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Direct Synthesis with Vanadium Atoms. 1. Synthesis of Hexacarbonylvanadium and Dodecacarbonyldivanadium

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Received November 13, 1975 AIC50823R

The compounds $V(CO)_6$ and $V_2(CO)_{12}$ are directly synthesized in CO and CO-doped rare gas matrices by cocondensing those gases with vanadium atoms. $V(CO)_6$ was investigated by infrared and uv–visible spectroscopy and $V_2(CO)_{12}$ by infrared spectroscopy subsequent to their formation. The distortion indicated for $V(CO)_6$ in pure CO is found to persist in Ne, Ar, Kr, and Xe matrices but with a magnitude which is of the same order or less than a matrix site splitting as seen by comparison with regular octahedral $M(CO)_6$ complexes in solid noble gas matrices (where M = Cr, Mo, or W). Polarizability–frequency plots imply that the larger splitting in solid CO arises from a matrix site splitting superimposed on a genuine molecular distortion splitting. The matrix-induced frequency shifts for $V(CO)_6$ in the inert gases yield linear Buckingham plots, consistent with the presence of nonspecific solute–matrix interactions. Two binuclear complexes could be generated in pure CO matrices, one of which (D_1) was thermally more stable than the other (D_2). Both were proven to be binuclear by quantitative V condensation experiments. From warmup studies, $^{12}C^{16}O/^{13}C^{16}O$ isotopic substitution, and comparison with the isoelectronic complex anion $[V_2(CO)_8(CN)_4]^{4-}$, the more stable dimer D_1 is best formulated as $(OC)_5V(\mu\text{-}CO)_2V(CO)_5$, containing two equivalent vanadium atoms and two bridging CO groups.

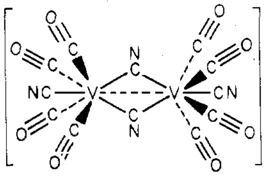
Introduction

Hexacarbonylvanadium was first synthesized in 1959 by Natta et al.[2a] via high-pressure reductive carbonylation of VCl_3 at 120 °C followed by separation from impurities. Since the original discovery of $V(CO)_6$, considerable effort has been devoted to the elucidation of the molecular and electronic properties of the molecule.

One predicts a 17-electron monomeric complex of this type to be paramagnetic with a magnetic moment corresponding to one unpaired electron. Since the ground state ($^2T_{2g}$) possesses a threefold orbital degeneracy, the molecule is expected to experience a distortion from its assumed octahedral symmetry, in compliance with the Jahn–Teller theorem. Not unexpectedly, a wide variety of experimental techniques have been employed to study the molecule in different phases. These include infrared,[2] uv–visible,[2b] ESR,[3] NMR,[4] ESCA,[5] and mass spectroscopy[6] and electron and x-ray diffraction,[7,8] as well as temperature-dependent magnetic measurements[9,10] and solution cryoscopy.[4,7] In summary, one can conclude that in the gaseous phase $V(CO)_6$ is subject to a dynamic Jahn–Teller effect and appears to be approximately octahedral. In benzene and toluene solutions at room temperature it is monomeric and paramagnetic, and in the solid phase above 66 K it is approximately octahedral with a magnetic moment corresponding to one unpaired electron. However, below 66 K a transformation occurs in the solid phase and both an axial distortion and an antiferromagnetic exchange interaction between pairs of molecules come into play, and at 4.2 K the solid is essentially diamagnetic.[10]

This anomalous magnetic behavior was originally and erroneously interpreted in terms of $V_2(CO)_{12}$ dimer formation.[9] However, this early claim for the existence of $V_2(CO)_{12}$ as well as the dimer proposals from molecular weight measurements in hydrocarbon solvents has been refuted,[10] and up to the time of writing, the authenticity of $V_2(CO)_{12}$ has remained uncertain.

Despite the overwhelming evidence against the dimer (presumably related to the kinetic and/or thermodynamic stability of the monomer), one would intuitively expect the molecule to have an independent existence, especially in view of the recent synthesis of $[V_2(CO)_8(CN)_4]^{4-}$ as the Et_4N^+ salt,[11] isoelectronic with the purported $V_2(CO)_{12}$. The cyanide complex is diamagnetic and contains equivalent vanadium atoms (from ^{51}V NMR) and bridging cyanide ligands (from infrared spectroscopy). The proposed structure for this complex is[11] and supposedly contains a vanadium–vanadium bond as in $(\eta\text{-}C_5H_5)_2V_2(CO)_5$.[12]



Our previous experience with binuclear metal carbonyls synthesized in low-temperature matrices[13] stimulated our search for the controversial $V_2(CO)_{12}$ dimer as well as its parent monomer, $V(CO)_6$, through the cocondensation reaction of atomic V and pure CO.

