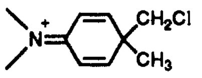
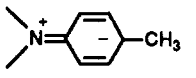


I



II

$NC_6H_4Me_2)(CO)_2(\mu\text{-dppm})_2]^+I^-$ (**4**) (eq 2). The spectral data[8]

$$\mathbf{1/2}\ (R = p\text{-}MeC_6H_4) + MeI \rightarrow [Rh_2(\mu\text{-}NC_6H_4Me_2)(CO)_2(\mu\text{-dppm})_2]^+I^- \quad (2)$$

for **4** are similar to those for **3**. Treating **1/2** (R = Ph) with MeI gives a product analogous to **4**,[9] but at least one other, as yet unidentified, product is also formed.

These results suggest a high degree of charge density in the imido and/or amido aryl ring. The formal positive charge on the nitrogen of the amido tautomer would not be expected to lead to such high charge density. On the other hand, the availability of the nitrogen lone pair in the imido tautomer makes possible the contribution of resonance form II (see above), which could lead to the observed reactivity.[10] However, the major resonance form should have most of the charge density on the nitrogen. This is consistent with the observed nitrogen protonation of **1/2** by acidic species.[1,2b,11] Why do we observe here CH_2Cl^+ and Me^+ addition to the ring and not to the nitrogen? The answer may be, at least partly, steric inaccessibility. A "space-filling" PLUTO diagram of **3** (Figure 1b) shows the derivatized imido ligand in a "pocket" formed by the dppm ligands. The structure of **3** is common to dppm A-frame complexes, and the parent imido complex is expected to have a similar structure with restricted access to the nitrogen. Consistent with steric control, we find no evidence of ring addition in the reaction of the analogous dmpm complex [dmpm = bis(dimethylphosphino)methane] with CH_2Cl_2.[12] The lower steric demand of the dmpm ligand may allow reaction to occur at the nitrogen.

Another consideration for these electron-rich species is electron transfer.[13] A single-electron-transfer (SET) mechanism[14] for the ring addition is a definite possibility. We have treated **1/2** with various oxidizing agents (I_2, Br_2, O_2) in an attempt to test for this. NMR evidence does suggest the formation of a ring addition product in the O_2 reaction. In addition, we have found that **1/2** (R = $p\text{-}MeC_6H_4$) undergoes a chemically reversible (cyclic voltammetric time scale) oxidation in THF at very low potentials (−0.6 V vs SCE). These and furthr results will be presented fully in a forthcoming full paper.

Acknowledgment. We thank ARCO Chemical Company, the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy (DE-FG02-88Er13880), and Johnson Matthey (loan of $RhCl_3$) for support of this work and Dr. C. Barnes for assistance with the X-ray work. The National Science Foundation provided a portion of the funds for the purchase of the X-ray (CHE-7820347) and NMR (PCM-8115599) equipment.

Supplementary Material Available: Table of fractional coordinates and thermal parameters (non-hydrogen) for **3** (2 pages). Ordering information is given on any current masthead page.

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[8] Data for $[Rh_2(\mu\text{-}NC_6H_4Me_2)(CO)_2(\mu\text{-dppm})_2]^+I^-$ (**4**): IR (CH_2Cl_2) 1988 (m), 1973 cm^{-1} (s); ^1H NMR (300 MHz, CD_2Cl_2) δ 7.2–7.5 (m, 40 H, Ph), 5.47 and 5.40 (2 d, J_{HH} = 10.4 Hz, 2 × 2 H, C_6H_4), 3.01 (m, 4 H, PCH_2P), 0.92 (s, 6 H, CH_3); ^{31}P NMR (36 MHz, CD_2Cl_2) δ 22.1 (dm, J^x_{RhP} = 137.9 Hz).

[9] On the basis of the observation of an A_2B_2 pattern and a high-field methyl group similar to that of **3** and **4**.

[10] An equivalent but opposite resonance form has been proposed for the addition of H^- to the para position of the tolylcarbyne ring of $[Os(CR)(CO)_2(PPh_3)_2]^+$ (R = $p\text{-}MeC_6H_4$). The resulting vinylidene complex is closely related to our product **3**: Roper, W. R.; Waters, J. M.; Wright, L. J.; Van Meurs, F. *J. Organomet. Chem.* **1980**, *201*, C27–C30.

[11] Proton attack on the dppm-H ligand of the amido tautomer is also possible.

[12] Work in progress.

[13] An oxidatively induced coupling of two Pt aryl amido complexes at para and ortho positions that may be related to our reactions has been reported: O'Sullivan, R. D.; Parkins, A. W.; Alcock, N. W. *J. Chem. Soc., Dalton Trans.* **1986**, 571–575.

