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Metal Atom Chemistry and Surface Chemistry. 2. Carbonylsilver(I) Superoxide, $(OC)Ag^+,O_2^-$, a Localized Bonding Model for Carbon Monoxide on an Oxidized Silver Surface

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The cocondensation reaction of Ag atoms with CO/O_2 mixtures is studied by matrix infrared and ultraviolet–visible spectroscopy and is found to yield just a single product. The identity of this compound is established from metal and ligand concentration studies, warm-up experiments, and $^{12}C^{16}O/^{13}C^{16}O/^{16}O_2/^{16}O^{18}O/^{18}O_2$ and $^{12}C^{16}O/^{13}C^{18}O/^{16}O_2/^{16}O^{18}O/^{18}O_2$ isotopic substitution to be carbonyl(dioxygen)silver, $(OC)Ag(O_2)$, most probably containing the dioxygen moiety side-on bonded with respect to the silver. The appearance of the carbonyl stretching mode in the frequency region above that of free CO (2165 cm^{-1}) and the occurrence of the dioxygen stretching mode at roughly the frequency of the superoxide anion (1110 cm^{-1}), when taken in conjunction with the presence of the characteristic uv absorption of superoxide (285 nm) yet absence of electronic transitions in the visible spectrum, provides convincing evidence in favor of the tight ion-pair formulation $(OC)Ag^+,O_2^-$ in which the silver can be considered to be acting as a strong σ acceptor yet a weak π donor with respect to the carbonyl group. The discovery of $(OC)Ag^+,O_2^-$ and its parent Ag^+,O_2^- raises the intriguing question as to whether or not they might serve as simple, localized bonding models for the molecular form of chemisorbed oxygen on silver $Ag(O_{2_{ads}})$ and the surface complex $Ag(O_{2_{ads}})(CO_{ads})$ which are thought by some to be involved in the silver-catalyzed oxidation of CO to CO_2.

Introduction

In part 1 of this paper we reported that silver atoms react with $^{16}O_2$ or dilute $^{16}O_2/Ar$ mixtures at cryogenic temperatures to produce oxidized silver in the form of the tight ion-pair silver(I) superoxide, Ag^+,O_2^-.[1] Experiments in concentrated $^{16}O_2/Ar$ mixtures led to the discovery of the novel silver(I) tetraoxygen complex Ag^+,O_4^-.[1]

The discovery of the tight ion pair Ag^+,O_2^- naturally raised the interesting question as to whether or not it could serve as a localized bonding model[2,3] for the molecular form of chemisorbed dioxygen $Ag(O_{2_{ads}})$ which is known to coexist with O^-_{ads} and O^{2-}_{ads} on oxidized silver surfaces.[4] Such a proposal has wide-ranging implications, as it is thought by some that the molecular form of chemisorbed oxygen on industrial silver catalysts, $Ag(O_{2_{ads}})$, may be the surface complex active in, for example, olefin[5] and carbon monoxide[6] oxidations.

It was therefore considered to be of interest to investigate some model reactions of Ag^+,O_2^- with other substrates, the aim being to fabricate localized bonding models for the surface complexes that have been postulated to occur on oxidized silver catalysts and which, generally speaking, appear to be poorly understood.[7]

What follows is a detailed account of our experiments with the silver atom–carbon monoxide–dioxygen system, the first investigation which sets out specifically to interrelate metal atom chemistry and surface chemistry.

Experimental Section

Monatomic silver was generated by directly heating a thin tantalum rod (0.025 in.) around the center of which was wound silver wire (0.005 in.). The silver metal (99.99%) was supplied by Imperial Smelting Co., Toronto. Research grade $^{12}C^{16}O$, $^{16}O_2$, and Ar (99.99%) were supplied by Matheson of Canada and $^{12}C^{18}O$ (90%), $^{13}C^{18}O$ (47%), and $^{18}O_2$ (90%) by Stohler Isotopes, Montreal. The furnace used for the evaporation of the metals has been described previously.[8] The rate of silver atom deposition was continuously monitored using a quartz crystal microbalance.[9] In the infrared experiments, matrices were deposited on either an NaCl or a CsI plate cooled to 10 K by means of an Air Products Displex closed-cycle helium refrigerator. Infrared spectra were recorded on a Perkin-Elmer 180 spectrophotometer. Uv-visible spectra were recorded on a standard Varian Techtron instrument in the range 190–900 nm, the sample being deposited on an NaCl optical plate.

