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(4) R. Koren, B. Perlmutter-Hayman, and R. Shinar, *Int. J. Chem. Kinet.*, **6**, 39 (1974).
(5) B. Perlmutter-Hayman and R. Shinar, *Inorg. Chem.*, **15**, 2932 (1976).
(6) B. Perlmutter-Hayman and R. Shinar, *Int. J. Chem. Kinet.*, **7**, 453, 798 (1975).
(7) B. Perlmutter-Hayman, R. Sarfaty, and R. Shinar, *Int. J. Chem. Kinet.*, **8**, 741 (1976).
(8) B. Perlmutter-Hayman and R. Shinar, *Int. J. Chem. Kinet.*, in press.
(9) B. Perlmutter-Hayman and R. Shinar, *Isr. J. Chem.*, in press.
(10) W. A. Johnson and R. G. Wilkins, *Inorg. Chem.*, **9**, 1917 (1970).
(11) D. W. Margerum, D. B. Rorabacher, and J. F. G. Clarke, Jr., *Inorg. Chem.*, **2**, 667 (1963).

(12) P. H. Tedesco and J. A. Gonzalez Quintana, *J. Inorg. Nucl. Chem.*, **37**, 1798 (1975).
(13) F. P. Cavasino, *Ric. Sci., Parte 2: Sez. A*, **8**, 1120 (1965); F. P. Cavasino, *J. Phys. Chem.*, **69**, 4380 (1965).
(14) B. Perlmutter-Hayman, *Adv. Mol. Relaxation Processes*, in press.
(15) J. Neely and R. Connick, *J. Am. Chem. Soc.*, **92**, 3476 (1970).
(16) M. Eigen and K. Tamm, *Z. Elektrochem.*, **66**, 107 (1962).
(17) M. C. Rose and J. E. Stuehr, *J. Am. Chem. Soc.*, **94**, 5532 (1972).
(18) L. G. Sillen and A. E. Martell, *Chem. Soc., Spec. Publ.*, No. 17 (1964); No. 25 (1971).
(19) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions", 2d ed, Reinhold, New York, N.Y., 1950, p 485.

Reactivity of Metal Radicals Generated Photochemically. Effects of Solvent and of Trapping Agent Concentrations on Quantum Yields for Photolysis of Hexacarbonylbis(π-cyclopentadienyl)ditungsten(I), [π-CpW(CO)₃]₂[1]

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The metal radical π-CpW(CO)₃, generated by the 520-nm photolysis of [π-CpW(CO)₃]₂, displays considerable selectivity in its reactions with various chlorocarbon trapping agents in solution. As reported previously, the principal metal-containing photolysis product is π-CpW(CO)₃Cl which results from the abstraction of chlorine from the chlorocarbon; however, another low-yield photodecomposition pathway is also evident in the absence of trapping agent. The sensitivity of the metal radical toward trapping agent follows the order CCl₄ ≫ CHCl₃ > PhCH₂Cl ≫ CH₂Cl₂ in a manner consistent with the reactivities of other radicals. The effects of lamp intensity and of trapping agent concentrations on quantum yields are reported and a kinetic scheme consistent with these results is proposed. In addition, quantum yields are reported for the reactions in carbon tetrachloride, chloroform, and dichloromethane as solvents, and it is noted that these values do not simply parallel the reactivities of the trapping agents but must reflect solvent effects on primary quantum yields for formation of the metal radicals.

Photolytic generation of reactive organometallic radicals has received considerable attention in the recent literature.[3-6] The interest in such species derives in part from the potential roles of metal radicals in the synthesis of new organometallic complexes (especially mixed polynuclear species),[3] in mechanisms of oxidative addition,[7,8] in metal carbonyl substitution reactions,[9,10] and in certain homogeneous catalysis processes.[6,11,12] Thus it is of interest to examine the reaction dynamics of photolytically generated metal radicals. Photolysis of neutral bimetallic complexes such as [π-CpW(CO)₃]₂ and [π-CpMo(CO)₃]₂ leads to homolytic metal–metal bond cleavage to give such species.[4,5] Reported here is a study of the reactions of the photolytically generated metal radical π-CpW(CO)₃ with a variety of chlorocarbon trapping agents as neat solvents and in tetrahydrofuran solution.

