arrangement in the isomorphous α-N_2 lattice.

8. Finally, EHMO calculations performed on the asymmetrical C-bonded dicarbonyl and the isocarbonyl–carbonyl complex predict shifts in the uv–visible transitions of both complexes compared to the symmetrical C-bonded dicarbonyl. However, an unreasonably large (~ 1.5 Å) perturbation of the unique CO group is required in the asymmetrical C-bonded dicarbonyl to simulate the changes observed on simply switching one CO group into the O-bonded configuration.

Moreover, the sensitivity of the high-energy transition compared to the low-energy transition on passing from the symmetrical C-bonded dicarbonyl to the isocarbonyl–carbonyl (although not in the right direction—which is not unexpected within the limitations of EHMO theory) is at least consistent with the trend observed in practice. On the other hand, on passing from the symmetrical C-bonded dicarbonyl to the asymmetrical C-bonded dicarbonyl, the calculations predict the reverse trend; that is, the low-energy transition is more sensitive than the high-energy transition to the mode of CO bonding. The EHMO calculations therefore suggest that the isocarbonyl–carbonyl formulation is a more acceptable model than a lattice-perturbed asymmetrical C-bonded complex.

In conclusion we would argue that five out of the eight pieces of evidence lean toward the isocarbonyl–carbonyl formulation. However, our data are not unequivocal and other experiments will be required to unravel this fascinating yet perplexing chemical problem.

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Metal Atom Chemistry and Surface Chemistry. 1. Dioxygensilver, Ag+,O2-, and Tetraoxygensilver, Ag+,O4-, Reactive Intermediates in the Silver Atom–Dioxygen System. Relevance to Surface Chemistry

D. McINTOSH and G. A. OZIN*

The cocondensation reaction of Ag atoms with $^{16}O_2$ and $^{16}O_2$/Ar matrices at 6–12 K has been investigated by infrared and ultraviolet–visible spectroscopy. Dioxygen and silver concentration experiments, warm-up studies, and $^{16}O_2$/$^{18}O_2$ and $^{16}O_2$/$^{16}O^{18}O$/$^{18}O_2$ isotopic substitutions establish that two mononuclear complexes are formed which are best formulated as AgO$_2$ and AgO$_4$. The isotopic data suggest that the oxygen atoms in AgO$_2$ are equivalent and the uv–visible data imply the presence of an Ag+,O2- ion pair. An ion-pair formulation is also arrived at for Ag+,O4- by comparison with Ag+,O2- as well as with the known alkali metal–dioxygen ion pairs Cs+,O2- and Cs+,O4-. The results for Ag/O$_2$ are found to be unique when compared with the available data for Cu/O$_2$ and Au/O$_2$ cocondensation reactions. The Ag/O$_2$ reaction products are further discussed in terms of their potential usefulness as localized bonding models for molecular dioxygen surface complexes which are known to participate in silver-catalyzed oxidation reactions.

Introduction

Molecular dioxygen surface species are of central interest in a variety of silver-catalyzed oxidation reactions.[1] Many of the mechanisms that have been proposed invoked Ag($O_{2_{ads}}$) complexes as reactive intermediates rather than O^-_{ads} and/or O^{2-}_{ads} surface oxide species, all of which are known to coexist on freshly oxygenated silver films and supported silver catalysts.[1] A potentially useful technique for gaining a localized bonding description[2] of metal–dioxygen surface interactions

involves the isolation and spectroscopic study of the primary reaction products of metal atom–dioxygen matrix reactions. Previous studies of this type have led to the discovery of binary dioxygen complexes, MO$_2$ and O$_2$MO$_2$ (where M = Ni, Pd, Pt,[3] Rh,[4] Cr,[5] or Cu[5,6]), which would appear at this stage to be useful models for exploring the transient steps prior to dissociative chemisorption of dioxygen on metal surfaces.