Infrared Experiments. (A) Pure Carbon Monoxide–Dioxygen Matrices. When silver atoms are cocondensed with roughly equimolar $^{16}O_2/^{12}C^{16}O$ matrices at 10–12 K (using very low concentrations of silver in order to minimize matrix surface diffusion and aggregation effects,[10] $Ag/^{16}O_2/^{12}C^{16}O \simeq 1/10^4/10^4$), the infrared spectrum (Figure 1B) shows, besides the characteristic absorptions of $^{12}C^{16}O$ (and $^{12}C^{18}O/^{13}C^{16}O$ in natural abundance, Figure 1A), *two* new absorptions, one in the carbonyl stretching region at 2165 cm^{-1} and one in the dioxygen stretching region at 1110 cm^{-1} (labeled I in Figure 1B).

Warming this matrix in the range 10–40 K simply causes the gradual diminution and eventual disappearance of both of these new lines at roughly the same rate, indicating that they are both associated with a single new species which clearly contains both CO and O_2 as ligands.

Three features of the infrared spectrum of I are particularly noteworthy. First, the absence of $Ag(CO)_{2,3}$[11] and AgO_2[1] is striking, as these would have been the major products anticipated in the corresponding silver atom, $CO/Ar \simeq 1/1$ and $O_2/Ar \simeq 1/1$ matrix reactions, respectively. Second, the carbonyl stretching of I occurs at a *higher* frequency than that of the free $^{12}C^{16}O$ in the matrix (2138 cm^{-1}), an unprecedented result when compared with other group 1B metal atom–carbon monoxide reaction products, $M(CO)_n$ (M = Cu or Ag, n = 1–3; M = Au, n = 1–2[11-13]), or in fact any of the available data for M/CO matrix cocondensations.[10] Finally, the observed dioxygen stretching frequency of I occurs roughly 20 cm^{-1} higher than that observed for silver superoxide,[1] Ag^+,O_2^-.

(B) Isotopic Substitution Experiments. To establish the identity of I we performed isotopic substitution experiments in which both the carbon monoxide and the dioxygen were labeled. In practice, compound I could be characterized in one experiment in which silver atoms were cocondensed with $^{12}C^{16}O/^{12}C^{18}O/^{16}O_2/^{16}O^{18}O/^{18}O_2 \simeq 1/1/1/2/1$ mixtures at 10–12 K. The resulting infrared spectrum, shown in Figure 2A, is particularly illuminating. Besides the absorptions of free $^{12}C^{16}O$ and $^{12}C^{18}O$ (and traces of $^{13}C^{18}O$, usually observable in commercially available $^{12}C^{16}O/^{12}C^{18}O$ mixtures), one observes an isotopic *doublet* for I in the carbonyl stretching region at 2165 and 2112 cm^{-1}, characteristic of a single carbonyl group coordinated to the silver. Furthermore, the dioxygen stretching mode of I originally observed at 1110 cm^{-1} appears in this experiment as an isotopic *triplet* at 1110, 1081, and 1050 cm^{-1} (Figure 2A), the intensities of which are approximately 1/2/1.

The isotopic patterns observed in the carbonyl and dioxygen stretching regions serve to characterize I as a carbonyl(dioxygen)silver complex.

