# Metal Atom Matrix Chemistry. Correlation of Bonding with Chemisorbed Molecules

Geoffrey A. Ozin

*Lash Miller Chemistry Laboratory and Erindale College, University of Toronto, Toronto, Ontario, Canada*

*Received July 1, 1976*

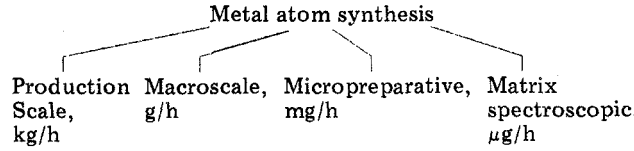
In this Account I will be mainly concerned with matrix scale chemistry of transition-metal vapors, particularly with the types of experiments and reactions which have a logical relationship to various aspects of chemisorption and catalysis. A feature common to both homogeneous and hetereogeneous catalysis is the prerequisite of a coordinatively unsaturated metal center or active surface site. However, because the active ingredients responsible for the mode of operation of a catalytic cycle have only a fleeting existence, their isolation and study by standard chemical procedures are often difficult if not impossible.

A novel approach to this type of problem is to employ "naked" metal atoms (or small, naked metal clusters) for tailor-making reaction intermediates with chemical and physical properties similar to those suspected to occur either on the surface of a heterogeneous catalyst or as part of a homogeneous catalytic cycle. To achieve this end, cryogenic trapping techniques and matrix isolation infrared, laser Raman, ultraviolet–visible, and ESR spectroscopy are employed to isolate and study the species and reactions of interest.

If one briefly surveys the field of metal vapor chemistry as it stands after roughly 6 years of intensive research, one discovers that four main subfields have emerged which are related to the scale of operation as shown in Scheme I. All of these experiments involve transporting the metal vapor (which is usually greater than 99% atomic) in a "collision-free" path to a cold surface (or cold solution) where it is arranged to react with another material (or solute) to form the desired product(s). The technology of efficient vapor sources is well understood,[1] and chemists and chemical engineers are now thinking about how to adapt industrial scale metal evaporators (for example, 32 kg of Ni can be easily vaporized in 1 h using a 164 kW electron gun) for the production of rare inorganic chemicals, organometallic compounds, and catalysts.

Macroscale (g/h) metal vapor techniques are most suitable for exploratory synthetic work in the research laboratory. At present, reactions are performed in static and rotary cryostats using either resistive, inductive, electron beam, or laser methods for vaporizing the metal. Some important new compounds, catalysts, and catalytic conversions have been realized using these techniques. Examples include the macroscale metal

**Scheme I**




atom catalysis work of Green[2a]—butadiene/metal atom polymerizations; Klabunde—RMX species previously proposed as catalysis intermediates[2b] and active metal powder catalysts;[2c] and Koerner von Gustorf's[2d] Cr–butadiene–CO complex; the reader is referred to a number of reviews on the subject.[3]

The micropreparative (mg/h) metal vapor experiment is a useful method for quickly checking the feasibility of a macroscale cryochemical synthesis. In brief, the metal vapor reaction is performed on an optical window at −196 °C, using conditions which duplicate the macropreparation, but of course on a spectroscopic scale. The product(s) is usually observed by infrared spectroscopy as the matrix is allowed to warm up and boil off, leaving the product(s) on the optical window in a pure state. In this way the product can be monitored from cryogenic to ambient temperatures, and its thermal stability and hence useful working range for chemical synthesis can therefore be established. This kind of experiment is beginning to provide the vital link between the macropreparative and matrix spectroscopic metal atom experiments.[4]

It is convenient at this point to subdivide the matrix approach to metal atom chemistry into four main areas, based on whether mononuclear or cluster compounds in inert or reactive matrices are the desired end product. For example, by using quantitative metal atom–inert gas cocondensation techniques it has proven possible to control and study the embryonic stages of the aggregation reaction:[5]

$$M \xrightarrow[k_1]{M} M_2 \xrightarrow[k_2]{M} M_3 \ldots$$

Geoffrey A. Ozin received his B.Sc. degree from Kings College, London, and in 1967 his D.Phil. degree from Oriel College, Oxford University, under Professor Ian Beattie. Following this, he spent 2 years as an ICI postdoctoral fellow in Professor Beattie's laboratories at Southampton University. In 1969 he joined the faculty of Erindale College, University of Toronto, where he is now Associate Professor. His present research effort is focused on the chemical reactions of transition-metal vapors as studied by matrix infrared, laser Raman, ultraviolet–visible, and ESR spectroscopies. He is the recipient of the 1973 Meldola Medal in Physical–Inorganic Chemistry of the Royal Institute of Chemistry, the 1976 Coblentz Medal in Molecular Spectroscopy of the Coblentz Society, and the 1977 Sherman Fairchild Scholarship from California Institute of Technology.

(1) (a) W. Reichelt, *Angew. Chem., Int. Ed. Engl.*, 14, 218 (1975); (b) "Cryochemistry", M. Moskovits and G. A. Ozin, Ed., Wiley, New York, N.Y., 1976.

(2) (a) V. M. Akhmedov, M. T. Anthony, M. L. H. Green, and D. Young, *J. Chem. Soc., Dalton Trans.*, 1412 (1975); (b) K. J. Klabunde and J. S. Roberts, *J. Organomet. Chem.*, 85, C13 (1975); K. J. Klabunde and J. Y. F. Low, *ibid.*, 51, C33 (1973); (c) K. J. Klabunde, J. F. Efner, T. O. Murdock, and R. Ropple, *J. Am. Chem. Soc.*, 98, 1021 (1976); (d) E. Koerner von Gustorf, O. Jaenicke, and O. E. Polansky, *Angew. Chem., Int. Ed. Engl.*, 77, 532 (1972).

