

(Table I).¹⁴ The isotropic tumbling times defined by the ³¹P experiments show the same sharp temperature dependence.⁷

Inversion recovery experiments were also performed at 80, 65, and 50 °C. The recovery curves were linear on a log plot to a good approximation except at 50 °C where a smaller signal-to-noise ratio leads to a higher uncertainty. The T_1 's from the log plots vary little from 80 to 50 °C (Table I), whereas the difference in line shapes over this temperature range is very significant. The data suggest that the T_1 's are dominated by a different motion from that which dominates line shapes and that this motion is less sensitive to the degree of base stacking. In the limit of relatively unrestricted and fast internal motion an isotropic model can be used to analyze T_1 data. From a value of $4.1 \times 10^7 \text{ s}^{-1}$ for the quadrupole coupling constant¹⁵ and the T_1 data at 80 °C, a correlation time of 0.06 ns is predicted. While this is somewhat shorter than the time assigned to internal motions from ³¹P data, both ³¹P and ¹⁷O data suggest that a motional model with two time scales is necessary. Quantitative differences in time scales may reflect departure of real motions from assumed models for these motions.

Even without further analysis, our experiments suggest that nucleic acid dynamics can be effectively studied with ¹⁷O NMR spectroscopy: the spectra are easily obtained and the relaxation data are readily interpreted by virtue of the dominating quadrupolar relaxation mechanism for ¹⁷O. We anticipate that more detailed analyses of relaxation data will be facilitated by both the examination of sequence-defined oligonucleotides and improvements in instrument design that allow more accurate measurements of line shapes.

Acknowledgment. This research was supported by grants (GM-30562 to J.A.G. and GM-19035 to J.H.P.) from the National Institutes of Health. The high-field NMR spectrometer used in this research is supported in part by a grant from the National Science Foundation (CHE-791620).

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Photofragmentation Dynamics of Cr(CO)₆ in the Gas Phase

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Received June 20, 1983

The photochemistry of Cr(CO)₆ has been extensively studied.¹⁻⁴ Nevertheless, important questions remain concerning the role of excited states and the timing of the various ligand-dissociation steps. We have used a method based on time-resolved CO laser absorption spectroscopy^{5,6} to address these questions.

In our experiments, a 1-m absorption cell is filled with 1-70 mtorr of Cr(CO)₆ at 300 K. The sample is photoactivated with a KrF* laser (249 nm, 15 ns, <0.5 mJ/cm²). A continuous-wave, grating-tuned CO laser⁷ is directed through the cell coaxially with the KrF* beam and then onto an InSb detector (rise time ≤ 100

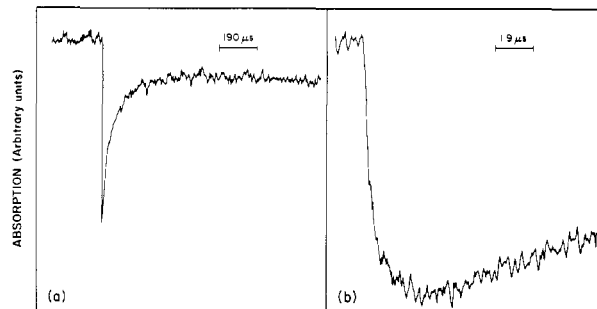


Figure 1. (a) Transient CO laser absorption [$P_{12}(1,0)$] produced by irradiating 49 mtorr of Cr(CO)₆ at 249 nm. (b) Rising portion of the CO laser absorption curve; Cr(CO)₆ pressure is 61 mtorr.

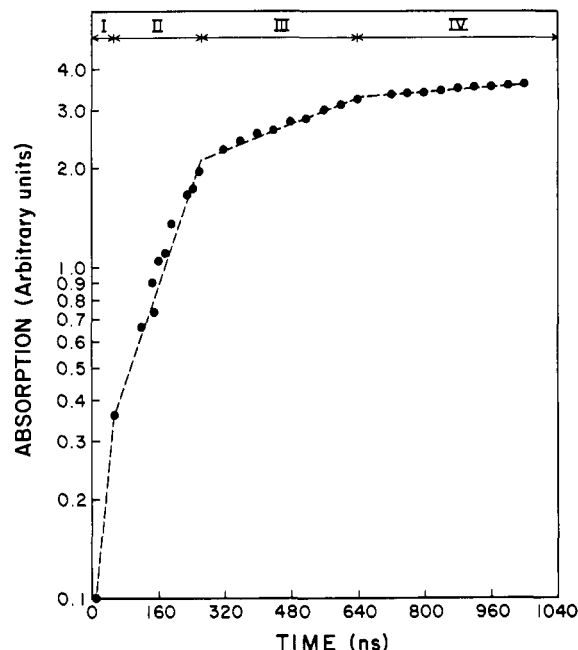


Figure 2. Semilog plot of data from Figure 1b. I-IV denote absorption regions described in text.