Experimental Section

Materials. Spectroscopic grade solvents were used. Chlorocarbon solvents and trapping agents were stored in the dark over molecular sieves and distilled in a nitrogen atmosphere immediately prior to use. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under nitrogen immediately prior to use. Hexane was stored over P₂O₅ and distilled under nitrogen prior to use. Manipulations of air-sensitive complexes were carried out under a nitrogen atmosphere. [π-CpW(CO)₃]₂ is an air- and light-sensitive compound; however, the following synthesis procedure gave pure material. To 20 ml of freshly distilled THF were added 0.036 g (1.5 × 10⁻³ mol) of NaH and 0.55 g (1.65 × 10⁻³ mol) of π-CpW(CO)₃H. The mixture was stirred magnetically until hydrogen evolution ceased. A 0.65-g (1.4 × 10⁻³ mol) portion of π-CpW(CO)₃I was added, the solution was stirred for 5 h and then was refluxed for 40 h. After the solution was allowed to cool to room temperature, 2 ml of acetic acid was added and the mixture was stirred for 1 h. The solvent and excess acetic acid were removed by high-vacuum evaporation, and then unreacted

π-CpW(CO)₃H was sublimed from the remaining material (60 °C at ~0.1 mmHg). Following the sublimation, the remaining residue was extracted with dichloromethane and filtered in a dark room. The [π-CpW(CO)₃]₂ was precipitated from the deep red solution by addition of hexane. Recrystallization from dichloromethane in the dark gave 0.75 g (68% yield) of crystalline [π-CpW(CO)₃]₂ with IR, UV, and mass spectral properties closely matching the literature values.[3,13] π-CpW(CO)₃Cl and π-CpW(CO)₃I were prepared from π-CpW(CO)₃H by the literature procedures[14] and were recrystallized from dichloromethane/hexane in the dark.

Photolysis Procedures. Solutions of THF, with or without measured quantities of trapping agent, were placed in a small Schlenk tube and degassed via three freeze–thaw cycles. Nitrogen was reintroduced, [π-CpW(CO)₃]₂ was added, and the resulting homogeneous solution was transferred by syringe to an airtight 2-cm quartz photolysis cell previously purged with nitrogen. The initial spectrum was recorded on a Cary 14 spectrophotometer. In most cases the initial solutions were relatively optically dense (OD > 0.5) at the irradiation wavelength. The cell was then placed in a thermostated compartment of the photolysis train equipped with a 150-W xenon short-arc lamp with interference filters of 520 or 460 nm for wavelength selection. Actinometry at each wavelength was accomplished using Reinecke's salt. The infrared solution spectra of reactants and products were recorded on a Perkin-Elmer Model 225 grating infrared spectrophotometer.

Results

The electronic spectrum of [π-CpW(CO)₃]₂ (A) displays two absorption bands in the near-UV–visible region. These are relatively insensitive to the solvent and in CCl₄ have absorption maxima at 493 and 362 nm (ε 3.05 × 10³ and 2.29 × 10⁴ M⁻¹ cm⁻¹, respectively) which have been assigned as π → σ* and σ → σ* transitions of the metal–metal bond.[4] Photolysis of A with 520-nm light in chlorocarbon solvent leads to a product identified from its IR and electronic spectrum

Table I. Quantum Yields for the Photolysis of $[\pi\text{-CpW(CO)}_3]_2$ in Various Neat Solvents

Solvent	λ_{irr} (intens)^a	$\Phi_d{}^b$
CCl_4	520 (3.4)	0.24 ± 0.02 (4)
	550^c	0.12
$CHCl_3$	520 (1.7)	0.31 ± 0.02 (4)
CH_2Cl_2	520 (2.9)	0.12 ± 0.01 (3)
THF	520 (1.8)	0.008 ± 0.001 (3)

