Table III

Complex	$\nu(CO)$, cm^{-1}		
$V(CO)_6$	1971	$\Delta = 113$ cm^{-1}	
$[V(CO)_6]^-$	1858		
"$V_2(CO)_{12}$" (D_1)	2050	$\Delta = 36$ cm^{-1}	
	2014		
	1852 ($\nu(CO)_b$)		$\Delta \simeq 260$ cm^{-1}
$[V_2(CO)_8(CN)_4]^{4-}$	1794^a	$\Delta = 46$ cm^{-1}	
	1748		

^{a} Contains two bridging cyanide groups.

4, where the proportionate relationship establishes that the lines belong to some binuclear carbonyl complex of vanadium. Annealing experiments performed on matrices containing the dimer (Figure 1C) establish that one of the dimers (D_2) (2030 cm^{-1}) is unstable with respect to the other (D_1) (2050, 2014, 1852 cm^{-1}). Moreover, warmup experiments suggest that the 2050-, 2014- and 1852-cm^{-1} absorptions belong to a single species. Although the stoichiometry of the complexes with respect to terminal CO groups cannot be ascertained from $^{12}C^{16}O/^{13}C^{16}O$ isotope experiments, owing to serious band-overlap problems in the 2050-1970-cm^{-1} region, it was possible to obtain mixed isotopic data for the 1852-cm^{-1} bridge mode (which is in a relatively clear region of the spectrum). The pattern obtained for the CO bridge mode was typical of a biscarbonyl, suggesting that the complex (D_1) can be formulated as $(OC)_nV(\mu\text{-}CO)_2V(CO)_n$.

Although the dimer D_1 is most probably $V_2(CO)_{12}$, we are obliged to base our final assignment on comparison with the data for the isoelectronic carbonyl–cyanide complex [V$_2$(CO)$_8$(CN)$_4$]$^{4-}$ as shown in Table III.[11] As can be seen, placement of a single electron charge on $V(CO)_6$ to form [$V(CO)_6$]$^-$ induces a shift to lower frequencies of 113 cm^{-1}. Thus the 260-cm^{-1} frequency shift for the $\nu(CO)_t$ modes of $V_2(CO)_{12}$, on passing to [V$_2$(CO)$_8$(CN)$_4$]$^{4-}$, is quite reasonable on the grounds that there is now a change of approximately two electron charges per vanadium atom in the carbonyl–cyanide dimer. Coupled with this is the fact that the frequency separation of 36 cm^{-1} of the $\nu(CO)_t$ modes in $V_2(CO)_{12}$ is approximately the same as the 46-cm^{-1} separation for the $\nu(CO)_t$ modes of [V$_2$(CO)$_8$(CN)$_4$]$^{4-}$. Although this remarkable correlation may be purely fortuitous, when combined with the binuclear character and biscarbonyl bridge formulation of our vanadium dimer complex D_1, it seems most plausible that the V/CO reaction has led to the production of the first authentic sample of $V_2(CO)_{12}$. Although we cannot assign dimer D_2 with any degree of certainty, it is conceivably a metastable metal–metal bonded form of D_1 or possibly

$V_2(CO)_{10}$, analogous to the recently reported metal–metal bonded dimer $Cr_2(CO)_{10}$.[13] Proof of this point will have to await further study. It is interesting, however, to note that dicobalt octacarbonyl also exists in two forms, (OC)$_3$Co(μ-CO)$_2$Co(CO)$_3$ (high-temperature isomer) and (OC)$_4$Co–Co(CO)$_4$ (low-temperature isomer).

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Kinetics of a Chemical Reaction in Low-Temperature Matrices: $2Ag(CO)_3 \rightarrow Ag_2(CO)_6$

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The dimerization reaction $2Ag(CO)_3 \rightarrow Ag_2(CO)_6$ has been studied in solid CO matrices at temperatures ranging from 30 to 37 K. The kinetics of this reaction appear to be diffusion controlled. The diffusion coefficient of the mobile species is found to have a value of 7×10^{-16} cm^2 s^{-1} at 35 K while the activation energy for the diffusion processes is calculated to be 1900 cal/mol. The binuclear carbonyl is found to be unstable at the temperatures used, presumably decomposing to give silver dimer and/or higher aggregates.