In the context of the Ag/O$_2$ cocondensation reaction one would anticipate that AgO$_2$ would be one of the products. A complex of this type could possibly serve as a simple model
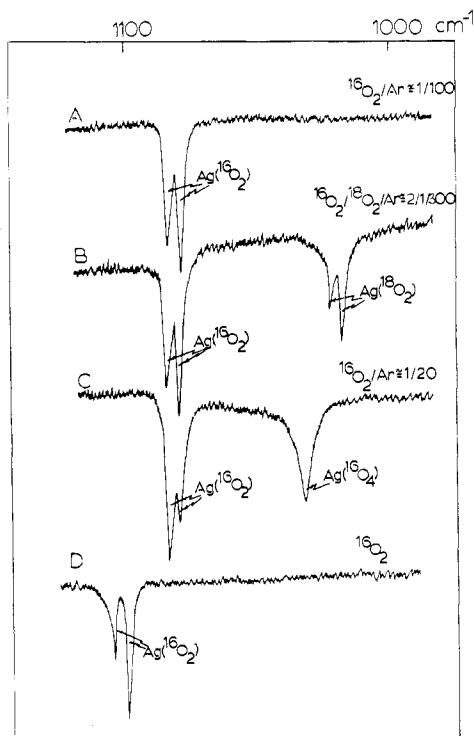
Figure 1. Matrix infrared spectrum observed on depositing Ag atoms with (A) $^{16}O_2/Ar \simeq 1/100$, (B) $^{16}O_2/^{18}O_2/Ar \simeq 2/1/300$, (C) $^{16}O_2/Ar \simeq 1/20$, and (D) $^{16}O_2$, at 6 K.

for $Ag(O_{2ads})$.[1] This expectation was realized in practice and led not only to the discovery of dioxygensilver, AgO_2, but to the interesting secondary reaction product tetraoxygensilver, AgO_4. What follows is a detailed account of these experiments.

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 $^{16}O_2$ and Ar (99.99%) were supplied by Matheson of Canada and $^{18}O_2$ (90%) was supplied by Stohler Isotopes, Montreal. The furnace used for the evaporation of the metals has been described previously.[7] The rate of silver atom deposition was continuously monitored using a quartz-crystal microbalance.[8] 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 or to 6 K by means of an Air Products Helitran system. 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.

Matrix Infrared Experiments. (A) Pure Dioxygen Matrices. When silver atoms are cocondensed with $^{16}O_2$ matrices at 6 K (using very low concentrations of Ag to eliminate complications due to cluster formation[9]), the resulting infrared spectrum shows a closely spaced doublet at 1102/1097 cm^{-1}, the absorbance of which increases at a rate proportional to the amount of silver deposited (Figure 1D). A very weak absorption is also observed at 440 cm^{-1}; its behavior appears to parallel that of the doublet absorption in the OO stretching region. A point to note here is that the intensity ratio and bandwidths of the component lines of this doublet are found to be particularly sensitive to the deposition conditions and thermal annealing history of the matrix and can appear as either a resolved doublet (1102/1097 cm^{-1}, Figure 1D) or a single, broadened band (1098 cm^{-1}, Figure 2A). In either case, warming the matrix from 6 to 40 K simply causes a gradual diminution of the absorbance of the band(s). The nonobservation of any other absorptions under these conditions implies that the Ag/O_2 matrix reaction yields just a single species. [The doublet splitting of the OO stretching mode is reminiscent of the matrix site effects observed for binary dioxygen complexes in solid dioxygen.[3] These
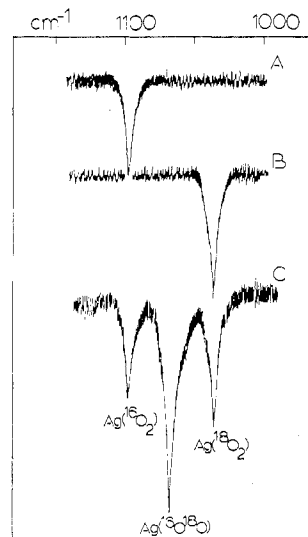

Figure 2. Matrix infrared spectrum observed on depositing Ag atoms with (A) $^{16}O_2$, (B) $^{16}O_2/^{18}O_2 \simeq 1/1$, and (C) $^{16}O_2/^{16}O^{18}O/^{18}O_2 \simeq 1/2/1$, at 10 K. The isotopic patterns in the OO stretching region are characteristic of dioxygensilver, AgO_2, probably containing a side-on bonded dioxygen moiety.

splittings were understood to originate from different matrix site perturbations experienced by the entrapped guest in the α and β crystalline phases of solid dioxygen.[10]]

