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Ab initio studies of the aluminum monocarbonyl species AlCO and AlOC have been performed to predict the geometries, fragmentation energies, and harmonic vibrational frequencies. Both species were optimized at the self-consistent field, configuration interaction, and coupled-cluster levels of theory with large basis sets. At the highest level of theory, AlCO was found to be 22 kcal/mol more stable than the isocarbonyl, AlOC. Al–CO was found to have a dissociation energy of 9 kcal/mol, with no barrier to dissociation to Al and CO fragments. Al–OC was found to have a dissociation energy of −13 kcal/mol with an energy barrier to dissociation of less than 5 kcal/mol. The dipole moment of AlCO is found to be small (around 0.1 D), while that of AlOC is significantly larger (around 2.8 D). The C–O harmonic vibrational frequencies were evaluated at all levels of theory. For AlCO at the highest level of theory, the C–O frequency was 1914 cm^{-1} compared to the experimental value of 1868 cm^{-1}, a 2.5% difference which may be attributed largely to anharmonic effects. The C–O frequency for AlOC is remarkably close to a tentative and disputed experimental spectral feature. © *1996 American Institute of Physics.* [S0021-9606(96)02910-7]

I. INTRODUCTION

The study of main group carbonyls has been of interest to surface chemists because of the possible use of these carbonyls as models for the interaction between main group elements and CO in chemisorption studies.[1] Furthermore, studies of these compounds reveal information about the bonding characteristics and ir identification of carbonyls when bound to atoms lacking valence *d* electrons.[2]

One particularly useful experimental technique employed in the study of metal carbonyls is matrix isolation of cocondensed M and CO and subsequent spectroscopic analyses.[3–5] Hinchliffe, Ogden, and Oswald[6] first isolated aluminum dicarbonyls in solid krypton and identified the species present utilizing the ir active CO stretching modes. Chertikhin, Rozhanskii, Serebrennikov, and Shevel'kov[7] later reported a CO stretch for AlCO in solid argon at 1872 cm^{-1} as well as a signal for the isocarbonyl, AlOC, at 1203 cm^{-1}, though this last assignment was made only tentatively. Further studies of Al–CO complexes in argon matrices by Kasai and Jones[8] suggested that Al(CO)$_2$ was the major product detected by EPR. With the exception of the work of Chertikhin *et al.*, there was no experimental evidence for the aluminum monocarbonyl, AlCO, or the aluminum isocarbonyl, AlOC, in these studies.

In 1983 Bagus, Nelin, and Bauschlicher[9] reported a theoretical study involving the linear AlCO $^2\Pi$ and $^2\Sigma^+$ ground states at the self-consistent field (SCF) level and concluded that the $^2\Pi$ state was more stable. A potential curve of the SCF energy as a function of the Al–CO bond distance was also constructed and revealed a very flat potential surface with a small well. In 1987 Balaji, Sunil, and Jordan[10] conducted an *ab initio* study of aluminum carbonyl compounds including AlCO, and concluded that this compound would be very weakly bound (less than 3 kcal/mol) if it existed at all. They also found the optimized geometry of AlCO to be linear even though it has a $^2\Pi$ ground state and a bent structure might be expected due to the Renner–Teller effect.[11] The association energy of two carbonyls to form Al(CO)$_2$ was predicted to be approximately six times greater than that of a single carbonyl in AlCO. Therefore, any experiments performed with a substantial concentration of CO present would be predicted to yield predominantly Al(CO)$_2$. This seemed to explain the lack of experimental ir and EPR signals which could be attributed to AlCO.

However, in a recent experimental ir study of aluminum carbonyl complexes in solid argon, Xu, Manceron, and Perchard[2] isolated and clearly identified AlCO. After cocondensing aluminum with dilute ^{12}C^{16}O in argon at 10–15 K and using very low concentrations of Al and CO, ir spectroscopy revealed a single absorption in the CO stretching region at 1867.7 cm^{-1}. At slightly different concentrations additional minor signals were present at 1874.1 and 1875.8 cm^{-1}. With increasing concentrations of CO, they asserted that the monocarbonyl was converted to the more stable dicarbonyl.

Although the 1872 cm^{-1} signal of Chertikhin *et al.*[7] may correspond to one of the minor signals of AlCO in this study, Xu *et al.*[2] found no signals at 1203 cm^{-1} corresponding to the O≡C stretch in AlOC at any point in their experiments—even when the 1867.7 cm^{-1} AlCO stretching signal was very strong. Since Chertikhin *et al.* also reported absorptions in the 1450–1300 cm^{-1} range due to Al$_2$CO$_3$, Xu *et al.* suggest that oxygen contamination may be the source of the 1203 cm^{-1} stretch as well.