Introduction

Matrix isolation, the technique whereby reactive species are immobilized by trapping them in cavities within low-tem-

perature solids, has been well established over the last 20 years.

In a typical experiment the species of interest is formed, trapped, and observed spectroscopically; then, usually it is

allowed to react by warming up the matrix to a temperature sufficiently high to allow motion within the matrix but not so high as to cause the matrix to vaporize. In this manner other species are formed which may help to establish the identity of the first or which are intersting in themselves. For example, warming a matrix containing Pd, CO, and excess Ar yields all the species Pd(CO)$_n$[1] via reactions of the sort Pd + CO → PdCO, PdCO + CO → Pd(CO)$_2$, etc.

Despite the universality of the "warm-up" technique, only a few accounts of quantitative matrix kinetics exist. Pimentel[2] reported kinetic data for the matrix cis–trans isomerization of HNO$_2$ and polymerization of ammonia, Ozin et al.[1] discussed the stepwise reaction of Pd atoms with CO, and Bos et al.[3] reported the dimerization and trimerization of tin atoms and tin oxide monomers followed by matrix Mössbauer spectroscopy.

The above studies illustrate several of the possible classes of reactions amenable to study under matrix conditions. These reactions are often difficult to probe by other means. For interest we list these various types of reaction below.

The first type involves a molecule which is stable to decomposition in the matrix but which is unstable with respect to an intramolecular rearrangement within the confines of the matrix cage.

The second type of molecule is one that is unstable to decomposition through one or more bond-rupture processes. The effect of matrix isolation upon this type of molecule is to provide a sufficiently low-temperature environment to reduce the thermal energy available to the molecule below that required to cause thermal decomposition.

Third, one can envisage a situation where the product of a cocondensation reaction may be a molecule which is itself stable to decomposition but which is unstable to further reaction with another species present in the matrix. Matrix isolation stabilizes coordinatively unsaturated molecules of this type by imposing a diffusion-controlled kinetic impediment to further reaction. By following the appearance and disappearance of product and reagent one has a means of determining the relative diffusion coefficients of the reacting species.

Finally, and of central interest to the present study, one can devise a situation where the product is an odd-electron species (atomic or molecular), unstable with respect to a dimerization or aggregation process. Reactive species of this type can be brought together within the confines of the matrix in a highly controlled manner, and measurable reaction rates will be observed even for activation energies of less than 1 kcal, a range difficult to study by other methods.

In this paper we discuss the matrix reaction

$$2Ag(CO)_3 \rightarrow Ag_2(CO)_6 \rightarrow \text{other products}$$
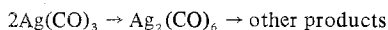
as performed in pure CO matrices which had been deposited at known Ag:CO ratios and temperatures, with warm-up experiments conducted in the accessible temperature range 25–39 K.

Experimental Section

The apparatus has been described elsewhere.[4] Monatomic Ag vapor was cocondensed with CO onto the tip of a liquid helium cooled cryostat. Silver vapor flux was measured with a quartz crystal balance[5] while gas flows were regulated with a precalibrated micrometer needle valve. Two sets of experiments were performed. In the first set four experiments were done, each with a different metal flux rate and a constant CO deposition rate of approximately 2 mmol/h. The metal-to-CO ratios in these experiments were approximately 7.4 × 10^{-5}, 2.9 × 10^{-4}, 4.4 × 10^{-4}, and 5.9 × 10^{-4}, which correspond to initial metal concentrations of 1.3 × 10^{18}, 5.0 × 10^{18}, 7.6 × 10^{18}, and 10.1 × 10^{18} silver atoms/cm^3, respectively, assuming that solid CO has a density of 0.8 g cm^{-3}. The temperature was fixed at 35 K by means of an electronic temperature regulator using a Au—0.7% Fe–chromel thermocouple sensor soldered to the copper plate holder.
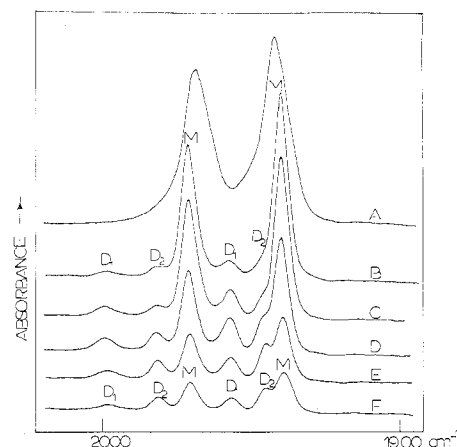

