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Carbon Dioxide Activation by Alkali Metals. 2. Infrared Spectra of $M^+CO_2^-$ and $M_2^{2+}CO_2^{2-}$ in Argon and Nitrogen Matrices

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Received July 7, 1983

The reactions of sodium, potassium, and cesium with carbon dioxide have been investigated in argon, nitrogen, and neat matrices. The spontaneous reduction of CO_2 to the radical anion, CO_2^-, and dianion, CO_2^{2-}, was successfully accomplished when potassium or cesium was used as the activating metal. $M^+CO_2^-$ (where M = Na, K, Cs) was found to have a rhombic ring structure of C_{2v} symmetry where the metal atom is interacting equally with the two oxygen atoms. Two geometrical isomers of $M_2^{2+}CO_2^{2-}$ (where M = K, Cs) have been isolated in argon and nitrogen matrices. Mixed $C^{18}O_2/C^{16}O_2$ studies suggest that one isomer has C_{2v} symmetry where the two oxygens are in equivalent positions whereas the second isomer has C_s symmetry and nonequivalent oxygen atoms. It is suggested that $M_2^{2+}CO_2^{2-}$ (C_{2v}) is formed as a result of the reaction between the alkali-metal dimer M_2 and CO_2. Photolysis of the C_{2v} form of the dimetal carbon dioxide dianion with the Nernst glower IR source causes its rearrangement to the C_s form. No bands associated with $Na_2^{2+}CO_2^{2-}$ have been detected in either argon or nitrogen matrices. Very small amounts of $Na^+CO_2^-$ were produced when Na was allowed to react with CO_2 in inert-gas matrices. This reaction was enhanced by photolysis with a medium-pressure 100-W Hg lamp during or after deposition. By using the triatomic molecule approximation, one can determine bond angles equal to 131.1 and 126.9° for the CO_2^- valence-bond angle in $K^+CO_2^-$ (C_{2v}) and $Cs^+CO_2^-$ (C_{2v}) and bond angles equal to 125.9 and 123.1° for the CO_2^{2-} valence-bond angle in $K_2^{2+}CO_2^{2-}$ (C_{2v}) and $Cs_2^{2+}CO_2^{2-}$ (C_{2v}).

Introduction

This investigation of the induced reductive coupling of CO_2 by different alkali metals is an extension of recent work[1,2] reported by our group on Li/CO_2 reactions in inert-gas matrices. Those studies have shown that $LiCO_2$ (C_{2v}), $LiCO_2$ (C_s), Li_2CO_2 (C_s), and LiC_2O_4 (C_{2v}) are formed in solid argon whereas $LiCO_2$ (C_{2v}) and Li_2CO_2 (C_s) are isolated in solid xenon and only $LiCO_2$ (C_{2v}) is detected in neat matrices. $LiCO_2$ (C_s) was found to be a necessary precursor to the formation of LiC_2O_4. Both species were photolytically converted to $LiCO_2$ (C_{2v}) and $LiCO_2{:}CO_2$, respectively, when exposed to IR radiation. These results are in good agreement with the theoretical studies of Jordan[3,4] on the stabilities and structures of lithium and sodium complexes with CO_2. Jordan has predicted two geometrical isomers for $LiCO_2$ that are close in energy (0.85 vs. 0.83 eV), with the C_{2v} structure being more stable. In contrast, the C_{2v} isomer of $NaCO_2$ was predicted to be considerably more stable than the C_s geometry. A CO_2^- valence-bond angle of 124.5° was calculated for $LiCO_2$ which is in good agreement with our value of 125.7°. A slightly larger CO_2^- valence-bond angle, 127.8°, has been determined for $NaCO_2$. Jacox and Milligan[5] reported a CO_2^- valence-bond angle equal to 130° for $CsCO_2$ from studies of reactions between Na, K, Cs, and CO_2 in solid argon. Hence, it is of interest to investigate the effect of the cation on the structures of the radical anion, CO_2^-, and dianion, CO_2^{2-}, as well as the different roles played by each metal in determining their chemistry with carbon dioxide.

Experimental Section

Vapors of sodium and potassium were obtained by either vaporizing the pure metal or the metal carbonates, which partially decompose to the alkali metal and carbon dioxide. Cesium vapors were produced by heating pure cesium metal to about 30 °C or, alternatively, a mixture of CsCl/Li to ~350–400 °C. In a typical experiment, the alkali metal was loaded inside a stainless-steel crucible that was then placed in a tantalum furnace. The whole assembly was resistively heated to the desired temperature (Na, ~200 °C; K, ~150 °C; Cs ~ 30 °C). The alkali-metal carbonates were placed inside a platinum boat and heated to 750 °C (Na_2CO_3), 950 °C (K_2CO_3), and 875 °C (Cs_2CO_3). An atomic beam of the metal was codeposited with carbon dioxide in excess argon or nitrogen onto a polished copper surface cooled to 15 K with a closed-cycle helium refrigerator. The period of deposition was usually fixed at 1 h. The copper mirror was then rotated 180° and the infrared reflection spectrum of the alkali metal/CO_2 reaction products measured with a Beckman IR-9 spectrophotometer. The rates of deposition of the alkali metal, carbon dioxide, nitrogen, and argon were measured with a quartz crystal microbalance. An alumel–chromel thermocouple affixed to the stainless-steel effusion cell was used to determine the vaporization temperatures of the various metals and/or metal carbonates. In some experiments, liquid nitrogen rather than water was passed through the heat shield that surrounded the furnace in order to reduce the amount of water present in the system. Matrices were photolyzed with IR radiation by exposure to the Nernst glower IR source during and after scanning. UV–vis photolysis was carried out during or after deposition by exposing the matrices to a medium-pressure 100-W Hg lamp. A water/Pyrex filter was usually used as an ultraviolet and infrared filter. Matrices were annealed in some experiments by heating to approximately twice the original temperature (~30 K) and then recooling back to 15 K. All spectra were calibrated against H_2O, CO_2, and NH_3, and frequencies were measured to an accuracy of ±0.5 cm^{-1}. A full description of the matrix-isolation apparatus has been given earlier.[5,6]