Experimental Section

Monatomic V was generated by directly heating a thin vanadium filament (0.025 in.). The vanadium metal (99.99%) was supplied by A. D. McKay, New York, N.Y., Research grade $^{12}C^{16}O$ (99.99%) was supplied by Matheson of Canada, and $^{12}C^{16}O/^{13}C^{16}O$ isotopic mixtures were supplied by Stohler, Montreal. The furnace used for the evaporation of the metals has been described previously.[14] The rate of metal atom deposition was continuously monitored using a quartz crystal microbalance.[14] To obtain quantitative data for V/CO cocondensations, it was necessary to calibrate carefully the rate of deposition of both metal and gas onto the sample window as described previously.[15] In the infrared experiments, matrices were deposited on a CsI plate cooled to 10–12 K by means of an Air Products Displex closed-cycle helium refrigerator or to 6 K by a liquid helium transfer system. Infrared spectra were recorded on a Perkin-Elmer 180 or 621 spectrophotometer. Uv–visible spectra were recorded on a standard Unicam SP 8000 instrument in the range 190–700 nm, the sample being deposited onto an LiF or NaCl optical plate cooled to 6–12 K.

Vanadium Atom–Carbon Monoxide Cocondensation Reactions

Synthesis and Characterization of $V(CO)_6$. When V atoms are cocondensed with pure CO at V:CO $\simeq$ 1:10^5 at 6–12 K, the infrared spectrum shown in Figure 1A is obtained. The spectrum essentially consists of an intense CO absorption centered at 1970 cm^{-1} with weaker high-frequency shoulders at 1976 and 1984 cm^{-1}. No other CO stretching modes are observed in the region 2080–1600 cm^{-1}. The similarity of this spectrum to that previously reported for $V(CO)_6$ (in the solid, solution, and gaseous phases) suggests that the V/CO reaction provides a direct and efficient route to pure $V(CO)_6$.

When vanadium is deposited in concentrated CO/Ne, CO/Ar, CO/Kr, or CO/Xe matrices, only a doublet is ob-

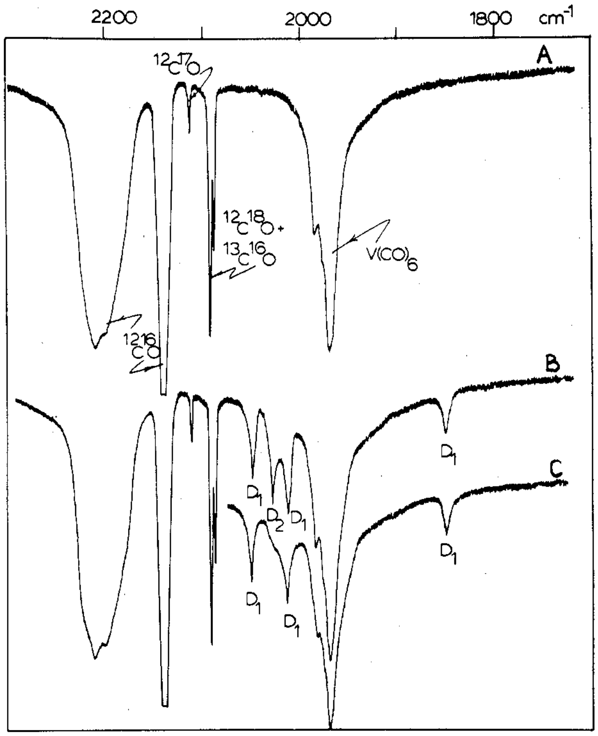


Figure 1. Infrared spectra of the cocondensation reaction of V atoms with CO at 6–10 K: (A) at low V concentrations; (B) at high V concentrations; (C) at the same concentrations as (B) but after warmup to 35 K.