^{a} Wavelength of irradiation (intensity in 10^{-6} einstein/l. s).
^{b} Quantum yield for disappearance of starting material calculated from spectral changes in the photolysis solution. Mean value, average deviation, and number of determinations (in parentheses) are listed; $T = 25$ °C. ^{c} Reference 4.
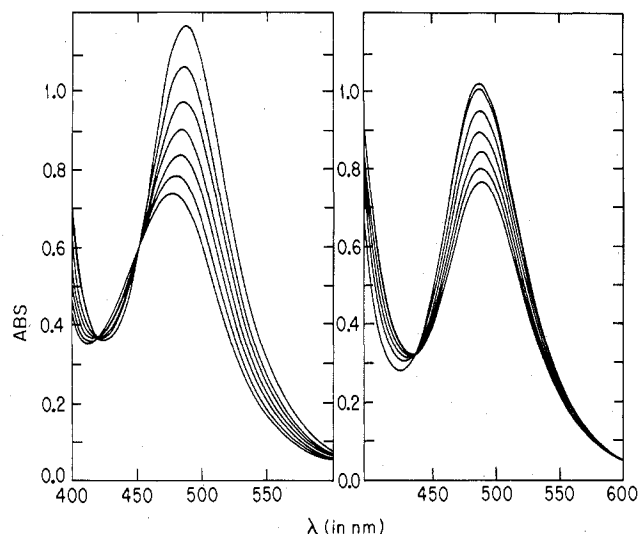

Figure 1. Right: Spectral changes observed when $[\pi\text{-CpW(CO)}_3]_2$ is photolyzed (520 nm, I_a(initial) $= 4.1 \times 10^{-6}$ einstein/l. s) in tetrahydrofuran solution. Irradiation time between the first curve (highest absorbance at 490 nm) and the last curve (lowest absorbance) is 3015 s. Left: Spectral changes observed when $[\pi\text{-CpW(CO)}_3]_2$ is photolyzed (520 nm, I_a(initial) $= 4.3 \times 10^{-6}$ einstein/l. s) in THF containing 0.4 M CCl_4. Irradiation time between the first and last curves is 110 s.

as $\pi\text{-CpW(CO)}_3\text{Cl}$ (B) (λ_{max} 460 nm, ϵ 580 nm, in CCl_4 solution), a result consistent with the previous report.[4] Quantum yields for the disappearance of starting material, Φ_d, are reported in Table I. These were determined for low conversion to product in order to deemphasize secondary photoreaction. However, secondary photolysis is of minor importance given the product's low extinction coefficient at 520 nm and relatively low photoreactivity. The photodecomposition of B to unknown products has a quantum yield of $\sim$0.02 mol/einstein when irradiated at 460 nm in $CHCl_3$. Similar decomposition with a comparable quantum yield is noted for the 520-nm photolysis of $\pi\text{-CpW(CO)}_3\text{I}$ (λ_{max} 468 nm, ϵ 830 M^{-1} cm^{-1}, in $CHCl_3$ solution). Mass spectral analysis of the solids isolated from the latter reaction indicated that $\pi\text{-CpW(CO)}_3\text{Cl}$ is not a photolysis product in $CHCl_3$ solution.

In THF solution, 520-nm photolysis of A leads to the slow disappearance of starting material as monitored spectrally. A clean isosbestic point was noted at 440 nm (Figure 1); however the reaction product(s) was (were) not identified. When the photolysis was carried out in THF solution containing various concentrations of CCl_4, the disappearance of A was much more rapid (Figure 1) and the IR and electronic spectral changes indicated the formation of B. Quantum yields Φ_d are clearly a function of the concentration of added CCl_4 in THF solution (Table II). A plot of these data shows that at low $[CCl_4]$ Φ_d extrapolates to the value observed in THF without added trapping agent and that, at high $[CCl_4]$, Φ_d levels off to a value

Table II. Quantum Yields for Disappearance^a of $[\pi\text{-CpW(CO)}_3]_2$ in THF Solution Containing Various Concentrations of Chlorocarbon Trapping Agents, T