(3) (a) P. L. Timms, *Adv. Inorg. Chem. Radiochem.*, 14, 121 (1972); (b) Merck Symposium Proceedings, "Metal Atoms in Chemical Synthesis", *Angew. Chem., Int. Ed. Engl.*, 4, 5 (1975); (c) G. A. Ozin and A. Vander Voet, *Acc. Chem. Res.*, 6, 313 (1973); (d) M. Moskovits and G. A. Ozin in "Vibrational Spectra and Structure", J. Durig, Ed., Elsevier, Amsterdam, 1976; (e) K. J. Klabunde, *Acc. Chem. Res.*, 8, 383 (1975).

(4) (a) L. A. Hanlan and G. A. Ozin, *J. Am. Chem. Soc.*, 96, 6324 (1974); (b) P. L. Timms, 170th National Meeting of the American Chemical Society, Chicago, Ill., Aug 1975, Paper INOR-119.

Small, well-defined clusters of metal atoms are of great and wide-ranging interest. They are the first stages in the metal nucleation process, and it is important to learn which geometries are favored and at which cluster sizes the electronic properties of the bulk material become evident. They may also be considered to be ideal models for high surface area catalysts. Hence the study of their interaction with reactive matrices can reveal information about the chemisorption process as well as about surface and catalytic intermediates.[3d,6] Similarly, metal atom cocondensation reactions can be designed to terminate at the mononuclear stage. In this way, coordinatively unsaturated transition-metal fragments, resembling the active species in a homogeneous catalytic cycle, can be isolated for study.[3]

For the remainder of this paper we will consider some localized bonding models[7] for the surface complexes $M(C_2H_{4\ ads})$, $M(O_{2\ ads})$, and $M(CO_{ads})$. Subsequently we will investigate some of their reactions with other substrates, the objectives being to provide a useful description of the chemisorption process and reactive intermediates and to study the origin of the reactivities of surface species and possibly mechanistic details of surface reactions.

## A Localized Bonding View of Carbon Monoxide Chemisorbed on Metal Surfaces

Metal atom synthesis of a series of triatomic monocarbonyls MCO (where M = V, Cr, Mn, Fe, Co, Ni, or Cu)[3d] has recently provided a unique opportunity to resolve a controversy that has existed for many years, concerning the mode of attachment of adsorbed CO on metal films and supported metal particles. The traditional view advocated by Eischens[8] relates the occurrence of low- and high-frequency CO stretching modes normally observed in the spectrum of chemisorbed CO to the simultaneous existence of terminally bonded and bridge-bonded CO groups on the metal sites, by analogy with stable metal carbonyls such as $Fe_2(CO)_9$. More recently, Blyholder[9] argued that the plurality of bands observed in the infrared spectrum of chemisorbed CO can be rationalized solely in terms of terminal CO groups adsorbed on corner, edge, and mid-plane sites of the metal. In support of his idea, the results of extended Hückel calculations for CO on a nine-atom model of a Ni surface[10] showed that the degree of $\pi$ overlap between metal d orbitals and the $\pi^*$ orbitals of terminal CO increased as one proceeded from central to corner sites, implying a concomitant shift of the CO stretching frequency to lower values. Blyholder's proposal is therefore physically understandable. A metal atom in a plane clearly has more metal atoms with which to share its d electrons than, for example, a metal atom in a corner site; therefore, the metal–CO $\pi$ overlap would be expected to increase in the same direction.

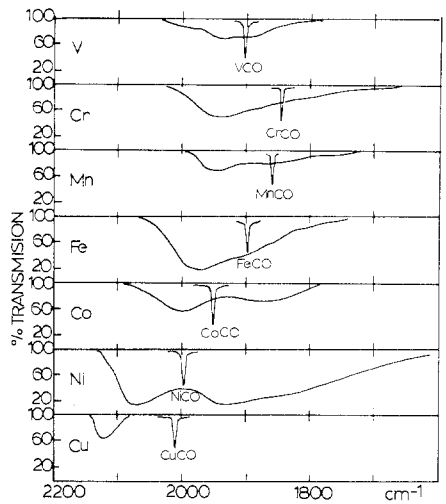



**Figure 1.** A superposition of the spectra reported by Blyholder and coworkers[8,9] for CO chemisorbed on metal particles with the frequencies reported for matrix isolated analogous monometal monocarbonyls. Taken from ref 1b.

Continuing this argument further, a MCO matrix isolated species should therefore absorb at a lower CO stretching frequency than the lowest observed for terminally adsorbed CO on bulk metal M. Figure 1 shows a superposition of Blyholder's spectra[9] of CO chemisorbed on various metals and the observed CO stretching frequency for the corresponding MCO species.[3d] The most significant point to note is that, aside from $Cu(CO_{ads})$,[16a] one observes an envelope of bands for $M(CO_{ads})$ *below* that of MCO, implying that these bands are most likely bridging CO groups. The metal atom data for MCO therefore indicate that the earliest picture of CO chemisorption on bulk metal is probably correct;[8] that is, both two-center and multicenter bonding of CO to surface metal atoms takes place.