Na metal and Li_2CO_3 were obtained from J. T. Baker Chemical Co., while K, Na_2CO_3, and K_2CO_3 were supplied by Allied Chemical. Pure cesium metal (99%) was purchased from Semi-Elements, Inc. CsCl (99.9%) and Li (99.9%) were bought from Alfa Inorganics. Carbon-13-enriched K_2CO_3 (90%) was obtained from U.S. Services Inc. Cs_2CO_3 (99.9%) was purchased from Research Organic/Inorganic Chemical Corp. Carbon dioxide (99.8%), $C^{18}O_2$, and $^{13}CO_2$ (98% and 90% enrichment, respectively) were bought from Matheson Gas Products, Prochem Isotopes Ltd., and Monsanto Research Corp., respectively. $C^{18}O^{16}O$ was produced via exchange between $C^{18}O_2$(g) and hot Li_2CO_3 (~500–550 °C) or by passing a mixture of $C^{18}O_2/C^{16}O_2$ gases through a hot alumina (~500 °C) tube. Argon (Matheson, 99.9%) was further purified by passing it through hot titanium. Nitrogen, obtained from Matheson Gas Products Co., was

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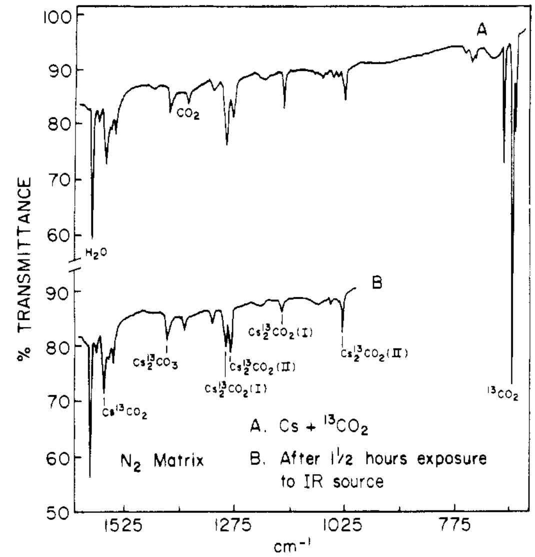

Figure 1. Infrared spectra of products from reaction of cesium metal with $^{13}CO_2$ in solid nitrogen (mole ratio of Cs:$^{13}CO_2$:N_2 is 0.9:6.0:1000): (A) spectrum measured immediately after 1-h deposition; (B) spectrum measured after 90-min exposure to Nernst glower IR source.

passed through a liquid-nitrogen trap during deposition. Carbon dioxide was passed through a dry ice bath to remove any volatile gases present as impurities.

Results

After the studies of the reactions of lithium with carbon dioxide were finished, it seemed appropriate to move to the end of the alkali-metal group and investigate the reactivity of cesium metal toward CO_2. Since cesium proved to be different from lithium in many ways, as will be discussed further, it appeared worthwhile to study potassium and compare its behavior to that of lithium and cesium. Finally, the reaction between Na and CO_2 was investigated, and it, in turn, gave unexpected results.

I. Infrared Spectra of Cs/CO_2 Reaction Products. Cocondensation of Cs metal with $^{13}CO_2/N_2$ (0.6%) gave rise to a bright turquoise matrix that yielded the spectrum shown in Figure 1A. New absorption bands appeared at 1567.3, 1424.1, 1294.7, 1280.4, 1165.9, and 1026.4 cm^{-1} along with weak features at 737.7 and 728.1 cm^{-1}. The strong absorption at 1597.2 cm^{-1} indicated the presence of H_2O traces in the system, which were difficult to eliminate. The 1567.3-cm^{-1} band was predominant in dilute matrices when the mole ratio of N_2 to Cs was ≥1000:1. A carbon-13 shift equal to 41.0 cm^{-1} was measured for this absorption. From the doublet (1:1) and triplet (1:2:1) intensity patterns observed in the mixed $^{12}CO_2/^{13}CO_2$ and $C^{16}O_2/C^{18}O_2$ isotopic studies as shown in Figures 2 and 3 C, respectively, we concluded that this absorbing species contained one carbon and two equivalent oxygen atoms. Since this absorption was observed in dilute matrices, we further concluded that only one cesium atom was present in this species. Thus, the bands at 1608.3 and 1567.3 cm^{-1} in Figure 2 and 1590.2 and 1580.7 cm^{-1} in Figure 3C have been assigned to $CsCO_2$, $Cs^{13}CO_2$, $CsC^{18}O^{16}O$, and $CsC^{18}O_2$, respectively.

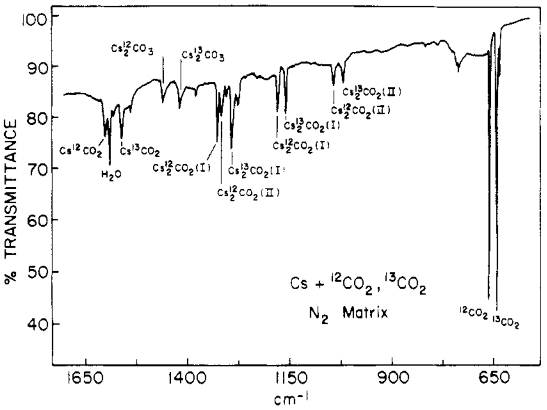

Figure 2. Infrared spectrum of products from reaction of cesium with a mixture of $^{12}CO_2/^{13}CO_2$ in a nitrogen matrix. Mole ratio of Cs:$^{12}CO_2/^{13}CO_2$:N_2 is 2.1:4.2:1000.