In light of the new experimental evidence for AlCO as well as the possibility for a more extensive examination opened by continuing advances in quantum chemical techniques, we present here a reinvestigation of the aluminum

TABLE I. Total energies (hartrees) for AlCO and AlOC.

	AlCO			
Basis set	SCF	CISD	CCSD	CCSD(T)
DZP	−354.606 896	−355.011 668	−355.105 293	−355.119 610
TZ2P	No minimum	−355.098 409	−355.208 947	−355.229 924
TZ2P+f	−354.648 007	−355.130 266	−355.244 513	−355.267 263

	AlOC			
Basis set	SCF	CISD	CCSD	CCSD(T)
DZP	−354.592 580	−354.985 831	−355.077 492	−355.089 240
TZ2P	−354.621 585	−355.067 193	−355.176 444	−355.195 118
TZ2P+f	−354.628 147	−355.100 428	−355.212 770	−355.232 966

monocarbonyl and aluminum isocarbonyl species in an effort to query the measured carbonyl vibrational frequencies and to re-examine the theoretically determined equilibrium geometries and fragmentation energies.

II. THEORETICAL METHODS

Three basis sets were employed in this study. The first was a double-zeta plus polarization (DZP) basis consisting of the standard Huzinaga–Dunning–Hay[12–14] set of contracted Gaussian functions with one additional of set of five d-type polarization functions on each atom.[15] The contraction scheme for the double-zeta portion of this basis set was Al($11s7p/6s4p$), C($9s5p/4s2p$), O($9s5p/4s2p$). A triple-zeta plus double polarization (TZ2P) basis set formed by augmenting the McLean–Chandler[16] triple zeta for Al and the Huzinaga–Dunning[12,17] triple zeta for C and O with two sets of five d-type functions[18] on each atom was also implemented. With further addition of seven f-type functions[19] on each atom the TZ2P+f basis set was formed. The contraction scheme for the triple-zeta portion of this basis set was Al($12s9p/6s5p$), C($10s6p/5s3p$), O($10s6p/5s3p$). The

DZP basis set contained 53 basis functions while the TZ2P and TZ2P+f contained 79 and 100 functions, respectively.

Energies were obtained using restricted open-shell Hartree–Fock (ROHF) self-consistent field (SCF) wave functions as well as single and double excitation configuration interaction (CISD), singles and doubles coupled-cluster (CCSD), and CCSD including perturbatively applied connected triple excitations [CCSD(T)]. At the correlated levels of theory the three lowest-lying molecular orbitals corresponding to the Al, C, and O $1s$ orbitals were held doubly occupied, and the corresponding three highest virtual orbitals were deleted. The ground state $^2\Pi$ occupation of the molecular orbitals in $C_{\infty v}$ symmetry is

$$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^4 6\sigma^2 7\sigma^2 8\sigma^2 2\pi^4 9\sigma^2 3\pi,$$

though it should be noted that all wave functions were constructed in the C_{2v} subgroup of $C_{\infty v}$. With the TZ2P+f basis, the number of configuration state functions incorporated in the CISD wave functions was 111 438.

The stationary point structures were completely optimized at all levels of theory within the linear symmetry constraints using analytic gradient techniques, until residual Cartesian coordinate gradients were less than 10^{-6} a.u. The SCF force constants were determined via analytic second derivatives, while the CISD, CCSD, and CCSD(T) force constants were determined by finite differences of analytic gradients. All computations were carried out using the PSI[20] (SCF and CISD wave functions) and ACESII[21] [CCSD and CCSD(T) wave functions] program packages.

III. RESULTS

The energies and bond lengths of AlCO and AlOC at their optimized linear geometries for all basis sets and theoretical methods used are presented in Tables I and II. Note that a bound state for AlCO for the TZ2P basis set at the SCF level was not found, due to the extreme flatness of the potential energy surface. The Al–C and Al–O bond lengths of

TABLE II. Equilibrium bond lengths (Å) for AlCO and AlOC.