## A Localized Model for the $\pi$-Complexed Form of Ethylene Chemisorbed on Palladium

The group 8 transition metals (Ni, Pd, Pt) are useful hydrogenation catalysts.[11] Infrared experiments suggest that ethylene is adsorbed on metal surfaces and supported metals in the form of the di-$\sigma$-bonded $M–CH_2–CH_2–M$ species.[12a,c] Very recently infrared evidence has been obtained for the presence of $\pi$-bonded species from ethylene chemisorbed on silica-supported Pd and Pt catalysts.[12b] These are proposed to coexist with the di-$\sigma$-bonded $M–CH_2–CH_2–M$ species and are found to be more readily removed by hydrogen than the latter. In line with these studies are the results obtained from photoemission experiments,[13] in which it is suggested that ethylene is bonded to the surface by means of its $\pi$ orbital. Interestingly, a recent secondary ion mass spectrometry study of ethylene adsorbed on Ni[14] showed the presence of two distinct types of adsorption, as indicated by the detection of the

(5) E. P. Kündig, M. Moskovits, and G. A. Ozin, *Nature (London)*, **254**, 503 (1975); R. Busby, W. Klotzbücher, and G. A. Ozin, *J. Am. Chem. Soc.*, **98**, 4013 (1976).

(6) (a) J. Hulse and M. Moskovits, *Surf. Sci.*, **57**, 125 (1976); (b) E. P. Kündig, M. Moskovits, and G. A. Ozin, *Angew. Chem., Int. Ed. Engl.*, **14**, 292 (1975); (c) H. Huber, E. P. Kündig, G. A. Ozin, and A. J. Poe, *J. Am. Chem. Soc.*, **97**, 308 (1975).

(7) (a) R. Ugo, *Cat. Rev.*, **11**, 225 (1975); (b) E. L. Muetterties, *Bull. Soc. Chem. Belg.*, **84**, 959 (1975).

(8) R. P. Eischens, W. A. Pliskin, and S. A. Frances, *J. Phys. Chem.*, **60**, 194 (1956).

(9) G. Blyholder, *J. Phys. Chem.*, **68**, 2772 (1964).

(10) G. Blyholder and M. C. Allen, *J. Am. Chem. Soc.*, **91**, 3158 (1969).

(11) (a) G. C. Bond, *Discuss. Faraday Soc.*, **41**, 200 (1966); (b) R. C. Burwell, Jr., in "Catalysis Progress in Research", F. Basolo and R. L. Burwell, Ed., Jr., Plenum Press, New York, N.Y., 1973.

(12) (a) B. A. Morrow and N. Sheppard, *J. Phys. Chem.*, **70**, 2406 (1966); *Proc. Roy. Soc., Ser. A*, 311, 391 (1969); (b) J. D. Prentice, A. Lesiunas, and N. Sheppard, *J. Chem. Soc., Chem. Commun.*, 76 (1976); (c) J. Erkelens and Th. Liefkens, *J. Catal.*, **8**, 36 (1967).

(13) J. E. Demuth and D. E. Eastman, *Phys. Rev. Lett.*, **32**, 1123 (1974).

(14) M. Barber, J. C. Vickerman, and J. Wolstenholme, *J. Catal.*, **42**, 48 (1976).

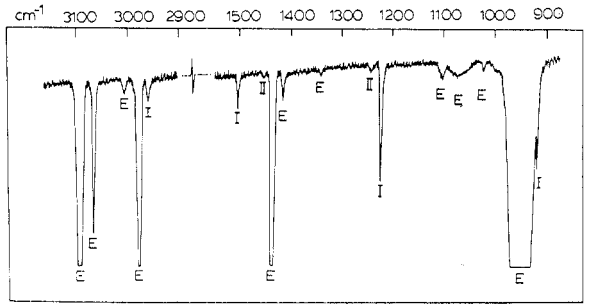



**Figure 2.** The matrix infrared spectrum observed on depositing Pd atoms with a $C_2H_4$:Xe ≃ 1:100 mixture at 15 K (Pd:Xe ≃ 1:$10^5$) showing the absorptions of $Pd(C_2H_4)$ (I). (The absorptions associated with free $C_2H_4$ in the matrix are labeled E. II represents a trace amount of $Pd(C_2H_4)_2$.) Taken from ref 15.

**Table I**
**Infrared Spectra of $Pd(C_2H_4)$ and $Pd(C_2H_4$ ads)**

| Approximate description of mode | $Pd(C_2H_4)$,[15] $cm^{-1}$ | $Pd(C_2H_4$ ads),[12] $cm^{-1}$ | Δ, $cm^{-1}$ |
|---|---|---|---|
| $\nu(CH_2)$ | 2952 | 2980 | 28 |
| $\nu(C{=}C)$ | 1502 | 1510 | 8 |
| $\delta(CH_2)$ | 1223 | Not obsd | |
| $\rho_w(CH_2)$ | 913 | Not obsd | |

ions $Ni(C_2H_4)^+$ and $Ni_2(C_2H_4)^+$.

By cocondensing Pd atoms with $C_2H_4$:Xe ≃ 1:100 matrices at 15 K (Pd/Xe ≃ 1/$10^5$) it proved possible to isolate $Pd(C_2H_4)$ as seen from its infrared spectrum (Figure 2).[15] Metal and ethylene concentration studies, warm-up experiments, and comparison with the data for $Ni(C_2H_4)$[17a] confirmed the 1:1 stoichiometry of monoethylenepalladium. Of central interest to this discussion is the remarkable similarity between the infrared spectra of $Pd(C_2H_4)$[15] and $Pd(\pi\text{-}C_2H_4$ ads),[12b] as shown in Table I. The close correspondence between the observed $\nu(CH_2)$ and $\nu(C{=}C)$ stretching modes strongly suggests that ethylene π-bonded to a single palladium atom in $Pd(C_2H_4)$ is an intuitively acceptable model for the π-complexed form of $C_2H_4$ chemisorbed onto Pd.

