The Infrared Spectrum of Dicarbonyl Aluminium(0), $Al(CO)_2$

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The i.r. spectrum of $Al(CO)_2$, observed in deposits of Al atoms and CO in adamantane at 77 K, has a symmetric CO stretching mode at 1985 cm^{-1} and an antisymmetric CO stretching mode at 1903.8 cm^{-1}; there is i.r. evidence for the formation of Al_2CO and $Al_2(CO)_4$ in this system.

There have been two[1,2] recent detailed e.s.r. studies of the reaction of aluminium atoms with carbon monoxide in inert matrices (argon and adamantane) at cryogenic temperatures (4—77 K) which have unambiguously demonstrated that $Al(CO)_2$ is the major paramagnetic reaction product. These studies have provided evidence that the bonding in this molecule involves donation of the 5σ electrons from the ligands into two empty sp^2 hybridized orbitals on aluminium, with a lone pair of electrons in the third sp^2 orbital. The unpaired electron is located in the remaining $3p_x$ orbital orthogonal to the molecular plane. Unpaired electron population is delocalized onto the ligands by back donation from the $3p_x$ orbital into the $2\pi^*$ orbitals. $Al(CO)_2$ is, therefore, a planar π radical with a $^2B_1$ electronic ground state in C_{2v} symmetry. The unpaired spin population distribution estimated from the magnetic parameters is consistent with a

C–Al–C angle of 110° obtained from INDO M.O. calculations.[1,2]

An earlier[3] i.r. study of codeposited Al and CO in solid krypton at 10 K gave two major bands in the CO stretching region at 1988 and 1890 cm^{-1}. The observation of these two bands in conjunction with the detection of two sets of triplets when Al atoms were allowed to react with a mixture of CO and $C^{18}O$ was consistent with the formation of an aluminium dicarbonyl with an unknown number of aluminium atoms, *i.e.*, $Al_x(CO)_2$. Moskovitz and Ozin[4] suggested that $x = 2$ because of the ease with which aluminium atoms undergo surface diffusion and dimerization.

We have recently performed *in situ* i.r. studies of Al–CO–adamantane codeposits on the drum of a rotating cryostat[5] which had been shown to contain substantial concentrations of $Al(CO)_2$ by e.s.r. spectroscopy[2] and now report the results.

The optical beam of a Mattson Sirius 100 Fourier transform i.r. spectrometer was deflected from the sample compartment on to the surface of the drum and the reflected beam was collected and diverted to a cooled mercury cadmium telluride (MCT) detector. Spectra were collected before deposition and after deposition of adamantane, adamantane and CO, and adamantane, CO, and Al, each spectrum being the average of 256 scans at a resolution of 4 cm^{-1}. Spectra of the products of reaction of Al with CO were obtained by subtracting spectra of adamantane and CO from spectra of adamantane, CO, and Al.

The i.r. spectrum of Al–CO–adamantane at 77 K in the CO stretching region (Figure 1a) has two narrow bands, A, at 1985 and 1903.8 cm^{-1} and broad bands, B and C, at 2078.5 and 1715 cm^{-1}. The two bands A are clearly those detected by Hinchcliffe, Ogden, and Oswald.[3] Upon annealing band C was the first to disappear and band B initially grew in intensity before disappearing along with bands A. The i.r. spectrum at ~160 K is shown in Figure 1b.

Spectra obtained from ^{13}CO and a 1 : 1 mixture of CO and ^{13}CO are shown in Figure 2. The four bands A, B, and C were observed in the spectrum from ^{13}CO (Figure 2a) at 1941, 1862.4, 2013, and 1682 cm^{-1}; *i.e.* they were all shifted down in frequency. They are readily assigned to aluminium carbonyls because the magnitudes of the frequency shifts are similar to those that have been obtained for other metallic carbonyls.[6–8]