		AlCO			
Basis set		SCF	CISD	CCSD	CCSD(T)
DZP	Al–C	2.145	2.076	2.070	2.076
	C–O	1.130	1.158	1.169	1.175
TZ2P	Al–C	No minimum	2.089	2.091	2.097
	C–O	No minimum	1.139	1.148	1.156
TZ2P+f	Al–C	2.136	2.066	2.068	2.074
	C–O	1.117	1.140	1.148	1.156

		AlOC			
Basis set		SCF	CISD	CCSD	CCSD(T)
DZP	Al–O	1.735	1.757	1.778	1.789
	O–C	1.263	1.271	1.268	1.267
TZ2P	Al–O	1.734	1.758	1.784	1.810
	O–C	1.247	1.250	1.244	1.238
TZ2P+f	Al–O	1.730	1.751	1.773	1.795
	O–C	1.246	1.247	1.242	1.238

TABLE III. Fragmentation energies (kcal/mol) for AlCO and AlOC to products Al+CO.

Basis set	$\Delta E(\text{AlCO} \rightarrow \text{Al+CO})$			
	SCF	CISD	CCSD	CCSD(T)
DZP	−4.4	3.4	5.9	7.5
TZ2P	No minimum	2.3	4.0	5.9
TZ2P+f	−4.5	4.5	6.5	8.6

Basis set	$\Delta E(\text{AlOC} \rightarrow \text{Al+CO})$			
	SCF	CISD	CCSD	CCSD(T)
DZP	−13.4	−12.8	−11.5	−11.6
TZ2P	−18.8	−17.3	−16.4	−15.9
TZ2P+f	−17.0	−14.2	−13.4	−12.9

FIG. 1. TZ2P+f-CCSD(T) potential energy curves (kcal/mol) for Al–CO and Al–OC as a function of the Al–C and Al–O distance (Å), respectively.

the two isomers are 2.074 and 1.795 Å, respectively for the TZ2P+f basis set at the CCSD(T) level, and these values are expected to be accurate to within 0.01 Å.[22] Since both molecules are predicted to be very weakly bound, these bond lengths are expected to be rather long. However, the much shorter Al–O bond distance compared to the Al–C bond distance may be evidence that the Al–O bond in AlOC is in some sense stronger than the Al–C bond in AlCO. This supposition is supported qualitatively by the greater electronegativity of oxygen compared to that of carbon as well as quantitatively by differences in calculated harmonic frequencies (*vide infra*). As expected, at the various levels of theory as the Al–C bond length becomes longer (weaker bond) the C–O bond distance becomes shorter (stronger bond). The AlOC isomer parallels this trend as well.

Dipole moments were determined at the optimized geometries for all levels of theory for both molecules. At the highest level of theory [TZ2P+f-CCSD(T)], the dipole moment of AlOC was found to be 2.75 D—significantly larger
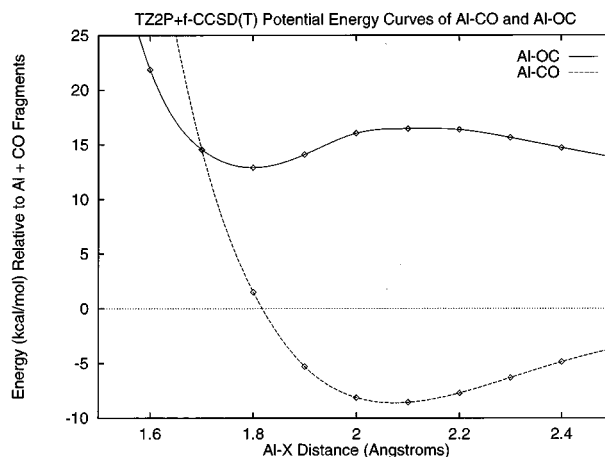
than that of AlCO at 0.1 D. These values are expected to be accurate to within 0.2 D. The dipole moment of each molecule remains relatively consistent at all levels of theory, to within 0.2–0.3 D, thus lending a high level of confidence to these results.

The fragmentation energies for each molecule are presented in Table III. In all cases AlCO is more stable than AlOC relative to the Al and CO fragments, with a 21.5 kcal/mol difference in stability at the highest level of theory. Furthermore, at all levels except SCF, AlCO is lower in energy than the fragments, while AlOC is higher in energy. Although one isomer may be more stable relative to the fragments, the question of which isomer might be detected experimentally cannot be addressed without some knowledge of the energy barriers between the bound states and the fragments. At the highest level of theory, TZ2P+f-CCSD(T), the

TABLE IV. Symmetric harmonic vibrational frequencies (cm^{-1}) for AlCO and AlOC. Infrared intensities (km/mol) are shown in parentheses.[a]

