the $\text{Cr}(\text{CO})_5$ ground state is almost certainly a singlet.¹⁷ Steric conditions may also play a role in the large difference in rates.

Using relative band-intensity arguments, kinetic evidence, and agreement with absorption frequencies of matrix-isolated $\text{Cr}(\text{CO})_5$, we have assigned the infrared absorptions observed subsequent to 351-nm photolysis of $\text{Cr}(\text{CO})_6$ to the pentacarbonylchromium fragment. These experiments have also essentially confirmed that the structure of "naked" $\text{Cr}(\text{CO})_5$ is square pyramidal, a result consistent with simple molecular orbital calculations.¹⁷

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Isotopic Multiplets in the ^{13}C NMR Spectra of Partially Deuterated Ammonium Derivatives. Spectral Effects of Isotopic Asymmetry at a Nitrogen Atom[†]

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Concurrent communications from two laboratories have recently demonstrated that the isotopic multiplets observed in the proton-decoupled ^{13}C NMR spectra of carbohydrates with partially deuterated hydroxyls can be very helpful in spectral assignments^{1,2} and molecular structure determinations.³ These multiplets are due to upfield deuterium isotope effects on the ^{13}C chemical shifts⁴ and can be observed when hydrogen exchange is slow relative to the magnitude of the isotope effect. Deuterium isotope effects have also been reported for amine, amide, and amino acid systems.⁵⁻⁹ The slow exchange of amide hydrogens has led to the

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