trasonic measurements (-10.1 ± 0.2 cm^3 mol^{-1}) and from two static perturbations of the equilibrium (-8.6 ± 0.3 cm^3 mol^{-1} from electronic spectra and -10.0 ± 0.1 cm^3 mol^{-1} from NMR contact shifts[4]).

A thorough analysis of the reaction mechanism is not possible in the absence of solvent exchange rate data, potentially obtainable from NMR studies. It is unlikely, however, that the water-exchange rate will be significantly more rapid than the octahedral–planar transformation. The measured rate constant k_{64} of 2.8×10^7 s^{-1} ($\Delta H_{64}^{*} = 9.3$ kcal mol^{-1}) is the minimum rate of exchange of *two* water molecules from the octahedral isomer. This is surprisingly close to the rate of acetonitrile exchange on the same complex of 1.5×10^7 s^{-1} ($\Delta H^{*} = 9.9$ kcal mol^{-1}) calculated per one acetonitrile molecule. It is also similar to the rate of water exchange (per water molecule) of 2.1×10^7 s^{-1} ($\Delta H^{*} = 7.8$ kcal mol^{-1}) on octahedral Ni([12]aneN$_4$)(H$_2$O)$_2^{2+}$ assumed to be in a cis configuration[17] and to the rate of water exchange (per water molecule) of $(2.1 \pm 0.7) \times 10^7$ s^{-1} ($\Delta H^{*} = 9.6 \pm 1.6$ kcal mol^{-1}) on Ni(cyclam)(H$_2$O)$_2^{2+}$.[9]

We assume that the five-coordinate species intermediate between the planar and trans-octahedral species is paramagnetic. In other words, it is distinguished from the solvated planar complex by the change in electron and nuclear configurations that result in high-spin, lenghtened nickel–nitrogen bonds. Hence, the transition from four- to five-coordinate nickel is accompanied by the exothermic formation of a new nickel–water bond and the endothermic lengthening of the nickel–nitrogen bonds. The transition from five- to six-coordinate nickel will be exothermic due to formation of the second nickel–water bond. The enthalpy profile of the reaction give in Figure 4 reflects this pattern. We conclude that the transition state closely resembles a paramagnetic five-coordinate intermediate.

Very accurate data under identical reaction conditions for both the planar–octahedral relaxation and the solvent-exchange process would be needed to determine whether the four–five or five–six coordinate step might be rate determining. Only if the solvent exchange rate were significantly more rapid than the establishment of the planar–octahedral equilibrium could it be concluded that the four–five coordinate transformation with the accompanying spin-state change were rate determining. For Ni(cyclam)(H$_2$O)$_2^{2+}$ the water-exchange rate of $(2.1 \pm 0.4) \times 10^7$ s^{-1} per water molecule corresponds to a minimum relaxation time of the planar–octahedral equilibrium of 80 ± 30 ns. This is within experimental error of the minimum of 10^{-7} s observed in the ultrasonic experiment. Hence, it is possible that for Ni(cyclam)(H$_2$O)$_2^{2+}$ the water-exchange process is effected by the planar–octahedral equilibrium with nearly concerted loss and addition of two water molecules.

There are small differences between Ni(Me$_4$cyclam)$^{2+}$ and Ni(cyclam)$^{2+}$, both in the trans configuration. Water addition to Ni(cyclam)$^{2+}$ is less exothermic (-5.0 kcal mol^{-1})[9] than to Ni(Me$_4$cyclam)$^{2+}$ (-6.9 kcal mol^{-1}). There is a slightly smaller decrease in entropy on water addition to Ni(cyclam)$^{2+}$ than to Ni(Me$_4$cyclam)$^{2+}$. In contrast, however, the rate of interconversion of the planar and octahedral species is slower for Ni(cyclam)$^{2+}$ than for Ni(Me$_4$cyclam)$^{2+}$. Finally, there is a 9–10 cm^3 mol^{-1} decrease in volume on adding two water molecules to Ni(Me$_4$cyclam)$^{2+}$ but only a 3–4 cm^3 mol^{-1} decrease in volume on the addition of two water molecules to Ni(cyclam)$^{2+}$. Since it is unlikely that there is a significant difference in the volume change due to expansion in the plane of the macrocycles, the differences probably arise from hydrogen-bonding effects associated with the amine protons. Further work is needed to elucidate these.

Acknowledgment. This work was supported by the Australian Research Grant Scheme. We appreciate enlightening discussions with both Dr. Michael Grant and Dr. Stephen Lincoln.

Registry No. Ni(Me$_4$cyclam)$^{2+}$, 48175-68-4.

