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# Kinetics of the Photolysis of Benzenetricarbonylchromium(0) in Chloroform

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In contrast to the photolysis of  $\text{Cr}(\text{CO})_3(\text{C}_6\text{H}_6)$  in nonhalogenated solvents, in which the products are  $\text{CrL}(\text{CO})_2(\text{C}_6\text{H}_6)$  in the presence of a donor L, or  $\text{Cr}(\text{CO})_6$  and  $\text{C}_6\text{H}_6$  if no donor is present, the photo-reaction in chloroform yields  $\text{CrCl}_3$ . No significant portion of the reaction occurs through absorption of 254 nm light by  $\text{CHCl}_3$ . The quantum yield is 1.4, consistent with a mechanism in which several radicals are formed upon chlorination of the chromium, which then cause further decomposition of the reactant. In 24%  $\text{CCl}_4$ , the reaction still occurs primarily through the excited state metal complex, but there is a solvent-initiated contribution, which is more significant the lower the reactant concentration. The quantum yield for the solvent-initiated pathway is 0.3 in 24%  $\text{CCl}_4$ .

*Keywords:* Benzenetricarbonylchromium, photochemistry, chloroform, solvent-initiated

## I. INTRODUCTION

Several workers have studied the photolysis of benzenetricarbonylchromium, beginning with Strohmeier in 1963 [1–3]. In donor solvents, or in the presence of electron pair donors, substitution of the donor for CO occurs [4–7]. In cyclohexane, the stoichiometric course of the reaction is

unknown, but  $\text{Cr}(\text{CO})_6$  and  $\text{C}_6\text{H}_6$  are the most commonly identified products [5,7,8]. In either case, the primary photochemical step appears to be dissociation of CO [6,9].

In chloroform, as in other halogenated solvents, there are several additional possibilities. Chloroform is reducible, and the excited state metal complex may be oxidized [9–12]. Oxidative addition [13,14] or substitution [15] may also occur. Alternatively, or in addition, chloroform may absorb light and undergo homolysis of the C–Cl bond, and the radicals produced may react with the ground state metal complex to yield almost any of the products that might form by reaction of the excited state metal complex with chloroform [16–19].

Thus in  $\text{CHCl}_3$  we may expect a different photochemical product than in nonhalogenated solvents. Distinguishing how the product is formed, through the excited state metal complex or through photodissociation of  $\text{CHCl}_3$ , is best done kinetically, by determining to what extent the reaction rate depends on the fraction of light absorbed at the irradiation wavelength by the reactant metal complex,  $f_R$ , and on the fraction of light absorbed by the solvent,  $f_S$ . These quantities

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are related to concentrations by the formulas [20]

$$f_R = \left\{ 1 - 10^{-(\epsilon_R[R] + \epsilon_P[P] + A_S)} \right\} \frac{\epsilon_R[R]}{\epsilon_R[R] + \epsilon_P[P] + A_S} \quad (1)$$

$$f_S = \left\{ 1 - 10^{-(\epsilon_R[R] + \epsilon_P[P] + A_S)} \right\} \frac{A_S}{\epsilon_R[R] + \epsilon_P[P] + A_S} \quad (2)$$

where  $[R]$  and  $[P]$  are the reactant and product concentrations,  $\epsilon_R$  and  $\epsilon_P$  are the molar absorption coefficients of the reactant and product at the irradiation wavelength, and  $A_S$  is the absorbance of the solvent at the same wavelength.

We have referred to reactions which proceed mostly or completely through the solvent homolysis pathway as solvent-initiated [20]. Such reactions are often characterized by an inverse relationship between reaction rate and the starting concentration of the metal complex, which can be baffling if the role of the solvent in the photoprocess is not recognized. One reason for examining the photolysis of  $\text{Cr}(\text{CO})_3(\text{C}_6\text{H}_6)$  in chloroform was to seek evidence of solvent-initiation.

