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Dissociation and Recombination Dynamics of the Complexes $[(\eta^5\text{-}C_5R_5)Cr(CO)_3]_2$ (R = H, Me)

Qin Yao, Andreja Bakac,* and James H. Espenson*

Ames Laboratory and Department of Chemistry, Iowa State University, Ames, Iowa 50011

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Summary: The kinetics of the thermal dissociation and subsequent recombination reactions of $[(\eta^5\text{-}C_5R_5)Cr(CO)_3]_2$ *and* $(\eta^5\text{-}C_5R_5)Cr(CO)_3$ *(R = H, Me) in solution have been investigated. The rapidly established dimer–monomer equilibrium was perturbed photochemically. The Cr–Cr bond efficiently cleaves in the laser flash to yield more of the 17-electron radicals* $(\eta^5\text{-}C_5R_5)Cr(CO)_3$*, which partially dimerize. The dissociation and recombination rate constants are* $k_1 = (1.2 \pm 0.1) \times 10^5$ s^{-1} *and* $k_{-1} = (2.7 \pm 0.2) \times 10^8$ L mol^{-1} s^{-1} *for* $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2$ *and* $k_1 = (5.6 \pm 0.5) \times 10^5$ s^{-1} *and* $k_{-1} = (7.0 \pm 0.6) \times 10^6$ L mol^{-1} s^{-1} *for* $[(\eta^5\text{-}C_5Me_5)Cr(CO)_3]_2$ *at 23 °C in acetonitrile. Very similar values were also found in tetrahydrofuran and toluene. The strength of the metal–metal bond is reflected in both forward and reverse rate constants not only for these complexes but also for the tungsten and molybdenum analogues.*

Introduction. In recent years, the chemistry of the metal–metal-bonded complexes $[(\eta^5\text{-}C_5R_5)Cr(CO)_3]_2$ (R = H, Me) has received considerable attention,[1–6] owing in part to their high chemical reactivity in solution. One issue of interest for these species is the extent of metal–metal interactions. The X-ray crystal structures reveal that the Cr–Cr bond lengths in these complexes are unusually long.[7,8] As a result, the electronically unsaturated, 17-electron monomers $(\eta^5\text{-}C_5R_5)Cr(CO)_3$ exist in equilibrium with the corresponding diamagnetic, closed-shell dimers in solution at room temperature as shown in eq 1. The monomer-dimer equilibration rates are extremely rapid at ambient temperature. Thus, the chemical reactivity of these species in solution is believed to be that of the monomers. This is supported by the fact that the related dimers $[(\eta^5\text{-}C_5H_5)M(CO)_3]_2$ (M = Mo, W), which do not thermally dissociate to an appreciable extent, are virtually unreactive. Despite the extensive studies carried out on these chromium species during the last several years, no kinetic data on metal–metal bond dissociation and recombination processes have been reported. We have therefore focused our research efforts on the metal–metal bond formation and cleavage dynamics.

$$[(\eta^5\text{-}C_5R_5)Cr(CO)_3]_2 \underset{k_{-1}}{\overset{h\nu,\,k_1}{\rightleftharpoons}} 2\{(\eta^5\text{-}C_5R_5)Cr(CO)_3\} \qquad (1)$$

In this paper we report the first such measurements for $[(\eta^5\text{-}C_5R_5)Cr(CO)_3]_2$ as shown in eq 1, where k_1 is the thermal dissociation rate constant and k_{-1} the recombination rate constant as defined by eq 2.

$$-\frac{d[\{(\eta^5\text{-}C_5R_5)Cr(CO)_3\}_2]}{dt} = \frac{d[(\eta^5\text{-}C_5R_5)Cr(CO)_3]}{2\,dt} = k_1[\{(\eta^5\text{-}C_5R_5)Cr(CO)_3\}_2] - k_{-1}[(\eta^5\text{-}C_5R_5)Cr(CO)_3]^2 \qquad (2)$$

The laser flash photolysis of $[(\eta^5\text{-}C_5R_5)Cr(CO)_3]_2$ in acetonitrile, tetrahydrofuran, and toluene has enabled us to observe and measure the metal–metal bond dissociation and recombination kinetics for these complexes at room temperature. The data have been compared with those for the molybdenum and tungsten analogues $[(\eta^5\text{-}C_5H_5)M(CO)_3]_2$ (M = Mo, W).