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The Role of Vibrational Energy in the Ultrafast Photodissociation of $Cr(CO)_6$

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In this paper, an investigation is presented of the photodissociation of $Cr(CO)_6$ and the subsequent reaction dynamics of the photoproducts using picosecond transient Raman spectroscopy. Contrary to the common perception that nonequilibrium vibrational energy does not contribute to condensed-phase reactions, it is found instead that the appearance time of the thermally equilibrated $Cr(CO)_5$ photoproduct is rate limited by vibrational energy decay. This result has important implications to recent ultrafast studies of the photochemistry of $Cr(CO)_6$. Transient absorption experiments have discovered[1-3] that photoexcitation of $Cr(CO)_6$ results in the formation of solvated $Cr(CO)_5$ which appears in a time of ≤0.8 ps in hydrocarbon solvents. However, in contrast to these results, a controversy now exists due to the experiments of Spears et al.[4,5] where transient picosecond infrared data has been interpreted to show that solvated $Cr(CO)_5$ appears to be produced by several different mechanisms on a much slower time scale. In contrast to this interpretation, time-dependent shifts in the absorption maximum of solvated $Cr(CO)_5$ have been attributed[2,6] to vibrational energy relaxation which occurs[6] in 17 ps.

The results reported in this paper remove the present controversy by directly probing the vibrational coordinates of the photoproducts using transient Raman spectroscopy. The experimental apparatus has been previously described in detail.[7-10] Figure 1 shows the picosecond transient Raman spectra obtained at various optical delays for 266-nm excitation of $Cr(CO)_6$ in cyclohexane. Two 5-ps pulses at 266 nm are used in this experiment. The first pulse photodissociates $Cr(CO)_6$, and the second probes the resonance Raman spectrum of $Cr(CO)_5$. The advantage of detecting resonance Raman scattering at this wavelength is that the ultraviolet absorption band of $Cr(CO)_5$ is very strong[14] ($\epsilon = 3 \times 10^4$ dm^3 mol^{-1} cm^{-1} at 240 nm) and relatively insensitive to solvent interactions. The spectra contain only pure transient Raman bands after removal of solvent and ground-state $Cr(CO)_6$ bands using a spectrum differencing technique. This was achieved by alternately exciting the sample with a single interrogation laser pulse or a double pump–probe laser pulse sequence. The pure transient spectrum shown in Figure 1 is obtained by subtracting the one-pulse background spectrum from that obtained in the double-pulse sequence.

Comparing frames A–D in Figure 1, it is readily apparent that a single transient appears with a time scale of roughly 100 ps. The metal–CO stretch at 381 cm^{-1} and the CO vibration at 1935

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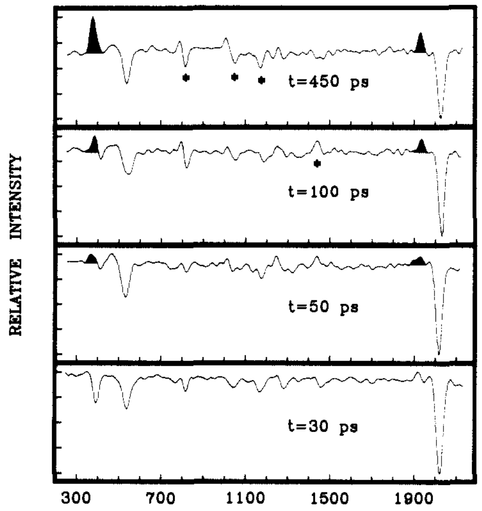

Figure 1. Pure transient picosecond Stokes Raman spectrum in cyclohexane obtained by two-pulse pump and probe at 266 nm as described in the text. Time delay between pump and probe lasers is given separately in each frame. The colored-in bands are those assigned to solvent-coordinated $Cr(CO)_5$. Asterisks are used to denote noise due to Raman bands of the solvent molecules which have been subtracted out of each spectrum. Laser intensity was 20 μJ/pulse at 2 kHz in a 0.2-mm beam waist. This laser intensity is 2 times less than that used in the previous transient infrared experiments.[4,5] Concentration is 10 mM. Frequency is in units of cm^{-1}.

cm^{-1} indicate that the transient is a metal carbonyl complex, which is assigned to $Cr(CO)_5$. The bands marked with asterisks are the result of noise generated by the spectrum differencing technique at the frequencies of the cyclohexane solvent bands. The negative peaks are ground-state $Cr(CO)_6$ bands which appear in the transient spectrum as a result of population bleaching. The ground-state 383-cm^{-1} metal–CO stretch of $Cr(CO)_6$ appears as a bleach in the 30-ps spectrum and gradually fills in at later times due to the growth of the $Cr(CO)_5$ transient band at 381 cm^{-1}.