Basis set		AlCO			
		SCF	CISD	CCSD	CCSD(T)
DZP	C–O	2069 (4391)	1997 (1798)	1922 (1446)	1888 (1167)
	Al–C	117 (10)	341 (0)	359 (0)	354 (1)
TZ2P	C–O	No minimum	2007 (1707)	1931 (1489)	1888 (1118)
	Al–C	No minimum	330 (0)	331 (0)	333 (1)
TZ2P+f	C–O	2089 (3493)	2023 (1556)	1953 (1351)	1914 (1025)
	Al–C	185 (47)	363 (0)	363 (2)	360 (4)

Basis set		AlOC			
		SCF	CISD	CCSD	CCSD(T)
DZP	O–C	1538 (539)	1462 (233)	1346 (10)	1285 (165)
	Al–O	639 (149)	612 (134)	568 (59)	536 (20)
TZ2P	O–C	1510 (473)	1427 (163)	1281 (117)	1152 (1027)
	Al–O	627 (153)	594 (135)	534 (34)	435 (24)
TZ2P+f	O–C	1535 (476)	1473 (174)	1346 (58)	1235 (632)
	Al–O	634 (150)	604 (135)	554 (48)	486 (0)

[a]Intensity in this context denotes an integrated absorption band intensity (extinction coefficient) related to the Einstein transition probability (Ref. 23).

fragmentation energies are 8.6 kcal/mol for AlCO and -12.9 kcal/mol for AlOC, and these values are expected to be accurate to within 3 kcal/mol.

In order to estimate these energy barriers, the procedure of Bagus et al.[9] in computing energy points as a function of the Al–CO and Al–OC bond distances was repeated at the TZ2P+f-CCSD(T) level of theory. For all values of the Al–C or Al–O bond distance shown in Fig. 1, the CO bond length was held fixed at its value in the equilibrium structure. As is clear from Fig. 1, the Al–CO potential energy curve is qualitatively similar to a diatomic potential, with no barrier to dissociation to Al and CO fragments. For Al–OC, a small barrier of less than 5 kcal/mol was found. With the absence of substantially deep binding wells for both of these molecules, it is reasonable that AlCO would be the isomer detected experimentally by Xu et al.[2] rather than AlOC, since the former is more stable with respect to the fragments.

The predicted harmonic vibrational frequencies and intensities for both AlCO and AlOC are summarized in Table IV. The units, km/mol, are given for the integrated absorption band intensities reported in this table, in order to conform to the accepted standards in the chemical literature. Bending frequencies at the SCF and CISD levels were evaluated and fell within the 75 to 300 cm^{-1} range for the basis sets employed. However, since only the C–O stretch is experimentally observable and is used in identification of these compounds, the bending frequencies at the CCSD and CCSD(T) were not calculated, and only the stretching vibrations are reported for all levels of theory in Table IV. The TZ2P+f-CCSD(T) C–O harmonic stretching frequency for AlCO was 1914 cm^{-1}, in good agreement with the experimental[2] fundamental frequency of 1867.72 cm^{-1}, attributing approximately 50 cm^{-1} to anharmonicity. However, since the experimental value of 1203 cm^{-1} tentatively assigned[7] to the C–O stretch in AlOC remains disputed in the literature,[2] one should be cautious in making comparisons of this with the TZ2P+f-CCSD(T) value of 1235 cm^{-1} determined in this study. However, for both of these molecules the TZ2P+f-CCSD(T) vibrational frequencies are expected to be accurate to within 50 cm^{-1},[22] and the match between theory and experiment is remarkably good.

IV. CONCLUSIONS

The aluminum monocarbonyl species, AlCO, is very weakly bound with a predicted dissociation energy of 8.6 kcal/mol. However, the theoretical Al–CO dissociation energy is much larger than that predicted by earlier studies.[9,10] AlCO is found to have no additional barrier to dissociation to fragments. However, AlOC has a barrier of less than 5 kcal/mol, prior to falling apart exothermically to Al+CO. The differences in the fragmentation energies suggest that AlCO is the more stable species, consistent with experimental evi-

dence. The harmonic vibrational frequency corresponding to the C–O stretch in AlCO was determined to be 1914 cm^{-1} at the TZ2P+f-CCSD(T) level of theory, in good agreement with the experimental fundamental frequency of 1867.72 cm^{-1}, leaving approximately 50 cm^{-1} accounted for by anharmonicity. The C–O stretch in the isocarbonyl AlOC was determined to be 1235 cm^{-1} at the TZ2P+f-CCSD(T) level of theory, in close agreement with the tentatively assigned and disputed experimental value of 1203 cm^{-1}. Further experiments to determine whether this agreement is merely accidental would be most welcome.

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