To provide additional support for this assignment, we deposited silver atoms with $^{12}C^{16}O/^{13}C^{18}O/^{16}O_2/^{16}O^{18}O/^{18}O_2 \simeq 1/1/1/2/1$ isotopic mixtures, the idea being to create a larger isotopic shift in the carbonyl stretching region (that is, roughly 100 cm^{-1} compared to 50 cm^{-1} in the $^{12}C^{16}O/^{12}C^{18}O$ experiment) and to check for any

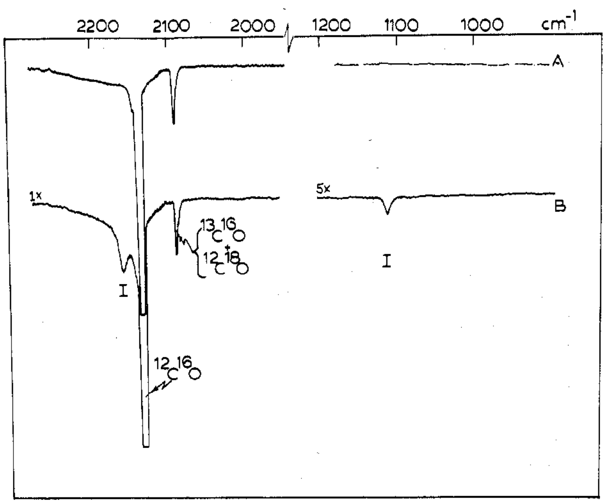


Figure 1. Matrix infrared spectrum of (A) $^{16}O_2/^{12}C^{16}O \simeq 1/1$ and (B) the products formed when silver atoms are deposited with $^{16}O_2/^{12}C^{16}O \simeq 1/1$ at 10–12 K, showing the formation of the carbonyl(dioxygen)silver complex, labeled I. Note that the OO stretching region is recorded on a 5× scale expansion.

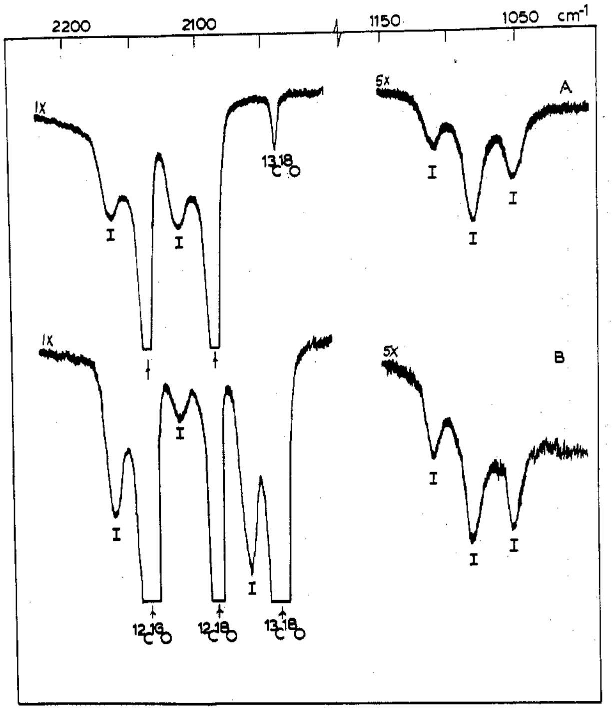


Figure 2. Matrix infrared spectrum of the products formed when silver atoms are cocondensed with (A) $^{12}C^{16}O/^{12}C^{18}O/^{16}O_2/^{16}O$-$^{18}O/^{18}O_2 \simeq 1/1/1/2/1$ and (B) $^{12}C^{16}O/^{13}C^{18}O/^{16}O_2/^{16}O^{18}O/^{18}O_2 \simeq 1/1/1/2/1$ at 10-12°K, showing the characteristic isotopic patterns for a (carbonyl)(dioxygen)silver complex (I). Note that the OO stretching region is recorded on a 5× scale expansion.

band overlap complications that might have confused the $^{12}C^{16}O/^{13}C^{16}O$ situation. The resulting spectrum, shown in Figure 2B, proved to be quite definitive. Besides the absorptions of free $^{12}C^{16}O$ and $^{13}C^{18}O$ (and roughly 7% of $^{12}C^{18}O/^{13}C^{16}O$ which is present even in the best commercial samples of doubly labeled $^{13}C^{18}O$), one observes an isotopic *doublet* for I in the carbonyl stretching region at 2165 and 2063 cm^{-1} (Figure 2B). Note also that the single carbonyl stretching mode of I associated with the small amount of $^{12}C^{18}O$ and $^{13}C^{16}O$ labeled (expected to be roughly coincident) can also be observed at 2116 cm^{-1} in this spectrum.

