$[\mathrm{Cr(CO)_5Xe}]$ in Solution; the First Spectroscopic Evidence

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$[\mathrm{Cr(CO)_5Xe}]$ is identified, from its $\nu_{\mathrm{C-O}}$ i.r. bands, as a relatively long-lived species ($t_{\frac{1}{2}}$ *ca.* 2 s at −98 °C) generated by u.v. photolysis of $[\mathrm{Cr(CO)_6}]$ dissolved in liquefied Xe or liquefied Kr doped with Xe.

Room-temperature flash photolysis[1] and low-temperature solution experiments[2] indicate rapid co-ordination of the $[\mathrm{Cr(CO)_5}]$ fragment by a saturated hydrocarbon [reaction (1)].‡ These experiments have confirmed the results of matrix isolation[3,4] which established a specific and significant interaction between the co-ordinatively unsaturated fragment $[\mathrm{Cr(CO)_5}]$ and supposedly innocuous matrix materials. The nature (*i.e.* chemical bond[4] or dispersion forces[5]) and magnitude of this $[\mathrm{Cr(CO)_5}]\cdots\mathrm{Q}$ interaction are not known but the energy of the visible absorption band of $[\mathrm{Cr(CO)_5}\cdots\mathrm{Q}]$ increases along the series $\mathrm{Ne}<\mathrm{SF_6}<\mathrm{Ar}<\mathrm{Kr}<\mathrm{Xe}\sim\mathrm{CH_4}$ indicating an increasingly strong interaction.[6] Thus, for

$$[\mathrm{Cr(CO)_6}] + \mathrm{RH} \xrightarrow{h\nu} [\mathrm{Cr(CO)_5}\cdots\mathrm{RH}] + \mathrm{CO} \qquad (1)$$

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‡ There is some evidence for the transient formation of these species in the gas phase (W. H. Breckenridge and N. Sinal, *J. Phys. Chem.*, 1981, **85**, 3557).