Table I. Infrared Spectroscopic Data for $V(CO)_6$ in CO, Ne, Ar, Kr, and Xe Matrices[c]

$V(CO)_6$ obsd freq, cm^{-1}	Matrix support	Doublet splitting, cm^{-1}
1986.0	Gas[a]	
1980.0, 1972.0	Ne	8.0
1976.0, 1970.0	Ar	6.0
1974.4, 1968.2	Kr	6.2
1976.0, 1966.4	Xe	9.6
1984, 1976.0, 1970.0	CO[b]	14.0 or 6.0[d]

[a] Reference 2b. [b] Shows additional splitting because of a C_2 site symmetry (see text). [c] CO:matrix ≃ 1:10 mixtures used. [d] Splitting between 1984 and 1970 and between 1976 and 1970 cm^{-1} pairs of lines.

served in each matrix. The frequencies of the components of these doublets are given in Table I.

Since one expects only a single infrared-active (T_{1u}) CO stretching mode for a regular O_h $V(CO)_6$ molecule, the presence of two lines suggests that one or several of three mechanisms are operating. These are (1) a static Jahn–Teller effect causing tetragonal distortion of $V(CO)_6$ to a D_{4h} complex, that is, an innate distortion of the molecule, (2) a matrix site effect, that is, the removal of degeneracy due to the interaction of the molecule with the host atoms forming its cage, and (3) a multiple-site effect in which the molecule retains its degeneracy but is trapped in two different matrix sites in which the interactions with the host atoms differ slightly. We will attempt to decide which of these mechanisms causes the observed degeneracy removal.

To begin with, a plot of the observed CO stretching frequencies of $V(CO)_6$ vs. the polarizability of the atoms of the matrix gas in which it is trapped (Figure 2) suggests that the interaction of $V(CO)_6$ with the matrix is largely nonspecific, that is, mainly of a van der Waals type.[17,18]

Second, we note that doublet splittings of the same order of magnitude as that observed in $V(CO)_6$ have been reported for 18-electron hexacarbonyls of chromium, molybdenum, and tungsten[19] under deposition conditions and in matrices similar to ours. These molecules are, of course, not subject to Jahn–Teller distortion.

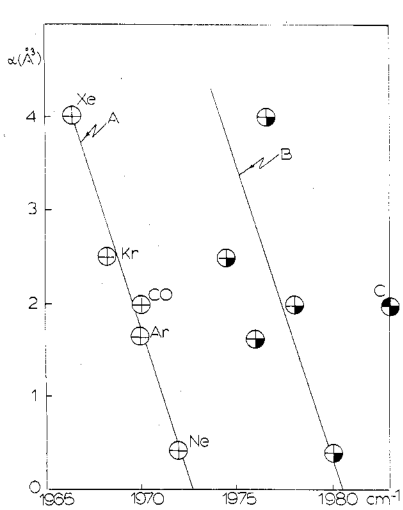


Figure 2. Graphical representation of the effect of the matrix polarizability on the doublet splitting of $V(CO)_6$ in Ne, Ar, Kr, and Xe matrices.

For the 18-electron systems, Graham et al.[19] have reported that the distortions in $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ virtually disappear when the matrices are heavily doped with CO. Since the doublet splitting for $V(CO)_6$ remains in CO/inert gas matrices, both heavily doped (10%) and lightly doped (0.5%)[23] with CO, a static distortion seems likely for $V(CO)_6$, although a small, superimposed site effect cannot be entirely discounted. Furthermore, the fact that the magnitude of the doublet splitting for $V(CO)_6$ remains approximately constant in Ne, Ar, Kr, and Xe matrices (Figure 2) would argue in favor of a genuine molecular distortion, rather than a site effect. In the event that the doublet splitting arises in part from a matrix effect, superimposed on a genuine distortion splitting, the following rationale would probably be justified.