## II. EXPERIMENTAL

$\text{Cr}(\text{CO})_3(\text{C}_6\text{H}_6)$ ,  $\text{CHCl}_3$ , and  $\text{CCl}_4$  were used as obtained from Aldrich. Chloroform and carbon tetrachloride were HPLC grade, the chloroform stabilized with ethanol. Samples (3.0 mL) were pipetted into 1.0 cm quartz cuvettes and irradiated at 254 nm with a 100-W mercury lamp in an Oriel Q housing, the light from which was passed through an Oriel 125 mm monochromator. After specified periods of irradiation, samples were removed from the beam and electronic spectra were measured on a Hewlett Packard model 8453 diode array spectrometer.

The starting concentration of benzenetricarbonylchromium in  $\text{CHCl}_3$  was determined from its molar absorption coefficient at its 315 nm peak,

$1.00 (\pm 0.03) \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  from a Beer's Law plot. The molar absorption coefficient of the product at 315 nm,  $100 \text{ M}^{-1} \text{ cm}^{-1}$ , was determined by irradiating five solutions of known concentration, and selecting the lowest absorption achieved before a colloidal precipitate began raising the baseline. The lowest value of  $\epsilon_P$  so calculated was taken as correct. The value is small enough, relative to  $\epsilon_R$ , that even large errors would have little effect on the calculated concentrations. Molar absorption coefficients for reactant and product were determined in a like manner in 24%  $\text{CCl}_4/76\%$   $\text{CHCl}_3$  by volume (this ratio was chosen to give a solvent absorbance above 1.0 at the exciting wavelength), and were the same as in pure  $\text{CHCl}_3$  within experimental error.  $A_S$ , the absorbance of the solvent at 254 nm, was 0.081 for  $\text{CHCl}_3$  and 1.18 for 24%  $\text{CCl}_4$  in chloroform.

Light intensities were measured in triplicate by ferrioxalate actinometry [21,22]. Initial rates of reaction for the photolysis of  $\text{Cr}(\text{CO})_3(\text{C}_6\text{H}_6)$  were determined by fitting the change in concentration with time to a straight line during approximately the first 5% of the reaction. Instantaneous rates during photolysis, i.e., the tangents to a concentration vs. time graph, were approximated as  $\Delta[R]/\Delta t$  for small time intervals.

## III. RESULTS

Irradiation at 254 nm of a  $2.1 \times 10^{-4} \text{ M}$  chloroform solution of  $\text{Cr}(\text{CO})_3(\text{C}_6\text{H}_6)$  ( $\epsilon_{254} = 8.2 \times 10^3$ ) led to the spectral changes shown in Figure 1. An isosbestic point at 440 nm was present until the baseline began to rise upon formation of a precipitate. Photolysis of a much more concentrated solution yielded a suspension of a fine, gray precipitate. Upon filtration the color changed to green, and its spectrum in  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{CN}$ , and  $\text{EtOH}$  matched that of *cis*- $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$  in the same solvents, including a shoulder in  $\text{EtOH}$  at about 690 nm. We assume that before filtration the product is primarily  $\text{CrCl}_3$ , which, because of the very small particle size, absorbs water rapidly

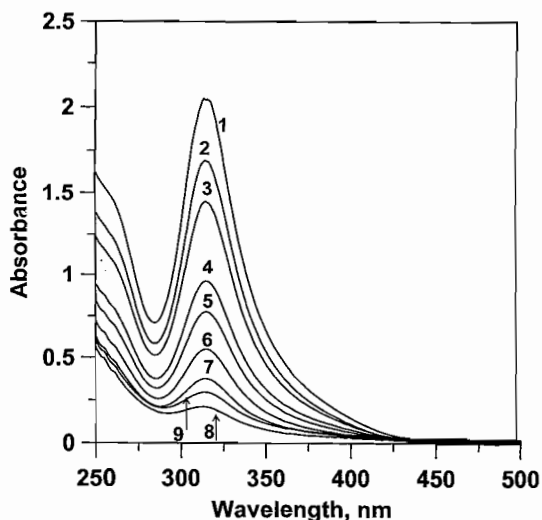


FIGURE 1 Sequential spectra from the 254 nm irradiation of a  $2.1 \times 10^{-4}$  M solution of  $\text{Cr}(\text{CO})_3(\text{C}_6\text{H}_6)$  in chloroform. Note the rise in the baseline in the last spectrum, consistent with dispersion from an incipient colloidal precipitate.

from the atmosphere, as well as adventitious and photolytically generated water from the solution. Samples of lower concentration than that used for Figure 1 were taken more nearly to completion without precipitation, and the spectrum of the product was featureless in the UV. There was no spectral evidence for the presence of either  $\text{Cr}(\text{CO})_6$  or  $\text{Cr}(\text{C}_6\text{H}_6)_2$ .

