

## Observation of Pentacarbonylchromium on Flash Photolysis of Hexacarbonylchromium in Cyclohexane Solution

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**Summary** The first observable transient (lifetime  $> 50$  ns) on flash photolysis of  $\text{Cr}(\text{CO})_6$  is  $\text{Cr}(\text{CO})_5$ , which is the precursor of two species previously assigned to the  $D_{3h}$  and  $C_{4v}$  forms of  $\text{Cr}(\text{CO})_5$ , and now shown to arise from reaction with impurities.

THERE is general agreement that the species seen after irradiation of  $\text{Cr}(\text{CO})_6$ ,  $\text{Mo}(\text{CO})_6$ , and  $\text{W}(\text{CO})_6$  in hydrocarbon glasses<sup>1–3</sup> at 77 K or in rare gas matrices<sup>4,5</sup> at 20 K are the  $C_{4v}$  forms of the respective metal pentacarbonyls, although the assignment of a further species observed on melting the hydrocarbon glasses as the  $D_{3h}$  form has been doubted by recent workers.<sup>2,5</sup> In solution, there have been qualitative studies<sup>4,6</sup> and millisecond flash photolysis has been performed. Nasielski *et al.*<sup>3</sup> reported the presence of two transient species having absorption in the visible region of the spectrum. The first ( $\lambda_{\text{max}}$  483 nm) did not react with CO, but instead formed, with a half-life of 6 ms, the second ( $\lambda_{\text{max}}$  445 nm) which slowly recombined with CO with a half-life of 25 s. These species were assigned to the  $C_{4v}$  and  $D_{3h}$  forms of  $\text{Cr}(\text{CO})_5$  by analogy with the study of Sheline and his co-workers.<sup>1</sup> On the other hand, Kelly and Morris<sup>7</sup> reported that under similar conditions, two transients could be observed but that the decay kinetics and the absorption spectra were irreproducible, presumably due to traces of impurities in the solvent.

We have examined this system further using a flash photolysis apparatus with a higher time resolution (flash half-width  $\leq 3 \mu\text{s}$ )<sup>8</sup> and with more extensively purified

solvent.<sup>†</sup> Under these conditions we have observed a species (P) immediately after the flash, which shows a broad band in the visible absorption spectrum with maximum absorption at  $503 \pm 5$  nm. This species has a lifetime  $> 200 \mu\text{s}$  and reacts to form further species ( $\lambda_{\text{max}}$  445 nm) which themselves decay away with lifetimes of  $< 1$  s to reform the hexacarbonyl.

TABLE. Formation of  $\text{Cr}(\text{CO})_5\text{X}$  from  $\text{Cr}(\text{CO})_6$  as a function of the concentrations of  $\text{Cr}(\text{CO})_6$  and  $\text{Cr}(\text{CO})_5$ <sup>a</sup>

$10^{-4} \times [\text{Cr}(\text{CO})_6]$ ( $\text{mol l}^{-1}$ )	Discharge energy (J)	Initial optical density of $\text{Cr}(\text{CO})_5$	$[\text{Cr}(\text{CO})_5\text{X}]^b$ / $[\text{Cr}(\text{CO})_6]$
0.2	25	0.24	$0.07 \pm 0.03$
	50	0.45	$0.07 \pm 0.02$
0.7	12.5	0.16	$0.10 \pm 0.03$
	25	0.41	$0.11 \pm 0.02$
1.1	50	0.93	$0.12 \pm 0.02$
	12.5	0.18	$0.10 \pm 0.03$
3.3	25	0.49	$0.10 \pm 0.02$
	50	1.20	$0.11 \pm 0.02$
	25	0.58	$0.11 \pm 0.02$
	50	1.48	$0.12 \pm 0.02$

<sup>a</sup> In cyclohexane solution under 1 atm of CO. <sup>b</sup> (O.D. of  $\text{Cr}(\text{CO})_5\text{X}$  at  $200 \mu\text{s}$ )/(Initial O.D. of  $\text{Cr}(\text{CO})_5$ ) multiplied by  $\epsilon[\text{Cr}(\text{CO})_6]/\epsilon[\text{Cr}(\text{CO})_5\text{X}]$ . The extinction coefficient ratio is known from photolysis of  $\text{Cr}(\text{CO})_6$  in argon-saturated solutions, where  $\text{Cr}(\text{CO})_6$  is completely converted into  $\text{Cr}(\text{CO})_5\text{X}$ .

