Aluminum Dicarbonyl: Matrix Isolation ESR Study

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Abstract: ESR spectra of an aluminum carbonyl generated in argon matrices by co-condensation of aluminum atoms and carbon monoxide were observed and analyzed. It is shown that the aluminum carbonyl consists of one aluminum atom and two CO molecules. It has a bent structure OC–Al–CO and a semifilled orbital representing the back-donation from the Al p_π orbital into the antibonding π^* orbitals of the CO moiety.

A variety of metal atom carbonyls have been generated by co-condensation of metal atoms and carbon monoxide molecules in inert gas matrices. The list includes $Co(CO)_{1-4}$, $Cu(CO)_{1-3}$, $Ag(CO)_{1-3}$, $Pd(CO)_4$, $Al_x(CO)_2$, and many others.[1-6] All of these carbonyls have been identified and examined by their vibrational spectra (IR and Raman). For $Co(CO)_4$, $Cu(CO)_3$, and $Ag(CO)_3$, ESR (electron spin resonance) spectra have also been observed.[1-3]

Ogden and his co-workers reported that co-condensation of aluminum atoms and carbon monoxide in a krypton matrix led to formation of an aluminum carbonyl.[5] On the basis of the effect of $C^{18}O$ upon the IR spectrum, they demonstrated that the species had the formula $Al_x(CO)_2$, but refrained from asserting the number of aluminum atoms involved. Ozin et al.[3] suggested that it might be $Al_2(CO)_2$.

We report here the ESR spectra observed from an aluminum carbonyl generated in argon matrices by the co-condensation technique. It is shown that the carbonyl involves one aluminum atom and two carbon monoxide molecules. It has a bent structure (OC)–Al–(CO) and the semifilled orbital representing the back-donation from the Al p_π orbital into the antibonding π^* orbitals of the carbon monoxide moiety.

Experimental Section

A liquid-helium cryostat that would enable trapping of vaporized species in an inert gas matrix and examination of the resulting matrix by ESR has been described earlier.[7] In the present series of experiments aluminum atoms were generated from a tantalum cell resistively heated to 1400 °C and were trapped in argon matrices containing controlled amounts of carbon monoxide (1–20%). The ESR spectrometer used was an IBM Model ER200D system. A low-frequency (375 Hz) modulation was employed for the signal detection. All the spectra reported here were obtained with the matrix maintained at ~4 K and the spectrometer frequency locked to the sample cavity at 9.4275 GHz.

Research grade argon and CP grade carbon monoxide were obtained from Matheson, while ^{13}C-enriched (enrichment >90%) carbon monoxide was obtained from MSD Isotopes.

Results

The ground-state electronic configuration of Al atoms is $3s^2\,3p^1$. Thus, owing to the degeneracy of the p orbitals, the ESR signal of the Al atoms situated at sites with a cubic symmetry would be broadened beyond detection. However, it has been shown that rare-gas matrices containing a high concentration (a few tenths of a percent) of Al atoms exhibit strong, well-defined ESR signals. The signals were designated as the Al–X signals[8] and were assigned to Al atoms occupying axially distorted substitutional sites of the host matrix.[9]

For the Al/CO/Ar system of the current study, only the Al–X signals were observed when the CO concentration was low (<2%). When the CO concentration was 3%, a set of new signals, due presumably to an aluminum carbonyl, began to appear at the expense of the Al–X signals. The two types of signals were equally intense in the Al/CO (5%)/Ar system. And only the carbonyl signals were observed when the CO concentration was 10% or higher. The color of the matrix changed from white to pink to dark red as the CO concentration increased from 1% to 5% to 10% or higher.

Figure 1a shows the carbonyl ESR spectrum observed from the Al/CO (20%)/Ar system in its entirety. The central section of the spectrum is shown expanded in Figure 2. Other than the signals due to inadvertently formed formyl radicals (HCO),[10] all features in the spectrum can be accounted for by a radical having a orthorhombic **g** tensor and an orthorhombic hfc (hyperfine coupling) tensor with one ^{27}Al nucleus (natural abundance 100%, $I = {}^5/_2$) as indicated in Figures 1a and 2. Thus the following assignments were made for the carbonyl radical.

axis	1	2	3
g	2.0021 (3)	2.0043 (3)	1.9990 (3)
A(Al), G	52.0 (2)	13.8 (1)	14.1 (1)

Figure 1b is a computer-simulated spectrum based upon these values.