## Metal Atom–Ethylene Reactions

A number of other monoethylene complexes, $M(C_2H_4)$, have been synthesized and studied using techniques similar to those described above. These include M = Co,[18] Rh,[18] Ni,[17a] Pd,[17a] Cu,[17b] Ag,[17c] Au,[17c] and are potentially useful candidates for modeling Co- and Rh-catalyzed hydroformylation reactions, Ni-, Pd-, and Pt-catalyzed hydrogenation reactions, and Cu-, Ag-, Au-catalyzed oxidation reactions, to name but a few.

By employing higher concentrations of ethylene it has also proven possible to obtain $M(C_2H_4)_2$ and $M(C_2H_4)_3$ complexes using M = Co,[18] Rh,[18] Ni,[17a] Pd,[17a] Pt,[17a] and Cu atoms.[17b] Let us illustrate the techniques by reference to the Ni:$C_2H_4$ reaction.[17a] A typical infrared spectrum using $C_2H_4$:Ar ≃ 1:10 matrices (Figure 3) shows the presence of the three complexes, $Ni(C_2H_4)_n$

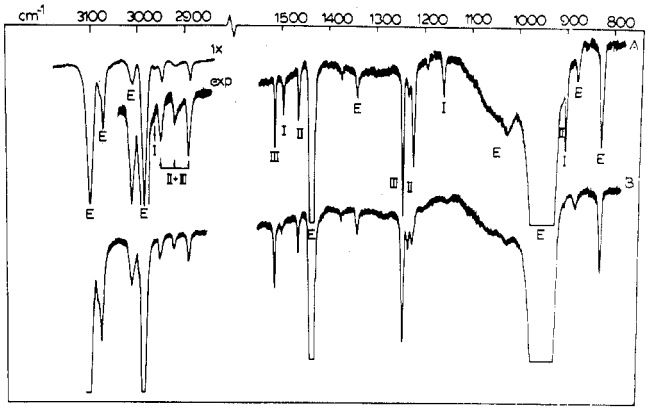



**Figure 3.** The matrix infrared spectrum observed (A) on depositing Ni atoms with a $C_2H_4$:Ar ≃ 1:10 mixture at 15 K and (B) after warm-up to 35 K, showing $Ni(C_2H_4)$, $Ni(C_2H_4)_2$, and $Ni(C_2H_4)_3$, labeled I, II, and III, respectively. (Absorptions associated with free ethylene in the matrix are labeled E.) Taken from ref 17a.

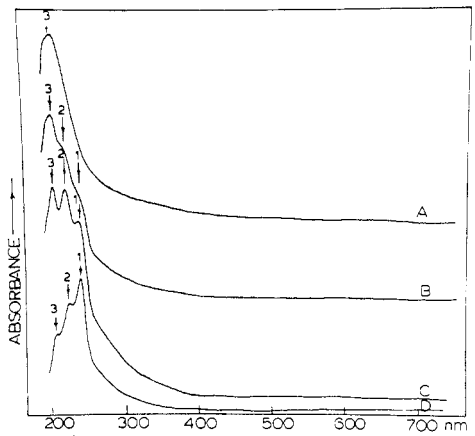



**Figure 4.** The ultraviolet–visible spectrum observed on cocondensing Pd atoms with (A) pure $C_2H_4$, (B) $C_2H_4$:Ar ≃ 1:10, (C) $C_2H_4$:Ar ≃ 1:50 and (D) $C_2H_4$:Ar ≃ 1:300 at 15 K showing the $Pd(d_\pi) \rightarrow C_2H_4(\pi^*)$ charge-transfer transitions of $Pd(C_2H_4)$, $Pd(C_2H_4)_2$, and $Pd(C_2H_4)_3$, labeled 1, 2, and 3, respectively. Taken from ref 17d.

(where $n$ = 1, 2 or 3), which were identified from their warm-up and ethylene concentration behavior.

It can be seen from the UV–visible spectra of a series of $M(C_2H_4)_n$ complexes that the $C_2H_4 \rightarrow M$ and $M \rightarrow C_2H_4$ σ- and π-charge transfers per $C_2H_4$ ligand decrease with increasing coordination number, $n$. For both M = Ni[17a] and Pd,[15] one observes an intense $M(d_\pi) \rightarrow C_2H_4(\pi^*)$ charge-transfer transition in the region 200–240 nm which shifts monotonically to higher energies with increasing $n$ (Figure 4), consistent with the idea of increasing C=C bond strength with $n$.

## Reactive Intermediates in the Catalytic Oxidation of Ethylene to Ethylene Oxide

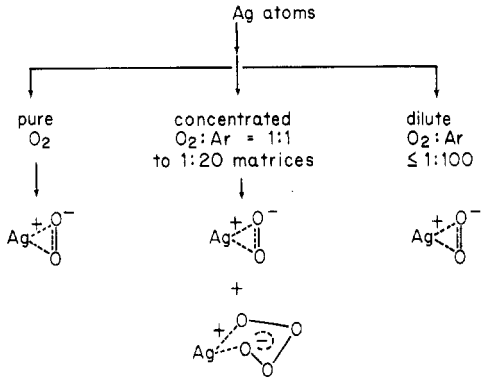
The modern petrochemical industry relies on several hydrocarbon raw materials, and oxidation reactions are some of the most important processes to which these materials are initially subjected. In the heterogeneous catalytic oxidation of ethylene

$$\underset{\text{(supported silver catalyst)}}{Ag|SiO_2} + C_2H_4 + O_2 \xrightarrow[150\text{–}250\ ^\circ C]{} \underset{\text{epoxidation}}{CH_2\text{-}CH_2 \diagdown\diagup O} + \underset{\text{complete combustion}}{CO_2 + H_2O}$$

