Photochemistry in Liquid Xenon: Synthesis of $[Cr(CO)_5N_2]$ from $[Cr(CO)_6]$ and N_2

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Summary $[Cr(CO)_5N_2]$ is produced by u.v. photolysis of $[Cr(CO)_6]$ dissolved in liquid xenon containing a trace of N_2 and is found to be stable in solution at −79 °C; $[Cr(CO)_5N_2]$ is converted back into $[Cr(CO)_6]$ by irradiation with 367 nm light.

BINARY compounds of the form $[M(CO)_x(N_2)_y]$, where M = transition metal, have been synthesised only in low-temperature matrices either by co-condensation on cold surfaces[1,2] or by u.v. photolysis of matrix-isolated metal carbonyls in N_2-doped matrices.[2–4] Although these compounds are well characterized in cold matrices, almost nothing has been reported about them in solution. Transient formation of $[Cr(CO)_5N_2]$ has been postulated to explain short-lived absorptions[5] and kinetic data[6] from flash photolysis of $[Cr(CO)_6]$ in fluoro- and hydro-carbon solvents at room temperature. No definitive evidence that $[M(CO)_{6-n}(N_2)_n]$ (M = Cr, Mo, W) can be produced by the photolysis of $[M(CO)_6]$ in liquid solutions has yet been published.

Here we report the production of $[Cr(CO)_5N_2]$ by the u.v. photolysis of $[Cr(CO)_6]$ in solution. Liquid xenon is used as the solvent because of its freedom from spectral absorptions and because the low temperature tends to stabilize unstable species.[7] We can thus use a longer optical path-length and achieve a higher concentration of $[Cr(CO)_5N_2]$ than would be possible in common room-temperature solvents.

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In this experiment, roughly 0·2 μmol of [Cr(CO)$_6$] were dissolved in liquid xenon containing a trace (<20 p.p.m.) of dissolved N$_2$. Our cryostat[7,8] had an optical pathlength of 1·3 cm and an internal volume of 2·5 cm^3. The cryostat can be pressurized to about 12,000 Torr, and xenon pressures > *ca.* 2,000 Torr were used in these experiments. The solution was irradiated and simultaneously stirred,[7,8] and the progress of the photolysis was monitored at intervals by changes in the i.r. absorption spectrum of the solution.‡

TABLE. I.r. absorption bands of [Cr(CO)$_5$N$_2$] and [Cr(CO)$_6$] in liquid xenon.

Wavenumber/cm^{-1}			Assignment[d]
Present[a]	Ref. 4[b]	Ref. 2[c]	
2237·2±0·5	2240·6	2243	ν(NN)a$_1$
2087·0±0·5	2086	2088	ν(CO)a$_1$
1975·5±0·3	1978·2[e]	1975	ν(CO)e
1966·8±0·3	1959·5	1962	ν(CO)a$_1$
1987·6±0·3	—	1986·5	ν(CO)t$_{1u}$[Cr(CO)$_6$]

[a] Dissolved in liquid xenon at −79 °C. [b] Raman lines of [Cr(CO)$_5$N$_2$] isolated in CH$_4$ matrices doped with N$_2$. [c] I.r. absorptions of [Cr(CO)$_5$N$_2$] isolated in a N$_2$-doped Ar matrix at 10 K. [d] Bands of the C_{4v} species [Cr(CO)$_5$N$_2$] unless otherwise noted. [e] I.r. absorption band.

Parts of the i.r. spectra before and after photolysis are shown in the Figure. Before photolysis only the i.r. absorption bands of [Cr(CO)$_6$] are prominent between 400 and 4000 cm^{-1}. Photolysis of the solution with unfiltered u.v. light causes the new bands listed in the Table to appear. In the C–O and N–N stretching regions of the spectrum, the wavenumbers of these new bands closely correspond to those of the known[2,4] bands of [Cr(CO)$_5$N$_2$], which has C_{4v} symmetry. The relative absorbances of the new bands are also similar to those found[2,4] for [Cr(CO)$_5$N$_2$]. The results indicate that the photochemical reaction (1) has occurred.

$$[\mathrm{Cr(CO)_6}] + \mathrm{N_2} \xrightarrow{\text{u.v.}} [\mathrm{Cr(CO)_5N_2}] + \mathrm{CO} \qquad (1)$$

Cooling the solution reduced the absorbances of the bands of both [Cr(CO)$_5$N$_2$] and [Cr(CO)$_6$]. Rewarming the solution caused the absorbances of the bands to increase, presumably because the two compounds were precipitating and redissolving.