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Structures and Kinetics of Cr(CO)$_5$ and Cr(CO)$_5$·H$_2$O in Cyclohexane Solution. Flash Photolysis Study of Cr(CO)$_6$ with Infrared and Visible Detection[†]

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Flash photolysis of Cr(CO)$_6$ in cyclohexane solution generates Cr(CO)$_5$ coordinated by the solvent, i.e., Cr(CO)$_5$·C$_6$H$_{12}$. The transient infrared spectrum obtained after flash photolysis of the monolabeled chromium hexacarbonyl, Cr(CO)$_5$(^{13}CO), proves that the pentacarbonylchromium fragment adopts a square-pyramidal (C_{4v}) geometry at room temperature. The axial–equatorial bond angle, determined as 93°, indicates that the structures of Cr(CO)$_5$ in solution and in low-temperature matrices are similar. The presence of a water trace impurity in CO-saturated cyclohexane solutions has been kinetically and spectroscopically identified. Studies in H$_2$O/CO-saturated cyclohexane solutions show that Cr(CO)$_5$·C$_6$H$_{12}$ is 13 times more reactive with H$_2$O than with CO. Activation parameters for the decay of Cr(CO)$_5$·H$_2$O allow an estimate of 75 ± 15 kJ mol^{-1} for the dissociation of the H$_2$O ligand.

Introduction

Cr(CO)$_5$ is a 16-electron coordinatively unsaturated species that displays a remarkable interaction toward normally inert substances. In low-temperature matrices, Perutz and Turner[1] demonstrated that the position of the visible absorption band of Cr(CO)$_5$ was extraordinarily sensitive to the nature of the matrix. This was interpreted in terms of a specific interaction between the Cr(CO)$_5$ fragment and the matrix material, a shift to shorter wavelength indicating a stronger interaction. Evidence for such shifts has also been found in the gas phase,[2] and flash photolysis experiments by Bonneau and Kelly[3] showed that similar interactions exist in room-temperature solution. The Cr(CO)$_5$ species generated in perfluoromethylcyclohexane reacts with CO and N$_2$ by nearly diffusion-controlled processes, whereas Cr(CO)$_5$ in cyclohexane (C$_6$H$_{12}$) is 3 orders of magnitude less reactive with these gases.[4,5] The Cr(CO)$_5$·C$_6$H$_{12}$ ($\lambda_{\max}$ 503 nm) interaction is similar to that

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[†] Dedicated to Professor Günther Wilke on the occasion of his 60th birthday.

(1) Perutz, R. N.; Turner, J. J. *J. Am. Chem. Soc.* **1975**, *97*, 4791.
(2) Breckenridge, W. H.; Sinai, N. *J. Phys. Chem.* **1981**, *85*, 3557.
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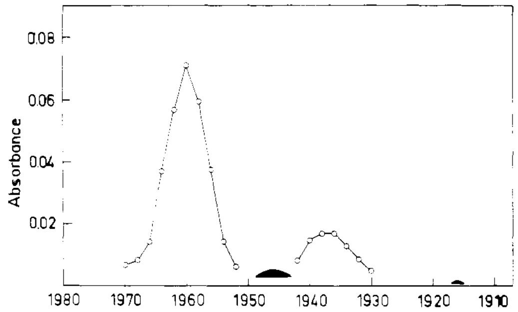

Figure 1. Transient IR spectrum of $Cr(CO)_5 \cdot C_6H_{12}$ generated by flash photolysis of 5×10^{-4} M $Cr(CO)_6$ in CO-saturated C_6H_{12} solution. Black regions show the quantity of $Cr(CO)_5 \cdot H_2O$ that grows in without H_2O added.

Table I. IR and Visible Absorptions of $Cr(CO)_5$ in Cyclohexane Solution and Solid Methane and Argon Matrices

		ν_{CO}, cm^{-1}			
medium	temp, K	a_1	e	a_1	λ_{max}, nm $E \leftarrow A_1$
C_6H_{12}	298	*a*	1960	1937	500
CH_4[b]	20	2088	1961	1932	489
Ar[b]	20	2093	1966	1936	533

[a] Not observed, predicted to be very weak. [b] Reference 9.

of, e.g., $Cr(CO)_5 \cdot CH_4$ (λ_{max} 489 nm)[1] and $Cr(CO)_5 \cdot Xe$[6] (λ_{max} 492 nm[1]), and it is considerably stronger than that of $Cr(CO)_5 \cdot C_7F_{14}$ (λ_{max} 620 nm). Indeed, $Cr(CO)_5 \cdot C_7F_{14}$ can even react with added C_6H_{12} to form $Cr(CO)_5 \cdot C_6H_{12}$ and with $Cr(CO)_6$ to form $Cr_2(CO)_{11}$ at nearly diffusion-controlled rates.[3] Recent picosecond flash photolysis experiments[7] indicated that in C_6H_{12} solution $Cr(CO)_5 \cdot C_6H_{12}$ is formed within 25 ps of the excitation of $Cr(CO)_6$. Hence, any preceding intermediates, such as excited states of $Cr(CO)_6$ and $Cr(CO)_5$, must have lifetimes on the picosecond time scale.