Experimental Section. Materials. Syntheses were carried out under an argon atmosphere. Special care was taken to exclude light. The solvents were dried and distilled over appropriate drying agents prior to use. The compounds $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2$[9] and $[(\eta^5\text{-}C_5Me_5)Cr(CO)_3]_2$[8] were prepared by literature procedures. Dicyclopentadiene, pentamethylcyclopentadiene, and $Cr(CO)_6$ were obtained from Aldrich and were used without further purification. Other chemicals were of the highest grade commercially available and were used as received.

The kinetic measurements were carried out under argon at room temperature. In a typical experiment, solutions of (0.2–2.4) × 10^{-4} M $[(\eta^5\text{-}C_5R_5)Cr(CO)_3]_2$ were prepared by dissolving the solid compound in the chosen solvent. The dimer concentrations in solution before the flash were determined spectrophotometrically from the visible electronic absorption spectra. The laser flash typically induced a concentration perturbation, $\Delta[(\eta^5\text{-}C_5R_5)Cr(CO)_3]_2$, of 2–18 μM.

Instruments. UV–visible absorption spectra were measured with a Shimadzu UV-3101PC scanning spectrophotometer. Flash photolysis experiments on the nanosecond time scale utilized a Nd:YAG laser which is a part of the LKS.50 laser photolysis spectrometer system from Applied Photophysics Ltd. The laser beam was set up perpendicular to the monitoring beam from a pulsed xenon lamp. The monitoring beam passed through the sample cell and a grating monochromator to a five-stage photomultiplier tube. Kinetic data from these experiments were recorded and analyzed on a PM3323 Philips digital oscilloscope interfaced to an Archimedes 420/1 computer. The frequency-doubled fundamental laser light at 532 nm was used for the photolysis of solutions of $[(\eta^5\text{-}C_5R_5)Cr(CO)_3]_2$ in all cases. The subsequent kinetic process was monitored directly at the UV–visible absorption bands of the dimers.

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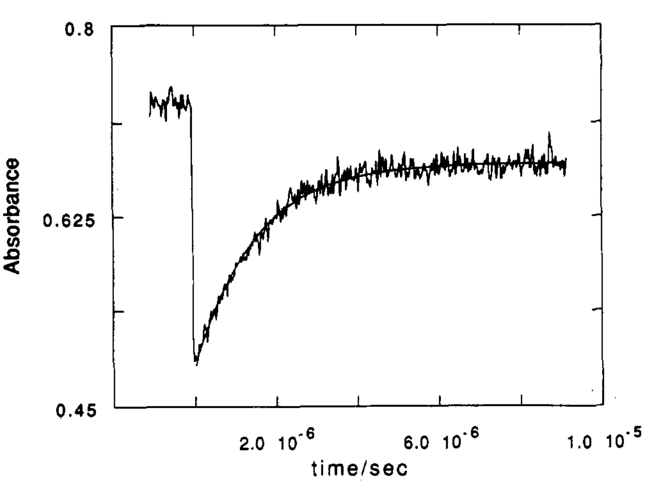

Figure 1. The time-resolved absorbance change recorded at 511 nm after the 532-nm laser flash photolysis of an argon-saturated solution of 37 μM $[(\eta^5\text{-}C_5Me_5)Cr(CO)_3]_2$ and ca. 1.7 mM monomer in CH_3CN. The smooth curve is the fit to a first-order rate law with $k = 6.8 \times 10^5$ s^{-1}.

Results and Discussion. The electronic spectrum of $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2$ shows a well-defined, intense absorption band at ~450 nm ($\epsilon = (1.8 \pm 0.1) \times 10^4$ M^{-1} cm^{-1}). The exact peak position varies somewhat with the solvent.[10,11] In the case of the more completely dissociated $[(\eta^5\text{-}C_5Me_5)Cr(CO)_3]_2$ dimer, for which no prior UV–vis absorption data were available, the measured spectrum shows an intense band at 511 nm in CH_3CN and 512 nm in toluene. These absorption bands are believed to be associated with the $\sigma \rightarrow \sigma^*$ transition of the Cr–Cr bond by analogy with the intense near-UV bands of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ and $[(\eta^5\text{-}C_5H_5)W(CO)_3]_2$.[12]