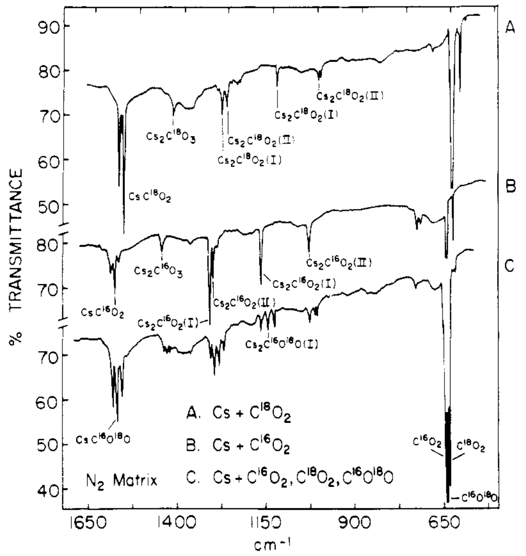

Figure 3. Infrared spectra of products from reactions in nitrogen matrices. Mole ratio of Cs:$C^{18}O_2$:$C^{16}O_2$:N_2 is 0.6:3.3:3.6:1000.

Other new absorption bands that occurred upon the cocondensation of cesium metal with CO_2 in N_2 matrices were more intense when the metal concentration was raised. During the measurement of the spectra, irradiation of the matrices with the Nernst glower IR source caused a simultaneous decrease of the 1294.7- and 1165.9-cm^{-1} bands and an increase of the 1280.4- and 1026.4-cm^{-1} bands. Furthermore, the relative intensity of the two peaks within each set remained constant. This observation is recorded in Figure 1B and suggested that the species absorbing at 1294.7 and 1165.9 cm^{-1} photolytically converted to the other absorbant that seemed to have a lower molar absorptivity. Mixed carbon-12/carbon-13 studies indicated that these two species contained only one carbon whereas the mixed oxygen-16/oxygen-18 work suggested that the species absorbing at higher frequencies had two equivalent oxygen atoms. This species photolytically rearranged to the other form containing two nonequivalent oxygen atoms. Assuming that the metals occupied equivalent positions, the bands at 1294.7 and 1165.9 cm^{-1} were assigned to $Cs_2{}^{13}CO_2$ (C_{2v}), while those peaks at 1280.4 and 1026.4 cm^{-1} belonged to a $Cs_2{}^{13}CO_2$ of C_s symmetry.

The carbon-12 counterpart of the 1424.1-cm^{-1} band fell 40.3 cm^{-1} to the blue, namely at 1465.1 cm^{-1}, as shown in Figure 2. The frequency for this absorption was very close to that reported for Cs_2CO_3 (1461.5 cm^{-1}) in a nitrogen matrix.[8] Oxygen-18 shifts of 21.3 and 9.0 cm^{-1} have been measured for the totally and partially isotopically substituted absorbant, respectively, as compared to shifts equal to 20.9 and 10.0 cm^{-1} reported[8] for $K_2C^{18}O_3$ and $K^{16}O_{18}OC^{16/18}OK$, respectively. To unravel the identity of this species, further experiments were conducted by vaporizing Cs_2CO_3 and $K_2{}^{13}CO_3$ into nitrogen matrices. Carbon-13 shifts equal to 40.3 and 41.3 cm^{-1} were measured for Cs_2CO_3 and $KCsCO_3$, respectively. The carbon-13 shift measured for cesium carbonate strongly suggested

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(8) Ogden, J. S.; Williams, S. J. *J. Chem. Soc., Dalton Trans. 2* **1981**, 456.

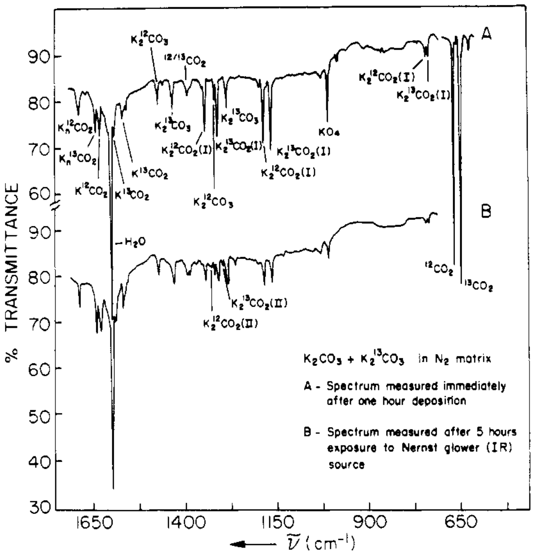

Figure 4. Infrared spectra obtained from the vaporization of a mixture of $K_2{}^{12}CO_3/K_2{}^{13}CO_3$ in solid nitrogen.

that the species absorbing at 1465.1 cm^{-1} is indeed Cs_2CO_3.

An absorption band predominant under high CO_2 concentrations at 1629.0 cm^{-1} was assigned to the adduct molecule, $CsCO_2{\cdot}CO_2$. Finally, a new band appeared in concentrated matrices at 1679.0 cm^{-1} and was assigned to $Cs_2C_2O_4$ since it grew in intensity on annealing the matrix and was present in spectra measured at room temperature when all the other absorbant species had disappeared.

Cocondensation of cesium metal with CO_2 in excess argon gave rise to spectra similar to those obtained in solid nitrogen with peaks due to $CsCO_2$ (C_{2v}), Cs_2CO_2 (C_s), $Cs_2C_2O_4$, and Cs_2CO_3. The intensity of the Cs_2CO_3 and $CsCO_2{\cdot}CO_2$ absorption bands was a function of the CO_2 concentration in the matrix. Increase of the concentration of CO_2 relative to that of the metal resulted in the decrease of the intensity of the $CsCO_2$ and Cs_2CO_2 peaks and the simultaneous increase of the $CsCO_2{\cdot}CO_2$ and Cs_2CO_3 absorption bands. When argon was totally substituted by carbon dioxide, all bands disappeared except those due to the adducted form of $CsCO_2$. When the matrix was annealed to room temperature ($\sim$300 K), the spectrum of the residue left after the vaporization of the matrix gas and the excess CO_2 reflected the disappearance of the $CsCO_2$ and Cs_2CO_2 absorption bands and the growth of new sets of bands in the oxalate absorption regions. The multiplicity of these bands suggests the possible presence of more than one geometrical form of $Cs_2C_2O_4$.