Figure 3a shows the ESR spectrum observed from the $Al/^{13}CO$ (20%)/Ar system. Though surprisingly small, effects of the hfc interaction with the ^{13}C nucleus/nuclei are conspicuous. They are manifested as broadening of the g_1 peaks and additional splittings of the g_2 and g_3 peaks. Thus $A_1(^{13}C)$ may be assessed from the line-width increase of g_1 peaks. Because of severe overlaps, individual peaks in the g_2 and g_3 regions are no longer resolved. $A_2(^{13}C)$ and $A_3(^{13}C)$, however, may be assessed from the low-field shift of the lowest field g_2 component and the high-field shift of the highest field g_3 component (see arrows in Figure 3a). The hfc tensor of the ^{13}C nucleus/nuclei was thus assessed as follows:

$$|A_1| = 1.5 \text{ (or 3.0) G}$$

$$|A_2| = 8.0 \text{ (or 16.0) G}$$

$$|A_3| = 10.0 \text{ (or 20.0) G}$$

The numbers in parentheses are for the case where only one carbonyl is assumed.

Parts b and c of Figure 3 are computer-simulated spectra based upon the **g** tensor, the Al hfc tensor determined earlier, and the ^{13}C hfc tensors given above for the bis- and monocarbonyl cases, respectively. Thus from a comparison of observed and simulated spectra, the number of carbon monoxide involved in the radical was firmly established as two.

The aluminum carbonyl observed here by ESR is thus $Al(CO)_2$. It must correspond to the dicarbonyl species detected in the IR study of Ogden and his co-workers. Throughout the CO con-

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[1] Hanlan, L. A.; Huber, H.; Kündig, E. P.; McGarvey, B. R.; Ozin, G. A. *J. Am. Chem. Soc.* **1975**, *97*, 7054.

[2] Huber, H.; Kündig, E. P.; Moskovits, M.; Ozin, G. A. *J. Am. Chem. Soc.* **1975**, *97*, 2097.

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[6] See, for example, a review by Sheline and Slater: Sheline, R. K.; Slater, J. L. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 309.

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[10] Adrian, F. J.; Cochran, E. L.; Bowers, V. A. *J. Chem. Phys.* **1962**, *36*, 1661.

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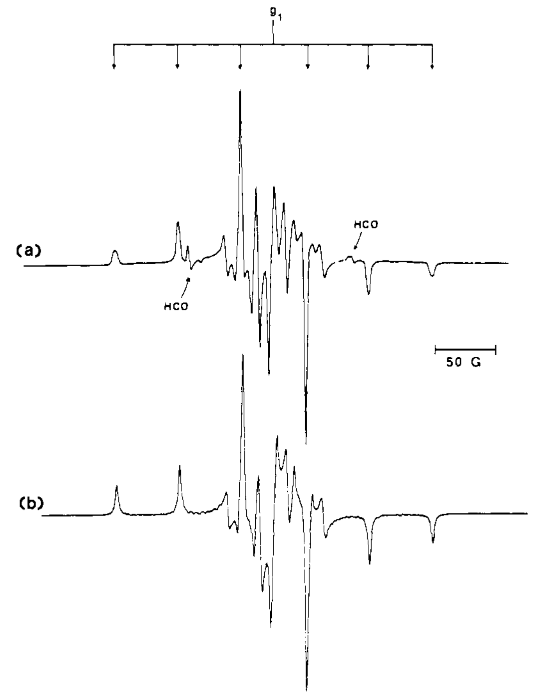


Figure 1. (a) ESR spectrum of aluminum carbonyl observed from the Al/CO (20%)/Ar system. Weak signals due to formyl radicals are indicated. (b) A computer-simulated spectrum based upon the g and Al hfc tensors given in the text.

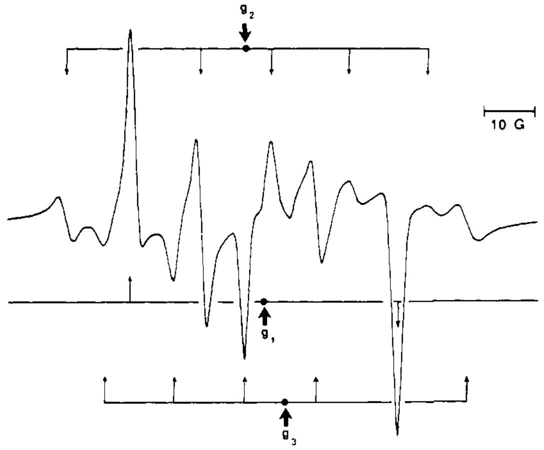


Figure 2. The central region of Figure 1a shown in an expanded scale; the g_2 and g_3 sextets and the innermost pair of the g_1 sextet are indicated.

centration range examined no ESR signals other than those discussed above were observed.