Figure 1. Portion of the spectrum of Ag(CO)$_3$ in a solid CO matrix showing the gradual decrease in reagent absorbance (M) and simultaneous growth and decay of product (D$_1$, D$_2$). A–F indicate increasing time.

(The temperature of the copper block was compared during a previous set of experiments with that measured at the center of the CsI plate on which the matrix was deposited. The two temperatures were found to be within 0.1 K of one another within 2 or 3 s after the heater was activated.)

In the second set the metal flux was kept constant so as to give a metal-to-CO ratio of approximately 2.9 × 10^{-4} and experiments were performed at 30, 33, and 37 K which, together with the previous set at 35 K, yielded results at four temperatures altogether.

The factors which govern these temperature limits are twofold. First, the lower limit is determined by the temperature at which measurable absorbance changes are observed for Ag(CO)$_3$, whereas the upper limit is critically governed by the temperature at which the matrix support begins to boil off at a measurable rate. The upper limit can be established by monitoring either the pressure in the sample vacuum shroud or the absorbances of the natural abundance ^{13}C^{16}O–^{12}C^{18}O isotope lines which serve as an "internal matrix reference" and which should remain strictly invariant throughout a run. In practice, slight matrix boil-off was difficult to avoid, especially at the high-temperature limit. This effect was corrected for by normalizing all absorbances with respect to the ^{13}C^{16}O–^{12}C^{18}O reference lines. Warm-ups were carried out by quickly warming the matrix to the appropriate temperature, a procedure which takes between 4 and 10 s to achieve 20 and 40 K, respectively, keeping the matrix at the required temperature for a measured length of time, and then quenching the matrix to liquid helium temperatures which took of the order of 2–5 s. Spectra were recorded on a Perkin-Elmer 180 infrared spectrometer used in the absorbance mode. Band heights were determined, when necessary, by using a Du Pont curve resolver.

A final point worth mentioning relates to photochemical complications. All of the kinetic runs described above were performed with a germanium filter inserted between the infrared source and the sample in order to reject the uv and visible components of the source beam. Without this precaution Ag(CO)$_3$ was found to disappear with extreme rapidity and at temperatures below 20 K, presumably as a result of CO photodetachment induced by uv or visible radiation from the source. Poliakoff and Turner et al.[6] have also reported such findings. In the photochemistry of Fe(CO)$_5$, the Fe(CO)$_4$–CO products were found by them to undergo "reverse" photolysis to Fe(CO)$_5$ in the beam of the infrared spectrometer, while the insertion of a germanium filter between the infrared source and the matrix sample eliminated the unwanted matrix photochemistry.

Results

The spectral changes observed during a typical kinetic run are shown in Figure 1. In brief, the spectra show a gradual and monotonic decrease in the absorbances of the Ag(CO)$_3$ starting material (labeled M), with the simultaneous growth and eventual decay of two sets of new lines at 1998, 1955 cm^{-1} and 1980, 1944 cm^{-1} (labeled D$_1$ and D$_2$). In addition to the changes described above, there was a simultaneous decrease in the absorbances of *all* species, becoming more pronounced
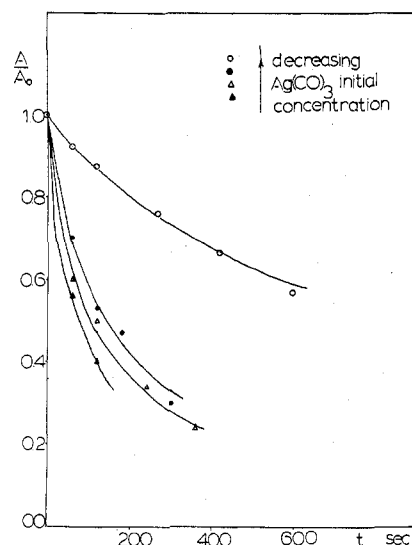
Figure 2. Absorbance of $Ag(CO)_3$ relative to initial absorbance plotted as a function of time for various initial reagent concentrations. Points are experimental data; lines are calculated values using eq 3.