Photolysis also occurs, at a similar rate, under 313 nm irradiation, which is strong evidence that the reaction is primarily (or completely) metal-initiated. Deoxygenation of a sample by bubbling  $\text{N}_2$  through it for 3 min did not change the reaction rate, within experimental error. When neat chloroform was irradiated for 10 min at 254 nm and then added to an approximately  $10^{-4}$  M solution of  $\text{Cr}(\text{CO})_3(\text{C}_6\text{H}_6)$ , the spectral changes were identical to those taking place during photolysis. However, it required about 1 min for complete reaction. Irradiated  $\text{CHCl}_3$  contains  $\text{CCl}_3\text{OOH}$  (if  $\text{O}_2$  has not been excluded) and  $\text{HCl}$ , and can accomplish some, though not all, of the reactions that can occur through photolysis of the solvent [16]. This result indicates that a solvent-initiated

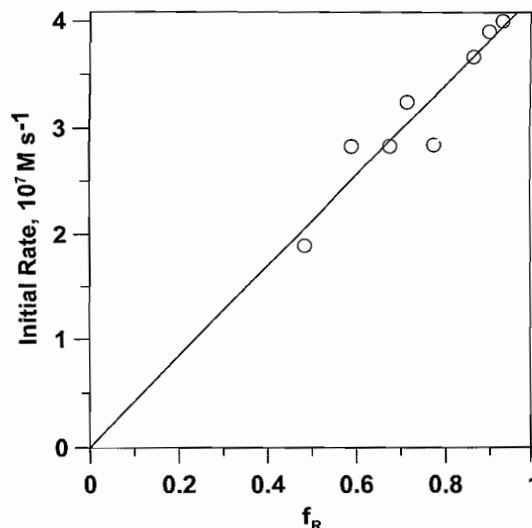


FIGURE 2 Initial rate of decomposition of  $4 \times 10^{-5}$  to  $3 \times 10^{-4}$  M solutions of  $\text{Cr}(\text{CO})_3(\text{C}_6\text{H}_6)$  in  $\text{CHCl}_3$  under 254 nm irradiation, plotted against the fraction of light absorbed by the complex.  $R^2$  for the linear fit is 0.89; slope =  $4.2 (\pm 0.1) \times 10^{-7} \text{ M s}^{-1}$ .  $I_0 = 9 \times 10^{-10}$  einstein/s.

pathway is possible, but it may be uncompetitively slow.

Initial rates for the disappearance of  $\text{Cr}(\text{CO})_3(\text{C}_6\text{H}_6)$  in  $\text{CHCl}_3$  under 254 nm irradiation were measured for several different starting concentrations at constant light intensity, and were plotted against  $f_R$ , the fraction of light absorbed by  $\text{Cr}(\text{CO})_3(\text{C}_6\text{H}_6)$ . The results, in Figure 2, indicate a direct dependence of  $f_R$  alone. Instantaneous rates up to approximately 75% disappearance also show the direct proportionality to  $f_R$  (Figure 3).

Initial rates for the disappearance of  $\text{Cr}(\text{CO})_3(\text{C}_6\text{H}_6)$  in  $\text{CHCl}_3$  under 254 nm irradiation were measured as a function of incident light intensity at a constant concentration of benzenetricarbonylchromium. There was a direct linear relationship ( $R^2 = 0.97$ ), and the slope corresponded to a quantum yield, based on light absorbed by the metal complex, of  $1.40 \pm 0.06$  mol/einstein.