The number of dioxygen molecules in this new complex was established to be *one* from $^{16}O_2/^{18}O_2 \simeq 1/1$ isotopic substitution experiments. This can be seen from the doublet isotope pattern in the OO stretching region at 1098 and 1036 cm^{-1} corresponding to $Ag^{16}O_2$ and $Ag^{18}O_2$, respectively. Note that the absence of a central component corresponding to $Ag^{16}O^{18}O$ demonstrates that dioxygen dissociation either on the silver source or from reaction with Ag atoms in the gas or matrix phase does not occur to any observable extent under the conditions of this experiment. The low-frequency mode observed at about 440 cm^{-1} by comparison with other monodioxygen complexes[3] is probably best assigned to a silver--oxygen stretching mode of AgO_2.

Strong support for the mononuclear AgO_2 formulation derives from the invariance of the matrix infrared spectrum to $Ag/^{16}O_2$ concentration changes[9] in the range $1/10^3$ to $1/10^6$.

To gain an insight into the mode of attachment of the dioxygen ligand to the Ag atom, scrambled $^{16}O_2/^{16}O^{18}O/^{18}O_2 \simeq 1/2/1$ mixtures were employed.[11] A characteristic 1/2/1 triplet was observed at 1098, 1068, and 1036 cm^{-1} (Figure 2) where the central component at 1068 cm^{-1} clearly is associated with $Ag^{16}O^{18}O$. This isotopic triplet with approximately equal $\Delta\nu_{1/2}$ values (6 cm^{-1}) for all three components might be taken as evidence that there is no linkage isomerism for the $Ag^{16}O^{18}O$ molecule and that the dioxygen ligand is side-on bonded with respect to the silver. The extremely low infrared absorbance of the OO stretching mode of AgO_2 even after a 5-h deposition (under normal flow conditions) would certainly support the contention of a side-on bonded dioxygen moiety.

Interestingly, this situation closely parallels the proposed side-on chemisorbed form of molecular dioxygen on a silver surface.[1] We recognize, however, that for AgO_2 the possibility of end-on bonded dioxygen cannot be dismissed for infrared bands roughly 6 cm^{-1} wide. For the purposes of this report we shall assume side-on bonding is an appropriate description.

(B) Dilute Dioxygen--Argon Matrices. Similar cocondensation reactions to those described in $^{16}O_2$ were conducted in $^{16}O_2/Ar \simeq 1/100$ mixtures (Figure 1A). Under these conditions an OO stretching mode was observed at 1082/1077 cm^{-1}, which is shifted only 20 cm^{-1} from the absorption assigned to $Ag^{16}O_2$ in $^{16}O_2$ matrices. The warm-up behavior and dioxygen isotope data for this species (Figure 1B) parallel closely those observed for AgO_2 and establish that one and the same species forms in both $^{16}O_2$ and dilute $^{16}O_2/Ar$ matrices, the only difference between the two situations being a matrix-induced frequency shift of the order of 20 cm^{-1}.

(C) Concentrated Dioxygen--Argon Matrices. Only under conditions of high-concentration $^{16}O_2/Ar$ mixtures (1/1 to 1/50) could a second
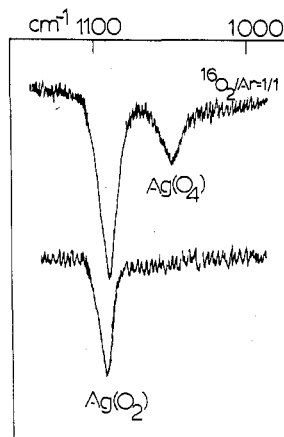
Figure 3. Matrix infrared spectrum observed on depositing Ag atoms with $^{16}O_2/Ar \simeq 1/1$ at 10 K and after warming the matrix to 30 K.
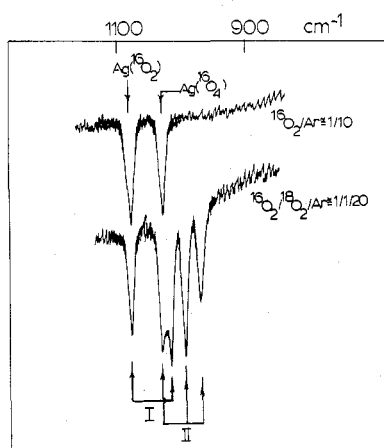

Figure 4. Matrix infrared spectrum observed on depositing Ag atoms with $^{16}O_2/Ar \simeq 1/10$ and $^{16}O_2/^{18}O_2/Ar \simeq 1/1/20$ at 10–12 K, showing the oxygen isotopic structure of AgO_2 (I) and AgO_4 (II).