Although flash photolysis experiments with UV–vis detection have been crucial in the study of $Cr(CO)_5$, they are very limited in providing structural information. The structural characterization of metal carbonyl fragments has therefore been almost solely restricted to IR spectroscopy in low-temperature matrices.[8] Perutz and Turner[9] showed that the structure of $Cr(CO)_5$ in CH_4 and Ar matrices is square pyramidal, with axial–equatorial bond angles of 93 and 94°, respectively. According to one report, however, $Cr(CO)_5$ adopts a D_{3h} geometry in Ar/CO matrices,[10] although this claim has been heavily disputed.[11] For $M(CO)_5$ species a combination of ^{13}CO enrichment and IR spectroscopy should readily distinguish between C_{4v} and D_{3h} geometries.

Part of this study is concerned with the detailed structure elucidation of $Cr(CO)_5 \cdot C_6H_{12}$ at room temperature by means of fast IR spectroscopy[5,12,13] and with use of $Cr(CO)_5(^{13}CO)$[5,16] as the starting material. This represents the first study of this kind, and it shows that the conclusions drawn from matrix isolation experiments may be extended to room-temperature solutions. Furthermore, we present kinetic and spectroscopic evidence that the only impurity that has been important in these CO-saturated C_6H_{12} solutions was H_2O. $Cr(CO)_5$ has been known[4,12] to coordinate an impurity at room temperature even in rigorously purified C_6H_{12}. Such impurities are important in view of the high reactivity of $Cr(CO)_5 \cdot$solv (solv = solvent) with donor ligands such as H_2O, acetone, and methanol. We have now unequivocally characterized the trace product as $Cr(CO)_5 \cdot H_2O$ and have quantified the kinetic effect of H_2O in these systems.

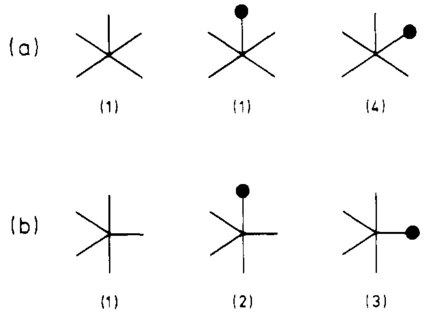

Figure 2. Isotopomers of $Cr(CO)_{5-x}(^{13}CO)_x$, $x = 0, 1$, with statistical probabilities in brackets (● = ^{13}CO group): (a) C_{4v} geometry; (b) D_{3h} geometry.

Results and Discussion

Identification of the $Cr(CO)_5 \cdot C_6H_{12}$ Complex. Flash photolysis of $Cr(CO)_6$ in CO-saturated C_6H_{12} solution generated a transient with a visible absorption at 500 nm and IR CO-stretching vibrations at 1960 and 1937 cm^{-1} (Figure 1, Table I).[17] This species, assigned as $Cr(CO)_5 \cdot C_6H_{12}$, disappeared on the same time scale[18] on which another species, displaying low-intensity absorptions under these conditions, grew in (λ_{max} 455 nm; ν_{CO} 1946, 1916 cm^{-1} (Figure 1)). This second transient, shown below to be $Cr(CO)_5 \cdot H_2O$, disappeared with a rate constant that varied from one experiment to another but lay in the region of 600–800 s^{-1}. All $Cr(CO)_6$ was subsequently regenerated.

These observations can be interpreted in terms of reactions 1–4, which have been adopted, together with the appropriate kinetic expressions (5), (6), and (7), from earlier work,[4] in which acetone, benzene, diethyl ether and ethyl acetate were used as added ligands. Under these conditions $k_2[CO] >> k_3[H_2O]$; therefore,

$$Cr(CO)_6 \xrightarrow[C_6H_{12}]{h\nu} Cr(CO)_5 \cdot C_6H_{12} + CO \qquad (1)$$

$$Cr(CO)_5 \cdot C_6H_{12} + CO \xrightarrow{k_2} Cr(CO)_6 + C_6H_{12} \qquad (2)$$

$$Cr(CO)_5 \cdot C_6H_{12} + H_2O \xrightarrow{k_3} Cr(CO)_5 \cdot H_2O + C_6H_{12} \qquad (3)$$

$$Cr(CO)_5 \cdot H_2O \xrightarrow[C_6H_{12}]{k_4} Cr(CO)_5 \cdot C_6H_{12} + H_2O \qquad (4)$$

it was possible to neglect eq 3 and 4 at this stage and a second-

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(13) Time-resolved IR spectroscopy is beginning to develop into an important tool to study structure and kinetics of transients in room-temperature solutions. As already shown in our initial and subsequent communications,[5,12,14] metal carbonyl photochemistry is a particularly well-suited field for our first-generation instrument,[15] the time resolution and sensitivity of which is presently improved (cf. ref 17 in ref 5).