Three sites are available to $V(CO)_6$, in a face-centered cubic noble gas crystal: the substitutional, octahedral, and tetrahedral. Only the substitutional site is large enough to accommodate a molecule of the dimensions of $V(CO)_6$ in all of the matrices used. This argues against a multiple-site effect as an explanation for the cause of the doublet, unless one postulates that the matrices are not crystalline but rather glassy, with two distinct substitutional trapping sites. Although one cannot outrule this possibility entirely, it seems unlikely that the same glassy structure should persist in all of the noble gas matrices used. Furthermore, the triplet structure obtained in pure CO suggests an orderly rather than random orientation of the CO molecules,[16] an unlikely state of affairs in a glass. One then concludes that part of the doublet splitting could arise from a matrix-site effect. If so, the $V(CO)_6$ molecule is aligned in a specific (and nonrandom) fashion, probably within *two* or more neighboring substitutional sites so as to generate the observed tetragonal distortion. An octahedral molecule situated at the center of this arrangement minimizes its interactions with the surrounding noble gas atoms if it aligns one of its axes along the diagonal of the middle layer of atoms while its other two axes point normal to the plane formed by three noble gas atoms, two from the top or bottom layers and one from the middle layer. Two trans ligands of a molecule oriented in this fashion would interact strongly with only one noble gas atom each, while the others interact with three each. This induces the required tetragonal distortion in the molecule, reducing its symmetry to D_{4h}. In solid CO matrices the alignment of the CO's vicinal to $V(CO)_6$ reduces the substitutional site symmetry further, thereby removing the re-

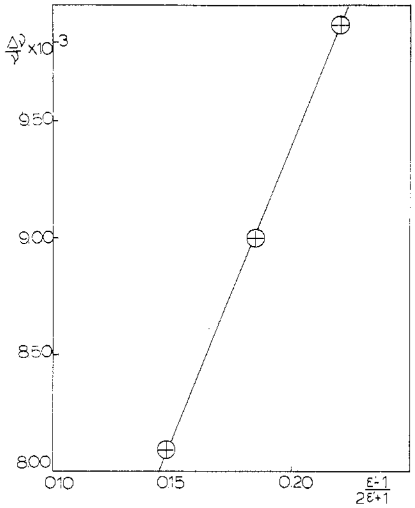


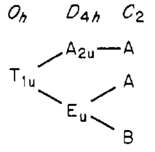
Figure 3. Buckingham plot for $V(CO)_6$ in Ar, Kr, and Xe matrices.

Table II. Matrix-Induced Frequency Shifts for $V(CO)_6$ in Ar, Kr, and Xe Matrices

Matrix	Obsd freq,[a] cm^{-1}	$\Delta\nu$, cm^{-1}	ν, cm^{-1}	10^{-3} $\Delta\nu/\nu$	$(\epsilon' - 1)/(2\epsilon' + 1)$[b]
Ar	1970.0	16.0	1978.0	8.09	0.148
Kr	1968.2	17.8	1977.1	9.00	0.185
Xe	1966.4	19.6	1976.2	9.92	0.221
Gas[c]	1986.0				

[a] Low-frequency component of $V(CO)_6$. [b] ϵ' (20 K): Ar, 1.63; Kr, 1.88; Xe, 2.19). (See H. Hallam, Ed., "Vibrational Spectra of Trapped Species", Wiley, New York, N.Y., 1974.) [c] See ref 2b.

maining degeneracy as shown below.



A second point to note about the data displayed in Table I and Figure 2 is the approximately linear and monotonically increasing "blue frequency shift" of the strongest component of the $V(CO)_6$ doublet on passing from Xe to Ne matrices (labeled A in Figure 2).

Using Buckingham's theory[17] of nonspecific solute–solvent interactions described in a previous publication as applied to matrix-isolated species,[18] we have computed the function $\Delta\nu/\nu$ vs. $(\epsilon' - 1)/(2\epsilon' + 1)$ (where $\Delta\nu = \nu_{gas} - \nu_{matrix}$ and $\nu = {}^1/_2(\nu_{gas} + \nu_{matrix})$ and ϵ' is the dielectric constant of the matrix support) as shown in Figure 3 and Table II. The excellent straight-line correlation implies that the forces between $V(CO)_6$ and the matrix material, responsible for the frequency shifts, are nonspecific in nature and do not arise from $V(CO)_6\cdots$matrix complexes as recently invoked for $Fe(CO)_4\cdots Xe$[20] and $Cr(CO)_5\cdots CH_4$.[21] This is not unreasonable in view of the coordinatively saturated nature of $V(CO)_6$.