Figure 5. Uv-visible spectrum observed on depositing Ag atoms with (A) $^{16}O_2$ and (B) $^{16}O_2/Ar \simeq 1/10$ at 10–12 K. Curve C shows the effect of warming matrix B to 35 K. Uv absorptions ascribed to Ag^+,O_2^- and Ag^+,O_4^- are indicated.

Scheme I

silver–dioxygen complex (II) be induced to form. For example, when Ag atoms were cocondensed with $^{16}O_2/Ar \simeq 1/20$ mixtures (Figure 1C), besides the absorption previously assigned to $Ag^{16}O_2$ (I), a new absorption to *lower* frequencies was observed at 1030 cm^{-1}. Warming the matrix in the range 10–30 K causes absorptions I and II to diminish gradually in intensity but at markedly different rates, species II apparently being less stable (Figure 3). Furthermore, on either increasing or decreasing the $^{16}O_2/Ar$ ratio above or below that of 1/20, the intensity of absorption II decreases relative to that of I. [It should be noted here that the OO stretching frequencies for species I and II are sensitive to the O_2/Ar ratio, showing *blue* shifts of roughly 10 and 18 cm^{-1} on changing from 1/50 to 1/1 mixtures, respectively.] However, this intensity ratio was insensitive to Ag/Ar variations in the range $1/10^3$ to $1/10^6$. These experiments serve to establish not only the mononuclear character[9] of compound II but also the optimum experimental conditions for its production.

The number of dioxygen molecules in compound II was established to be *two* by $^{16}O_2/^{18}O_2/Ar \simeq 1/1/20$ isotopic substitution. A typical infrared spectrum is shown in Figure 4 and shows, besides the characteristic $Ag^{16}O_2/Ag^{18}O_2$ doublet, a *triplet* isotope pattern at 1030, 996, and 971 cm^{-1} in place of the original OO absorption of compound II. These data adequately serve to characterize II as a complex containing *two* dioxygen moieties in which the $^{16}O_2$ and $^{18}O_2$ molecules retain their identity.

To obtain information as to the relative disposition of the two dioxygen moieties in II, we performed $^{16}O_2/^{16}O^{18}O/^{18}O_2/Ar \simeq 1/2/1/40$ experiments. Unfortunately these data did not prove to be very informative owing to the relatively large $\Delta\nu_{1/2} \simeq 6-8$ cm^{-1} of the isotopic components of II and the resulting difficulties in resolving the isotopic structure, so vital for drawing meaningful stereochemical conclusions.
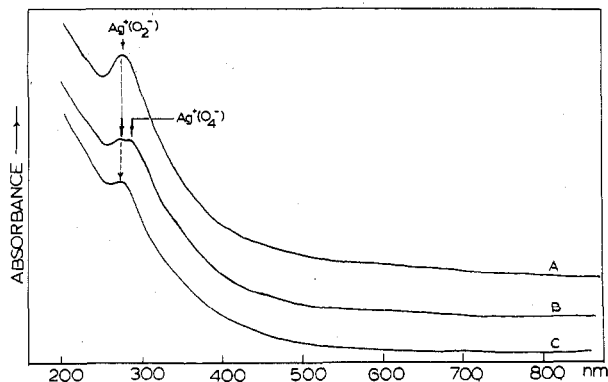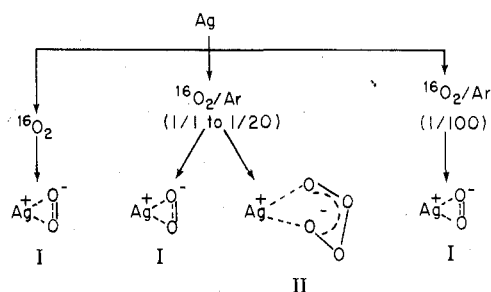
Ultraviolet–Visible Experiments. The ultraviolet–visible spectra of compounds I and II were recorded in order to derive some information about their electronic properties. Visible absorptions were not observed (cf. $(C_2H_4)Ag$—purple;[12] $(C_2H_4)Au$—green;[13] Ag-$(CO)_3$—green;[14] $Au(CO)_2$—green;[15] $Au(O_2)$—green[16]) for either I or II, although weak absorptions were observed in the ultraviolet regions of the spectrum at roughly 275 nm for I and 290 nm for II. For example, in $^{16}O_2$ matrices a single absorption was observed in the uv (Figure 5A) centered at 275 nm which is the region characteristic of the $\pi \rightarrow \pi^*$ electronic transition of superoxide.[22] Knowing that AgO_2 is the sole reaction product under these conditions, one may conclude that the observation of a superoxide absorption in the uv (and infrared) spectrum as well as the absence of electronic transitions in the visible spectrum provide strong evidence in favor of silver oxidation state I and the tight ion-pair formulation Ag^+,O_2^-.