T	10^3[T], M	$10^6 I_a$, ein-steins/l. s	$\Phi_d{}^{a,b}$ mol/einstein	Φ_d(calcd),^{c} mol/einstein
CCl_4	0.17	2.9	0.020 ± 0.003 (3)	0.018
	0.66	2.9	0.043 ± 0.001 (3)	0.047
	1.0	2.8	0.060 ± 0.003 (3)	0.065
	1.3	2.9	0.071 ± 0.003 (3)	0.083
	2.3	3.1	0.12 ± 0.01 (3)	0.13
	3.3	2.8	0.19 ± 0.01 (3)	0.18
	5.0	0.6	0.31 ± 0.02 (3)	0.35
		2.9	0.25 ± 0.02 (3)	0.23
		4.1	0.19 ± 0.02 (3)	0.20
	8.3	2.8	0.32 ± 0.01 (3)	0.31
	10.5	2.8	0.34 ± 0.02 (2)	0.35
	12.5	2.7	0.37 ± 0.02 (2)	0.38
	83	2.5	0.49 ± 0.01 (2)	0.49
	400	2.7	0.45 ± 0.01 (2)	0.49
CH_2Cl_2	20	1.9	0.008 ± 0.001 (2)	
	400	1.8	0.008 ± 0.001 (2)	
$CHCl_3$	5	1.9	0.009 ± 0.001 (2)	
	80	1.9	0.017 ± 0.001 (2)	
	400	1.7	0.060 ± 0.003 (2)	
$PhCH_2Cl$	200	2.7	0.024 ± 0.002 (2)	
	400	2.2	0.037 ± 0.003 (2)	
	760	2.6	0.053 ± 0.002 (2)	

^{a} Φ_d calculated from extinction coefficient differences between starting material and product assuming the stoichiometry
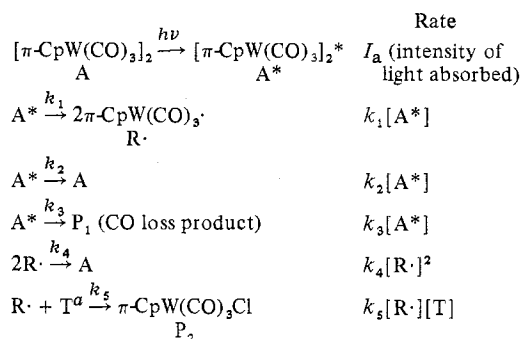
$$[\pi\text{-CpW(CO)}_3]_2 \xrightarrow[\text{trapping agent}]{h\nu} 2[\pi\text{-CpW(CO)}_3\text{Cl}]$$
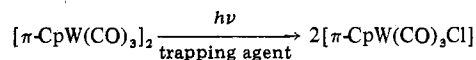
^{b} Average value of Φ_d, standard deviation, and number of determinations (in parentheses) listed; $T = 25$ °C, [A]$_{initial} \simeq (3 \pm 1) \times 10^{-4}$ M. ^{c} Quantum yield calculated from eq 4 using the parameters $\Phi_R. = 0.98$ and $k_s{}^2/k_4 = 0.042$ M^{-1} s^{-1} in CCl_4/THF solution.

approximating 0.5 mol/einstein. When other chlorocarbons are present in the THF solution, the efficiency of radical trapping is a function of the identity of the trapping agent (Table II) and follows the order $CCl_4 \gg CHCl_3 > PhCH_2Cl \gg CH_2Cl_2$. Last, it is noteworthy that, at a constant concentration of CCl_4 (0.005 M) below the saturation limit, Φ_d is clearly also a function of the absorbed light intensity (Table II).

Discussion

Photolysis of $[\pi\text{-CpW(CO)}_3]_2$ with 520-nm light in CH_2Cl_2, $CHCl_3$, or CCl_4 solvent leads to the formation of $\pi\text{-CpW-(CO)}_3\text{Cl}$ as the only detectable tungsten product. Previous studies have shown that in CCl_4 the stoichiometric ratio of chloride formation to dimer consumption is 2:1,[4] and this result has been interpreted in terms of the photolysis-induced homolytic cleavage of the metal–metal bonds and subsequent trapping of the metal radical $\pi\text{-CpW(CO)}_3$.[15] Quantum yields for the disappearance of the starting material are somewhat dependent on the identity of the chlorocarbon solvent (Table I). However, Φ_d values do not correlate simply with a macroscopic property of the solvent such as viscosity or dielectric constant or with the stability of the chloromethyl radicals formed by chlorine abstraction (vide infra).[15b] Thus, it appears likely that the differences may be due to microscopic solvation effects on the ground state, excited states, or probable intermediates or to effects on the nonradiative deactivation rates of relevant excited states. The effect of the solvent on the photoreaction is emphasized by the observation that Φ_d measured in a THF solution containing 0.083 M CCl_4 is a factor of 2 larger than Φ_d measured in pure CCl_4. Since any $\pi\text{-CpW(CO)}_3$ formed in CCl_4 solvent would be efficiently trapped, the lower Φ_d value in CCl_4 apparently reflects a