Indications of band overlap in both of these experiments were not evident and the observed isotopic patterns provide strong support for the monocarbonyl nature of I. Moreover, the dioxygen stretching region in the $^{12}C^{16}O/^{13}C^{18}O$ experiment displays an isotopic *triplet* at 1110, 1081, and 1050 cm^{-1}, essentially identical with the dioxygen triplet of the corresponding $^{12}C^{16}O/^{13}C^{16}O$ experiment, confirming the monodioxygen nature of I.

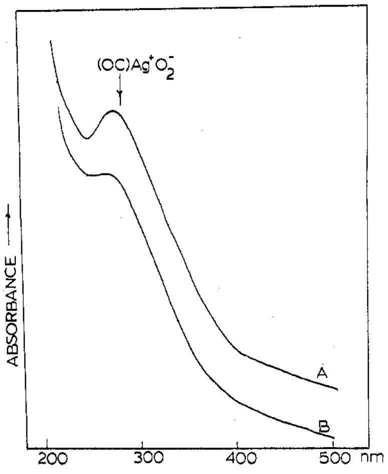


Figure 3. Matrix uv-visible spectrum of the products formed when silver atoms are cocondensed with $^{16}O_2/^{12}C^{16}O \simeq 1/1$ mixtures (A) at 10–12 K and (B) after warm-up to 25 K for 10 min.

The approximately 1/2/1 intensity pattern observed for the dioxygen isotopic triplet and roughly equal $\Delta\nu_{1/2}$ values ($\simeq$10 cm^{-1}) for all three components (in both the $^{12}C^{16}O/^{12}C^{18}O$ and $^{12}C^{16}O/^{13}C^{18}O$ experiments) might be taken as evidence that there is no linkage isomerism for the (OC)Ag($^{16}O^{18}O$) molecule and that the dioxygen ligand is side-on bonded with respect to the silver. This assignment, however, must be treated with caution as the magnitude of the splitting of the linkage isomers (OC)Ag($^{16}O^{18}O$)/(OC)Ag($^{18}O^{16}O$) could be quite small and for a band roughly 10 cm^{-1} wide could remain unresolved. We therefore recognize that the possibility of end-on bonding in (OC)Ag(O$_2$) cannot be dismissed, as was the case for the parent molecule AgO$_2$.[1] For the purposes of the following discussion we shall assume side-on bonded dioxygen for (OC)Ag(O$_2$).

Ultraviolet–Visible Experiments. The uv–visible spectrum of compound I in $^{16}O_2/^{12}C^{16}O \simeq 1/1$ mixtures was recorded at 10–12 K and showed a uv absorption centered at about 285 nm (Figure 3). This should be compared with 275 nm in Ag$^+$,O$_2^-$. The presence of the 285-nm absorption in I is characteristic of the $\pi \rightarrow \pi^*$ electronic transition of superoxide,[14] and the absence of electronic transitions in the visible provides strong evidence for the presence of silver oxidation state I.

Discussion of Results

The infrared and uv–visible data for the Ag/O$_2$/CO cocondensation reaction serve adequately to define the new carbonyl(dioxygen)silver complex, (OC)Ag(O$_2$). The nature of the bonding remains to be ascertained.

The appearance of the carbonyl stretching mode in the frequency region above that of free CO (2138 cm^{-1}), taken together with the occurrence of a dioxygen stretching mode in the infrared region and an electronic transition in the uv region at roughly the frequencies expected for a superoxide anion, as well as the absence of electronic transitions in the visible region, would argue strongly in favor of silver oxidation state I and a tight ion-pair formulation, (OC)Ag$^+$,O$_2^-$.