By experimenting in $^{16}O_2/Ar \simeq 1/10$ matrices where AgO_2 and AgO_4 are known to coexist with roughly equal absorbances, one observes in the uv spectrum (Figure 5B) a shoulder at roughly 290 nm on the absorption at 275 nm previously ascribed to Ag^+,O_2^-. On warming of the matrix to 30 K, the shoulder at 290 nm gradually disappears (Figure 5C), leaving the 275-nm absorption as the only observable spectral feature in the range 190–900 nm.
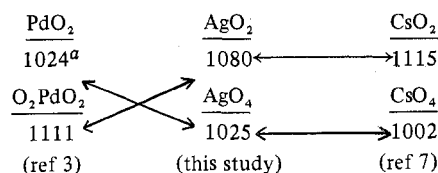
These data closely parallel those observed in the infrared region for AgO_2 and AgO_4 and permit one to assign the uv absorption at 290 nm to an electronic transition characteristic of AgO_4.

The absence of visible transitions for AgO_4 and the close proximity of its 290-nm absorption to the 275-nm absorption of AgO_2 suggest an assignment to silver oxidation state I and a Ag^+,O_4^- ion-pair formulation.

We note that the *red* frequency shift of the OO stretching mode on passing from Ag^+,O_2^- to Ag^+,O_4^- is consistent with the *red* frequency shift in their respective uv absorptions. In brief, the lower OO bond order for O_4^- compared to that for O_2^-, as seen from the infrared data, implies a smaller $\pi \rightarrow \pi^*$ energy separation in the weakly coupled component dioxygen moieties of O_4^- and hence a *red* shift in its uv transition energy compared to the corresponding transition of O_2^-.

We therefore suggest that these data are consistent with an assignment of silver oxidation state I in both Ag^+,O_2^- and Ag^+,O_4^-. We shall proceed to discuss these results and the corresponding infrared data in the following sections.

Chart I

$\underline{PdO_2}$	$\underline{AgO_2}$	$\underline{CsO_2}$
1024^a	$1080 \longleftrightarrow 1115$	

$\underline{O_2PdO_2}$	$\underline{AgO_4}$	$\underline{CsO_4}$
1111	$1025 \longleftrightarrow 1002 \longleftrightarrow$	
(ref 3)	(this study)	(ref 7)

^{a} All units: cm^{-1}.

Results and Discussion

The results of the Ag/O$_2$ experiments can be summarized in the flow diagram shown in Scheme I. It can be seen that a single compound I can be generated in $^{16}O_2$ or dilute $^{16}O_2$/Ar matrices. The absence of visible transitions for I and the presence of a uv transition at 275 nm which could be associated with an O$_2^-$ anion[22] (cf. Cs$^+$,O$_2^-$ [17c]) tempt one to propose that an Ag$^+$,O$_2^-$ ion-pair formulation is an appropriate description for I.