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(15) For a more recent report on results achieved with a related instrument, see: Moore, B. D.; Simpson, M. B.; Poliakoff, M.; Turner, J. J. *J. Chem. Soc., Chem. Commun.*, in press. We thank the authors for communication prior to publication.

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(17) The 1937-cm^{-1} band of $Cr(CO)_5 \cdot C_6H_{12}$ was not observed in our previous study[12] since higher impurity levels led to the grow-in of species such as $Cr(CO)_5 \cdot H_2O$, which obscured this region.

(18) The pseudo-first-order rate constant for the disappearance of $Cr(CO)_5 \cdot C_6H_{12}$ is 43 000 s^{-1} at 1.3 bar of CO and 298 K; cf. 28 000 s^{-1} at 1 bar of CO and room temperature.[4]

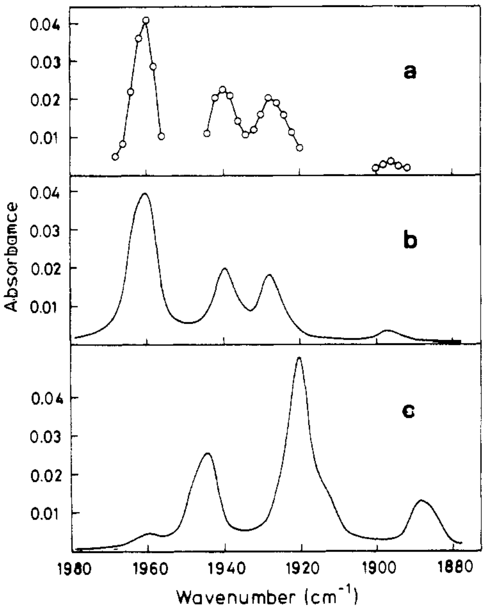

Figure 3. (a) Transient IR spectrum of the photoproducts of a 6 × 10^{-4} M solution of $Cr(CO)_5(^{13}CO)$ in CO-saturated C_6H_{12} solution. The spectrum is a superposition of the IR frequencies of $Cr(CO)_{5-x}(^{13}CO)_x$, $x = 0, 1$. Fresh solution had to be used for each measured point since scrambling occurs in regenerated $Cr(CO)_6$. (b) Simulated IR spectrum for $Cr(CO)_{5-x}(^{13}CO)_x$, $x = 0, 1$, calculated assuming a C_{4v} structure, axial–equatorial bond angle 93°, $\mu_{ax}'/\mu_{eq}' = 1$, and the force constants given in Table II (Lorentzian band shapes, 7 cm^{-1} fwhm). (c) Simulated IR spectrum for $Cr(CO)_{5-x}(^{13}CO)_x$, $x = 0, 1$, calculated assuming a D_{3h} structure, $\mu_{ax}'/\mu_{eq}' = 1$, and Timney force constants (N m^{-1}) $k_{ax} = 1589.6$, $k_{eq} = 1540.8$, $k_{trans} = 60.7$, $k_{eq,eq} = 49.2$, $k_{ax,eq} = 34.6$ (Lorentzian band shapes, 7 cm^{-1} fwhm).

order rate constant k_2 of 3.6 × 10^6 dm^3 mol^{-1} s^{-1} could be determined (CO pressure 1.3 bar, [CO] = 1.2 × 10^{-2} M, 298 K[19]). This value agrees, within experimental error, with that determined by Kelly et al.[4] for $Cr(CO)_5{\cdot}C_6H_{12}$ in conventional flash photolysis. The assignment of this first transient is further supported by the following facts. (i) It is the only species formed within the pulse half-life of 1.5 μs used in the IR experiments, or of 10 ns used in the UV–vis experiments. (ii) The visible transient spectrum corresponds to that observed by Welch et al.[7] 25 ps after the excitation of $Cr(CO)_6$ in C_6H_{12}. (iii) No impurities were detected in the solvent by GLC. (iv) The transient is the precursor to the second species, $Cr(CO)_5{\cdot}H_2O$, formed on reaction with traces of H_2O in the C_6H_{12} solution undetected by GLC.

Structure of $Cr(CO)_5{\cdot}C_6H_{12}$. The transient IR spectrum of $Cr(CO)_5{\cdot}C_6H_{12}$ is shown in Figure 1. For a trigonal-bipyramidal $Cr(CO)_5$ fragment (D_{3h} geometry), two infrared-active CO-stretching vibrations are expected, a$_2''$ and e′, with approximate relative intensities of 2:3. A square-pyramidal $Cr(CO)_5$ fragment (C_{4v} geometry) should have three infrared-active CO-stretching vibrations, two a$_1$ and one e. The high-frequency a$_1$ vibration is usually very weak and may well to be too weak to be observed under our conditions,[20] whereas the e vibration should be about 4 times stronger than the low-frequency a$_1$ vibration. On the basis of these simple arguments, the spectrum in Figure 1 is clearly consistent with a C_{4v} structure.

