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Preliminary communication

Matrix isolated metal carbonyl anions

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SUMMARY

Cocondensation at 20K of sodium atoms with transition metal carbonyls (*e.g.* $Cr(CO)_6$) diluted in argon gives IR spectroscopic evidence for carbonyl anions (*e.g.* $Cr(CO)_5^-$).

Several carbonyl anions ($Fe(CO)_4^{2-}$, $V(CO)_6^-$) have been well characterised. Evidence for many others is rather tenuous. Recently anionic species (*e.g.* $B_2H_6^-$ [1], NO_2^- [2]) have been generated in low temperature rare gas matrices by a variety of techniques, and in particular by cocondensation of some parent compounds with alkali metal atoms as electron donors.

We describe preliminary experiments applying this technique to carbonyl chemistry; in particular to chromium carbonyls. Our results demonstrate the possibility of preparing carbonyl anions and identifying them spectroscopically.

Figure 1(i) shows the infrared spectrum in the carbonyl stretching region obtained on cocondensing a stream of sodium atoms, from a furnace, with a gas stream of $Cr(CO)_6$ in argon (dilution 1/2000) on to a CsBr window maintained at 20 K. In addition to the $Cr(CO)_6$ bands (labelled '6'-1995, 1990 and 1959 cm^{-1} the latter due to $Cr(CO)_5(^{13}CO)$) there are two weak bands at 1855 and 1838 cm^{-1} labelled 'a', 'b' respectively.

Figure 1(ii) shows the infrared spectrum obtained after photolysis of the initial matrix and then repeated spray on and photolysis to obtain increased intensities of product bands. A medium pressure mercury arc with a water filter was used for photolysis. 'a' and 'b' have increased in intensity and a new band has appeared at 1852 cm^{-1} ('c'). In addition new bands have appeared at 1965 and 1936 cm^{-1}, which are labelled '5' since they have been previously assigned to the C_{4v} form of $Cr(CO)_5$ formed by CO loss from $Cr(CO)_6$ [3].

On annealing the matrix to about 35 K, band 'c' disappeared and band 'a' increased in intensity, band 'b' being unaffected. Further photolysis regenerated band 'c' at

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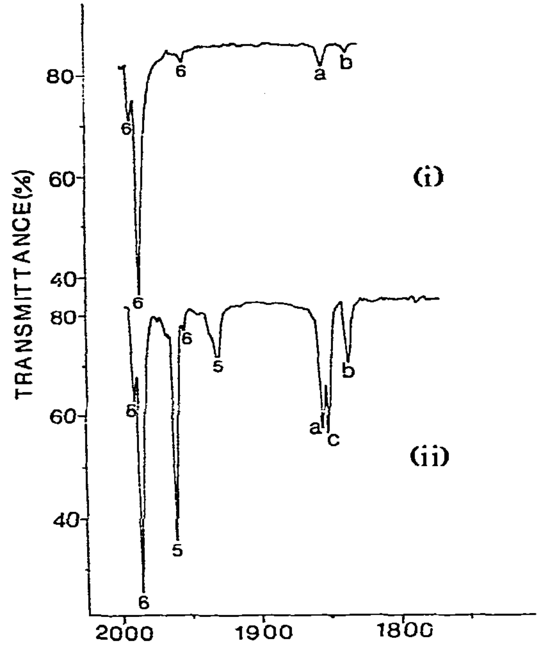

Fig. 1. (i) IR spectrum of Na + $Cr(CO)_6/Ar$ after 40 min spray on. (ii) IR spectrum of Na + $Cr(CO)_6/Ar$ after 40 min spray on + 2 min photolysis, 80 min further spray on + 2½ min photolysis.

the expense of band ‘a’, band ‘b’ again remaining unaffected.

In a corresponding experiment using sodium and $W(CO)_6/Ar$, bands appeared at 1861.5 and 1846 cm^{-1} on spray on, *i.e.* shifted from those in the chromium system. With potassium and $Cr(CO)_6/Ar$, bands appeared in the 1850 cm^{-1} region within 2 cm^{-1} of those in the $Na/Cr(CO)_6$ experiments.

Bands ‘a’, ‘b’ and ‘c’ do not correspond to those of any of the lower carbonyl species $Cr(CO)_{1-4}$ [4] and we assign them to C_{4v} $Cr(CO)_5^-$ for the following reasons.

(i) The bands must be assigned to a Cr/CO species, rather than say Na/CO since otherwise there would be no shift in going from $Cr(CO)_6$ to $W(CO)_6$.

(ii) The separation of bands ‘a’, ‘b’ and ‘c’ from $Cr(CO)_5$ suggests the species is an anion and the following comparison suggests a singly rather than doubly charged species.

The overall shift in frequency from $Cr(CO)_5$ to $Cr(CO)_5^-$ is approximately 106 cm^{-1}; the shifts in other systems are $Co(CO)_4$ [5] to $Co(CO)_4^-$ [6] 80–100 cm^{-1}; $V(CO)_6$ [7] to $V(CO)_6^-$ [8] approximately 117 cm^{-1} whereas the shift $Fe(CO)_4$ [9] to $Fe(CO)_4^{2-}$ is much larger, approximately 200 cm^{-1}.

(iii) In experiments with $Cr(CO)_6$ and Na in hexamethylphosphoramide[10] (HMPT) Kaska has assigned bands in the infrared spectrum at 1869 and 1842 cm^{-1} to $[Cr(CO)_5HMPT]^{2-}$. A model by Drago and Wayland[11] indicates how HMPT may delocalise considerable electron density from metal orbitals so the carbonyl part of the system probably resembles $Cr(CO)_5^-$.

(iv) The observed band pattern in the IR is consistent with a C_{4v} $Cr(CO)_5^-$ system, although we have not as yet observed the high frequency A_1 band expected for this structure.

Perturbation of the anion by alkali metal cations seems to be small as otherwise a greater shift on changing from Na to K would be expected.

The reversible intensity changes of the 1855/1852 bands on photolysis and annealing is probably due to slight matrix perturbation[3] rather than a photochemical change.

We have also extended this work to other systems, for example the system $Co(CO)_3NO/CO/Na$. Initial results suggest the formation of $Co(CO)_3NO^-$ on spray with a nitrosyl stretch at 1488 cm^{-1}, and other species, probably including $Co(CO)_4^-$, on photolysis.

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