Only in concentrated $^{16}O_2$/Ar matrices can we generate compound II, which is known from isotopic substitution to contain two dioxygen units. Particularly noteworthy is the fact that the OO stretching mode of II occurs at lower frequencies than that of I, which is *not* the behavior expected for a bis-(dioxygen) complex, as seen in Chart I. Thus in O$_2$PdO$_2$ the infrared-active OO stretching mode is predicted and observed[3] at higher frequencies than PdO$_2$ which is not the case for II compared to I. However, the infrared data for I and II closely resemble those for Cs$^+$,O$_2^-$ and Cs$^+$,O$_4^-$.[17a,b]

A point to appreciate about a tetraoxygen complex of this type is that intermolecular interaction between the component dioxygens must lead to a concomitant weakening of the intramolecular oxygen–oxygen bonds and hence a lowering of the OO stretching mode in M(O$_2$···O$_2$) relative to MO$_2$. On the other hand, a bis(dioxygen) formulation O$_2$MO$_2$ must lead to a strengthening of the intramolecular oxygen–oxygen bonds relative to MO$_2$. The former set of circumstances appears to prevail in the silver–dioxygen complex II. When taken in conjunction with the absence of visible transitions for II and the presence of a uv transition at 290 nm which could be associated with an O$_4^-$ anion, as well as the close similarity to Cs$^+$,O$_4^-$,[17] this evidence favors an Ag$^+$,O$_4^-$ ion-pair formulation for II.

Although we cannot determine the detailed geometry of AgO$_4$, it is worth mentioning that the equilibrium structure calculated for a gaseous O$_4^-$ anion from approximate SCF–MO theory[18] is that of a trans chain (cf. the Pimentel–Spratley bonding description of O$_2$F$_2$[19]) with a weak intermolecular bond between the two dioxygen moieties. This structure receives support from Jacox and Milligan's observation of O$_4^-$ in their matrix photolysis studies of Na atom/O$_2$/Ar mixtures.[17d] Pertinent to the present study, CNINDO–MO calculations[17b] have been performed to investigate possible O$_4^-$ geometries and Na$^+$ positions in the Na$^+$,O$_4^-$ molecular system and tend to favor a five-membered, puckered-ring geometry, as we have indicated for Ag$^+$,O$_4^-$ in Scheme I.

An intriguing observation in the Ag atom–O$_2$ system relates to the ability to generate AgO$_4$ only in O$_2$/Ar matrices, within a narrow concentration range 1/1 to 1/50. Not unexpectedly, the probability of forming AgO$_4$ relative to AgO$_2$ diminishes as the O$_2$/Ar dilution increases. At dilutions greater than 1/50, AgO$_2$ is the only observable species. Surprisingly, however, AgO$_4$ does *not* form in *pure* O$_2$ and under these conditions AgO$_2$ is the only detectable species.
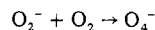
This is a difficult result to rationalize unless one invokes an unfavorably high activation energy for an ion–molecule matrix reaction of the kind

$$Ag^+,O_2^- + O_2 \rightarrow Ag^+,O_4^-$$
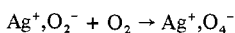
Scheme II
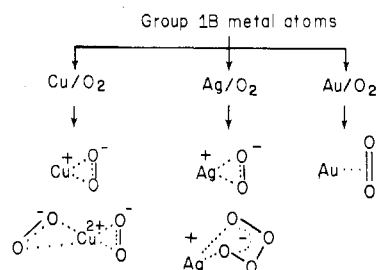
in a solid dioxygen lattice. This reaction should be compared with the gas-phase ion–molecule reaction

$$O_2^- + O_2 \rightarrow O_4^-$$

which can be monitored by mass spectroscopy.[20] It seems clear that no obvious lattice restriction can affect the formation of Ag$^+$,O$_2^-$ for a silver atom in the substitutional site of an O$_2$ or O$_2$/Ar lattice. On the other hand, the lattice requirements of the dioxygen molecules in crystalline O$_2$ could well impose a substantial kinetic impediment to Ag$^+$,O$_4^-$ formation, on the grounds that the site symmetry requirements of α- or β-O$_2$[10] are likely to be incompatible with the conformation of an O$_4^-$ anion relative to the Ag$^+$ cation. In concentrated O$_2$/Ar matrices the dioxygen lattice structure no longer dominates and the formation of Ag$^+$,O$_4^-$ is not expected to be lattice constrained. In this way we can rationalize the observation of Ag$^+$,O$_4^-$ in O$_2$/Ar matrices as concentrated as 1/1.