Much more information can be gained by using $Cr(CO)_5(^{13}CO)$[5,16] as a starting material. A superposition of the absorptions of three isotopomeric products is now to be expected for the transient IR spectra of both a square-pyramidal (Figure 2a) and a trigonal-bipyramidal geometry (Figure 2b). The initial spectrum formed by flash photolysis of the labeled compound in CO-saturated C_6H_{12} solution is shown in Figure 3a. The observed pattern of frequencies and intensities is reproduced fairly well by calculation[21] using Timney force constants[22] and a dipole derivative ratio, μ_{ax}'/μ_{eq}', of 1. The assumption of a dipole derivative ratio of 1 is based on the values determined for $Cr(CO)_5$ in low-temperature matrices: $Cr(CO)_5{\cdot}CH_4$, 0.877; $Cr(CO)_5{\cdot}Ar$, 1.080.[9] An independent determination of values for the dipole derivative ratio and the bond angle was not possible since no high-frequency a$_1$ vibration was observed.

Table II. Observed and Calculated Wavenumbers (cm^{-1}) of the IR Bands of $Cr(CO)_{5-x}(^{13}CO)_x$, $x = 0, 1$, in Room-Temperature Cyclohexane Solution

molecule	mode	obsd	calcd[a]
$Cr(CO)_5$	a$_1$	*b*	2087
(C_{4v} geometry)	b$_2$	*c*	1998
	e	1960	1961
	a$_1$	1937	1937
$Cr(CO)_4(^{13}CO,ax)$	a$_1$	*b*	2083
(C_{4v} geometry)	b$_2$	*c*	1998
	e	1960	1961
	a$_1$	1896	1897
$Cr(CO)_4(^{13}CO,eq)$	a′	*b*	2079
(C_s geometry)	a′	*d*	1991
	a″	1960	1961
	a′	1940	1940
	a′	1928	1928

[a] Each frequency was only entered once into the least-squares refinement; force constants (N m^{-1}): $k_{ax} = 1540$, $k_{eq} = 1613.7$, $k_{ax,eq} = 37.0$, $k_{eq,eq(cis)} = 30.4$, $k_{eq,eq(trans)} = 60.0$. [b] Not observed, predicted to be very weak. [c] Formally IR inactive. [d] Not observed, predicted to be obscured by a band of $Cr(CO)_5(^{13}CO)$.

However, an even better fit is obtained for the observed frequencies simply by modifying the value of the force constant k_{ax} for $Cr(CO)_5$ in a CH_4 matrix (1531.45 N m^{-1})[9] to 1540 N m^{-1} and keeping the other force constants the same.[9] The error between observed and calculated frequencies is then better than the experimental error (±2 cm^{-1}) for the measured values (Table II). The simulated spectrum (Figure 3b), calculated by using these modified force constants, an axial–equatorial bond angle of 93°, and $\mu_{ax}'/\mu_{eq}' = 1$, is in excellent agreement with the observed spectrum (Figure 3a).

The observed spectrum (Figure 3a) could not be accommodated by a D_{3h} structure. The isotopic frequencies calculated from force constants obtained by the Timney method[22] (Figure 3c) were in very poor agreement. Attempts to refine the D_{3h} force constants to produce a significantly better fit proved fruitless. The simulated D_{3h} isotopic spectrum, generated by Timney force constants and $\mu_{ax}'/\mu_{eq}' = 1$, is shown in Figure 3c. Clearly, the $Cr(CO)_5$ fragment in C_6H_{12} has a square-pyramidal structure very similar to that of $Cr(CO)_5$ in Ar and CH_4 matrices, and the D_{3h} structure must be rejected.

Identification of the $Cr(CO)_5{\cdot}H_2O$ Complex. Kelly et al.[4] described the formation of a $Cr(CO)_5{\cdot}X$ complex (λ_{max} ca. 450 nm) from reaction of $Cr(CO)_5{\cdot}C_6H_{12}$ with a trace impurity X in the flash photolysis of $Cr(CO)_6$ in CO-saturated C_6H_{12} solution. X was not identified but could be quantitatively accounted for in the kinetic analysis. A subsequent similar study using IR detection[12] indicated that X was likely to be moisture.

When $Cr(CO)_6$ was subjected to microsecond flashes in C_6H_{12} solutions saturated with CO and H_2O ("added" H_2O; see Experimental Section), $Cr(CO)_5{\cdot}C_6H_{12}$ was barely discernible by

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(19) Extrapolated from [CO] = 9.2 × 10^{-3} M at 1 bar and 298 K: Wilhelm, E.; Battino, R. *J. Chem. Thermodyn.* **1973**, *5*, 117 (cf. Wilhelm, E.; Battino, R. *Chem. Rev.* **1973**, *73*, 1).