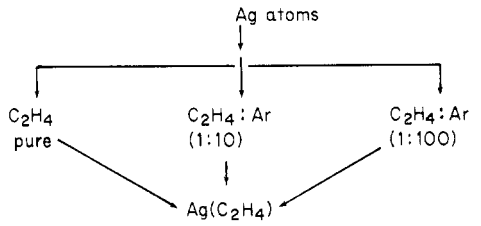
silver is unique in giving a high selectivity to ethylene

(15) G. A. Ozin and W. J. Power, *Inorg. Chem.*, **16**, 212 (1977).
(16) (a) It is interesting to note that neither $Cu_2(CO)_6$[16b] nor $Cu(CO_{ads})$ shows evidence for bridge bonded CO groups; (b) H. Huber, E. P. Kündig, M. Moskovits, and G. A. Ozin, *J. Am. Chem. Soc.*, **97**, 2097 (1975).
(17) (a) H. Huber, G. A. Ozin, and W. J. Power, *J. Am. Chem. Soc.*, **98**, 6508 (1976); (b) H. Huber, D. McIntosh, and G. A. Ozin, *J. Organomet. Chem.*, **112**, C50 (1976); (c) D. McIntosh and G. A. Ozin, *ibid.*, **120**, 127 (1976); (d) H. Huber, G. A. Ozin, and W. J. Power, *Inorg. Chem.*, in press.
(18) L. A. Hanlan, G. A. Ozin, and W. J. Power, unpublished work.

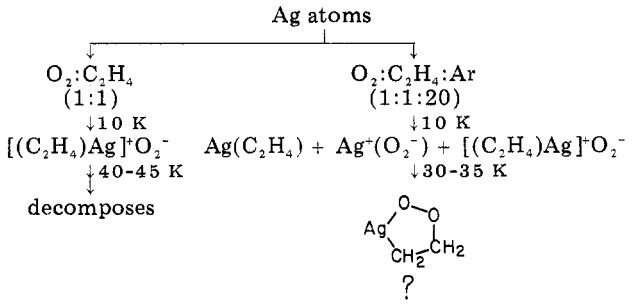
**Scheme II**[20]




**Scheme III**[17c]




**Scheme IV**[21]




oxide. As in most heterogeneous oxidations, the mechanism proposed involves the interaction between an ethylene and oxygen species on the silver surface. The general consensus appears to be that the chemisorbed state of freshly oxygenated silver surfaces[19] consists of $O_2^-{}_{ads}$, $O^-{}_{ads}$, and $O^{2-}{}_{ads}$. The molecular oxygen adsorption complex $Ag(O_{2,ads})$ has evoked considerable interest because it is thought by some to be the surface species active in olefin oxidation reactions.[19] Therefore, from a localized bonding point of view[7] a "molecular" $Ag(O_2)$ complex is a potentially interesting model for $Ag(O_{2,ads})$. Similarly, $Ag(C_2H_4)$ could serve as a model intermediate for $Ag(C_2H_{4,ads})$. For brevity the experimental details for the $Ag:O_2$[20] and $Ag:C_2H_4$[17c] matrix reactions are summarized in Schemes II and III.

To probe the actual oxidation process, reactions in $O_2:C_2H_4$ and $O_2:C_2H_4$:Ar matrices were conducted under a variety of conditions.[21] The infrared and UV–visible data for the $Ag:O_2:C_2H_4$ matrix reaction are summarized in Scheme IV and Figure 5, where it can be seen that the primary product is the reactive intermediate $[(C_2H_4)Ag]^+O_2^-$. Warming this complex up to the point where the matrix is beginning to sublime from the optical window simply causes the compound to decompose without noticeable production of ethylene

(19) P. A. Kilty and W. M. H. Sachtler, *Catal. Rev.*, **10**, 1 (1974).
(20) D. McIntosh and G. A. Ozin, *Inorg. Chem.*, **16**, 59 (1977).
(21) H. Huber, D. McIntosh, and G. A. Ozin, in preparation.

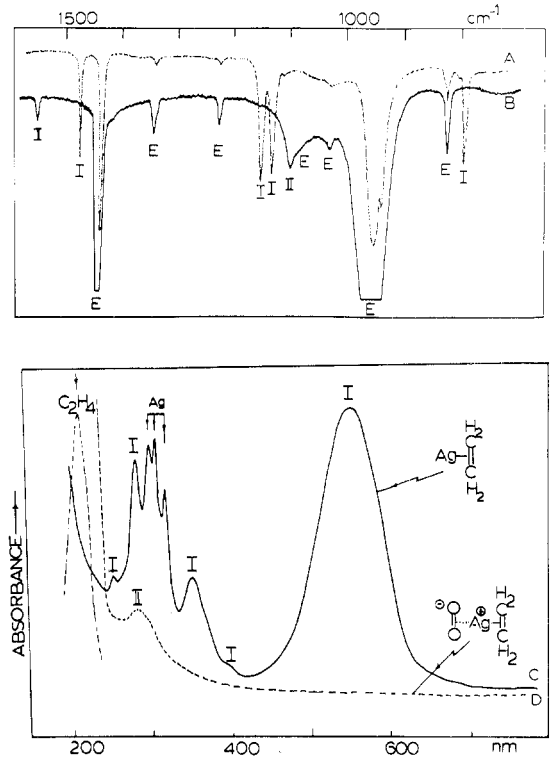
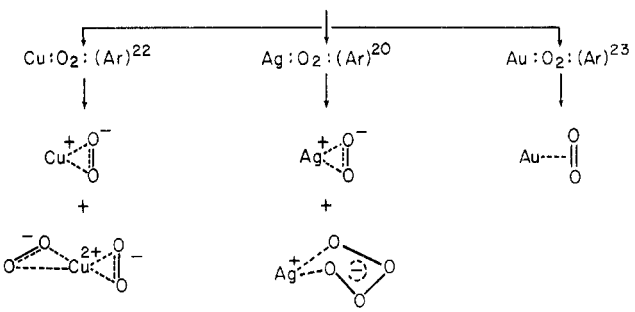
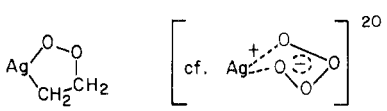