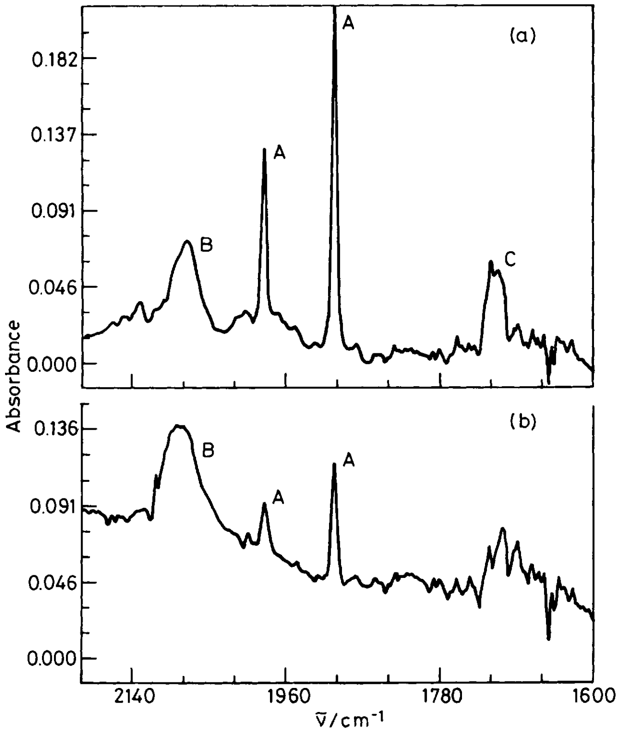

Figure 1. I.r. spectra of Al–CO–adamantane at (a) 77 K and (b) 160 K in the CO stretching region.

I.r. spectra from Al–CO–^{13}CO mixtures (Figure 2b) had all the bands in spectra from CO and ^{13}CO plus narrow bands at 1968.5 and 1879 cm^{-1}. The broad band C was, however, not always observed and its observation seemed to depend on the relative ratios of Al and CO deposited. It is apparent from a comparison of spectra given in Figures 1a, 2a, and 2b that the doublet A in spectra from pure CO becomes a doublet of triplets in the spectrum from CO–^{13}CO. The bands at 1985 and 1903.8 cm^{-1} can, therefore, be unambiguously assigned to a bent dicarbonyl with the higher frequency band assigned to the symmetric stretching mode and the lower frequency band to the asymmetric stretching mode.[9]

If we assume that the dipole moment derivatives are directed along the CO bonds relative band intensities can be used to give the C–Al–C angle θ by using the equation[10] $I_{sym.}/I_{asym.} = \cot^2 \theta/2$ where $I_{sym.}$ and $I_{asym.}$ are the intensities of the symmetric and asymmetric bands, respectively. Measurement of the areas under these two bands gave $\theta = 110 \pm 5°$ at 77 K. This angle is identical, within experimental error, to the C–Al–C angle of $Al(CO)_2$ obtained from a comparison of e.s.r. spectra with INDO M.O. calculations.[1,2] We thus assign the i.r. bands at 1985 and 1903.8 cm^{-1} to this mononuclear species and not to the dinuclear species, $Al_2(CO)_2$, suggested previously.[4]

These frequencies can be used to calculate the force constant k_{CO} and the interaction constant $k_{CO.CO}$ if we make the Cotton–Kraihanzel approximation[11] which essentially

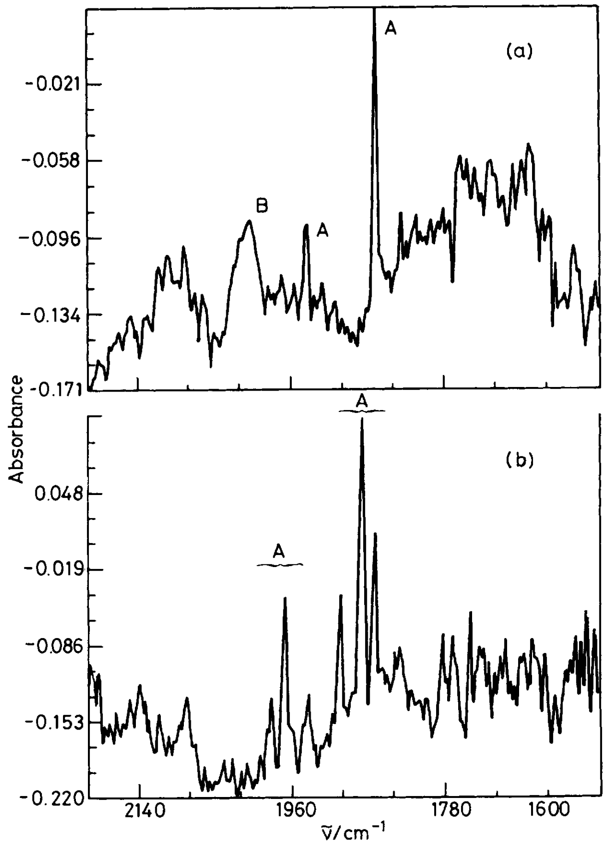

Figure 2. I.r. spectra of (a) Al–^{13}CO–adamantane and (b) Al–CO–^{13}CO–adamantane in the CO stretching region at 77 K.