Table I. Rate Constants and Diffusion Coefficients Obtained from the Dimerization of $Ag(CO)_3$ with Varying Initial Reagent Concentrations

$10^{-18}X_0$, molecules cm^{-3}	$10^3\,aX_0$, s^{-1}	$10^3\,abX_0$, s$^{-1/2}$	$r_0{}^a$, Å	$10^{16}D$,[b] cm^2 s^{-1}
1.3	1.11	0.947	5.4	5.2
5.0	6.15	5.23	6.1	7.5
7.6	7.83	6.66	5.7	6.3
10.1	10.55	8.98	5.7	6.4
			Av 5.7	Av 6.8

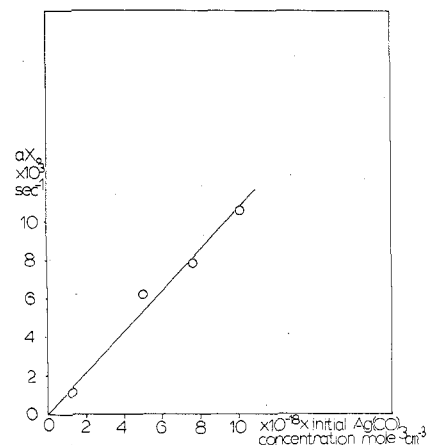[a] Obtained from $ab^2 = 4r_0{}^3$. [b] Obtained from aX_0 using eq 4 and $r = 5.7$ Å.

Figure 3. Plot of the parameter aX_0 (defined in the text) as a function of initial $Ag(CO)_3$ concentration showing the proportional relationship between the two quantities.

at the high-temperature limit. This was proven not to be an artifact related to matrix boil-off, as the $^{13}C^{16}O-^{12}C^{18}O$ reference absorbances remained essentially unchanged throughout the runs.

This observed behavior can be accounted for, qualitatively, by assuming that $Ag(CO)_3$ is either decomposing unimolecularly or dimerizing, or both. The observed metal concentration dependence of the rate of disappearance of the absorptions attributed to $Ag(CO)_3$ eliminates the first explanation. The last mechanism was also cast out on the basis of the observation that in solid Xe, which can be warmed to 80–100 K, $Ag(CO)_3$ is not found to decompose.[7] We therefore conclude that the observed removal of $Ag(CO)_3$ results from dimerization alone (followed by other reactions). This mechanism will therefore be considered in detail.

Diffusion-Controlled Kinetics. Reactions occurring in solids are often diffusion limited. The rate of a diffusion-limited bimolecular reaction differs from a normal one in that the apparent rate constant is time dependent.[8] Smoluchowski[9] has derived the following rate equation for such reactions

$$-\frac{dX}{dt} = 4\pi r_0(D_X + D_Y)\left[1 + \frac{r_0}{(\pi(D_X + D_Y)t)^{1/2}}\right]XY \quad (1)$$

where X and Y are the concentrations of reagents X and Y, D_X and D_Y are their respective diffusion coefficients, and r_0 is the X–Y separation below which reaction is ensured.

For a dimerization process

$$2X \rightarrow X_2$$

eq 1 reduces to

$$-\frac{dX}{dt} = 8\pi r_0 D\left[1 + \frac{r_0}{(2\pi Dt)^{1/2}}\right]X^2 \quad (2)$$

and eq 2 integrates to give

$$X/X_0 = 1/(aX_0 t + 2abX_0 t^{1/2} + 1) \quad (3)$$

where

$$a = 8\pi r_0 D \quad b = r_0/(2\pi D)^{1/2} \quad (4)$$

D being the diffusion coefficient of X. For spectroscopic data, X/X_0 equals A/A_0, the absorbance ratio. Equation 3 reduces to a normal second-order rate law if b vanishes.