**Figure 5.** The matrix infrared and ultraviolet–visible spectra observed on depositing Ag atoms at 10 K with (A, C) $C_2H_4$:Ar $\simeq$ 1:10 matrices showing the absorption of $Ag(C_2H_4)$ (I) and (B, D) $C_2H_4:O_2 \simeq$ 1:1 matrices showing the absorptions of $[(C_2H_4)Ag]^+O_2^-$ (II). (The absorptions associated with free ethylene in the matrix are labeled E.)

**Scheme V**




oxide or a peroxy intermediate. On the other hand, preliminary results in dilute $O_2:C_2H_4$:Ar matrices, in which all three species $Ag(O_2)$, $Ag(C_2H_4)$, and $[(C_2H_4)Ag]^+O_2^-$ coexist on deposition, show the gradual disappearance of $Ag(O_2)$ and $Ag(C_2H_4)$ at 30 K with the concomitant growth of a new species which appears to be a reaction intermediate of the form




not unlike the proposed surface peroxy species in the actual catalytic system.[19] Further experiments along these lines may be able to provide evidence for or against $Ag(O_{2,ads})$ as the active species in the silver-catalyzed epoxidation of ethylene.

## Reactive Intermediates in the Oxidation of Carbon Monoxide to Carbon Dioxide

The discovery of the tight ion pair $Ag^+(O_2^-)$ described in the previous section stimulated a search for similar

**Scheme VI**[24]

Ag atoms

| CO (pure) | CO:Ar (1:10) | CO:Ar (1:100) |
|---|---|---|
| ↓ | ↓ | ↓ |
| $Ag(CO)_3$ | $Ag(CO)_{1,2,3}$ | Ag(CO) |
| ↓ 30-40 K | ↓ 30-40 K | ↓ 30-40 K |
| $Ag_2(CO)_6$ (pale yellow) | $Ag(CO)_3$ (green) | $Ag(CO)_2$ |
| | | ↓ |
| | | $Ag(CO)_3$ |

**Scheme VII**[25]

Au atoms

| CO (pure) | CO:Ar (1:10) | CO:Ar (1:100) |
|---|---|---|
| ↓ | ↓ | ↓ |
| (OC)Au(OC) carbonylisocarbonyl gold (green) | $Au(CO)_{1,2}$ | Au(CO) |
| | ↓ 30 K | ↓ 30 K |
| | $Au(CO)_2$ (green) | $Au(CO)_2$ (green) |

compounds of the group 1B metals with the intention of examining their activity toward carbon monoxide oxidation. A summary of the results for the reactions of group 1B metal atoms with dioxygen is shown in Scheme V, from which it can be seen that monodioxygen complexes can be generated for all three metals. In the cases of $Cu^+(O_2^-)$ and $Ag^+(O_2^-)$ they are best formulated as metal superoxide molecular species. However, the optical data for the "green" compound $Au(O_2)$ are unusual, especially when compared with the "green" compound $Au(C_2H_4)$,[17c] and suggest that the dioxygen moiety in $Au(O_2)$ is olefinic in its bonding properties to gold. In view of the high first ionization potential for Au (9.22 eV), compared to Cu (7.72 eV) and Ag (7.57 eV), this set of circumstances is not too surprising.

The obvious differences in the nature of the dioxygen binding to Ag and Au in these complexes naturally raised the question as to which would serve better as a localized bonding model for studying reactive intermediates in CO oxidation to $CO_2$. To fully appreciate the subtleties of the Ag:$O_2$:CO and Au:$O_2$:CO matrix reactions, the relevant details of the corresponding Ag:CO[24] and Au:CO[25] matrix reactions are summarized in Schemes VI and VII.

Let us first consider the results of the Ag:$O_2$:CO reaction.[26] A typical infrared spectrum in $O_2$:CO $\simeq$ 1:1 matrices shows a single $\nu$(CO) stretching mode at 2165 $cm^{-1}$ (note, above that of free CO, 2138 $cm^{-1}$) and a single $\nu$(OO) stretching mode at 1110 $cm^{-1}$ (note, close to that of free $O_2^-$, 1097 $cm^{-1}$). The UV–visible spectrum shows an absorption at 285 nm in a region associated with that of superoxide (free $O_2^-$, 250 nm). An Ag:$^{12}C^{16}O$:$^{13}C^{18}O$:$^{16}O_2$:$^{16}O^{18}O$:$^{18}O_2$ isotope experiment (Figure 6) unequivocally proved that the complex contained a single CO and $O_2$ (the latter probably side-on bonded). With this knowledge one is compelled to formulate the complex as $[(OC)Ag]^+O_2^-$.