The observation of the carbonyl stretching mode at higher frequencies than free CO frequencies is the situation expected for a CO ligand coordinating to a "hard" metal center in the Pearson sense. That is, silver(I) is acting as a strong σ acceptor but a weak π donor toward the carbonyl group. These circumstances are reminiscent of the spectroscopic and bonding properties of carbon monoxide in the recently reported complexes MF$_2$·CO (M = Ca, Cr, Mn, Ni, Cu, Zn; ν_{CO} 2210–2165 cm^{-1})[15] in which one can consider the coordinated CO group to donate electrons from its 5σ-donor orbital (which is slightly antibonding with respect to the CO bond) to the central metal, causing an increase in the CO bond order (and

Chart I

	ν_{CO}	Ref
Ag(CO)	1950	11
$Ag(CO_{ads})$	2110	18
CO_{free}	2138	
$[Ag(CO)]^+$	2165	This study
$[Ag(CO)_2]^+$	2193	16

ν_{CO} stretching frequency) compared to that of free CO. However, the extent of charge transfer from the metal π-type orbitals into the 2π antibonding orbitals on the CO is expected to decrease as the metal oxidation state increases, the outcome being a strengthening of the carbon–oxygen bond when CO is coordinated to a hard metal center. This certainly appears to be the case for $(OC)Ag^+,O_2^-$ and, incidentally, for the recently reported silver dicarbonyl cation $[Ag(CO)_2]^+$ (ν_{CO} 2193 cm^{-1}) which forms when Ag_2O reacts with CO in strong acid media.[16] In this context one should mention the results of extended Hückel molecular orbital calculations[17] for the model systems Ni^0CO, Ni^ICO, $Ni^{II}CO$, and $Ni^{III}CO$, which confirm the idea that the extent of σ-charge transfer from the 5σ orbital of the CO to the metal center increases, while the π-charge transfer from the metal to the 2π orbitals of the CO decreases as the metal oxidation state increases, the overall result being a concomitant increase in the CO bond order.

The results for the carbonyl(dioxygen)silver complex are certainly consistent with the idea of silver(I). Further support for this view stems from the monotonic frequency order shown in Chart I. We have included in this list the CO stretching frequency of CO chemisorbed onto silver films[18] which, as expected, occurs at lower frequencies than CO in $(OC)Ag^+,O_2^-$. Surprisingly, the infrared-active CO stretching frequency of the dicarbonyl cation[16] $[Ag(CO)_2]^+$ is 28 cm^{-1} higher than that in $[Ag(CO)]^+$. This would imply that some residual π back-donation from the 4d orbitals of Ag(I) to the coordinated CO group(s) persists in these carbonyl cations and decreases on passing from $[Ag(CO)]^+$ to $[Ag(CO)_2]^+$.

An additional point worth mentioning is the relatively large, *blue* frequency shift in the CO stretching mode on passing from Ag(CO) to $(OC)Ag^+,O_2^-$ ($\Delta \simeq 215$ cm^{-1}) yet correspondingly small shift in the OO stretching mode on passing from Ag^+,O_2^- to $(OC)Ag^+,O_2^-$ ($\Delta \simeq 20$ cm^{-1}). This set of circumstances parallels closely the results observed for the analogous set of complexes $(N_2)M(O_2)$ (M = Ni, Pd, Pt),[19] in which the $(N_2)M^{\delta+},O_2^{\delta-}$ formulation was proposed. The extent of charge transfer from M to O_2 was certainly such that $1 < \delta < 2$.[19] In essence the NN stretching frequency experienced a large blue shift compared to that of the respective MN_2 complex,[20] yet the OO stretching frequency was hardly perturbed from the value observed in the respective MO_2 complex.[21]

The arguments put forward to rationalize the spectroscopic properties of the $(N_2)M(O_2)$ complexes are clearly applicable to the carbonyl–dioxygen complex of the present study and lend credence to the tight ion-pair description, $(OC)Ag^+,O_2^-$. This formulation is meant to imply that the odd 5s valence electron of silver has been completely transferred to the $3\pi_g$ molecular orbital of the dioxygen.