(20) Cf. $Mn(CO)_5$, which has recently been reported in hydrocarbon solution.[14a]

(21) The application of ^{13}CO isotopic substitution and IR spectroscopy to the structural characterization of metal carbonyl complexes has been extensively reviewed.[8] Timney's[22] empirical method of obtaining a starting set of energy-factored force constants works well for $M(CO)_x$ complexes with regular bond angles, i.e., 90, 109, 120, 180°. Thus, accurate force constants are generated for $Mo(CO)_5$ (C_{4v} geometry, axial–equatorial bond angle 91°[9]), but the method is less reliable for $Mn(CO)_5$ (C_{4v} geometry, axial–equatorial bond angle 96°[23]).

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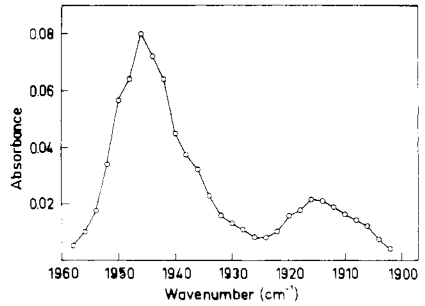

Figure 4. Transient IR spectrum of $Cr(CO)_5{\cdot}H_2O$ generated by the thermal reaction of $Cr(CO)_5{\cdot}C_6H_{12}$ with H_2O following the flash photolysis of 5×10^{-4} M $Cr(CO)_6$ in CO/H_2O-saturated C_6H_{12} solution.

Table III. IR and Visible Absorptions of $Cr(CO)_5{\cdot}H_2O$ in Cyclohexane Solution and Hydrocarbon Glasses

medium	temp, K	ν_{CO}, cm⁻¹ a_1	b_2	e	a_1	λ_{max}, nm $E \leftarrow A_1$
C_6H_{12}[a]	298	*b*	*c*	1946	1916	455
methylcyclohexane–isopentane[d]	>150	2080	1975	1936	1908	
	<120					435

[a] This work. [b] Not observed, predicted to be weak. [c] Formally IR inactive. [d] Reference 24.

either visible or IR detection. Only the final portion of the transient decay signal was observed, evidently because $Cr(CO)_5{\cdot}C_6H_{12}$ was mostly consumed within the duration of the flash. However, laser experiments on the nanosecond time scale showed that the product, identified by its visible absorption maximum at 500 nm, was formed within 10 ns of the excitation of $Cr(CO)_6$. Concurrent with the disappearance of $Cr(CO)_5{\cdot}C_6H_{12}$, a second prominent transient appeared at 455 nm by first-order kinetics, $k_{app} = 1.8 \times 10^5$ s⁻¹ (298 K). The decay of this second transient was too slow to be monitored on the nanosecond apparatus, but complete reversibility of the system was ascertained since no loss of the $Cr(CO)_6$ was detected after 200 laser pulses. The slower decay could be established by microsecond techniques with IR detection. It followed excellent first-order kinetics; $k_{exptl} = 160$ s⁻¹ (298 K). The absorptions of the second transient are the same as those observed for the impurity complex, i.e., in the absence of added H_2O (see above and Figures 1 and 4 and Table III). However, its formation from $Cr(CO)_5{\cdot}C_6H_{12}$ in H_2O-saturated solution is now much more efficient. We assign this second species to $Cr(CO)_5{\cdot}H_2O$. Its spectrum is compatible with that observed by Boylan et al.[24] in hydrocarbon glasses (Table III). Interestingly, the IR bands of $Cr(CO)_5{\cdot}H_2O$ (Figure 4) are approximately twice as broad as those of $Cr(CO)_5{\cdot}C_6H_{12}$ (Figure 1). The reasons for this difference are not yet clear.

The rate constant for the grow-in of Cr(CO)5·H_2O (suitably monitored either by the decay of $Cr(CO)_5{\cdot}C_6H_{12}$, measured at 560 nm, or by the grow-in of $Cr(CO)_5{\cdot}H_2O$, measured at 450 nm) is given[4] by

$$k_{app} = k_2[CO] + k_3[H_2O] \tag{5}$$

($k_{app} \equiv k_f$ in ref 4). Note that, in the absence of added H_2O, $k_2[CO] >> k_3[H_2O]$. The rate constant for the disappearance of $Cr(CO)_5{\cdot}H_2O$ is given by

$$k_{exptl} = \frac{k_4k_2[CO]}{k_2[CO] + k_3[H_2O]} \tag{6}$$

and

$$\frac{1}{k_{exptl}} = \frac{1}{k_4} + \frac{k_3[H_2O]}{k_4k_2[CO]} \tag{7}$$

Table IV. Rate Constants and Stability Constants for $Cr(CO)_5(R_2O)$ Complexes in Cyclohexane Solutions