Scheme I

$$[\pi\text{-CpW(CO)}_3]_2 \xrightarrow{h\nu} [\pi\text{-CpW(CO)}_3]_2^*$$

	Rate
$[\pi\text{-CpW(CO)}_3]_2 \xrightarrow{h\nu} [\pi\text{-CpW(CO)}_3]_2^*$ A $\qquad$ A*	I_a (intensity of light absorbed)
A* $\xrightarrow{k_1}$ 2π-CpW(CO)$_3\cdot$ R$\cdot$	$k_1[\text{A}^*]$
A* $\xrightarrow{k_2}$ A	$k_2[\text{A}^*]$
A* $\xrightarrow{k_3}$ P$_1$ (CO loss product)	$k_3[\text{A}^*]$
2R$\cdot$ $\xrightarrow{k_4}$ A	$k_4[\text{R}\cdot]^2$
R$\cdot$ + T^a $\xrightarrow{k_5}$ π-CpW(CO)$_3$Cl P$_2$	$k_5[\text{R}\cdot][\text{T}]$

^{a} T is the chlorocarbon trapping agent.

solvent effect on the quantum yield for formation of the reactive radicals (vide infra).

In THF solution with no chlorocarbon present, the dimer is much less photoactive. Thus, if metal radicals are formed by photolysis under these conditions, they must recombine efficiently. The hydride complex π-CpW(CO)$_3$H is stable under the reaction conditions, but none was detected. Thus, hydrogen atom abstraction from THF appears to be an unlikely pathway, and the minor photodecomposition observed very likely involves loss of CO. Such CO loss was postulated[5] for the formation of an intermediate during flash photolysis of the molybdenum analogue of A in THF. This intermediate was suggested to react with CO to re-form $[\pi$-CpMo(CO)$_3]_2$ or to lose another CO to produce $[\pi$-CpMo(CO)$_2]_2$. Similarly, the photodecomposition of π-CpW(CO)$_3$I very likely involves CO loss since B would have been expected if π-CpW(CO)$_3$ had been formed. In addition, CO loss has been seen for photolysis of π-CpW(CO)$_3$Cl in pyridine solution.[16]

The dependence of Φ_d on the CCl$_4$ concentration (Table II) suggests that the principal photoreaction pathway in THF involves cleavage of the metal–metal bond to form radicals which undergo competitive trapping by CCl$_4$ or dimerization to re-form A. The current data do not differentiate whether the photodecomposition in the absence of CCl$_4$ (proposed CO loss) also occurs as a result of radical formation[10] or as an independent pathway from excited A.[5] Scheme I summarizes the proposed reactions based on the latter of these pathways. This scheme suggests that in the absence of trapping agent the radicals return to starting material, and the quantum yield for disappearance of A is

$$\Phi_d = \Phi_1 = \frac{k_3}{k_1 + k_2 + k_3} = 0.008 \text{ mol/einstein} \quad (1)$$

In the presence of T a more complicated relationship results

$$\Phi_d = -\frac{d[\text{A}]/dt}{I_a} = \frac{dP_1/dt + (0.5)dP_2/dt}{I_a} \quad (2)$$

According to this scheme, the radical formation path does not affect the formation of P$_1$; therefore

$$\Phi_d = \frac{k_5[\text{R}\cdot][\text{T}]}{2I_a} + \Phi_1 \quad (3)$$

Application of the steady-state approximation to [R$\cdot$] and to [A*] gives

$$\Phi_d = \frac{-k_5{}^2[\text{T}]^2(1 - (1 + 4k_4I_a\Phi_{\text{R}\cdot}k_5{}^{-2}[\text{T}]^{-2})^{1/2})}{4k_4I_a} + \Phi_1 \quad (4)$$