decouples the high-frequency ligand stretching modes from the other vibrations in the molecule. The secular equations (1) and (2) are used in this calculation for the A_1 and B_1 stretching modes, respectively where $\lambda = (5.8890 \times 10^{-2})\nu^2$, μ is the reciprocal of the reduced mass of the CO group, *viz*, $(16.00 + 12.01)/(16.00 \times 12.01) = 0.14583$, and ν is the frequency in cm^{-1}. These equations have been used for a range of metallic dicarbonyls and are valid when comparing closely related compounds.[6—8] Substitution of the two frequencies into equations (1) and (2) gives $k_{CO} = 15.3$ mdyn/Å and $k_{CO.CO} = 0.64$ mdyn/Å (1 dyn = 10^{-5} N).

Intensity and frequency measurement for the symmetric and antisymmetric CO stretching modes of $Al(^{13}CO)_2$ in cyclohexane showed that the C–Al–C angle, k_{CO}, and $k_{CO.CO}$ are the same in cyclohexane and adamantane.

$$\lambda = \mu(k_{CO} + k_{CO.CO}) \qquad (1)$$

$$\lambda = \mu(k_{CO} - k_{CO.CO}) \qquad (2)$$

This value of k_{CO} for $Al(CO)_2$ is identical within experimental error to the values of this force constant for linear $Cu(CO)_2$ (15.35 mdyn/Å) and linear $Ag(CO)_2$ (15.30 mdyn/Å) while the value of $k_{CO.CO}$ is somewhat smaller than interaction constants for the group 11 (Ölander numbering) dicarbonyls.[6,7] In the group 11 dicarbonyls bonding is believed to involve donation of 5σ electrons from the ligands into two sp hydridized orbitals on the metal with some back donation of the unpaired electron located in the degenerate p_x and p_y orbitals into the antibonding $2\pi^*$ orbitals of the ligands which results in a decrease in k_{CO} from that in carbon monoxide. Our results imply that there is a similar amount of π charge transfer in $Al(CO)_2$ as there is in $Cu(CO)_2$ and $Ag(CO)_2$ even though no d electrons are available for donation from aluminium.

The broad, somewhat irreproducible band, C, at 1715 cm^{-1} gave a broad doublet in Al–CO–^{13}CO experiments indicating a monocarbonyl species. The frequency is too low to assign it to bent AlCO since the σ radicals CH_3CO[12] and HCO[13] have CO stretching frequencies of 1796 and 1861 cm^{-1}, respectively. Furthermore there was no evidence in e.s.r. spectra from Al–CO codeposits for transitions which could be assigned to a bent aluminium monocarbonyl.[2] This band is in fact in the range (1620—1730 cm^{-1}) expected for a triply bridging CO group[14] and we tentatively assign it to Al_3CO because of the ease with which Al atoms form Al_3 on the rotating cryostat[15] although Al_2CO is also a possible assignment. There was no evidence in the e.s.r. spectra of Al–CO–adamantane codeposits for such a cluster carbonyl but it could have been masked by the spectrum of the more intense $Al(CO)_2$.

The observation that band B at 2078.5 cm^{-1} first grew in intensity as the bands from $Al(CO)_2$ decreased in intensity upon warm-up suggests that it is from the diamagnetic dimerization product $Al_2(CO)_4$ and not from the linear monocarbonyl AlCO. Although there was no evidence for linear AlCO by e.s.r. spectroscopy it could have gone undetected because it is a $^2\Pi_{\frac{1}{2}}$ species. If, however, band B was due to $^2\Pi_{\frac{1}{2}}$ AlCO it should have a lower CO stretching than $Al(CO)_2$, not higher as observed.[7] Unfortunately band B was too broad for Al–CO–^{13}CO experiments to allow us to determine the stoicheiometry with respect to CO.

In conclusion by using e.s.r. and i.r. spectroscopic evidence we have been able to assign symmetric and antisymmetric CO stretching modes to $Al(CO)_2$ produced by reaction of Al atoms with CO at 77 K on a solid hydrocarbon surface. Moreover we have tentative evidence for the formation of Al_3CO with a triply bridged CO ligand and $Al_2(CO)_4$ under these reaction conditions.

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