All the kinetic results, together with the reactivity under higher wavelength irradiation, are consistent with a completely metal-initiated

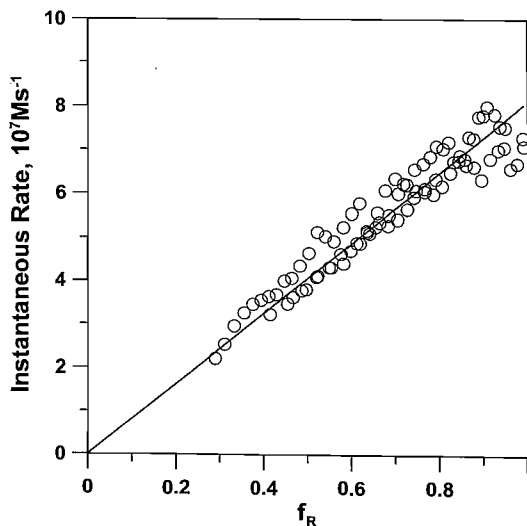


FIGURE 3 Instantaneous rates of reaction during the course of the 254 nm irradiation of three solutions (initial concentrations from  $9 \times 10^{-5}$  to  $3 \times 10^{-4}$  M) of  $\text{Cr}(\text{CO})_3(\text{C}_6\text{H}_6)$  in  $\text{CHCl}_3$ , plotted against the fraction of light absorbed by the reactant.  $R^2$  for the linear fit is 0.90.  $I_0 = 1.8 \times 10^{-9}$  einstein/s.

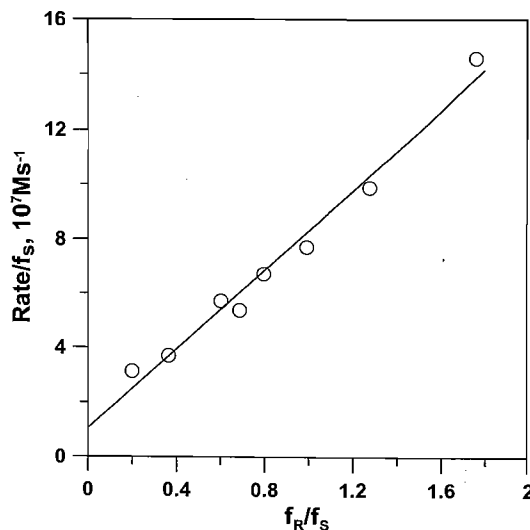


FIGURE 4 Initial rate of decomposition of  $3 \times 10^{-5}$  to  $3 \times 10^{-4}$  M solutions of  $\text{Cr}(\text{CO})_3(\text{C}_6\text{H}_6)$  in 24%  $\text{CCl}_4$ /76%  $\text{CHCl}_3$  by volume under 254 nm irradiation, plotted to show the fit to the expression  $af_R + bf_S$ . Slope of least squares line  $a = 7.3(\pm 0.4) \times 10^{-7} \text{ M s}^{-1}$ ; intercept  $b = 1.1(\pm 0.4) \times 10^{-7} \text{ M s}^{-1}$ ;  $R^2 = 0.98$ .  $I_0 = 1.2 \times 10^{-9}$  einstein/s.

photolysis. One further test was performed – photolysis was carried out on two solutions of the same concentration, one in chloroform, the other in carbon tetrachloride. The absorbance of  $\text{CCl}_4$  at 254 nm is approximately 60 times that of  $\text{CHCl}_3$ . Consequently, the fraction of light absorbed by the metal complex is greatly reduced while that of the solvent is greatly increased. Any radical reactions initiated by  $\text{Cl}^\bullet$  or  $^\bullet\text{CCl}_3$  in chloroform should also take place in  $\text{CCl}_4$ . Thus, as a general rule, solvent-initiated reactions should be much faster in  $\text{CCl}_4$  and metal-initiated reactions much slower. An exception can occur when HCl is a critical reactant in chloroform, in which case a solvent-initiated reaction can be retarded or extinguished. The intrinsic reactivity through a metal-initiated pathway may also be different in the two solvents, but the great difference in  $f_R$  should be decisive.

When  $\text{Cr}(\text{CO})_3(\text{C}_6\text{H}_6)$  solutions in  $\text{CHCl}_3$  and  $\text{CCl}_4$ , in like concentration, were irradiated at 254 nm, the reaction rate in carbon tetrachloride was almost exactly the same as that in chloroform.