where $\Phi_{\text{R}\cdot}$ is the quantum yield for formation of the metal radical R$\cdot$ and equals $2k_1/(k_1 + k_2 + k_3)$. At high CCl$_4$ concentrations the limiting value of Φ_d is approximately 0.50 mol/einstein. Since under these conditions the radicals are
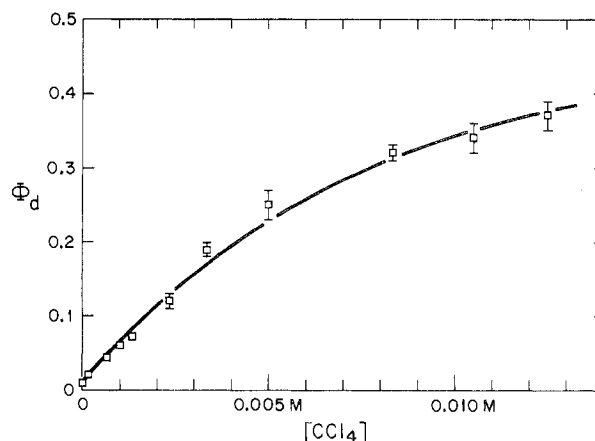

Figure 2. Φ_d as a function of carbon tetrachloride concentration at an approximately constant intensity of absorbed light ($I_a = (2.9 \pm 0.2) \times 10^{-6}$ einstein/l. s). The solid curve represents the theoretical Φ_d values calculated according to eq 4 and the parameters $k_5{}^2/k_4 = 0.042$ M^{-1} s^{-1}, $\Phi_{\text{R}\cdot} = 0.98$, and $I_a = 2.9 \times 10^{-6}$ einstein/l. s. Note that some of the differences between the experimental Φ_d values and calculated curve are due to minor variations in the experimental I_a values (see Table II).

apparently efficiently scavenged, the $\Phi_{\text{R}\cdot}$ may be estimated as $2(\Phi_d(\text{limiting}) - \Phi_1) = 0.98$ mol/einstein in THF solution.

Equation 4 predicts that Φ_d is a function of [T] and of the intensity of absorbed light, I_a. Also, if the metal radicals do not react with T upon every collision, then Φ_d will depend on the nature of T. Each of these general features is realized in the present data (Table II). Quantitative evaluation of the model suffers from the experimental problem that light intensity absorbed is an exponential function of the distance from the front cell face. The optical densities used were such that the majority of the light was absorbed into the first 35% of the cell volume; however, the absorbed intensities reported are averages for the full cell volume. No systematic variation in Φ_d with solution optical density over the range 0.7–1.5 was observable which could not be accounted for by the resulting small changes in average I_a. In this regard, increases in the light intensity incident on otherwise analogous solutions led to decreases in Φ_d as predicted by eq 4.[17]

Despite the stated difficulties in evaluating the model quantitatively, it is possible to extend the evaluation and to approximate the relative reactivity of the metal radical toward dimerization vs. trapping by CCl$_4$. Rearrangement of eq 4 gives

$$\frac{k_5{}^2}{k_4} = \frac{4I_a}{[\text{T}]^2}\left[\frac{(\Phi_d - \Phi_1)^2}{\Phi_{\text{R}\cdot} - 2(\Phi_d - \Phi_1)}\right] \quad (5)$$

From the data in THF solution for [CCl$_4$] ≤ 0.013 M and $\Phi_{\text{R}\cdot} = 0.98$ mol/einstein, one can calculate an average value: $k_5{}^2/k_4 = 0.042 \pm 0.010$ M^{-1} s^{-1}. The self-consistency of Scheme I is illustrated by using this value plus $\Phi_{\text{R}\cdot}$ to calculate Φ_d. The calculated and observed values for Φ_d give an excellent numerical fit for the data obtained under conditions of approximately equal I_a (Table II, Figure 2) and demonstrate with reasonable accuracy the effect of I_a variation at constant [CCl$_4$] (5×10^{-3} M).

It is evident from the calculated $k_5{}^2/k_4$ ratio that even with CCl$_4$ the rate constant for chlorine abstraction is much smaller than that for radical dimerization. The flash photolysis of the molybdenum analogue indicates that radical recombination occurs with a rate constant of 2×10^9 M^{-1} s^{-1} in THF solution,[5] and a rate constant of 3.8×10^9 M^{-1} s^{-1} has been measured for the tungsten radical recombination.[18] If one uses the latter value for k_4, k_5 for CCl$_4$ can be estimated at ap-

proximately 1.3×10^4 M^{-1} s^{-1}. Similar treatment using eq 5 and the data from Table II give the respective $k_5{}^2/k_4$ ratios and estimated k_5 values: for $CHCl_3$, $k_5{}^2/k_4 = (1.2 \pm 0.2) \times 10^{-7}$ M^{-1} s^{-1} and $k_5 \simeq 21$ M^{-1} s^{-1}; for $PhCH_2Cl$, $k_5{}^2/k_4 = (5.5 \pm 2) \times 10^{-8}$ M^{-1} s^{-1} and $k_5 \simeq 14$ M^{-1} s^{-1}; for CH_2Cl_2, $k_5{}^2/k_4 < 10^{-10}$ M^{-1} s^{-1} and $k_5 < 0.6$ M^{-1} s^{-1}.