Summary of the Reactions of Group 1B Metal Atoms with Dioxygen

Scheme II summarizes the matrix reactions of group 1B metal atoms with dioxygen under various dilution conditions. Mono(dioxygen) complexes can be generated for all three metals which, in the cases of Cu$^+$,O$_2^-$ and Ag$^+$,O$_2^-$, are best formulated as metal–superoxide molecular species. However, the optical data for AuO$_2$, especially when compared with those for (C$_2$H$_4$)Au,[13] strongly suggest that the dioxygen moiety is olefinic in its bonding properties to gold. This is not unexpected in view of the high first ionization potential for Au (9.22 eV) compared to those for Cu (7.72 eV) and Ag (7.57 eV).

Silver would appear to be unique in group 1B in view of a secondary reaction of AgO$_2$ with O$_2$ to yield a complex which is best formulated as tetraoxygensilver, AgO$_4$, rather than a bis(dioxygen) description as favored for O$_2$CuO$_2$.[5] By contrast, AuO$_2$ is the only species that can be generated from Au atoms and O$_2$ under cryogenic conditions.[16]

The behavior of this group of metal atoms with dioxygen is most fascinating. The reluctance of Au to accept more than a single O$_2$ might be related to the extremely high first-ionization potential of Au which in turn may be interconnected with the inability of Au to chemisorb O$_2$.[21] A superoxide–copper(I) assignment and bis(superoxide)–copper(II) assignment is not unexpected for the Cu/O$_2$ reaction products in view of the accessibility of the Cu(I)/Cu(II) oxidation states. However, the extremely unfavorable second-ionization potential for silver may preclude the attainment of this state under cryogenic conditions and a lower activation energy pathway to Ag$^+$,O$_4^-$ is favored. In this way silver oxidation state I is preserved.

This idea receives strong support from the corresponding alkali metal atom–dioxygen matrix reactions, which show that the ease of formation of the analogous M$^+$,O$_4^-$ species relative to that of the M$^+$,O$_2^-$ species decreases in the order Cs > Rb > K > Na.[17]

In view of the Cu/O$_2$ and Ag/O$_2$ reaction products, it does not seem too surprising that Au can only be induced to form

AuO_2 with an olefinic type of gold–dioxygen bonding interaction.[16]

Relevance to Dioxygen Chemisorption on Silver

Various groups have investigated the species present on freshly oxygenated silver surfaces over a wide range of temperatures.[1] The general consensus appears to be that the chemisorbed state consists of $O_2^-{}_{ads}$, $O^-{}_{ads}$ and $O^{2-}{}_{ads}$. The molecular oxygen adsorption complex has evoked considerable interest because it is thought by some to be the surface species active in olefin oxidation reactions.[1] Therefore, from a localized bonding point of view,[2] the AgO_2 complex of the present study is an interesting model for $Ag(O_{2_{ads}})$.

Unfortunately, spectroscopic comparisons between $Ag(O_{2_{ads}})$ and AgO_2 are not possible at the present time owing to the paucity of vibrational and optical data for O_2 chemisorbed onto silver. However, by utilizing AgO_2 as a model reaction intermediate for studying oxidation reactions with other substrates, such as ethylene or carbon monoxide, one may be able to gain a rather novel insight into the usefulness of AgO_2 as a localized bonding model for $Ag(O_{2_{ads}})$ (see part 2 of this study[24]).

In practice AgO_2 may not prove to be a suitable model for $Ag(O_{2_{ads}})$ because of the prerequisite of, for example, multiatom surface sites, to enhance $Ag \rightarrow O_2$ charge transfer prior to dissociative chemisorption. If this is the case, then molecular AgO and/or Ag_2O (as localized bonding models for $O^-{}_{ads}$ and $O^{2-}{}_{ads}$, respectively) may be more appropriate synthetic goals. In this event the matrix reactions of small, well-defined silver clusters Ag_n (where $n = 2, 3, ...$)[23] with dioxygen should be interesting and could serve two purposes. First, to simulate dissociative chemisorption of dioxygen on silver surfaces and, second, to utilize the resulting molecular oxides as model reaction intermediates for studying silver-catalyzed oxidation reactions. In this context we note that the nonobservation of OO bond rupture in silver atom–dioxygen matrix reactions probably reflects a kinetic rather than a thermodynamic impediment at the low temperatures employed. Presumably, dioxygen dissociation can be induced by working at higher deposition temperatures or under conditions which favor silver cluster formation. Further experiments will be required to clarify these proposals.

Registry No. $Ag(O_2)$, 12321-65-2; $Ag(O_4)$, 60606-83-9.

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