Dilute Carbon Monoxide–Dioxygen–Argon Matrices. The reaction of silver atoms with $^{16}O_2/^{12}C^{16}O/Ar \simeq 1/1/50$ mixtures at 10–12 K was also investigated by infrared spectroscopy. The major effect of dilution was the generation of observable quantities of $Ag(CO)_{2,3}$ together with compound I. This can be seen in Figure 4 from the carbonyl absorptions at 1954/1943 cm^{-1} for $Ag(CO)_3$,[11] 1842/1827 cm^{-1} for $Ag(CO)_2$,[11] and 2166/2155 cm^{-1} for I. Interestingly, the anionic portion of I favored under these conditions appears to be O_4^- as seen by the OO stretching mode at 1058 cm^{-1}, which should be compared with 1030 cm^{-1} for Ag^+,O_4^-.[1]

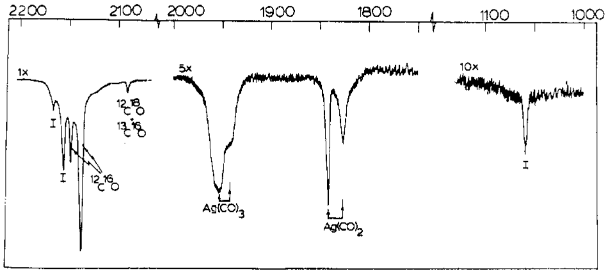
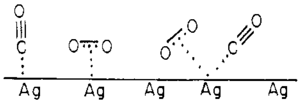


Figure 4. Matrix infrared spectrum of the products formed when silver atoms are cocondensed with $^{16}O_2/^{12}C^{16}O/Ar \simeq 1/1/50$ mixtures at 10–12 K.

Scheme I



Mixed isotopic substitution experiments (similar to those described in the earlier part of this paper) were performed in dilute Ar matrices and confirmed the cationic part of I to be $[(OC)Ag]^+$ (the 2166/2155 cm^{-1} being a multiple trapping site effect) and the anionic part to be O_4^- (by comparison with the results for $Ag^+O_4^-$ in part 1 of this study[1]).

Discussion

We now return to the question of the suitability of $(OC)Ag^+,O_2^-$ as a localized bonding model for the more complex situation $Ag(O_{2_{ads}})(CO_{ads})$, which could be a reasonable description of the transient surface species active in the silver-catalyzed oxidation of CO to CO_2. To begin with, published data for oxidized silver surfaces and supported silver catalysts point to the existence of three types of chemisorbed oxygen in the form of $O_2^-{}_{ads}$, $O^-{}_{ads}$, and $O^{2-}{}_{ads}$, the predominant species being a function of temperature and surface coverage.[4-6] For example, at high to moderate surface coverages and temperatures from 0 to 100 °C, the predominant form is $O_2^-{}_{ads}$. This form of chemisorbed oxygen is considered by some to be the species active in silver-catalyzed oxidation reactions as exemplified by the selective oxidation of ethylene to ethylene oxide.[5] On the other hand, the $O^-{}_{ads}$ species is supposed to be responsible for the oxidation channel which leads ultimately to complete combustion to CO_2/H_2O.[5] However, even in the 1975 literature, conflicting opinions still exist as to the actual role of these two surface oxygen species.[22]

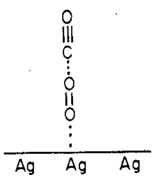
In part 1 of this study we presented a detailed report of the synthesis and characterization of Ag^+,O_2^- and suggested that it might serve as a localized bonding model for $Ag(O_{2_{ads}})$. Let us consider this idea in the context of the $Ag/O_2/CO$ cocondensation reaction.

Published results indicate that the oxidation of CO at 100 °C over silver may proceed by an Eley–Rideal mechanism in which CO reacts with chemisorbed oxygen.[7] The reactive CO is thought to be weakly adsorbed on the chemisorbed oxygen and not on the silver surface itself. In addition, the product CO_2 has also been shown to be adsorbed on the chemisorbed oxygen and not on the silver surface.[7]

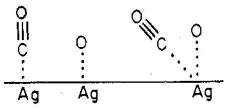
Published data show that CO does not adsorb on a silver catalyst at 100 °C unless the catalyst contains preadsorbed oxyen.[7] Under these circumstances CO adsorbs rapidly on the preadsorbed oxygen. Only when the CO dose size exceeds roughly half that of the preadsorbed O_2, is CO_2 evolution observed.[7]