ns). Photogenerated CO produces a transient decrease in CO laser intensity reaching the InSb detector, and the resulting signal change is recorded. A typical transient absorption is shown in Figure 1a. These data provide information on the rates of CO formation, vibrational relaxation, and metal carbonyl-CO recombination. It is apparent that all of the photogenerated CO is not consumed by recombination on a millisecond time scale, i.e., some of the unsaturated metal carbonyls irreversibly recombine with one another or with Cr(CO)₆. This will be discussed subsequently.⁸ Here we discuss the portion of Figure 1a where CO absorption grows in, which provides information on the dynamics of CO generation. See Figure 1b, where CO absorption at early times is displayed with higher resolution. These data were obtained by observing CO($v = 0$) with the $P_{12}(1,0)$ CO laser line, but qualitatively similar results are obtained if CO($v = 1$) is observed with the $P_{10}(2,1)$ CO laser line. A comparison of absorption amplitudes using these two laser lines indicates that $[\text{CO}(v = 0)]/[\text{CO}(v \geq 1)] \approx 10$. The data shown in Figure 1b cannot be fit by a single exponential and, as shown in Figure 2 and subsequent pressure-dependence studies, consist of at least four components (I-IV): I, a region of rise time < 100 ns, independent of pressure, constituting ca. 20% of the total absorption amplitude; II, a region where the rise time is pressure dependent with a CO appearance rate⁹ $k_{II} \approx 7 \times 10^6 \text{ s}^{-1}$ at 26 mtorr, corresponding

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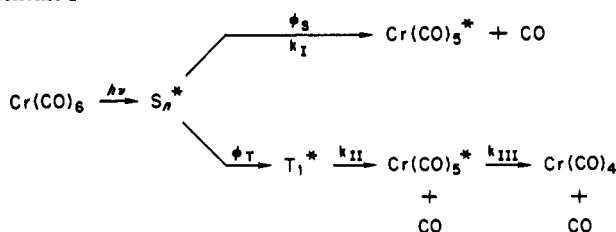
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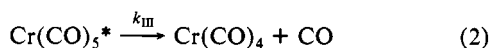
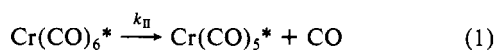
(9) The rate constants were determined from a least-squares fit to the data in the indicated region.

Scheme I



to ca. 36% of the total absorption amplitude at low pressure; III, a region where the rise time is more strongly pressure dependent than in II with a CO appearance rate⁹ $k_{\text{III}} \approx 2 \times 10^6 \text{ s}^{-1}$ at 26 mtorr, corresponding to ca. 35% of the total absorption amplitude at low pressure; IV, a region where $\text{CO}(v=0)$ is produced by collisional relaxation of $\text{CO}(v \geq 1)$ as determined by control experiments and pressure-dependence studies using argon buffer gas. The contribution from IV represents $\leq 9\%$ of the total absorption amplitude. In Figure 2, the slope for I is pressure independent while the slopes for II-IV each have a different pressure dependence. This provides good evidence that CO formation is occurring as a result of at least four processes. Neither II or III can be due to rotational relaxation of nascent CO, since in both cases, the observed rate constants decrease with increasing pressure. The processes associated with I-III can occur in the absence of collisions since they are observed even at $p[\text{Cr}(\text{CO})_6] < 5$ mtorr where the time between collisions is ≥ 10 μs .