II. Infrared Spectra of K/CO_2 Reaction Products. Cocondensation of potassium with carbon dioxide in solid nitrogen gave rise to a royal blue matrix. Identical spectra were obtained when potassium carbonate was vaporized and deposited in excess nitrogen. This result suggests that K and CO_2 are the main species present in the vapors over hot K_2CO_3 and agrees with the mass spectrometric studies carried out on K_2CO_3.[9] Figure 4 presents infrared spectra obtained from the deposition of vapors of a mixture of $K_2{}^{12}CO_3$ and $K_2{}^{13}CO_3$ in a nitrogen matrix. Bands appear at 1689.8, 1634.2, 1630.8, 1609.9, 1471.1, 1342.3, 1317.1, 1184.0, 1007.1, and 738.8 cm^{-1}. The absorptions at 1471.1 and 1317.1 cm^{-1} agree very well with the reported[8] frequencies for K_2CO_3 (1471.6 and 1317.4 cm^{-1}). The 1007.1-cm^{-1} peak is assigned to KO_4, which formed from the reaction of K and O_2. It is also present in considerable amount in the spectrum of heated K_2CO_3.[8] The bands at 1342.3, 1184.0, and 738.8 cm^{-1} decrease in intensity when the matrix is exposed to the Nernst glower IR source, as shown in Figure 4B, with the growth of new peaks at 1328.6 and 1052.1 cm^{-1}, respectively. The relative intensities of the decreasing peaks remain unaltered. The behavior of these two sets of bands is very similar to those bands due to Cs_2CO_2 (C_{2v}) and Cs_2CO_2 (C_s), discussed in the previous paragraph. Thus, by analogy to the Cs/CO_2 system, the peaks at 1342.3, 1184.0, and 738.8 cm^{-1} are assigned to K_2CO_2 (C_{2v}). This assignment is further supported by the mixed $C^{18}O_2/C^{16}O_2$ study, which indicates that the molecule contains two equivalent atoms. Similarly, the bands at 1328.6 and 1052.1 cm^{-1} are assigned to K_2CO_2 (C_s). This is further supported by the unresolved quartet intensity pattern that appears as a doublet in the spectrum of the mixed $C^{18}O_2/C^{16}O_2$/K reaction products shown in Figure 5.

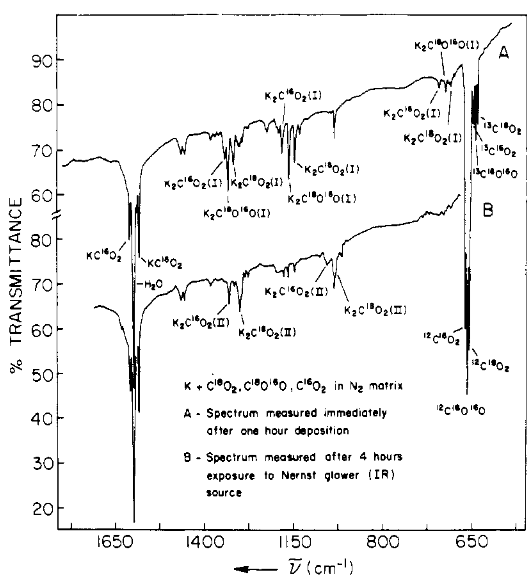

Figure 5. Infrared spectra of products from reaction of potassium with $C^{16}O_2/C^{18}O_2$ in solid nitrogen. Unlabeled peak at 1035.1 cm^{-1} does not arise from K/CO_2 reaction products.

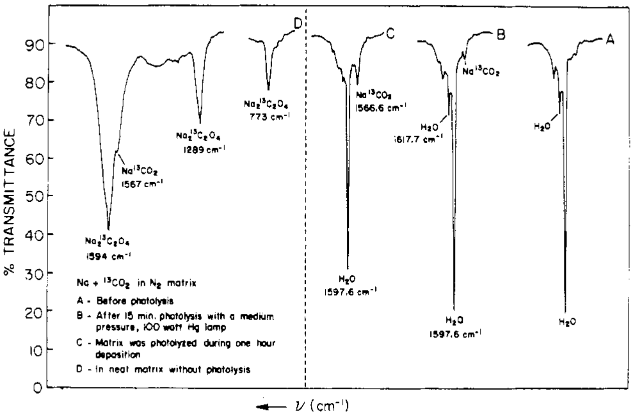

Figure 6. Infrared spectra of products from reactions of sodium with $^{13}CO_2$ in nitrogen (A (mole ratio of $^{13}CO_2$:N_2 1.4:1000), B, C) and in neat (D (mole ratio of Na:$^{13}CO_2$ 1.1:100)) matrices.

The absorption at 1609.9 cm^{-1} is prominent in dilute matrices and exhibits carbon-13 and oxygen-18 shifts similar to those of $CsCO_2$. Hence, it should belong to KCO_2. The "solvated" form of KCO_2 is responsible for the peaks at 1634.2 and 1630.8 cm^{-1}, which are predominant at high carbon dioxide concentrations. These bands shift to 1590.6 and 1588.0 cm^{-1}, respectively, upon carbon-13 substitution. The 1689.8-cm^{-1} absorption is present under very high metal concentrations. It exhibits a 1:1 and a 1:2:1 intensity pattern in a 1:1 isotopic mixture of $^{12}CO_2/^{13}CO_2$ and $C^{16}O_2/C^{18}O_2$, respectively. Furthermore, the carbon-13 and oxygen-18

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(9) Simmons, L. L.; Lowden, L. F.; Ehlert, T. C. *J. Phys. Chem.* **1977**, *81*, 706.

isotopic shifts measured for these species are of the same order of magnitude as those of KCO_2. Hence, one tentatively assigns this absorption to K_nCO_2 where $n \geq 3$.