R_2O	$10^{-7}k_3$, dm³ mol⁻¹ s⁻¹	k_4, s⁻¹	$10^{-4}k_3/k_4 = 10^{-4}K$, dm³ mol⁻¹
H_2O[a]	4.5_5	670	6.8
diethyl ether[b]	1.1	140	7.6
tetrahydrofuran[c]	4		

[a] This work; $[H_2O] = 3.01 \times 10^{-3}$ M in H_2O-saturated C_6H_{12} at 298 K.[25] [b] Reference 4. [c] Reference 26.

With use of eq 5 and 6, the rate constants k_3 and k_4 and the equilibrium constant K (= k_3/k_4) can now be calculated from the values of $k_2[CO]$ and k_{app}, measured in the absence of added H_2O and in H_2O-saturated solution, respectively (see above) (Table IV). The value of k_3 is very close to that reported for diethyl ether[4] and tetrahydrofuran[26] as added ligands, and the K values for the H_2O and diethyl ether systems are almost identical. The kinetic role of water is therefore very similar to that of ethers (R_2O). The strength of the interaction with the ligands R_2O can be gauged from the visible absorptions of the $Cr(CO)_5{\cdot}R_2O$ complexes at about 450 nm compared with, e.g., λ_{max} 620 nm for $Cr(CO)_5{\cdot}C_7F_{14}$, 500 nm for $Cr(CO)_5{\cdot}C_6H_{12}$, and 370 nm for $Cr(CO)_5{\cdot}N_2$. The IR absorptions of $Cr(CO)_5{\cdot}H_2O$ at frequencies as low as 1946 and 1916 cm⁻¹ suggest that H_2O is a good donor ligand.

For the identification of the impurity complex as $Cr(CO)_5{\cdot}H_2O$ the calculated k_4 value of 670 s⁻¹ (298 K) is of particular significance. It is apparent from eq 6 and 7 that k_4 becomes equal to k_{exptl} at zero concentration of H_2O. And indeed, without the addition of H_2O k_{exptl} lies in the region of 600–800 s⁻¹, i.e., within the experimental error of k_4. The error in these rate constants is too large to determine the trace level concentration of H_2O. However, we estimate that a maximum of 5% of $Cr(CO)_5{\cdot}C_6H_{12}$ is converted to $Cr(CO)_5{\cdot}H_2O$ (cf. Figure 1). Thus, under these conditions (see eq 5), $k_2[CO] \approx 20\ k_3[H_2O]$, which suggests an upper limit for the H_2O concentration of 5×10^{-5} M (≤1 ppm). Hence, the correction term for k_2 at trace levels of H_2O is less than 5%, i.e., within the experimental error of the measured rate constants.

Further support for the identification of $Cr(CO)_5{\cdot}H_2O$ from the two extreme cases described above, i.e., in H_2O-saturated solution and in the absence of added H_2O, comes from the effect of liquid pumping in the sample preparation. From a H_2O-saturated solution H_2O can in fact be drastically removed in this way (see Experimental Section). This is manifested by an increase in k_{exptl} with continued liquid pumping within the range 160–800 s⁻¹ and a drop to the lower limit upon subsequent saturation with H_2O. Correspondingly, the IR absorption intensities of the complex showed a decreasing trend. Since the CO absorptions of $Cr(CO)_5{\cdot}H_2O$ could be practically suppressed in only three liquid-pumping steps, the method should certainly receive greater attention for H_2O-sensitive systems.

Temperature-Dependence Measurements. The temperature dependence of k_2, monitored by IR detection, was measured at 295–315 K in CO-saturated C_6H_{12} solutions. The CO concentration is practically constant within this temperature range and is estimated as 1.2×10^{-2} M.[19] The rate constants k_{app} (see eq 5, determined by visible detection) and k_{exptl} (see eq 6, determined by IR detection) were measured in the same temperature range in H_2O/CO-saturated C_6H_{12} solutions. Appropriate corrections were made for the variation of the H_2O concentration in C_6H_{12} with temperature.[25]

The activation energies for reactions 2 and 3 were the same within experimental error, both determined as 22 ± 5 kJ mol⁻¹. This suggests that the 13-fold higher value of k_3 over k_2 is determined by the preexponential factor. However, since the errors involved in these measurements are large, such consideration

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necessarily remains speculative.