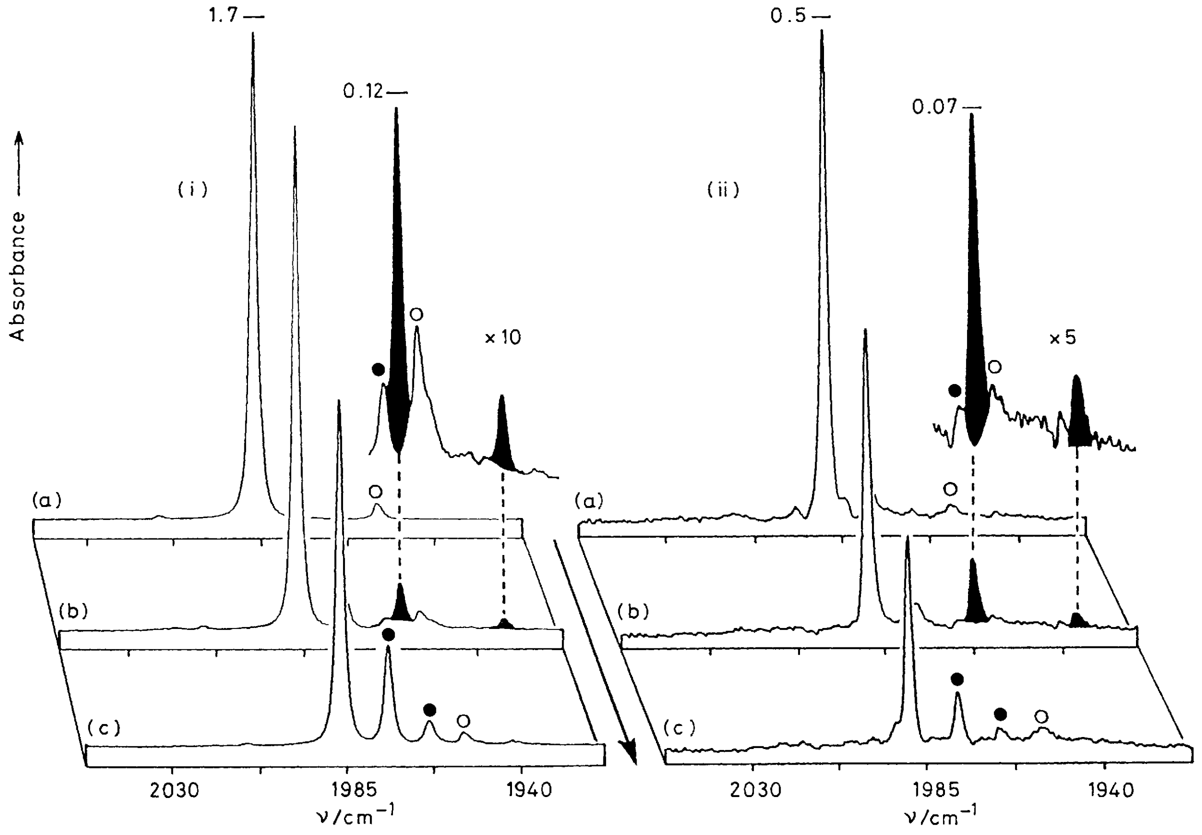

Figure 1. FTIR spectra¶ of $[\mathrm{Cr(CO)_6}]$ dissolved in (i) pure liquid Xe, −98 °C and (ii) liquid Kr containing 5% Xe, −122 °C. (a) Spectra before photolysis; (b) spectra taken during u.v. photolysis (250 W high-pressure Hg arc); (c) spectra after photolysis. Each spectrum took 17 s to scan and the total time of the experiment (a) → (c) is about 1 min. In each spectrum, the strongest band is due to $[\mathrm{Cr(CO)_6}]$ and other bands are assigned as follows: Black, $[\mathrm{Cr(CO)_5Xe}]$; ○, $[\mathrm{Cr(CO)_5(^{13}CO)}]$ (nat. abundance); ●, $[\mathrm{Cr(CO)_5N_2}]$. The concentration of $[\mathrm{Cr(CO)_6}]$ was *ca.* 10^{-5} M and the solutions contained <1 p.p.m. of N_2 impurity, which accounts for the small quantities of $[\mathrm{Cr(CO)_5N_2}]$ formed during photolysis.

example, $[\mathrm{Cr(CO)_5\cdots Xe}]$ is produced by photolysis of matrix-isolated $[\mathrm{Cr(CO)_6}]$ in the presence of Xe at 20 K [reaction (2)].

$$[\mathrm{Cr(CO)_6}] + \mathrm{Xe} \xrightarrow[20\,\mathrm{K}]{\mathrm{u.v.}} [\mathrm{Cr(CO)_5\cdots Xe}] + \mathrm{CO} \qquad (2)$$

Here, we present evidence which shows that in liquid noble gas solution at −100 °C the solvated species $[\mathrm{Cr(CO)_5Xe}]$ is sufficiently stable to be detected by conventional Fourier-transform i.r. (FTIR) interferometry.

The experimental arrangement for obtaining low-temperature liquefied noble gas solutions has been described previously.[7] Our four-windowed cell allows i.r. spectra to be recorded during u.v. photolysis of a solution.

We have already reported[8] that brief u.v. photolysis of $[\mathrm{Cr(CO)_6}]$ in liquefied xenon or krypton solution with added N_2 generates a long-lived $[\mathrm{Cr(CO)_5N_2}]$ species, identified by i.r. spectroscopy and thermally stable to −35 °C. On the other hand, photolysis of $[\mathrm{Cr(CO)_6}]$ in pure liquefied xenon or in liquefied krypton doped with 5% Xe produces a much shorter-lived species ($t_{\frac{1}{2}}$ *ca.* 2 s at −98 °C, in liq. Xe); see the bands coloured black in Figure 1.

This species has i.r. bands in the C–O stretching region, characteristic of a $[\mathrm{Cr(CO)_5Q}]$ compound. The bands are close in frequency to those of matrix-isolated $[\mathrm{Cr(CO)_5Xe}]$ and are significantly different from those of more obvious $[\mathrm{Cr(CO)_5(impurity)}]$ species § (see Table 1) which are all known to have much longer lifetimes under these conditions. The transient species is not observed at all when small quantities of oxygen are added to the solution [reaction (3)].

$$[\mathrm{Cr(CO)_6}] \xrightarrow[\text{Liq. Xe or liq. Kr/Xe}]{\mathrm{u.v.}} [\mathrm{Cr(CO)_5Q}] \qquad (3)$$

$$Q \neq N_2,\ H_2O,\ O_2,\ \text{or}\ H_2$$

The experiment, illustrated in Figure 2, elimimates the possibility that the transient $[\mathrm{Cr(CO)_5Q}]$ species could be an isomer of $[\mathrm{Cr(CO)_6}]$, *e.g.* $[\mathrm{Cr(CO)_5OC}]$, or some polymeric species, *e.g.* $[\mathrm{Cr_2(CO)_{11}}]$. This experiment was designed to compare directly the photolysis of $[\mathrm{Cr(CO)_6}]$ in pure liq. Kr with photolysis of $[\mathrm{Cr(CO)_6}]$ in liq. Kr *containing* 5% *Xe*. It is clear that the absorption of the transient $[\mathrm{Cr(CO)_5Q}]$, arrowed in Figure 2, was only observed in the Xe-doped solution. The two photolyses were *identical* {*i.e.* the same lamp intensity, the same temperature, the same initial concentration of $[\mathrm{Cr(CO)_6}]$}, apart from the addition of Xe to

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¶ All spectra were run with a Nicolet MX 3600 FTIR interferometer with 32 K data points (0.7 $\mathrm{cm^{-1}}$ resolution) and one degree of zero filling in the Fourier transform. The spectra in Figure 1 each represent a single data collection while these in Figure 2 are the co-addition of six separate data collections.