The kinetic data from the first set of experiments (Figure 2) were fit to eq 3 using a nonlinear least-squares program. The eight adjustable parameters, aX_0 and abX_0 for each of the four runs, were reduced to five by requiring the ratio abX_0/aX_0 to be constant. The fit so obtained was superior to that obtained by setting b identically equal to zero; i.e., diffusion-limited kinetics described the data better than ordinary second-order kinetics, implying that the kinetics are indeed diffusion limited. The data obtained from the fit are given in Table I. A plot of the parameter aX_0 obtained from the kinetic data as a function of X_0 as determined from the actual metal deposition rates used is shown in Figure 3. The two quantities are proportional to one another as required.

Using eq 4 one can show that the quantity $X_0ab^2 = 4r_0{}^3X_0$. This quantity can be obtained from the two parameters aX_0 and abX_0 used in fitting the kinetic data by taking a ratio of the second parameter to the first, squaring that quantity, and multiplying the result by aX_0. Using these quantities and the tabulated values of X_0, an average value of 5.7 Å was obtained for r_0, and with this value of r_0, D was calculated from aX_0 and eq 4. An average value of 6.8×10^{-16} cm^2 s^{-1} was obtained. This value of D is in remarkably close agreement with that obtained by Bos et al.[3] for the diffusion of tin in nitrogen and by Kündig, Moskovits, and Ozin[1] for the diffusion of CO in argon, while 5.7 Å is an entirely feasible value of r_0.

Rate of Diffusion as a Function of Temperature. The kinetic data for the dimerization of $Ag(CO)_3$ at various matrix temperatures is shown in Figures 4 and 5. These data were fit to the Smoluchowski equation as before with the data for each temperature being treated independently. The kinetic parameters so obtained are listed in Table II. Much greater scatter is evident in the r_0 values calculated from aX_0 and abX_0 of these experiments than in the previous set. In view of the error inherent in these measurements, however, the average value of 10 Å for r_0 is in acceptable agreement with the
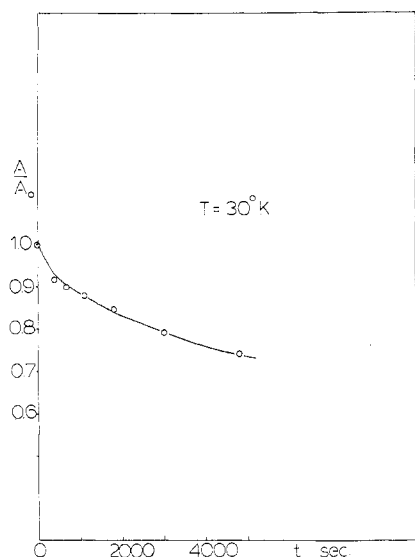
Figure 4. Absorbance of $Ag(CO)_3$ relative to its initial absorbance plotted as a function of time at 30 K. Points are experimental data; lines are calculated using eq 3.
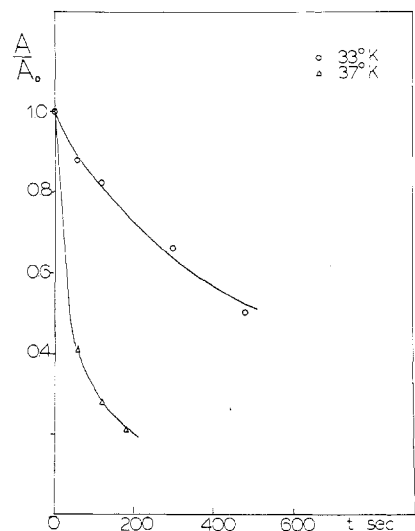

Figure 5. Absorbance of $Ag(CO)_3$ relative to its initial absorbance plotted as a function of time at 33 and 37 K. Points and lines are as in Figure 4.