The activation energy for reaction 4 was calculated as 75 ± 15 kJ mol^{-1}. This value can be taken as a good estimate of the dissociation energy in going from $Cr(CO)_5{\cdot}H_2O$ to the "naked" $Cr(CO)_5$ and H_2O, since $Cr(CO)_5$ in noncoordinating solvent is known[3] to possess only negligible activation barriers for reaction. The value is reasonable for a loosely bound H_2O ligand and can be compared with the following activation energies for dissociation of stable complexes:

$$Cr(CO)_6 \rightarrow Cr(CO)_5 + CO \qquad E_a \approx 170 \text{ kJ mol}^{-1}\,{}^{27}$$

$$Cr(CO)_5PR_3 \rightarrow Cr(CO)_5 + PR_3 \qquad E_a \approx 130 \text{ kJ mol}^{-1}\,{}^{28}$$

Conclusion

This study, using time-resolved IR spectroscopy,[12,13] has helped to bridge the gap between the results obtained in low-temperature matrices and room-temperature solutions. In particular, the structure of the $Cr(CO)_5$ fragment, a transient with a half-life <20 μs in CO-saturated C_6H_{12} solution at room temperature, correlates with that found at low temperature.

Moreover, further insight into the nature of $Cr(CO)_5$ interactions has been gained, which are important in the photochemistry of $Cr(CO)_6$. This also includes the role of impurities in these reactions (q.v.). Thus, $Cr(CO)_5{\cdot}C_6H_{12}$ is 13 times more reactive with H_2O ($k_3 = 4.6 \times 10^7$ dm^3 mol^{-1} s^{-1}) than with CO ($k_2 = 3.6 \times 10^6$ dm^3 mol^{-1} s^{-1}). Other ligands such as acetone, methanol, acetonitrile, diethyl ether,[4] and tetrahydrofuran[26] are also highly reactive with the C_6H_{12} complex. Any trace impurity of this kind can therefore play a significant role in the photochemistry of $Cr(CO)_6$.

Experimental Section

The instrumental design[12] and improved sample preparation procedures[5] for flash photolysis experiments with IR detection have been previously described. The importance of rigorous precautions throughout sample preparations cannot be overstressed.[5] In addition to the previously described IR cell, a thermostated cell was also used in this study. CaF_2 windows were mounted in a VA steel block (1 mm path length) fitted with electrical heater and thermocouple giving a temperature accuracy of ±1 °C.

Laser flash photolysis experiments were conducted with an EMG 200 excimer laser (Lambda Physics, Göttingen, West Germany) emitting at 248 nm (KrF) with a pulse half-life of ca. 10 ns. Laser and analyzing beams were arranged in a crossed-beam setup. The detection system has been described elsewhere.[29] Samples were prepared in 1-cm cuvettes and vacuum degassed by liquid pumping.[4,5] For temperature measurements the solution was heated manually and the temperature measured by a thermocouple.

CO was research grade quality (99.997%) supplied by Messer Griesheim. $Cr(CO)_6$ was purchased from Merck (z. S.), and $Cr(CO)_5(^{13}CO)$ was prepared by the published procedure.[16] Typical concentrations of $Cr(CO)_6$ were 5×10^{-4} M for IR experiments and 6×10^{-5} M for laser flash experiments, which ensured homogeneity of the C_6H_{12} solutions. When H_2O-saturated solutions were required, triply distilled H_2O was degassed by liquid pumping and distilled into the solution vessel[5] until a two-phase system was obtained. The solutions were finally saturated with CO to a pressure of 1.3 bar. Thorough shaking ensured saturation of C_6H_{12} with the gas and also with H_2O when added.

For the removal of H_2O from the H_2O-saturated C_6H_{12} solution by liquid pumping[30] the organic layer was first decanted from the H_2O phase and then subjected to three freeze–pump–thaw cycles before 1.3 bar of CO was added to the solution vessel and the first flash experiment performed. Subsequently the vapor phase was allowed to expand at room temperature into a flask of a ca. 7-fold volume previously evacuated. The flask was then disconnected, the solution vessel refilled with 1.3 bar of CO, and the next experiment carried out.

All rate constants measured in this study (k_2[CO], k_{app}, k_{exptl}) unquestionably obeyed first-order kinetics. With allowance for concentration uncertainties in the additives CO and H_2O, the derived rate constants k_2, k_3, and k_4 contain a possible error of 20%. At or near the maximum transient absorption one signal sweep was sufficient to give excellent S/N ratios in experiments with both IR and visible detection. Signal averaging in the IR experiments was employed (up to 16 scans) for weaker transient signals in order to accurately determine rate constants and absorbances throughout the entire spectral range.

Force constant calculations were performed on an Apple II computer using iterative refinement programs.[9] IR spectra were simulated on a Nicolet 1280E computer using a program that constructed Lorentzian band shapes around the frequency and intensity data derived from the Apple programs. All such calculations were carried out at the University of Nottingham, England.

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Registry No. $Cr(CO)_6$, 13007-92-6; $Cr(CO)_5(^{13}CO)$, 17594-10-4; $Cr(CO)_5$, 39586-86-2.

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