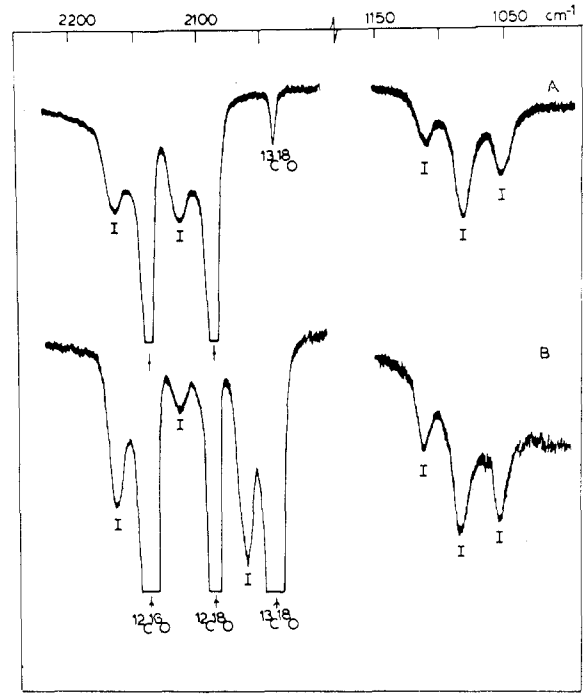



**Figure 6.** The matrix infrared spectrum of the products formed when Ag atoms are cocondensed with (A) $^{12}C^{16}O$:$^{12}C^{18}O$:$^{16}O_2$:$^{16}O^{18}O$:$^{18}O_2$ = 1:1:1:2:1 and (B) $^{12}C^{16}O$:$^{13}C^{18}O$:$^{16}O_2$:$^{16}O^{18}O$:$^{18}O_2$ = 1:1:1:2:1 at 10–12 K showing the characteristic isotopic patterns for an $[(OC)Ag]^+O_2^-$ complex (labeled I). (Note that the commercially available $^{12}C^{16}O$:$^{13}C^{18}O$ mixtures contain about 7% of $^{12}C^{18}O$:$^{13}C^{16}O$ as seen in (B).) Taken from ref 26.

The intriguing question therefore arises as to the suitability of $[(OC)Ag]^+O_2^-$ as a localized bonding model for the more complex $Ag(O_{2,ads})(CO_{ads})$ situation[27] used to describe the silver-catalyzed oxidation of CO to $CO_2$. Utilization of $[(OC)Ag]^+O_2^-$ as a model for CO on an oxidized Ag catalyst would imply the association of both CO and $O_2$ simultaneously with one or more silver surface sites, in contrast to an Eley–Rideal type mechanism.

Warm-up experiments for our model complex $[(OC)Ag]^+O_2^-$ demonstrate that decomposition occurs at roughly 40 K. Neither $CO_2$ production nor $CO_3$–$CO_2$ intermediates were observed at any stage of the decomposition process. One can deduce from this type of experiment that, although $[(OC)Ag]^+O_2^-$ may be a suitable localized bonding model for CO:$O_2$ surface complexes, the oxygen moiety is not sufficiently active to permit either a CO insertion process or O–O bond rupture to occur. This may be the result of a kinetic impediment at the low temperatures employed; alternatively, $O^-_{ads}$ may be the active species in the oxidation process, and a complex such as $[(OC)Ag]^+O^-$ might be a more appropriate synthetic goal.

Of special interest is the discovery that the dioxygen moiety in the "green" complex $Au(O_2)$[23] appears to be more active toward CO oxidation. A typical infrared spectrum for the corresponding Au:$O_2$:CO reaction[28] is shown in Figure 7A. Compared to the Ag:$O_2$:CO reaction, certain features are most intriguing. To begin with, CO coordinated to cationic Au is apparent from

(22) (a) J. H. Darling, M. B. Garton-Sprenger, and J. S. Ogden, *Faraday Symp. Chem. Soc.*, 8, 75 (1973); (b) D. McIntosh and G. A. Ozin, in preparation.
(23) D. McIntosh and G. A. Ozin, *Inorg. Chem.*, **15**, 2869 (1976).
(24) D. McIntosh and G. A. Ozin, *J. Am. Chem. Soc.*, **98**, 3167 (1976).
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(27) G. W. Keulks and J. F. Outlaw, Jr., "Proceedings of the Fifth International Conference on Catalysis, 1973", J. W. Hightower, Ed., North-Holland Publishing Co., Amsterdam, 1973 paper 65, p 945.
(28) H. Huber, D. McIntosh, and G. A. Ozin, *Inorg. Chem.*, in press.

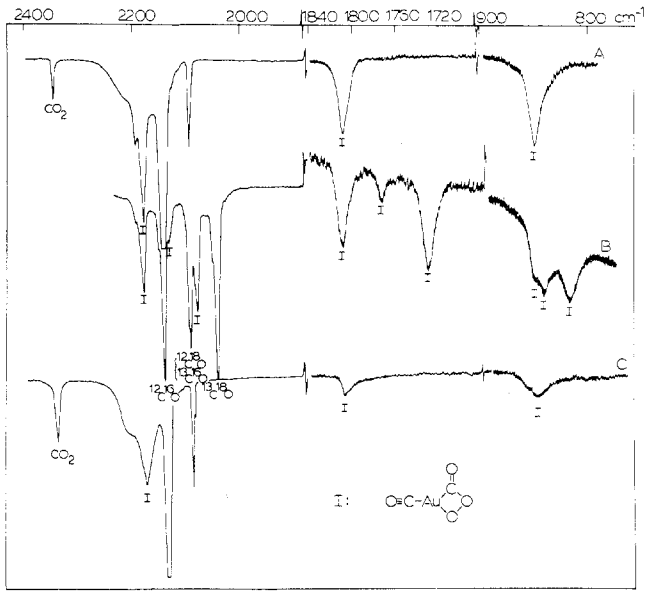
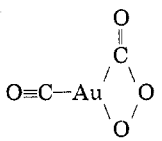
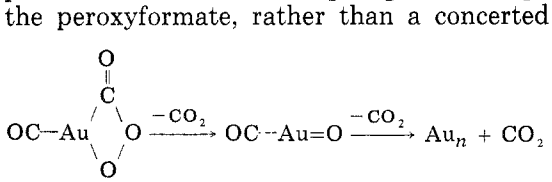