Previous experiments[2,4] have shown that [Cr(CO)$_5$N$_2$] can be converted back into [Cr(CO)$_6$] in a matrix by 367 nm light. In the present experiment in liquid xenon, 367 nm light caused a large decrease in the absorbances of the [Cr(CO)$_5$N$_2$] bands and a smaller increase in the absorbance of the [Cr(CO)$_5$^{13}CO] band shown in the Figure. A detailed analysis of the spectra shows that this increase in absorbance is within experimental error of that which would be expected for the reaction (2).

$$[\mathrm{Cr(CO)_5N_2}] + \mathrm{CO} \xrightarrow{367\ \text{nm}} [\mathrm{Cr(CO)_6}] + \mathrm{N_2} \qquad (2)$$

Preliminary results indicate that u.v. photolysis of [Cr(CO)$_5$N$_2$] in liquid xenon causes further substitution of N$_2$ for CO, *e.g.* formation of [Cr(CO)$_4$(N$_2$)$_2$].

The following points are clear from this work. (i) The positive identification of [Cr(CO)$_5$N$_2$] relied on the results of matrix-isolation studies. Preliminary matrix-isolation

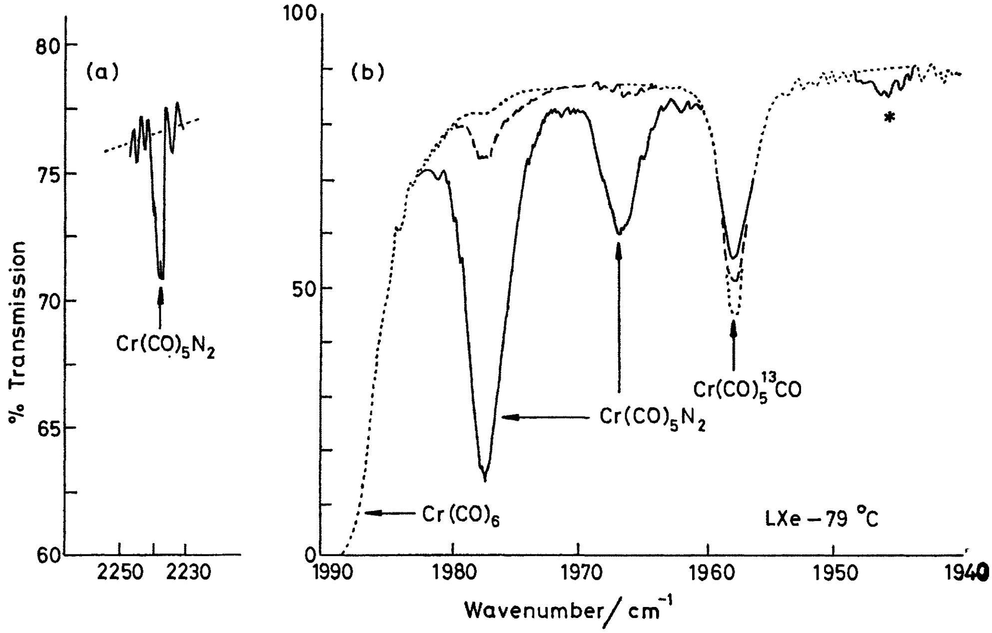

FIGURE. Absorption spectra of [Cr(CO)$_5$N$_2$] and [Cr(CO)$_6$] dissolved in liquid xenon at −79 °C. The spectra are represented by the following curves: (· · · ·) before photolysis; (———) after 3·3 min irradiation with an unfiltered Hg arc lamp placed 28 cm from the centre of the cryostat; (– – – –) after irradiation for about 12 min with the Hg arc lamp and Balzers 367 nm filter about 14 cm from the centre of the cryostat. Where these curves are indistinguishable, only the dotted curve is shown. For clarity, the noise has been omitted from the dotted curve in part (a). The feature marked with an asterisk (*) is tentatively assigned to [Cr(CO)$_4$(N$_2$)$_2$].

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‡ All spectra were obtained with a Perkin-Elmer Model 283B spectrophotometer. The u.v. light source was a Philips HPK-125W medium pressure Hg arc lamp used in conjunction with a Balzers 367 nm u.v. interference filter when appropriate.

studies can therefore be very suggestive for solution photochemistry. (ii) The band splitting observed in matrix-isolated compounds does not occur for molecules dissolved in liquids, so that there are no ambiguities about band positions. (iii) The solution technique promises to be a method for the synthesis and study of many unstable compounds. For example we have evidence for the photolytic production of $[Mo(CO)_5N_2]$ and $[Ni(CO)_3N_2]$. (iv) In matrices it is possible to isolate highly reactive species. In solutions we expect to observe only moderately unstable molecules, but we can obtain both kinetic and energetic data for the reactions in which these unstable species participate.

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