Synthesis and Characterization of $V_2(CO)_{12}$. Evidence for the dimerization of $V(CO)_6$ to give $V_2(CO)_{12}$ originally stemmed from temperature-dependent magnetic measurements for solid $V(CO)_6$.[9] However, the magnetic behavior of $V(CO)_6$ has recently been reinterpreted in terms of the vibronic coupling model of Van Vleck–Kotani on the one hand and the exchange magnetic interaction between two magnetic centers on the other.[10]

To test this proposal for $V(CO)_6$ we have synthesized $V(CO)_6$ in CO matrices at 10 K and then allowed the CO matrix gradually to sublime away from the compound at about 50 K. In this way isolated $V(CO)_6$ molecules aggregate to form solid $V(CO)_6$, the infrared spectrum of which can then be studied from 6 to 100 K. Apart from very slight changes in band shape, the spectrum gave no indication for the formation of $V_2(CO)_{12}$ and is consistent therefore with the proposed magnetic exchange interaction model[10] rather than binuclear complex formation.[9]

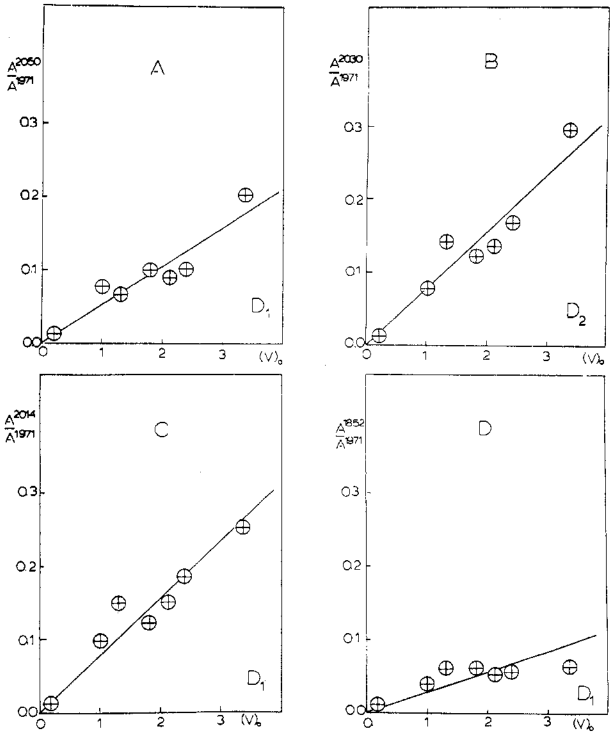


Figure 4. Plots of the ratios of absorbances of the lines attributed to $V_2(CO)_{12}$ to those of the $V(CO)_6$ lines as a function of the V metal deposition rate at constant CO deposition rate.

As mentioned earlier, the problems experienced in trying to synthesize $V_2(CO)_{12}$ from $V(CO)_6$ may be kinetic in origin, relating to the difficulty of rearranging an essentially octahedral $V(CO)_6$ complex to the steric and electronic configurations demanded for dimer formation. If this rationale is correct, then a synthetic pathway to the dimer which probably has a greater chance of success is from the V/CO reaction under conditions which favor binuclear complex formation. Using high V concentrations, reactions of the following type become favored processes.

$$V(CO)_n + V(CO)_m \rightarrow V_2(CO)_q$$

$$V_2(CO)_q + (12 - q)CO \rightarrow V_2(CO)_{12}$$

(where n, m = 0–6) which in pure CO matrices should lead to the complex of highest stoichiometry. This technique has been described in detail[13] and used to advantage in the synthesis of other so-called "nonexistent" binuclear complexes such as $Rh_2(CO)_8$, $Ir_2(CO)_8$[15] and $Cu_2(CO)_6$.[22] The anticipated product of the V/CO reaction should therefore be $V_2(CO)_{12}$.

Using metal concentration studies and kinetic analyses similar to those described for the V/V$_2$/Ar system,[24] we have studied the V/CO reaction products as a function of the V concentration in the matrix. A typical infrared spectrum is shown in Figure 1B at V:CO $\simeq$ 1:10^2 on deposition at 6–12 K, where besides the $V(CO)_6$ absorption, four other lines have appeared at 2050, 2030, 2014, and 1852 cm^{-1}. These new absorptions grow in relative to $V(CO)_6$ as the V concentration increases. The absorbances of these four new lines relative to those of $V(CO)_6$ as a function of [V$_0$] are shown in Figure

Table III

Complex	ν(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}	$\Delta \simeq 260$ cm^{-1}
	2014		
	1852 ($\nu(CO)_b$)		
$[V_2(CO)_8(CN)_4]^{4-}$	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, $(OC)_3Co(\mu\text{-}CO)_2Co(CO)_3$ (high-temperature isomer) and $(OC)_4Co\text{–}Co(CO)_4$ (low-temperature isomer).