This unexpected result led us to suspect that a solvent-initiated pathway does exist, but is too slow in pure chloroform to compete with the metal-initiated pathway.

To test this, initial rates of reaction were determined for a range of concentrations of  $\text{Cr}(\text{CO})_3(\text{C}_6\text{H}_6)$  in 24%  $\text{CCl}_4$ /76%  $\text{CHCl}_3$  by volume under 254 nm irradiation. A plot of rate against  $f_R$  was approximately linear, but definitely did not pass through the origin. Assuming that both metal- and solvent-initiated processes contributed to the overall rate, as expressed by

$$-\frac{d[R]}{dt} = af_R + bf_S \quad (3)$$

the coefficients  $a$  and  $b$  may be found from a plot of  $-(d[R]/dt)/f_S$  vs.  $f_R/f_S$ . The corresponding plot, Figure 4, yields the values  $a = 7.3(\pm 0.4) \times 10^{-7} \text{ M s}^{-1}$  and  $b = 1.1(\pm 0.4) \times 10^{-7} \text{ M s}^{-1}$ . In 24%  $\text{CCl}_4$ ,  $f_R$  and  $f_S$  have similar magnitudes over the range of concentrations used, in contrast to  $\text{CHCl}_3$  solutions, in which  $f_S$  is small. The

substantially greater value for the  $a$  coefficient indicates that even under these conditions the reaction is still primarily metal-initiated. Assuming the coefficients are also valid in pure  $\text{CCl}_4$ , in a  $10^{-4}$  M solution of  $\text{Cr}(\text{CO})_3(\text{C}_6\text{H}_6)$ ,  $f_R$  and  $f_S$  would be about 0.2 and 0.8, respectively, and the contributions from the two pathways would be close to equal. In going from  $\text{CHCl}_3$  to  $\text{CCl}_4$ , the increased participation of the solvent-initiated pathway serves to maintain the overall rate of photolytic decomposition.

Separate quantum yields may be calculated for the two pathways, based on Equation 3 and the experimental coefficients, which may be expressed as  $a = I_0\phi_R/V$  and  $b = I_0\phi_S/V$ . From this  $\phi_R$  is 1.9 and  $\phi_S$  is 0.3 mol/einstein. The solvent-based quantum yield,  $\phi_S$ , incorporates the quantum yield for the primary bond homolysis as well as the efficiency with which the radicals so formed decompose  $\text{Cr}(\text{CO})_3(\text{C}_6\text{H}_6)$ .

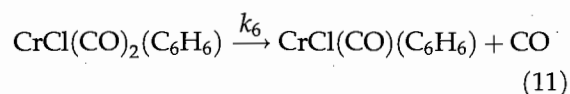
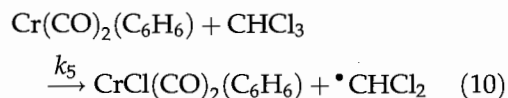
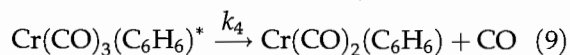
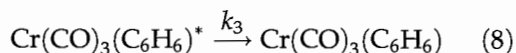
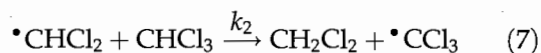
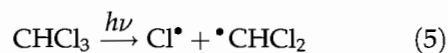
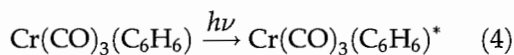
#### IV. DISCUSSION

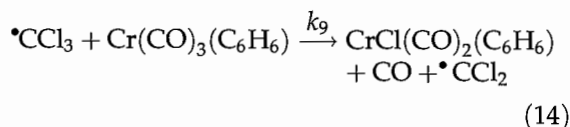
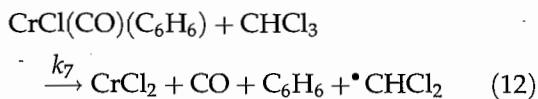
That the photolysis rate in  $\text{CCl}_4$  was the same as that in  $\text{CHCl}_3$  in our experiment was at least partly accidental. The solutions tested were optically dense, and at lower concentrations the rates would no longer be the same. Part of the reason that the rates were equal, despite a smaller fraction of light absorbed by the metal complex, was the role played by the solvent-initiated pathway in  $\text{CCl}_4$ . However, another significant reason was that the quantum yield for the metal-initiated pathway appears to be greater in  $\text{CCl}_4$ . There can be several reasons for this, including a greater probability for the reaction between the excited state complex and  $\text{CCl}_4$ , or a smaller rate of deactivation in a  $\text{CCl}_4$  cage.