Table II. Rate Constants and Diffusion Coefficients Obtained from the Dimerization of $Ag(CO)_3$ at Various Temperatures

T, K	aX_0, s^{-1}	abX_0, s^{-1}	r_0, Å	D,[a] cm^2 s^{-1}
30	2.32×10^{-5}	1.73×10^{-3}	18.6	1.8×10^{-18}
33	1.81×10^{-3}	7.28×10^{-4}	2.4	1.4×10^{-16}
35	6.15×10^{-3}	5.23×10^{-3}	6.1	4.7×10^{-16}
37	1.57×10^{-2}	3.15×10^{-2}	14.7	1.2×10^{-15}
			Av 10.4	

[a] Obtained from aX_0 using eq 4, $r_0 = 10.4$ Å, and $X_0 = 5.0 \times 10^{18}$ molecules/cm^3.

previously calculated value of 6 Å. The diffusion coefficient D was calculated from the aX_0 values, as before, for each of the temperatures and it too is listed in Table II. An Arrhenius plot of ln D as a function of $1/T$ is shown in Figure 6, indicating acceptable Arrhenius behavior, implying thereby a functional form for D of the type $D = D_0 \exp(-E_a/RT)$. A nonlinear least-squares fit of the D values as a function of temperature yields a value of 1860 ± 300 cal/mol for the activation energy of the process while the preexponential factor was found to be 1.9×10^{-4} cm^2 s^{-1}, with a standard deviation roughly 4 times this number making the diffusion coefficients

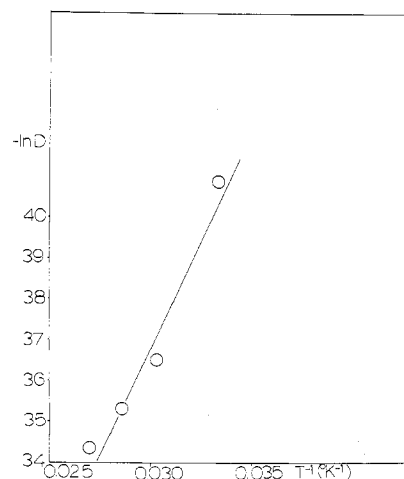**Figure 6.** Arrhenius plot of ln D vs. inverse temperature, D being the diffusion coefficient of $Ag(CO)_3$ in the solid CO matrices used.

uncertain by a factor of 8. Thus, as often happens, the activation energy can be calculated with considerably greater accuracy than the preexponential factor. The rather large uncertainty attests to the difficulty of performing kinetics of this sort at such low temperatures. This may also explain the paucity of data available for diffusion in solids of permanent gases at cryogenic temperatures. The calculated values of D depend critically on the value of r_0 used. By using an r_0 value of 6 Å rather than 10 Å, D would increase by the ratio of the two values. In view of the large error in the preexponential factor, however, such a correction is not justified.

Discussion

Diffusion studies in low-temperature van der Waals solids are not plentiful in the literature. Self-diffusion in neither solid CO nor N_2 has been reported. Diffusion data for the noble gas solids are, however, available with Ar being the noble gas whose properties most closely approximate those of CO. Berne et al.[10] have measured the self-diffusion of Ar in the neighborhood of 79 K where the diffusion coefficient of Ar is of the order of 10^{-10} cm^2 s^{-1}, and they arrived at the expression

$$D = 45e^{-3860/RT}$$

If one were justified in using this expression at lower temperatures, which one is probably not, D for argon at 35 K would be 5×10^{-23} cm^2 s^{-1}, that is, much lower than our measured rate of diffusion of $Ag(CO)_3$ in CO. Diffusion coefficients of the order of 10^{-16} cm^2 s^{-1} at 30 K have been previously reported for CO in Ar[1] and Sn in N_2,[3] however. One should keep in mind that self-diffusion studies are carried out in pure single crystals while the system we are studying is either polycrystalline or glassy and contains a large concentration of guests, all factors which tend to increase the rate of diffusion. In a glassy solid, diffusion through interstitial sites as well as through vacancies is possible, while in a polycrystalline solid the presence of grain boundaries facilitates molecular migration. The presence of guest species increases the concentration of vacancies, which would increase the preexponential factor in the expression for D but not necessarily the activation energy for vacancy migration. Accordingly if one assumes that $Ag(CO)_3$ moves through solid CO via a CO vacancy mechanism, then the activation energy for this process would not be greatly different from that of self-diffusion in CO. An estimate for the value of this activation energy may be obtained from Oshcherin's empirical relationship[11]

$$E_a = k(4.85 \times 10^{-7})a^2\theta_D^2M \text{ kcal/mol}$$

where θ_D is the Debye temperature, a the lattice parameter,

and M the molecular weight of the solid. k is a constant depending on lattice type, with $k = 0.75$ for noble gas fccub crystals. Using Oshcherin's expression and $\theta_D = 79.5$ K[12] and $a = 5.65$ Å[13] for CO, one obtains $E_a = 2.05$ kcal/mol, in remarkably good agreement with our measured value of 1.9 kcal/mol.