Our proposed localized bonding model for CO on an oxidized silver surface, namely, $(OC)Ag^+,O_2^-$, would imply the association of both CO and O_2 with one or more silver surface sites (Scheme I) in contrast to the Eley–Rideal type mechanism (Scheme II). On the other hand, if $O^-{}_{ads}$ is the surface

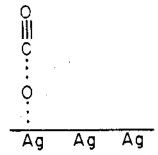
Scheme II



Scheme III



Scheme IV



species active in oxidation, one would envisage corresponding Schemes III and IV.

From our matrix warm-up experiments (OC)Ag$^+$,O$_2^-$ appears to be a very unstable compound which certainly decomposes at temperatures exceeding 40 K. It would therefore appear exceedingly unlikely that a related surface complex could have anything other than a very transient existence on a silver catalyst in the working temperature range of 100 °C. However, such a species could be a short-lived precursor to the CO$_3$ surface intermediate which is supposed to be formed from the CO and preadsorbed oxygen on silver and which is thought to be responsible for ^{16}O/^{18}O isotopic exchange processes between ^{12}C^{16}O and ^{18}O$_2$.[7]

In our Ag/O$_2$/CO matrix experiments, only *very small* quantities of CO$_2$ were detected on deposition, indicating that oxidation reactions on the hot silver source, in the gas phase or in the matrix, were insignificant. Of greater importance is the fact that CO$_2$ generation was not observed on warming (OC)Ag$^+$,O$_2^-$ to 40 K at which temperature the complex was undergoing some kind of decomposition. Furthermore, evidence for a Ag–CO$_3$ or Ag–CO$_2$ reaction intermediate was not observed at any time during the matrix decomposition of (OC)Ag$^+$,O$_2^-$.

Conclusion

One may conclude that although (OC)Ag$^+$,O$_2^-$ does not act as a precursor for CO$_2$ under cryogenic conditions, it may nevertheless be a suitable localized bonding model for CO/O$_2$ surface complexes. It certainly displays all of the properties anticipated for CO coordinated to an oxidized silver atom even though it does not simulate the actual oxidation process to CO$_2$. This may be the result of a kinetic impediment to OO bond rupture at the low temperatures employed. Alternatively, the O$_2^-{}_{\text{ads}}$ species may not be active in CO oxidation, in which case a complex such as [(OC)Ag]$^+$O$^-$ would be a more appropriate synthetic goal. In the event that the Eley–Rideal type of mechanism is a better description of the surface oxidation process, then modeling the CO/O$_2$ oxidation on a silver atom may prove to be impossible.

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Registry No. (OC)Ag(O$_2$), 60594-86-7; [Ag(CO)]$^+$, 60594-87-8.

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Metal Carbonyl Induced Reactions of Azirines. Coupling and Insertion by Diiron Enneacarbonyl

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Azirines undergo coupling and insertion reactions with diiron enneacarbonyl in benzene to give pyrroles, ketones, ureadiiron hexacarbonyl complexes, and diimine complexes. Substituent effects have a significant influence on the course of the reaction. A mechanism is proposed which involves carbon–nitrogen bond cleavage of the azirine ring. Treatment of 1-azidostyrene with Fe$_2$(CO)$_9$ results in the formation of some of the same products as obtained using azirines as the substrates.

The chemistry of azirines has been a subject of great interest in recent years. Splendid work by Hassner,[1a] Padwa,[1b,c] Schmid,[1d] and others has resulted in new synthetic routes to heterocycles via cycloaddition to the ring-opened azirine. In addition, metal carbonyls can effect fascinating ring-cleavage reactions of small ring systems [e.g., vinyloxiranes,[2a] vinylcyclopropanes[2b]] to give interesting organic or organometallic products.

On the basis of these results, it seemed conceivable that metal carbonyls might induce azirines to form novel organometallic complexes and/or to provide simple and convenient synthetic approaches to heterocyclic systems. The