Discussion

Perhaps the most intriguing revelation of the early IR study and the present ESR study of the Al atom carbon monoxide interaction is that, while aluminum dicarbonyl is readily formed, aluminum monocarbonyl is not. Aluminum monocarbonyl is a thirteen-electron system, and, following the Walsh rule,[11] would have a linear structure. It would then be a $^2\Pi$ radical and may not be detectable by ESR. However, it would surely be detected by IR. No carbonyl bands other than those of the dicarbonyl system and isolated carbon monoxide were observed in the IR study.

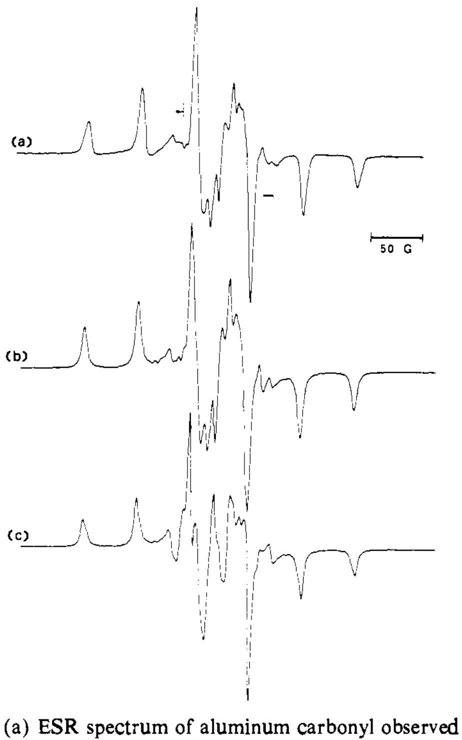
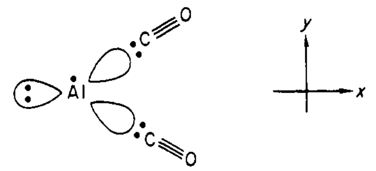


Figure 3. (a) ESR spectrum of aluminum carbonyl observed from the Al/^{13}CO (20%)/Ar system. The arrows indicate the low-field shift of the lowest field g_2 component and the high-field shift of the highest field g_3 component. (b and c) Computer-simulated spectra based upon the g and Al hfc tensors used earlier and additional ^{13}C hfc tensors given in the text for the bis- and monocarbonyl cases, respectively.

Stability of transition-metal carbonyls $M(CO)_n$ has been attributed to a σ bond resulting from dative interaction between the lone-pair electrons of the carbon atom of CO and a vacant σ orbital of M and a π bond resulting from back-donation from a filled d_π orbital of M into a vacant π^* orbital of CO.[12] Importance of synergism between the two dative interactions has been emphasized. An $sp_{x,y}{}^2$-hybridized aluminum atom with its lone-pair electrons in one of the hybridized orbitals and the unpaired electron in the remaining p_z orbital should be receptive to a σ-type dative approach of two carbon monoxides as depicted below.



The possibility of π-type back-bonding from the semifilled p_z orbital of Al into the vacant $\pi_z{}^*$ orbitals of CO follows naturally. The symmetric and antisymmetric stretching bands of $Al(CO)_2$ occur at 1988 and 1890 cm^{-1}, respectively,[5] indicating a significant degree of back-donation into the $\pi_z{}^*$ orbitals. The intensity ratio of the two bands is $\sim 1/2^5$, indicating the angle between the carbonyls of $\sim 110°$. We hence conclude that $Al(CO)_2$ has the structural and bonding features illustrated above, and its semifilled orbital is given by eq 1. Here $\pi_z{}^*$ and $\pi_z{}^{*\prime}$ represent the antibonding $\pi_z{}^*$ orbitals of the two carbonyls.