Visible laser flash photolysis of $[(\eta^5\text{-}C_5R_5)Cr(CO)_3]_2$ in solution has been carried out in various solvents. In every case, the laser flash causes the bleaching of the absorbance, which then recovers to the extent of 80–90%. A typical trace following the laser flash photolysis of $[(\eta^5\text{-}C_5Me_5)Cr(CO)_3]_2$ is displayed in Figure 1. We interpret these data to mean that the light-induced cleavage of the Cr–Cr bond is followed by the monomer–dimer reequilibration as shown in eq 1. This is as expected, since the excited state should be antibonding with regard to the Cr–Cr bond. After several flashes, the absorbance of the dimer had decreased substantially. We associate this with the loss of CO and conversion of the singly bonded dimer to the more stable triply bonded analogue, $[(\eta^5\text{-}C_5R_5)Cr(CO)_2]_2$, upon flash photolysis. These reactions have been well documented and are believed to be irreversible for the chromium complexes under standard conditions.[11] The recombination of CO and $Cp_2W_2(CO)_5$ occurs on a much longer time scale;[13] we presume the same is true for the chromium complexes, since the dimer recovery after the flash is largely but not entirely complete. Thus, it will not interfere with the determination of the kinetics for eq 1.

The concentration-jump method used in this work[13,14] involves a sudden perturbation (by the laser flash) of an equilibrated system, followed by the kinetically controlled reestablishment of the equilibrium. The perturbation must be rapid compared to the rate of reequilibration. Our conditions obviously satisfy this requirement. The kinetic expressions can be simplified by noting that they reduce to a first-order expression since the value of the perturbation is at least 1 order of magnitude smaller than the monomer concentration under the experimental conditions. Thus, the data should fit first order kinetics according to eq 3.

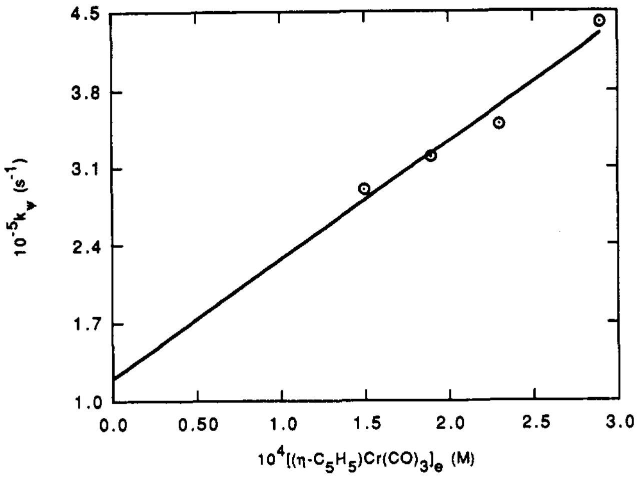

Figure 2. Plot of the apparent rate constant versus $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_e$ for argon-saturated solutions in CH_3CN at 23 °C ($[\{(\eta^5\text{-}C_5H_5)Cr(CO)_3\}_2]_e = (0.5\text{–}1.8) \times 10^{-4}$ M and $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_e = (1.5\text{–}2.9) \times 10^{-4}$ M).

$$k_\psi = k_1 + 4k_{-1}[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_e \qquad (3)$$

The data for the Cp complex indeed fit first-order kinetics well and yielded values of k_ψ. A plot of k_ψ against the equilibrium concentration of the monomer was linear and yielded k_1 as intercept and $4k_{-1}$ as slope (Figure 2). The least-squares values are $k_1 = (1.2 \pm 0.3) \times 10^5$ s^{-1} and $k_{-1} = (2.7 \pm 0.4) \times 10^8$ L mol^{-1} s^{-1}. The summary of the kinetic data for $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2$ in different solvents is given in Table I.