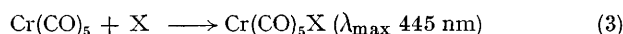
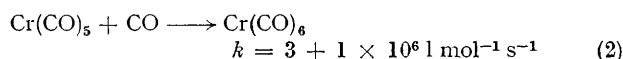
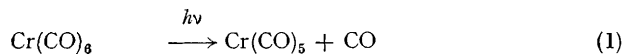
If the solution is saturated under 1 atm of CO, P reacts to reform  $\text{Cr}(\text{CO})_6$  with a half-life of  $25 \mu\text{s}$ . In addition a

<sup>†</sup> The cyclohexane (spectroanalytical grade or g.c. purified material) was dried by distillation from  $\text{P}_2\text{O}_5$  under argon, and all sample preparation was carried out under argon. Samples ( $[\text{Cr}(\text{CO})_6] = 10^{-5} - 2 \times 10^{-4}$  M) were degassed either by flushing with purified argon or by a series of freeze at 77 K, pump, and thaw cycles, followed by pumping at room temperature. None of the residual impurities in the g.c. purified material exceeded 20 p.p.m.

small quantity ( $\leq 10\%$ ) of other products is simultaneously formed. The pseudo first order rate constant for disappearance of P under these conditions is  $2.8 \pm 0.3 \times 10^4 \text{ s}^{-1}$ . Assuming the concentration $\ddagger$  of CO in solution at  $25^\circ$  to be  $1.1 \times 10^{-2} \text{ mol l}^{-1}$  a rate constant for the recombination process of  $3 \pm 1 \times 10^6 \text{ l mol}^{-1} \text{ s}^{-1}$  can be derived.

The rate constant of decay of P is sensitive to the purity of the solvent and to the method of degassing. If the degassing is performed by the conventional "freeze, pump, and thaw" method used in earlier studies,<sup>3,7</sup> a further species ( $\lambda_{\text{max}} 470\text{--}480 \text{ nm}$ ) is formed. We presume that this latter species is formed by some artifact. $\S$

We believe that these findings are consistent with the mechanisms (1), (2), and (3) and with P being  $\text{Cr}(\text{CO})_5$ .



In solution under 1 atm of CO, varying the concentrations of  $\text{Cr}(\text{CO})_5$  and  $\text{Cr}(\text{CO})_6$  did not affect the proportion of  $\text{Cr}(\text{CO})_5\text{X}$  produced from  $\text{Cr}(\text{CO})_5$  (see Table). Thus under these conditions X is neither  $\text{Cr}(\text{CO})_5$  nor  $\text{Cr}(\text{CO})_6$ . There is, however, a slight variation when cyclohexane from

$\ddagger$  This value is for heptane,<sup>9</sup> as no value for cyclohexane has been reported.

$\S$  Prof. Nasielski has confirmed this conclusion.

$\P$  In further studies we have shown that complexes of  $\text{Cr}(\text{CO})_5$  with acetone, methanol, ethyl acetate, and diethyl ether have  $\lambda_{\text{max}}$  in the range 435–465 nm. Therefore X may be a related oxygen containing compound.

different sources is used. Further, we could observe no products from decomposition of cyclohexane after irradiation of solutions of  $\text{Cr}(\text{CO})_6$ ,<sup>10</sup> and we therefore conclude that X is not the solvent, but rather that P is able to scavenge slight traces of impurities contained in solution. $\ddagger\P$  The extreme sensitivity of P is illustrated by the fact that, for instance, species P produced under argon has a lifetime of less than  $50 \mu\text{s}$  in the presence of  $10^{-4} \text{ mol l}^{-1}$  acetone (7 p.p.m.).

By use of a laser flash photolysis apparatus (Applied Photophysics Ltd) we have shown that species P is formed within 50 ns of excitation of  $\text{Cr}(\text{CO})_6$ .<sup>11</sup> Therefore should an isomerisation process be taking place, it must do so with a rate constant  $> 2 \times 10^7 \text{ s}^{-1}$ , provided that the isomers have detectably different absorption spectra.

We do not know the structure of  $\text{Cr}(\text{CO})_5$  in solution. However, its absorption maximum in both cyclohexane and in 1:1 methylcyclohexane-isopentane solutions at room temperature is at somewhat longer wavelengths than those observed for the  $C_{4v}$  form of  $\text{Cr}(\text{CO})_5$  in methylcyclohexane glasses at 77 K (483 nm,<sup>2</sup> 485 nm<sup>3</sup>) and in methane matrices at 20 K (492 nm).<sup>5</sup>

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