$$\Phi = a\varphi_{Al}(3p_z) + b(\pi_z{}^* + \pi_z{}^{*\prime}) \qquad (1)$$

It has been shown that, for a radical having a nondegenerate ground state $|0\rangle$, deviation of the g tensor from the spin-only value g_e (=2.0023) is given by eq 2.[13] Here i (=x, y, z) represents an

$$g_i - g_e = -2\lambda \sum_n \frac{\langle 0|L_i|n\rangle\langle n|L_i|0\rangle}{E_n - E_0} \qquad (2)$$

axis of the principal g tensor, L_i the orbital angular momentum operator, and λ the one-electron spin-orbit coupling constant. The summation is performed over all the excited states. In evaluating

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(11) Walsh, A. D. *J. Chem. Soc.* **1953**, *22*, 2266.

(12) See, for example: Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; John Wiley & Sons: New York, 1980; pp 82-86 and 1049-1079.

(13) Pryce, M. H. L. *Proc. Phys. Soc., London, Sect. A* **1950**, *63*, 25.

eq 2 in terms of LCAO–MO's, only one-centered integrals need to be retained, and for each atomic integral the spin–orbit coupling constant of the particular atom is used. Thus for the ground state $|0\rangle$ given by eq 1, we can immediately state $\Delta g_z = 0.0$. Also the highest doubly occupied MO ($E_n - E_0 < 0$) of the carbonyl would be that of the Al lone-pair electrons. A large positive **g** shift is hence expected along the y axis. Thus axis 1 of $Al(CO)_2$, showing the smallest deviation from the spin-only value, is identified as the z axis and axis 2 as the y axis.

Anisotropy of the hfc tensor to a magnetic nucleus should reflect the symmetry of the distribution of the unpaired electron in the vicinity of the nucleus. Thus the hfc tensors of both the ^{27}Al and ^{13}C nuclei in $Al(CO)_2$ should be approximately axially symmetric about the z axis. The hfc tensors determined above for the ^{27}Al and ^{13}C nuclei are indeed nearly axially symmetric about the z axis. Small deviation from the axial symmetry is expected since the molecule itself lacks axial symmetry. It has been shown that the principal elements, $A_\parallel$ and $A_\perp$, of an axially symmetric hfc tensor are related to the isotropic term A_{iso} and the anisotropic term A_{dip} as follows.[14]

$$A_\parallel = A_{iso} + 2A_{dip}$$

$$A_\perp = A_{iso} - A_{dip} \tag{3}$$

where

$$A_{iso} = g_e\beta_e g_n\beta_n\frac{8\pi}{3}\left|\Phi(0)\right|^2$$

$$A_{dip} = g_e\beta_e g_n\beta_n\left\langle\frac{3\cos^2\theta - 1}{2r^3}\right\rangle = g_e\beta_e g_n\beta_n\frac{2}{5}\left\langle\frac{1}{r^3}\right\rangle$$

Here $|\Phi(0)|^2$ represents the spin density at the nucleus, r the separation between the unpaired electron and the nucleus, and θ the angle between r and the symmetry axis. Only a spin density in an s orbital contributes to A_{iso}, and that in a non-s orbital contributes to A_{dip}. The second expression for A_{dip} applies when a unit spin density is located in a p orbital of the magnetic nucleus.

Equation 3 states that, for a p orbital case, A_{dip} is positive, and hence $A_\parallel > A_\perp$. From the observed ^{27}Al and ^{13}C hfc constants the hf tensors of axial symmetry (with signs) are thus deduced as follows.

$$A_\parallel(^{27}\mathrm{Al}) = +52.0\ \mathrm{G}$$

$$A_\perp(^{27}\mathrm{Al}) \simeq \pm(|A_2| + |A_3|)/2 = \pm 14.0\ \mathrm{G}$$

$$A_\parallel(^{13}\mathrm{C}) = \pm 1.5\ \mathrm{G} \qquad A_\perp(^{13}\mathrm{C}) = -(|A_2| + |A_3|)/2 = -9.0\ \mathrm{G}$$

Let us assume $A_\perp(^{27}\mathrm{Al}) = +14.0$ and $A_\parallel(^{13}\mathrm{C}) = +1.5$ G. Analysis of the tensors in terms of eq 3 yields the following

$$A_{iso}(^{27}\mathrm{Al}) = 26.7\ \mathrm{G} \qquad A_{dip}(^{27}\mathrm{Al}) = 12.7\ \mathrm{G}$$

$$A_{iso}(^{13}\mathrm{C}) = -5.5\ \mathrm{G} \qquad A_{dip}(^{13}\mathrm{C}) = 3.5\ \mathrm{G}$$

The positive signs were chosen for $A_\perp(^{27}\mathrm{Al})$ and $A_\parallel(^{13}\mathrm{C})$, since they led to a spin-density distribution with a better overall agreement with that predicted by a molecular orbital calculation (vide infra).