Acknowledgment. We wish to thank the National Research Council of Canada and the Atkinson Foundation for financial support. M.M. thanks the Connaught Foundation for financial assistance and T.A.F thanks the South African Council for Scientific and Industrial Research for financial support.

Registry No. $V(CO)_6$, 14024-00-1; $V_2(CO)_{12}$, 58815-50-2; V, 7440-62-2.

References and Notes

(1) On leave from the Chemistry Department, University of Witwatersrand, Johannesburg, South Africa.

(2) (a) G. Natta, R. Ercoli, F. Calderazzo, A. Alberola, P. Corradini, and G Allegra, *Atti Accad. Naz. Lincei, Cl. Sci. Fis., Mat. Nat., Rend.*, **27**, 107 (1959); R. Ercoli, F. Calderazzo, and A. Alberola, *J. Am. Chem. Soc.*, **82**, 2966 (1960); (b) H. Haas and R. K. Sheline, *ibid.*, **88**, 3219 (1966).

(3) D. W. Pratt and R. J. Myers, *J. Am. Chem. Soc.*, **89**, 6470 (1967).

(4) R. L. Pruett and J. E. Wyman, *Chem. Ind. (London)*, 119 (1960).

(5) S. Evans, J. C. Green, A. F. Orchard, T. Saito, and D. W. Turner, *Chem. Phys. Lett.*, **4**, 361 (1969).

(6) R. E. Sullivan, M. S. Lupin, and R. W. Kiser, *Chem. Commun.*, 655 (1969).

(7) F. Calderazzo, R. Cini, P. Corradini, R. Ercoli, and G. Natta, *Chem. Ind. (London)*, 500 (1960).

(8) D. G. Schmidling, *J. Mol. Struct.*, **24**, 1 (1975).

(9) H. J. Keller, P. Laubereau, and D. Nöthe, *Z. Naturforsch., B*, **24**, 257 (1969).

(10) J. C. Bernier and O. Kahn, *Chem. Phys. Lett.*, **19**, 414 (1973).

(11) D. Rehder, *J. Organomet. Chem.*, **37**, 303 (1972).

(12) F. A. Cotton, B. A. Frenz, and L. Kruczynski, *J. Am. Chem. Soc.*, **95**, 951 (1973).

(13) E. P. Kündig, M. Moskovits, and G. A. Ozin, *Angew. Chem., Int. Ed. Engl.*, **14**, 292 (1975).

(14) M. Moskovits and G. A. Ozin, *Appl. Spectrosc.*, **26**, 481 (1972); E. P. Kündig, M. Moskovits, and G. A. Ozin, *J. Mol. Struct.*, **14**, 137 (1972).

(15) L. Hanlan and G. A. Ozin, *J. Am. Chem. Soc.*, **96**, 6324 (1974).

(16) R. W. G. Wyckoff, "Crystal Structures", Vol. 7, Interscience, New York, N.Y., p 29.

(17) A. D. Buckingham, *Proc. R. Soc., Ser. A*, **248**, 1969 (1958); **255**, 32 (1960); *Trans. Faraday Soc.*, **56**, 753 (1960).

(18) L. Hanlan, H. Huber, E. P. Kündig, B. McGarvey and G. A. Ozin, *J. Am. Chem. Soc.*, **97**, 7054 (1975).

(19) M. A. Graham, M. Poliakoff, and J. J. Turner, *J. Chem. Soc. A*, 2939 (1971); R. Perutz and J. J. Turner, *J. Am. Chem. Soc.*, **97**, 4791 (1975).

(20) J. J. Turner and M. Poliakoff, *J. Chem. Soc., Dalton Trans.*, 2276 (1974).

(21) R. N. Perutz and J. J. Turner, *Inorg. Chem.*, **14**, 262 (1975).

(22) H. Huber, E. P. Kündig, M. Moskovits, and G. A. Ozin, *J. Am. Chem. Soc.* **97**, 2097 (1975).

(23) L. A. Hanlan, H. Huber, and G. A. Ozin, submitted for publication in *Inorg. Chem.*

(24) T. A. Ford, H. Huber, W. Klotzbücher, E. P. Kündig, M. Moskovits, and G. A. Ozin, *J. Chem. Phys.*, in press.

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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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Received December 9, 1975

AIC50875G

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-temperature 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