III. Infrared Spectra of Na/CO_2 Reaction Products. A lilac-colored matrix was obtained upon the cocondensation of sodium and CO_2 in solid argon or nitrogen. Very little reaction product was detected in the infrared spectrum shown in Figure 6A. A small absorption at 1566.6 cm^{-1} grows in intensity when the matrix is irradiated with a medium-pressure 100-W mercury lamp. Spectra of matrices photolyzed during and after deposition are given in Figure 6C,B, respectively. It is clear that photolysis enhances the yield of the reaction product especially when it is carried out during deposition. This product enhancement is also obtained when the reaction is carried out in neat matrices. One notices that the 1567-cm^{-1} absorption shown in Figure 6D is much stronger than its counterpart when photolysis was carried out. New bands grow in at 770, 1292, and 1590 cm^{-1} when sodium is allowed to react with $^{13}CO_2$ in a neat matrix as shown in Figure 6D. A similar set of bands was obtained when Na was codeposited with $^{12}CO_2$. Their frequencies at 774, 1306, and 1633 cm^{-1} are very similar to the literature values[10] for solid sodium oxalate. The carbon-12 counterpart of the 1567-cm^{-1} band was only seen in neat matrices at ~1612 cm^{-1} since it was masked by strong water bands in argon and nitrogen matrices. Its frequency value is close to that measured by Jacox and Milligan[5] for $NaCO_2$ in an argon matrix. Thus, it seems reasonable to assign the 1566.6-cm^{-1} absorption to $Na^{13}CO_2$.

Discussion

I. Reaction of an Alkali Metal with CO_2. A. Cesium. The reaction of cesium metal with CO_2 in an argon matrix was first investigated by Jacox and Milligan.[5] Absorption bands due to $Cs^+CO_2^-$ were identified, and a C_{2v} structure with a CO_2^- valence-bond angle close to 130° was assigned to this molecule on the basis of the measured asymmetric CO_2^- stretching frequencies of the different isotopomers. Unidentified bands were observed at 1336 cm^{-1} with a shoulder at 1342 and 1017 cm^{-1}. The 1336- and 1017-cm^{-1} peaks shifted to 1307 and 997 cm^{-1} on oxygen-18 substitution. Weak absorptions were also measured at 1654 and 1658 cm^{-1}, which were replaced by peaks at 1630, 1636, and 1640 cm^{-1} in the oxygen-18 study.

Our present studies of the reactions of cesium with carbon dioxide in argon and nitrogen matrices have revealed the formation of $Cs_2^{2+}CO_2^{2-}$ besides the already observed Cs^+-CO_2^-. $Cs^+CO_2^-$ was produced in dilute matrices whereas the formation of $Cs_2^{2+}CO_2^{2-}$ was more favored at a higher metal concentration. Two geometrical isomers were isolated for the dicesium carbon dioxide dianion. On the basis of mixed $C^{16}O_2/C^{18}O_2$ studies, one geometrical isomer was found to have a C_{2v} geometry where the two oxygen atoms are in equivalent positions and each is interacting with one of the two metals. This C_{2v} form of Cs_2CO_2 was found to photolytically convert to another geometrical isomer of C_s symmetry where the two oxygen atoms are nonequivalent. The effect of photolysis was discovered by coincidence when the matrix was exposed to the Nernst glower IR source during scanning. This isomeric rearrangement may possibly be taking place through the excitation of one of the vibrational modes of Cs_2CO_2 (C_{2v}). At high CO_2 concentrations, $CsCO_2$:CO_2 as well as Cs_2CO_3 were formed while absorptions exhibited by either form of Cs_2CO_2 disappeared. Occasionally, weak bands that could be assigned to cesium oxalate were observed. It is interesting that reaction of Cs_2CO_2 with another molecule of CO_2 leads to the formation of cesium carbonate rather than cesium oxalate. This implies that the carbonate of cesium is relatively more stable when compared to its oxalate than is the case for the lithium compounds.[2] For the reaction of lithium with CO_2, $Li_2C_2O_4$ was initially formed. However, subsequent heating of the matrix to room temperature does cause the decomposition of lithium oxalate to Li_2CO_3 and CO.

B. Potassium. Results similar to those of the Cs/CO_2 reactions were obtained when potassium was allowed to react with CO_2 in argon and nitrogen matrices. Bands were first observed and assigned to the C_{2v} forms of KCO_2 and K_2CO_2. Irradiation of the matrix with the Nernst glower IR source caused the disappearance of the absorptions exhibited by K_2CO_2 (C_{2v}) and the growth of very weak features that were assigned to K_2CO_2 (C_s). The only difference observed in the Cs/CO_2 and K/CO_2 reactions is that only the C_{2v} form of K_2CO_2 was initially formed in the case of potassium. IR photolysis did cause bands due to K_2CO_2 (C_s) to grow in the spectrum, along with the simultaneous disappearance of those exhibited by K_2CO_2 (C_{2v}). In the case of cesium, both Cs_2CO_2 (C_{2v}) and Cs_2CO_2 (C_s) were initially formed and IR photolysis caused the rearrangement of the C_{2v} to the C_s form. This observation leads us to believe that M_2CO_2 (C_{2v}) is formed as a result of the reaction of a dimetal molecule with CO_2; this conclusion is based on the assumption that the O–C–O + M–M reaction orientation where CO_2 is parallel to M_2 will produce the C_{2v} form of M_2CO_2. It is also interesting that no bands due to Li_2CO_2 (C_{2v}) were observed in the Li/CO_2 studies. This phenomenon might be explained in terms of the strength of the Li–Li bond, which has to be broken in order to react with CO_2 and form Li_2CO_2 (C_{2v}). The Li_2 bond is more than twice as strong as that of the K–K or Cs–Cs bond. The formation of M_2CO_2 (C_s) (where M = Li, K, Cs) can be postulated as a result of the reaction of a second metal atom with MCO_2 (C_{2v}). For the metals K and Cs, K_2CO_2 (C_s) and Cs_2CO_2 (C_s) are also formed from the photolytic conversion of K_2CO_2 (C_{2v}) and Cs_2CO_2 (C_{2v}), respectively. This observation suggests that the C_s form of M_2CO_2 is more stable than the C_{2v} isomer. This conclusion is also supported by the theoretical studies[4] carried out by Jordan on the stabilities and structures of lithium and sodium complexes. Jordan has predicted the two forms of $LiCO_2$ of C_{2v} and C_s symmetries to be close in energy, a prediction that has been verified by our earlier experiments.[2] He has also predicted only one stable form of $NaCO_2$ of C_{2v} symmetry, which agrees with our present studies. In the case of Li_2CO_2 and Na_2CO_2, he has calculated potential minima for one geometry of C_s and two geometries of C_{2v} symmetries, with the C_s form being the most stable in each case. Again, this is in a accord with our experimental results on potassium and cesium dimetal carbon dioxide dianion molecules.