The reactivity order observed here for the trapping of the metal radical by the various chlorocarbons has analogy in other examples of halogen abstraction from halocarbons. For example, rates of bromine atom abstraction as illustrated in eq

$$R' \cdot + R''-Br \to R'-Br + R'' \cdot \qquad (6)$$

6 have been reported for cases where $R' \cdot$ is the methyl radical[19] or where $R' \cdot$ is the tri-*n*-butyltin radical[20] in hydrocarbon solvents. In both cases, the relative reactivities for the trapping agents $R''Br$ followed the order $CCl_3Br > CHCl_2Br > PhCH_2Br > CH_2ClBr$. Also, for the tri-*n*-butyltin radical, chloride abstraction from CCl_4 is about three orders of magnitude faster than from $PhCH_2Cl$.[20] Other chloride abstractions analogous to eq 6 display similar orders of halocarbon reactivities. The gas-phase chlorine atom abstraction from the chloromethanes by sodium atoms displays a strong dependence on the number of chlorines $CCl_4 > CHCl_3 > CH_2Cl_2 > CH_3Cl$ with each chlorine increasing the rate by roughly an order of magnitude.[21] A closer analogy to the present case is the use of chromium(II) as a reducing agent in mixed aqueous solvents.[22,23] With the chloromethanes, the rate of chloride abstraction by Cr(II) follows the order seen with the gas-phase sodium atom reaction.[23] Furthermore, comparison of the Cr(II) reductions of $CHCl_3$ and $PhCH_2Cl$ under somewhat different conditions ($CHCl_3$ in 29.8 °C, 50% aqueous dimethylformamide;[23] $PhCH_2Cl$ in 27.5 °C, 22% aqueous ethanol[22]) indicates that chloroform is an order of magnitude the more reactive.

In summary, the proposed model (Scheme I) provides a reasonable explanation of the variations of Φ_d measured for the irradiation of $[\pi\text{-}CpW(CO)_3]_2$ in THF solution containing different concentrations of the halocarbon trapping agents. The quantum yield data demonstrate that the metal radicals produced display considerable selectivity in their chemical reactions. This selectivity includes the failure to abstract hydrogen from solvent, various reactivities with chlorocarbon trapping agents in a manner consistent with other radicals, and much more rapid reaction with another radical to re-form the starting material. In addition, it is clear that the quantum yields observed in the different chloromethane solvents do not reflect simply the ease of chlorine abstraction from the solvent

trapping agent and instead indicate solvent effects on the primary quantum yields for the formation of reactive metal radicals.

Registry No. $[\pi\text{-}CpW(CO)_3]_2$, 12566-66-4; $\pi\text{-}CpW(CO)_3H$, 12128-26-6; $\pi\text{-}CpW(CO)_3I$, 31870-69-6.