The Decomposition of Ag$_2$(CO)$_6$. The low absorbance of the lines attributed to Ag$_2$(CO)$_6$ prevented a quantitative analysis of the data to determine whether it decomposes unimolecularly to form Ag$_2$ or whether it reacts with yet another Ag(CO)$_3$ to form a trimer and eventually a higher aggregate upon further reaction. If the reaction

$$Ag_2(CO)_6 \rightarrow Ag_2 + 6CO$$
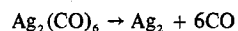
is the one which takes place, one has to explain the apparent instability of the hexacarbonyl in view of the low values of the CO stretching frequencies in this compound and in Ag(CO)$_3$. In an earlier publication,[14] Moskovits and Ozin have related ΔF_{CO}, the change in CO stretching constant on going from free CO to the complex, with $\bar{D}^*$, the M–CO bond dissociation energy to the valence state of the metal. Thus, $\bar{D}$, the bond dissociation energy with respect to ground-state metal, is equal to $\bar{D}^* - E^*/n$, where E^* is the promotion energy to the valence state and n is the number of ligands involved. It is possible that the large value of ΔF_{CO} in silver reflects a large promotion energy rather than a large value of $\bar{D}$ and that $\bar{D}$ is sufficiently small so that $6\bar{D}$ plus the metal–metal bond energy in Ag$_2$(CO)$_6$ is still less than the Ag$_2$ dissociation energy of 38 kcal/mol.[15]

If $\bar{D}$ is in fact sufficiently small, and assuming the $\bar{D}$ for Ag(CO)$_3$ is of the same order of magnitude of that of the dimer, then the high mobility of Ag(CO)$_3$ in solid CO may result from a lattice-assisted diffusion process whereby Ag atoms are the mobile species rather than the whole Ag(CO)$_3$ moiety. However, in dilute CO–inert gas matrices, the chances of a neighboring molecule being CO are small, and the "lattice-assisted diffusion mechanism" described above becomes unfavorable.

Conclusion

In 1958 Pimentel[2] had the foresight to outline the unique possibilities that matrix isolation spectroscopy offers for the study of chemical reactions with low activation energies. However, since Pimentel's 1958 paper, the usefulness of the technique remained questionable.

The present study may be considered to serve two main purposes. First, the Ag(CO)$_3$ system is particularly well suited for matrix isolation kinetic measurements and can be used as a model to examine critically and evaluate the experimental procedures involved and the precautions and complications that may arise in practice. Second, the matrix reactions which are responsible for the gradual diminution of Ag(CO)$_3$ in CO at

10–40 K are themselves of considerable chemical interest.

If we have reincarnated nothing less than the viability, usefulness, and wide-ranging implications of the matrix isolation kinetics experiment in this paper (20 years after its original conception), then we have achieved something worthwhile, because the number of possible kinetic experiments involving organic and inorganic reaction intermediates (which are difficult to study by other techniques) are limitless and worthy of study.

As far as the Ag(CO)$_3$ system is concerned, we recognize the limitations of our measurements and that the final mechanism proposed is not totally without question. Nevertheless, certain features of the system are clear.

The silver concentration dependence of the rate of disappearance of Ag(CO)$_3$ and the concomitant diminution of the ESR signal intensity of Ag(CO)$_3$, together with the agreement between the observed and calculated kinetics for a diffusion-controlled dimerization process, are indicative that our basis proposal of 2Ag(CO)$_3$ → Ag$_2$(CO)$_6$ is chemically acceptable. Further studies will however be required to elucidate the exact nature of the other processes that may be occurring in this system at the high-temperature limit, such as the decomposition of Ag$_2$(CO)$_6$ and/or further clustering reactions.

Registry No. Ag(CO)$_3$, 58832-57-8; Ag$_2$(CO)$_6$, 58933-79-2.

References and Notes

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