Other molecules that are formed at high metal concentrations are K_nCO_2 (C_{2v}) where $n \geq 3$. This molecule was found to have equivalent oxygen atoms and was only present at high concentrations of potassium. At high concentrations of CO_2, the "solvated", $KCO_2 \cdot CO_2$ was observed. Bands due to K_2CO_3 were also identified under the same conditions.

It is interesting to note that identical products were obtained either from the vaporization of K_2CO_3 or from the cocondensation of potassium with carbon dioxide in inert-gas matrices. However, this result is not too surprising since mass spectrometric studies[9] on the vaporization of K_2CO_3 have suggested that the most abundant species in the vapor phase are K, CO_2, and O_2, in that order. This is further supported by the matrix-isolation studies on K_2CO_3 carried out by Ogden and co-workers.[8] Besides absorptions due to K_2CO_3, these investigators observed unidentifiable bands at 1340, 1180, and 720 cm^{-1} that were found to maintain the same relative intensities throughout a range of experimental conditions. An

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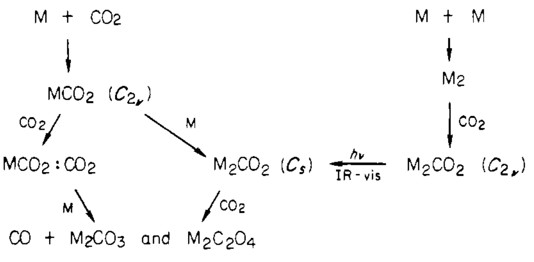
(10) Schmeltz, M. J.; Mizazawa, T.; Mizushima, S.; Lane, T. J.; Quagliano, J. V. *Spectrochim. Acta* **1957**, *9*, 51.

Table I. Measured Infrared Frequencies (cm^{-1}) for $CsCO_2$, KCO_2, and $NaCO_2$ Isotopomers in Ar and N_2 Matrices

vibrational mode	M	MCO_2		$M^{13}CO_2$		$MC^{18}O_2$		$MC^{18}O^{16}O$	
		N_2	Ar	N_2	Ar	N_2	Ar	N_2	Ar
$\nu_1(A_1)$	Cs	1345.5	1352.8	1324.1					
	Cs	1608.3	1595.3 1596.2[a]	1567.3	1553.8 1554.2[a]	1580.7	1568.9 1569.0[a]	1596.2	1583.0
$\nu_4(B_2)$	K	1609.9	1609[a]	1567.9		1582.6			
	Na		1601.6 1608[a]	1566.6	1560.9				

[a] Reference 5.

Scheme I



M = K, Cs

identical set of bands was observed in our experiments and was assigned to K_2CO_2 (C_{2v}).

Thus, we can summarize the chemistry that takes place between K or Cs and CO_2 in Scheme I.

C. Sodium. Reaction of sodium with carbon dioxide led to very little reaction product. Only bands assigned to Na^+-CO_2^- were observed. This result is rather surprising in light of the reactivity of lithium metal toward CO_2. However, one might explain this reactivity in terms of the rather stable isomer $LiCO_2$ (C_s) that lithium initially forms with CO_2 which may be the reaction intermediate that leads to the final product $LiCO_2$ (C_{2v}). Since $NaCO_2$ (C_s) is more unstable relative to $NaCO_2$ (C_{2v}),[3] this reaction pathway may not be feasible. Thus, the reactivity of the alkali metals toward CO_2 follows the expected order Cs > K > Na with the exception of lithium for the above-mentioned reason. No bands were observed in the spectra of Na/CO_2 reaction products that could be assigned to Na_2CO_2. Again, this result is not surprising since it was concluded that the C_s isomer of M_2CO_2 (where M = K, Cs) is formed from the reaction of MCO_2 and M and/or from the photolytic rearrangement of M_2CO_2 (C_{2v}). The latter molecule is thought to be formed from the reaction of Na_2 and CO_2. The lack of reaction of Na_2 might be explained by the higher energy required to break the stronger Na–Na bond compared to K–K and Cs–Cs.

Interestingly, the yield of $NaCO_2$ is increased by UV–vis photolysis during or after deposition. One may postulate that there is an energy barrier to the formation of this molecule, which is circumvented by irradiating the matrix with the mercury lamp. The yield of this molecule also increased in neat matrices. However, absorption bands assigned to sodium oxalate were the predominant features in the neat matrix. The intensity of the oxalate bands was slightly reduced when the matrix was heated to room temperature. This behavior was also observed in the case of potassium and cesium reactions in neat matrices. Bands due to the metal carbonate appeared upon annealing, which suggests that the metal oxalate partially decomposed to the metal carbonate and carbon monoxide.