If photoexcitation of $\text{Cr}(\text{CO})_6$ at 249 nm were followed by rapid internal conversion to yield the vibrationally hot ground state with unit efficiency, then the yield of CO must remain constant or decrease over the sequence I-III (Figure 2). This is clearly not the case. Moreover, RRKM estimates of the decomposition rates^{10,11} for $\text{Cr}(\text{CO})_n^*$ ($n = 5, 6$) in the ground state are too fast (by ca. 10^4) to be consistent with the observed decarbonylation rates in regions II and III. Thus, most of the CO formed in our experiments must come from a relatively long-lived excited electronic state (or states) of $\text{Cr}(\text{CO})_6$, e.g., a low-lying triplet state.¹² By contrast, the CO in region I is formed from a state whose lifetime is < 100 ns. Pressure-dependence studies using pure $\text{Cr}(\text{CO})_6$ and $\text{Cr}(\text{CO})_6/\text{argon}$ mixtures demonstrate that under all conditions $k_{\text{III}} < k_{\text{II}}$ and that the yield (absorption amplitude) associated with region III is less than or equal to that for II. This suggests the sequential nature of the associated decarbonylation steps, i.e.,



Thus, the yield for II is a measure of the efficiency, ϕ_{T} , with which the $\text{Cr}(\text{CO})_6$ state initially prepared at 249 nm, S_n^* , decays to the long-lived triplet state, T_1^* . Similarly, the yield for I is a measure of the efficiency, ϕ_{S} , of the detector-limited decarbonylation, which likely results from the rapid predissociation of S_n^* (or its internal conversion to the ground electronic state). Our data demonstrate that $\phi_{\text{S}} \leq 0.36$ and $\phi_{\text{T}} \leq 0.64$. With increasing pressure, vibrational energy is removed from T_1^* via collisions, so that the decarbonylation rates of this species and the subsequently generated fragments decrease. The model proposed is summarized in Scheme I. It is possible that the process k_{I} forms $\text{Cr}(\text{CO})_5^*$ with sufficient internal energy to decarbonylate further within our 100-ns detector rise time. In this case, the value determined for ϕ_{S} is an upper limit and that for ϕ_{T} is a lower limit. The mechanistic model suggested here is not unique and will undoubtedly be refined as further data become available. It is,

nevertheless, the simplest model consistent with our observations and the findings of Yardley and co-workers,⁴ who report that $\text{Cr}(\text{CO})_4$ is the species formed in greatest abundance upon the 249-nm photolysis of $\text{Cr}(\text{CO})_6$ vapor.

In summary, CO laser absorption spectroscopy has been used to study the dissociation dynamics of $\text{Cr}(\text{CO})_6$ following photoactivation. Our results suggest that the excited state prepared at 249 nm yields CO both by rapid predissociation, with an efficiency $\phi_{\text{S}} \leq 0.36$, and by intersystem crossing to a long-lived triplet, with an efficiency $\phi_{\text{T}} \geq 0.64$. The triplet state thus formed undergoes serial decarbonylation yielding $\text{Cr}(\text{CO})_5$ and $\text{Cr}(\text{CO})_4$.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. We are grateful to Dr. Gregory Smith and Karen Lewis of SRI, International, for communicating the results from their laser pyrolysis studies of $\text{Cr}(\text{CO})_6$ to us prior to publication.

Registry No. $\text{Cr}(\text{CO})_6$, 13007-92-6; $\text{Cr}(\text{CO})_5$, 26319-33-5; $\text{Cr}(\text{CO})_4$, 56110-59-9; CO, 630-08-0.

Evidence for Rapid Pseudorotation in Triphenylcyclopropenyl Anion

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Received June 13, 1983

The Jahn-Teller theorem¹ predicts that the lowest singlet state ($^1E'$) of a symmetrically substituted cyclopropenyl anion will show first-order instability to C-C bond-length distortions that lower the symmetry from D_{3h} . Nevertheless, time-averaged equivalence of the three ring carbon atoms can be restored by pseudorotation.² Ab initio calculations have been used to locate the stationary points on the lowest energy pseudorotation pathway for the planar cyclopropenyl anion³ and for the isoelectronic $(\text{NH})_3^{2+}$.⁴ In this Communication we present evidence that pseudorotation in triphenylcyclopropenyl anion is faster than proton capture.

Previous attempts to probe the symmetry of cyclopropenyl anions with three identical substituents⁵ have been frustrated by the high pK_a of even triphenylcyclopropene.^{6,7} When, in order to increase the acidity, the cyclopropene ring is substituted with groups that are more electron withdrawing than phenyl, Michael addition of the base to the strained-ring double bond occurs.⁸ We sought to overcome these problems by using fluorodesilylation for carbanion generation.^{9,10}

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