**Figure 7.** The matrix infrared spectra observed on depositing Au atoms with (A) $CO:O_2 \simeq 1:1$, (B) $^{12}C^{16}O:^{13}C^{18}O:^{16}O_2:^{16}O^{18}O:^{18}O_2 \simeq 1:1:1:2:1$ matrices at 10 K, and (C) the same as (A) but after warm-up to 30–40 K. Taken from ref 28.

the observation of a $\nu$(CO) stretching mode at 2176 $cm^{-1}$. However, a ketonic CO group absorbing at 1807 $cm^{-1}$ and an extremely low mode in the oxygen region at 850 $cm^{-1}$ are also observed and can be associated with a single complex—labeled I in Figure 7A. A $^{12}C^{16}O:^{13}C^{18}O:^{16}O_2:^{16}O^{18}O:^{18}O_2$ isotope experiment (Figure 7B) established the complex to be the novel peroxyformate[28,29]

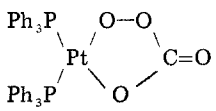


which at 30–40 K acts as a precursor for $CO_2$. The breakdown of this novel metallocycle to $CO_2$ has been monitored by infrared spectroscopy using $^{13}C^{16}O:^{16}O_2$ and $^{12}C^{16}O:^{18}O_2$ mixtures, from which it could be deduced that cleavage of the peroxy group is the primary step leading to $CO_2$ production. The identification of an intermediate (OC)AuO during these warm-up experiments favored a two-step fragmentation process of the peroxyformate, rather than a concerted reduc-

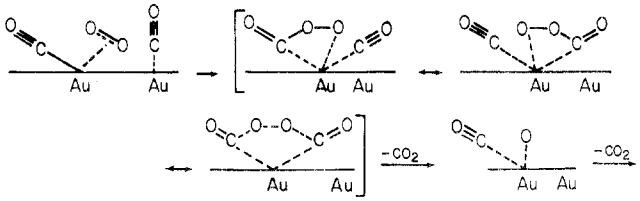


tive-elimination of two molecules of $CO_2$ from the peroxyformate. These data are particularly significant

(29) It is worth noting here that the reaction proposed as a route to the peroxyformate is not an unprecedented occurrence. For example, $CO_2$ is known to insert into the platinum–dioxygen linkage of $(Ph_3P)_2PtO_2$ (P. J. Hayward, D. M. Blake, G. Wilkinson, and C. J. Nyman, *J. Am. Chem. Soc.*, **92**, 5873 (1970)) to yield the peroxycarbonate species



**Scheme VIII**



as they point to a localized bonding description of CO oxidation, at least on gold surfaces, through the intermediacy of a "peroxyformate" species, as illustrated in Scheme VIII.

Whether the CO adsorbs on the same metal site as the $O_2$ and is subsequently responsible for the insertion process, or whether an adjacent CO group migrates to the adsorbed $O_2$ and then inserts, cannot be established from the Au atom experiments. However, the formation of an $Au(O_{2,ads})(CO_{ads})$ species and its conversion to a reactive $Au(CO_{3,ads})$ species from which $CO_2$ is eliminated seem a likely description of the oxidation of CO to $CO_2$ by freshly oxidized Au (and possibly, at higher temperatures, by Ag[27]).

## Conclusion

The results presented in this Account illustrate some of the strengths and shortcomings of metal atom based, localized bonding models for chemisorption complexes and surface intermediates in a number of selected heterogeneous catalytic reactions. At this stage, the systematic similarities between the atom-based models and the surface situation are encouraging indicators of the usefulness of the method. One can certainly enquire how the molecular, electronic, and chemical properties of ligands are modified when bonded to a single metal atom site and how these compare with the metal surfaces.

Bridging the gap between the atom-based approach and real surfaces will ultimately require experiments in high-temperature matrix supports and/or with small, well-defined metal clusters. To this end, alkane matrices $C_nH_{2n+2}$ (where $n$ = 1–12)[30,31] and controlled matrix diffusion experiments with metal atoms are enjoying some early successes,[4-6,16] and $M_n$ aggregates with $n$ = 2, 3, and 4 have been recently isolated and reacted with other substrates in an effort to unravel the changes that ensue on passing from an isolated metal atom to a small metal cluster to the bulk material. Hopefully, one will soon be able to compare the results of such experiments with the exciting new results of self-consistent-field–$\alpha$-scattered wave molecular orbital calculations of metal clusters and their chemisorption complexes.[32]

*I am happy to acknowledge the invaluable collaboration of my students and colleagues whose names appear in the cited articles and to express my special indebtedness to Mr. Ted Huber for his invaluable technical assistance. I am also deeply grateful to the National Research Council of Canada and the Atkinson Foundation for financial support of this research.*

(30) W. Klotzbücher, G. A. Ozin, and D. Singh, to be published.
(31) W. Klotzbucher, S. Mitchell, G. A. Ozin, and D. Singh, in preparation.
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