§ We have repeated the observation with at least four independent Xe samples with no change in result. In addition, mass spectrometric and detailed i.r. examination of the Xe reveals no significant impurity.

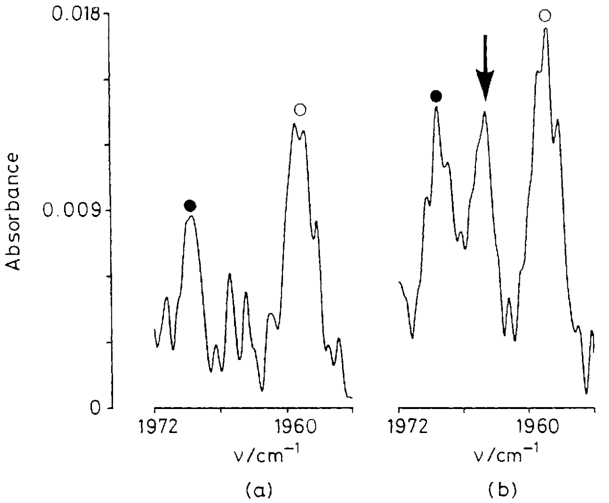

Figure 2. FTIR spectra, recorded during the u.v. photolysis of $[Cr(CO)_6]$ in (a) pure liquid Kr and (b) liquid Kr doped with 5% Xe. The bands are assigned: ●, $[Cr(CO)_5N_2]$; ↓, $[Cr(CO)_5Xe]$; ○, $[Cr(CO)_5{}^{13}CO]$. The same solution was used for both spectra, and all experimental conditions were identical apart from the addition of Xe between the recording of the two spectra. $[Cr(CO)_6]$ is substantially less soluble in pure liq. Kr than liq. Kr/Xe mixtures so a higher temperature (−111 °C) and lower lamp intensity were used than in the experiment illustrated in Figure 1(ii). The vapour pressure of Kr at this temperature is *ca.* 1.3 MPa (170 psig).

the solution. Xe is therefore necessary for the formation of the transient species, which can only be $[Cr(CO)_5Xe]$ [reaction (4)].

$$[Cr(CO)_6] + Xe \xrightarrow[\text{Liq. noble gas}]{\text{u.v.}} [Cr(CO)_5Xe] + CO \quad (4)$$

The thermal decay of $[Cr(CO)_5Xe]$ in liq. Kr + 5% Xe has a low activation energy,** 15 ± 2 kJ mol^{-1}. Any Cr–Xe interaction might be expected to be weak[5] but, unfortunately, the precise interpretation of this activation energy must await further evidence for the mechanism of the decay of $[Cr(CO)_5Xe]$. However, the surprisingly long lifetime of $[Cr(CO)_5Xe]$ (*i.e.* a half-life of a few seconds) must be due, in part, to the high concentration of Xe, *ca.* 1.5—27 M, and the extremely low concentrations of the other reactants, 10^{-7}—10^{-5} M.

Table 1. Wavenumbers (in cm^{-1}) of bands due to $[Cr(CO)_5Q]$ species dissolved in liquid Xe at −98 °C.

ν_{C-O}	Q = Xe	Xe[a]	H_2O[b]	N_2[c]	H_2[d]
a_1	**2085.9**	**2086**	2073.9	2086	2093.6
e	**1960.3**	**1956**	1944.5 1938.5	1974.4	1973.3
a_1	**1934**	**1929**	1913.3	1963.8	1957

[a] Xe matrix, 20 K, ref. 3. [b] Ref. 8; strictly this molecule has C_{2v} symmetry. [c] Ref. 8. [d] Tentative assignment, ref. 9.

Our experiments provide evidence for the existence of $[Cr(CO)_5Xe]$ *in solution*. The interaction of $[Cr(CO)_5]$ with Xe is not therefore restricted to solid state matrices, and our results further underline the remarkable reactivity of co-ordinatively unsaturated metal carbonyl species.

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** Determined by assuming the steady state approximation and measuring the concentration of transient at different temperatures. This is consistent with the observation that $[Cr(CO)_5Xe]$ has similar lifetimes in liq. Kr/Xe at −122 °C and in pure liq. Xe at −98 °C, where the concentration of Xe is, of course, higher.