The dynamics of vibrational cooling can be investigated by comparing the Stokes and anti-Stokes band intensities. Figure 2 illustrates the *transient* anti-Stokes spectrum in the region of the 381-cm^{-1} band assigned to $Cr(CO)_5$. The results indicate that the anti-Stokes spectrum from the hot vibrational state decays in 100 ps. The observation that the anti-Stokes and Stokes spectra have complementary dynamics is consistent with vibrational relaxation. The appearance of thermally equilibrated $Cr(CO)_5$ is therefore believed to represent the time required for the photoproduct to approach thermal equilibrium with the solvent. This conclusion clearly demonstrates the importance of nonequilibrium vibrational energy in condensed-phase photochemistry and provides an alternative explanation for the dynamics observed in the transient infrared[4,5] experiments.

It is interesting to note that the time scale we observe for complete vibrational relaxation is approximately the same as that observed[11] for the CO stretching vibration in $Cr(CO)_6$. In that experiment, a relaxation time of 145 ± 25 ps was observed in *n*-hexane. Similar rates would be expected in these two experiments if the latter dynamics represent the time required for energy randomization followed by vibrational relaxation through the entire manifold of vibrational levels. There is no direct way to compare our results to the faster dynamics attributed to vibrational decay in the transient absorption[2,6] experiments. It is likely that the latter results represent initial decay from upper vibrational levels which are difficult to characterize by using electronic absorption spectroscopy.

In summary, results are presented that demonstrate the importance of vibrational energy in the photodissociation of $Cr(CO)_6$. A single Stokes transient is observed to appear at a rate similar to the decay rate of a species with a vibrationally hot anti-Stokes spectrum. The probe wavelength (266 nm) should[14] be equally sensitive to detection of both naked $Cr(CO)_5$ and $Cr(CO)_5{\cdot}C_6H_{12}$. Even so, we do not find a thermally equilibrated precursor to the final product. This suggests that one of the following two reaction schemes[15] is operative. Here # indicates nonthermal vibrational energy and ·S solvent coordination.

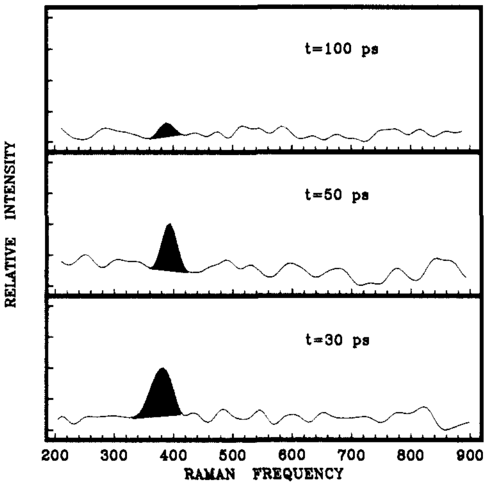

Figure 2. Transient anti-Stokes Raman spectrum obtained under similar conditions to those given in Figure 1. Time delay between pump and probe pulses is given separately in each frame. Ground-state bands have been subtracted out of the spectrum as described in the text. Spectra are normalized to the intensity of the ground-state chromium band at 532 cm^{-1} in the unsubtracted spectrum. Frequency is in units of cm^{-1}.

$$Cr(CO)_5\# \xrightarrow{100\ ps} Cr(CO)_5 \xrightarrow{fast} Cr(CO)_5{\cdot}S \qquad (1)$$

$$Cr(CO)_5\# \xrightarrow{fast} Cr(CO)_5\#{\cdot}S \xrightarrow{100ps} Cr(CO)_5{\cdot}S \qquad (2)$$

In both mechanisms, vibrational relaxation is the rate-limiting step and is found to be remarkably long, requiring over 100 ps for complete thermalization.

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(15) The anti-Stokes and Stokes vibrational frequencies for the transient species are identical and therefore suggest that both can be assigned to the solvated pentacarbonyl indicating that eq 2 is correct. However, we do not know how much solvent coordination will shift the Raman frequencies and cannot rule out eq 1.

Identification of a Unique Glutathione Conjugate of Trichloroacrolein Using Heteronuclear Multiple Quantum Coherence ^{13}C Nuclear Magnetic Resonance Spectroscopy

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The proton-detected heteronuclear multiple quantum coherence (HMQC) NMR experiment is a unique spectroscopic technique that permits the assignment of proton–heteroatom connectivity in a variety of nuclear environments.[1] Proton-detected HMQC methods, typically used for two-dimensional applications,[2] provide significant increases in sensitivity over conventional ^{13}C- and ^{15}N-detected experiments. We describe here a one-dimensional application of the proton-detected HMQC experiment for the assignment of proton–carbon connectivity in a xenobiotic animal metabolite. This method offers a powerful approach to metabolite

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