II. Bonding and Structure of MCO_2. Jacox and Milligan[5] were the first investigators to observe $CsCO_2$, KCO_2, and $NaCO_2$ in an argon matrix. They have measured the asymmetric CO_2 stretching frequency for all $CsCO_2$ isotopomers and have concluded that the molecule has a C_{2v} symmetry with an OCO valence-bond angle close to 130°. Recent theoretical calculations carried out by Jordan and co-workers[3] have shown that the most stable structure for the Li–CO_2 and Na–CO_2 complexes is a planar rhombus (C_{2v} symmetry), where the metal is equally interacting with the two oxygen atoms. Assuming C_{2v} symmetry for MCO_2, six vibrational modes are expected to be infrared active. Frequencies of only two of the five in-plane modes have been measured for $CsCO_2$ isotopomers in our laboratory and are listed in Table I. There is quite good agreement between these frequencies and those measured in the earlier studies.[5] From the location of the absorption bands and from the carbon-13 and oxygen-18 shifts, these frequencies have been assigned to the symmetric and asymmetric stretching modes of CO_2^- in $CsCO_2$. In the cases of KCO_2 an $NaCO_2$, we were only able to measure frequencies for the asymmetric stretching mode given in Table I. Assuming little interaction between M^+ and CO_2^-, one can apply the triatomic molecule approximation to the CO_2^- portion of the molecule and calculate a valence-bond angle for CO_2^-. The validity of applying this approximation to those molecules has been tested and proved to be acceptable for $LiCO_2$.[2] Table II gives upper and lower limits as well as average values for CO_2^- valence-bond angles calculated for $CsCO_2$, KCO_2, $NaCO_2$, and $LiCO_2$ in different matrices. This bond angle calculation can be further refined by correcting for anharmonicity with use of Green's formula.[11] In each case, correction for anharmonicity has raised the value of the bond angle approximately 3°. A list of calculated anharmonicities for CO_2^- in KCO_2, $CsCO_2$, and $LiCO_2$ is given at the bottom of Table II.

Table II. Valence-Bond Angles (deg) and Calculated Anharmonicities (cm^{-1}) for CO_2^- in $M^+CO_2^-$ (C_{2v}) from the Triatomic Molecule Approximation

	$CsCO_2$		KCO_2	$NaCO_2$	$LiCO_2$	
	Ar	N_2	N_2	Ar	Ar	Xe
$MCO_2/MC^{18}O_2$	142.7	134.8	137.2		129.8	126.5
$MCO_2/M^{13}CO_2$	119.5	114.1	118.3	113.3	115.5	123.5
value (av)	131.1	124.5	127.8		122.6	125.0
best matrix value[a]	133.9	126.9	131.1		125.7	125.5
Jacox and Milligan[4]	130					
Jordan[3]				128.4	124.5	

MCO_2	$-X$		MCO_2	Ar
	Ar	N_2		
$CsCO_2$	65.8	70.2	$LiCO_2$	60.2
KCO_2		51.2		

[a] Bond angle calculated after corrections for anharmonicity, X.

The value of the calculated CO_2^- bond angle seems to be dependent on the matrix in which the molecule is trapped. For instance, $CsCO_2$ exhibits a difference of 7° in the OCO bond angle between nitrogen and argon matrices. One expects the MCO_2 molecule to be better "solvated" in nitrogen matrices, and hence nitrogen should allow more of an electron transfer from the metal to the CO_2 molecule. Thus, in a N_2 matrix

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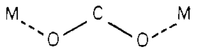
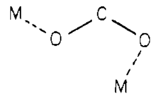
(11) Green, D. W.; Ervin, K. M. *J. Mol. Spectrosc.* **1981**, *88*, 51.

Chart I



C_{2v}



C_s

Table III. Measured Infrared Frequencies (cm^{-1}) for All Cs_2CO_2 (C_{2v}) and K_2CO_2 (C_{2v}) Isotopomers in Ar and N_2 Matrices

vibrational mode	M	M_2CO_2		$M_2{}^{13}CO_2$	$M_2C^{18}O_2$	$M_2C^{18}O^{16}O$
		N_2	Ar	N_2	N_2	N_2
$\nu_5(B_2)$	Cs	1328.7	1341.0	1294.7	1305.0	1318.1
	K	1342.3		1307.4	1318.6	1331.7
$\nu_1(A_1)$	Cs	1186.7	1174.0	1165.9	1151.9	1167.8
	K	1184.0		1163.9	1148.3	1164.5
$\nu_2(A_1)$	Cs	745.2	744.5	737.7		
	K	738.8		731.8	706.2	723.0

the CO_2^- portion of MCO_2 will more closely resemble a free CO_2^- than in an argon matrix. The effect of the cation on the CO_2^- bond angle seems to be quite pronounced if one compares the OCO bond angles calculated for $LiCO_2$ and $CsCO_2$ in argon matrices, which show a difference of 8.2°. This result does not seem to be too surprising since CO_2 is expected to interact more strongly with the small lithium ion because of its much smaller ionic radius ($r_{Cs^+} \simeq 3r_{Li^+}$). Thus, a greater overlap between lithium and oxygen orbitals results in a more bent CO_2^-. On the other hand, the ionic radius of the cation does not seem to be the only factor that affects the size of the CO_2^- bond angle. Comparing the CO_2^- bond angles calculated for KCO_2 and $CsCO_2$ from frequencies measured in nitrogen matrices, one notices that the bond angle obtained for KCO_2 is about 3° higher than that of $CsCO_2$. However, there is a difference of about 10 kcal between the ionization potentials of potassium and cesium, which may explain the decrease in the CO_2^{2-} bond angle in going from K to Cs since there will be more of an electron transfer between Cs and CO_2 than between K and CO_2. The bond angle calculated for CO_2^- by Jordan et al.[3] of 134.9° is in close agreement with the measured value[12] for the isoelectronic molecule NO_2 (134.1°) but higher than the experimental values obtained from $LiCO_2$, KCO_2, and $CsCO_2$. Thus, we can only conclude that the CO_2^- valence-bond angle calculated in this study has a value close to that of "free" CO_2^-. It is clear that more than one factor affects the size of the CO_2^- bond angle, such as matrix effect, the ionic radius, and the ionization potential of the alkali metal. Total electron transfer from the alkali metal to CO_2 seems to be unlikely because of the small electron affinity[13] of CO_2, on the order of −0.6 eV.