References and Notes

(1) Reported initially at the 1975 Pacific Conference on Chemistry and Spectroscopy, Los Angeles, Calif., Oct 1975.
(2) Camille and Henry Dreyfus Foundation Teacher-Scholar, 1971–1976.
(3) (a) M. S. Wrighton and D. S. Ginley, *J. Am. Chem. Soc.*, **97**, 2065 (1975); (b) *ibid.*, **97**, 4908 (1975).
(4) M. S. Wrighton and D. S. Ginley, *J. Am. Chem. Soc.*, **97**, 4246 (1975).
(5) J. L. Hughey, C. B. Bock, and T. J. Meyer, *J. Am. Chem. Soc.*, **97**, 4440 (1975).
(6) B. H. Byers and T. L. Brown, *J. Am. Chem. Soc.*, **97**, 3260 (1975).
(7) A. V. Kramer and J. A. Osborne, *J. Am. Chem. Soc.*, **96**, 7832 (1974).
(8) M. F. Lappert and P. W. Lednor, *J. Chem. Soc., Chem. Commun.*, 948 (1973).
(9) J. P. Fawcett, R. A. Jackson, and A. Poe, *J. Chem. Soc., Chem. Commun.*, 733 (1975).
(10) B. H. Byers and T. L. Brown, *J. Am. Chem. Soc.*, **97**, 947 (1975).
(11) E. L. Muetterties, B. A. Sosinsky, and K. I. Zamaraev, *J. Am. Chem. Soc.*, **97**, 5299 (1975).
(12) J. Halpern and M. Pribonie, *Inorg. Chem.*, **9**, 2616 (1970).
(13) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956).
(14) T. E. Sloan and A. Wojcicki, *Inorg. Chem.*, **7**, 1268 (1968).
(15) (a) In the present study, the fate of the organic radical produced by abstraction of Cl· from the trapping agent T was not determined; however, in a previous study[4] with benzyl chloride as trapping agent, 1,2-diphenylethane was isolated as the other reaction product. (b) The reason for the difference between the present measurement of Φ_d in CCl_4 solution and the previously reported value at 550 nm (Table I) is unclear.
(16) (a) L. H. Ali, A. Cox, and T. J. Kemp, *J. Chem. Soc., Dalton Trans.*, 1475 (1973); (b) D. M. Allen, A. Cox, T. J. Kemp, and L. H. Ali, *ibid.*, 1899 (1973).
(17) Attempts were made to determine Φ_d at low solution optical density (<0.2 at 520 nm) so that I_a is more nearly a constant throughout the cell volume. Large experimental uncertainties in the incremental Φ_d values resulted and can be attributed to uncertainties in the small OD differences measured and to the possible roles of solution impurities having an inflated importance with these low concentrations. For example, with [A] = 5 × 10^{-5} M and [CCl_4] = 0.005 M, I_a(av) = 0.77 × 10^{-6} einstein/l. s in THF and Φ_d = 0.40 ± 0.05 mol/einstein. The expected value calculated according to eq 4 is 0.33 mol/einstein indicating that while the model is qualitatively successful, it suffers some quantitative uncertainties when $k_5{}^2/k_4$ ratios obtained at the higher optical densities are employed.
(18) J. L. Hughey, IV, Ph.D. Dissertation, University of North Carolina, Chapel Hill, N.C., 1975. Professor T. J. Meyer, private communication.
(19) K. U. Ingold in "Free Radicals", J. K. Kochi, Ed., Wiley, New York, N.Y., 1973, Chapter 2.
(20) L. W. Menapace and H. G. Kuivila, *J. Am. Chem. Soc.*, **86**, 3047 (1964).
(21) (a) B. G. Gowenlock and K. E. Thomas, *J. Chem. Soc.*, 5068 (1965); (b) E. Warhurst, *Q. Rev., Chem. Soc.*, **5**, 44 (1951).
(22) J. K. Kochi and D. D. Davis, *J. Am. Chem. Soc.*, **86**, 5264 (1964).
(23) C. E. Castro and W. C. Kray, *J. Am. Chem. Soc.*, **88**, 4447 (1966).

Conjugate Addition of Enolate Anions to Vinylcarbene Complexes

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The lithium enolate of cyclopentanone and the potassium enolate of isobutyrophenone conjugately add to (isobutenylmethoxycarbene)pentacarbonylchromium(0), **1**, and to (styrylmethoxycarbene)pentacarbonylchromium(0), **2**, to form new carbene complexes. The lithium enolate of acetone reacted with **1** and **2** to give products derived from addition to the carbene carbon atom. Reaction of the lithium enolate of cyclopentanone with (phenylmethoxycarbene)pentacarbonyltungsten(0), **12**, gave 2-benzylidenecyclopentanone via attack of the enolate carbon on the carbene carbon while the reaction of the potassium enolate of isobutyrophenone and **12** proceeded by attack of the enolate oxygen.

Introduction

The evolution of metal–carbene complexes into useful reagents for organic synthesis[1,2] requires the development of general synthetic methods for the preparation of a wide variety

of metal–carbene complexes. Recently, we demonstrated that anions generated α to the carbene carbon of metal–carbene complexes are synthetically useful intermediates for the elaboration of metal–carbene complexes.[3–7] These carbene