In the case of $[(\eta^5\text{-}C_5Me_5)Cr(CO)_3]_2$, the dimer is almost completely dissociated in solution at ambient temperature. Its extreme air sensitivity in solution prevented us from obtaining a reliable value for the molar absorptivity (ϵ) of $[(\eta^5\text{-}C_5Me_5)Cr(CO)_3]_2$. Fortunately, the calculation of the dissociation rate constant k_1 is quite insensitive to the ϵ value. An error of 50% in this value (with $\epsilon = 20\,000 \pm 50\%$ L mol^{-1} cm^{-1}) would correspond to an error of <3% in the derived k_{-1} value.

To obtain k_1, we used the value of the equilibrium constant K of 0.08 M, which is an average of literature values[8] obtained by different methods in toluene (FTIR 0.11 M; magnetic susceptibility 0.058 M). The derived dissociation and recombination rate constants k_1 and k_{-1} for $[(\eta^5\text{-}C_5Me_5)Cr(CO)_3]_2$ in different solvents are shown in Table I. Also listed for the purpose of comparison are the literature data[13,16,17] for the molybdenum and tungsten analogues $[(\eta^5\text{-}C_5H_5)M(CO)_3]_2$ (M = Mo, W).

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(17) The value of k_1 was calculated on the basis of K for the molybdenum analogue,[16] corrected for the difference in $\Delta H°$ in the homolytic dissociation of the W compound (234 kJ mol^{-1}: Krause, J. R.; Bidinosti, D. R. *Can. J. Chem.* **1975**, *53*, 628) as compared to Mo (136 kJ mol^{-1}: Amer, S.; Kramer, G.; Pöe, A. *J. Organomet. Chem.* **1981**, *209*, C28). This is a large correction, amounting to ca. 10^{40} in the equilibrium constant ratio and thus to an extraordinarily low value of k_1 for $[(C_5H_5)W(CO)_3]_2$.

Table I. Dissociation and Recombination Rate Constants for $[(\eta^5\text{-}C_5R_5)M(CO)_3]_2$ (M = Cr, R = H, Me; M = W, R = H)

complex	solvent	k_1 (s^{-1})	k_{-1} ($L\ mol^{-1}\ s^{-1}$)	ref
$[(\eta^5\text{-}C_5Me_5)Cr(CO)_3]_2$[a]	CH_3CN	$(5.6 \pm 0.5) \times 10^5$	$(7.0 \pm 0.6) \times 10^6$	*b*
	toluene	$(6.2 \pm 0.5) \times 10^5$	$(7.6 \pm 0.6) \times 10^6$	*b*
$[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2$[a]	CH_3CN	$(1.2 \pm 0.3) \times 10^5$	$(2.7 \pm 0.4) \times 10^8$	*b*
	THF	$(1.2 \pm 0.3) \times 10^5$	$(3.0 \pm 0.4) \times 10^8$	*b*
	toluene	$(2.0 \pm 0.6) \times 10^5$	$(3.1 \pm 0.5) \times 10^8$	*b*
$[(\eta^5\text{-}C_5H_5)MoCO)_3]_2$	CH_3CN	2.8×10^{-8}	3.9×10^9	13, 16
$[(\eta^5\text{-}C_5H_5)W(CO)_3]_2$	CH_3CN	7×10^{-47}	6.2×10^9	13, 17

[a] The equilibrium constants used here are 4.5×10^{-4} M for $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2$[10] and 8×10^{-2} M (an average of values obtained with different techniques) for $[(\eta^5\text{-}C_5Me_5)Cr(CO)_3]_2$.[8] [b] This work.

Inspection of our results reveals that the rate constants for both chromium systems show no appreciable change with solvent (see Table I), polar or nonpolar, or with initial concentrations. However, it is noticed that the recombination rate constants vary by almost 10^3-fold among the four species. The kinetic data thus parallel the thermodynamic parameters associated with the metal–metal bond stability in the order $[(\eta^5\text{-}C_5H_5)W(CO)_3]_2 \approx [(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2 > [(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2 > [(\eta^5\text{-}C_5Me_5)Cr(CO)_3]_2$.

A striking feature of this thermodynamic series is that both k_1 and k_{-1} separately follow the same trend. One might have anticipated the family of k_{-1} values to be (nearly) constant, with the bond strength change reflected mainly in the k_1 values. The fact that this is not the case suggests a transition state with an appreciable Cr–Cr bond, since k_1 is well below what it would have been were k_{-1} at the diffusion-controlled limit.

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