The atomic values $A_{iso}{}^0$ and $A_{dip}{}^0$ for a unit spin density in the valence s and p orbitals of atoms have been computed theoretically.[15] The results for Al and C are $A_{iso}{}^0(^{27}\mathrm{Al}) = 1400$ G, $A_{dip}{}^0(^{27}\mathrm{Al}) = 30$ G, $A_{iso}{}^0(^{13}\mathrm{C}) = 1350$ G, and $A_{dip}{}^0(^{13}\mathrm{C}) = 38$ G. The spin-density distribution in $Al(CO)_2$ was thus determined as follows.

$$\rho(3\mathrm{s})_{\mathrm{Al}} = 0.02 \qquad \rho(3\mathrm{p}_z)_{\mathrm{Al}} = 0.42$$

$$\rho(2\mathrm{s})_{\mathrm{C}} = -0.004 \qquad \rho(2\mathrm{p}_z)_{\mathrm{C}} = 0.09$$

The balance of spin density must be at oxygens. Thus $\rho(2\mathrm{p}_z)_{\mathrm{O}} = 0.19$. The small but non-zero spin densities computed above for the Al 3s and C 2s orbitals should not be taken too literally. Small A_{iso}'s determined here are the sum attributes of the spin polarization in all the filled s orbitals of the respective atoms. However, A_{iso} of the ^{13}C nucleus induced by spin polarization by an unpaired electron in the 2p orbital of the same atom is usually positive.[16] A negative spin density determined above for the C 2s orbital is hence particularly interesting. It can be best accounted for by polarization of electrons in the σ dative bond by the large spin density in the Al 3p$_z$ orbital.

In order to gain further insight into the carbonyl system and provide further support for the assignment presented above, an INDO molecular orbital calculation was performed.[17] The structural parameters assumed were the following: OC–Al–CO angle = 110°, r(Al–C) = 1.80 Å, and r(C–O) = 1.15 Å. The theory predicted the semifilled orbital given by eq 1 and the highest doubly occupied orbital for the Al lone-pair electrons. It also yielded the following spin-density distribution: $\rho(3\mathrm{s})_{\mathrm{Al}} = 0.02$, $\rho(3\mathrm{p}_z)_{\mathrm{Al}} = 0.42$, $\rho(2\mathrm{s})_{\mathrm{C}} = 0.01$, $\rho(2\mathrm{p}_z)_{\mathrm{C}} = 0.15$, and $\rho(2\mathrm{p}_z)_{\mathrm{O}} = 0.14$. Though it failed to generate a negative spin density in the C 2s orbital, the overall agreement is considered reasonable.

The present ESR and earlier IR studies of aluminum atoms and carbon monoxide co-condensed in rare-gas matrices thus completely affirmed the formation of bis(carbonyl)aluminum(0). The bis(carbonyl) state is formed as the result of σ-type dative interaction between the lone-pair electrons of CO and the vacant $\mathrm{sp}_{x,y}{}^2$ hybridized orbitals of Al and π-type back-donation of the unpaired electron from the Al p$_z$ orbital into the vacant antibonding $\pi_z{}^*$ orbitals of CO. Synergism between the two types of dative interactions must be crucial; aluminum monocarbonyl does not appear to have a bound state.

Registry No. (OC)-Al-(CO), 12691-52-0; Al, 7429-90-5; CO, 630-08-0.

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(14) See, for example: Atkins, P. W.; Symons, M. C. R. "The Structure of Inorganic Radicals"; Elsevier: Amsterdam, 1967.

(15) Morton, J. R.; Preston, K. F. *J. Magn. Reson.* **1978**, *30*, 577.

(16) See a review article by Morton: Morton, J. R. *Chem. Rev.* 1964, *64*, 453.

(17) Pople, J. A.; Beveridge, D. L. "Approximate Molecular Orbital Theory"; McGraw-Hill: New York, 1970.