The magnitude of  $\phi_R$  suggests that a chain reaction may be involved. However, this need not be true, and in fact, if it were true, there would most likely be a square root dependence of the rate on intensity due to a bimolecular termination step [16,20]. It is much more likely that each

photon can initiate decomposition of two or more reactant molecules. This can readily occur in  $\text{CHCl}_3$  or  $\text{CCl}_4$ , because each of the three chlorine atoms eventually acquired by the chromium can generate a radical through the encounter of an intermediate metal complex with chloroform. The radical may then attack the reactant to displace a carbonyl, magnifying the initial photochemical event. Of course, the radicals would be exactly those generated through direct photodissociation of  $\text{CHCl}_3$  or  $\text{CCl}_4$ , which would bring in a solvent-initiated path. However, the efficiency of the primary metal-centered photochemical step is apparently so great that, at least in chloroform, the solvent-initiated pathway is insignificant.

A sample mechanism is shown below for  $\text{CHCl}_3$ . Similar steps would occur in  $\text{CCl}_4$ . The steps in which  $\text{CO}$  or  $\text{C}_6\text{H}_6$  is lost and in which  $\text{CHCl}_3$  reacts with an intermediate may occur in an order quite different from that illustrated. However, the order of these steps is without kinetic consequences.





The last step, Equation 14, illustrates the reaction of the trichloromethyl radical with the starting complex to yield the intermediate from Equation 10, at which point the metal-initiated and solvent-initiated pathways converge. The rate of the primary metal-initiated photochemical step, Equation 4, is  $I_{0fR}/V$ . The rate of the primary solvent-initiated photochemical step, Equation 5, is  $I_{0fs}\phi_C/V$ , where  $\phi_C$  represents the quantum yield for bond homolysis.

Given the steady state approximation for all intermediate species, the rate of reaction from the sequence above is

$$-\frac{d[R]}{dt} = 4 \left( \frac{k_4}{k_3 + k_4} \right) \frac{I_{0fR}}{V} + 2 \frac{I_{0fs}\phi_C}{V} \quad (15)$$

Thus the maximum quantum yield for the metal-initiated pathway would be 4, corresponding to the primary event plus three radicals formed, while the maximum quantum yield for the solvent-initiated pathway is 2, because of the two radicals formed by homolysis.

In this light, the quantum yield of 1.4 in chloroform is reasonable. The quantum yield observed for the photodecomposition of  $\text{Cr}(\text{CO})_3(\text{C}_6\text{H}_6)$  in isooctane is approximately 0.1 under 365 nm irradiation, but increases if  $\text{CCl}_4$  is added [5]. In methyl methacrylate the quantum yield is 0.4 [5]. In isooctane, loss of CO is followed by further decomposition, and eventually rearrangement [5]. In methyl methacrylate, the solvent replaces carbon monoxide, or benzene, as a ligand [5]. In the presence of pyridine, photolysis of  $\text{Cr}(\text{CO})_3(\text{C}_6\text{H}_6)$  to form  $\text{Cr}(\text{CO})_2(\text{C}_6\text{H}_6)\text{py}$

proceeds with a quantum yield of 0.7 in several different solvents, and independently of wavelength [4]. The much higher value of  $\phi$  in chloroform is consistent with the multiplicative effect of radical formation as chromium-chlorine bonds are formed. It is also consistent with the observation that the photodecomposition of  $\text{Cr}(\text{CO})_3(\text{C}_6\text{H}_6)$  can be used to initiate polymerization of methyl methacrylate, but only when some  $\text{CCl}_4$  is added [5].

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