III. Bonding and Structure of M_2CO_2. Two geometrical isomers were isolated for K_2CO_2 and Cs_2CO_2 in argon and nitrogen matrices. One isomer has C_{2v} geometry with equivalent oxygen atoms as confirmed from the mixed $C^{18}O_2/C^{16}O_2$ studies whereas the other isomer is of C_s symmetry with nonequivalent oxygen atoms. Chart I shows possible structures for these two isomers.

The bonding interaction between the metal atoms and the CO_2 molecule in the C_{2v} geometry may take two forms: one alkali atom may be bonded to each oxygen or the alkali atoms may bridge the oxygen and carbon atoms. Indeed, theoretical studies[3] have shown the existence of two minima for the C_{2v} isomers of Na_2CO_2 and Li_2CO_2 with these two kinds of interaction. It was found that the structure where the metal bridges the oxygen and carbon atoms is slightly more stable than the other. However, the most stable structure of all was shown[3] to be that of C_s symmetry. Again, in this structure each of the metal atoms may be interactive with one oxygen or one metal may bridge the two oxygen atoms as in MCO_2 (C_{2v}), and the other metal may bridge one carbon and one oxygen atom. The latter structure seems to be more favorable since our experiments show that M_2CO_2 (C_s) is predominantly formed from the addition of one metal atom to MCO_2 (C_{2v}) whereas M_2CO_2 (C_{2v}) is obtained as the result of the reaction of M_2 with CO_2.

Table IV. Valence-Bond Angles (deg) for CO_2^{2-} in $M_2^{2+}CO_2^{2-}$ (C_{2v}) from the Triatomic Molecule Approximation

	Cs_2CO_2	K_2CO_2	Na_2CO_2	Li_2CO_2
$M_2CO_2/M_2C^{18}O_2$	126.4	129.5		
$M_2CO_2/M_2{}^{13}CO_2$	115.7	117.0		
value (av)	121.1	123.3		
best matrix value[a]	123.2	125.9		
Jordan[3]			127.4	125.2
			119.8	112.9

[a] Bond angle calculated after corrections for anharmonicity, *X*. $X = -38.3$ cm^{-1} for Cs_2CO_2, and $X = -29.0$ cm^{-1} for K_2CO_2.

Table V. Measured Infrared Frequencies (cm^{-1}) for all Cs_2CO_2 (C_s) and K_2CO_2 (C_s) Isotopomers in Ar and N_2 Matrices

vibrational mode	M	M_2CO_2		$M_2{}^{13}CO_2$		$M_2C^{18}O_2$	
		N_2	Ar	N_2	Ar	N_2	Ar
$\nu_1(A')$	Cs	1320.0	1334.8	1280.4	1304.8	1289.9	1305.9
	K	1328.6		1295.4		1299.1	
$\nu_2(A')$	Cs	1050.0	1017.6	1026.4		1028.7	996.5
	K	1052.1		1028.2		1030.2	

Table VI. Measured Infrared Frequencies (cm^{-1}) for all K_nCO_2 (C_{2v}) Isotopomers in N_2 Matrix and CO_2^- Valence-Bond Angles (deg) from the Triatomic Molecule Approximation

IR Frequencies

K_nCO_2	1689.8	$K_nC^{18}O_2$	1664.1
$K_n{}^{13}CO_2$	1642.9	$K_nC^{18}O^{16}O$	1677.7

CO_2^- Bond Angles

$K_nCO_2/K_nC^{18}O_2$	>180
$K_nCO_2/K_n{}^{13}CO_2$	146.2
best matrix value[a]	164.3

[a] Average bond angle calculated after correction for anharmonicity, $X = -34.3$ cm^{-1}.

Three frequencies have been measured for M_2CO_2 (C_{2v}) and have been assigned to the asymmetric and symmetric stretching as well as to the bending modes of CO_2^{2-}. A list of these frequencies for all K_2CO_2 (C_{2v}) and Cs_2CO_2 (C_{2v}) isotopomers is given in Table III. Frequencies measured for K_2CO_2 (C_{2v}) are very close to those of Cs_2CO_2 (C_{2v}), which suggests similar bonding in each molecule. Assuming small metal interaction with the CO_2^{2-} portion of the molecule, one can apply the triatomic molecule approximation and calculate valence-bond angles in K_2CO_2 (C_{2v}) and Cs_2CO_2 (C_{2v}). Table IV gives lower and upper limits as well as average values for the CO_2^{2-} bond angle calculated for K_2CO_2 (C_{2v}) and Cs_2CO_2 (C_{2v}). Correction for anharmonicity using Green's formula[11] causes an increase in the CO_2^{2-} bond angle of approximately 2°. The bond angle obtained for K_2CO_2 (C_{2v}) is about 2.7° higher than that calculated for Cs_2CO_2 (C_{2v}), which suggests that there is more electron transfer from the metal atom to CO_2 in the case of Cs_2CO_2 because of its lower ionization potential. Theoretical CO_2^{2-} valence-bond angles are also listed in Table IV for both structures of Na_2CO_2 (C_{2v}) and Li_2CO_2 (C_{2v}). The structure with the metal atoms bridged to a carbon

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[12] Bird, G. R.; Baird, J. C.; Jacke, A. W.; Hodgeson, J. A.; Curl, R. F., Jr.; Kunkle, A. C.; Bransford, J. W.; Rastrup-Andersen, J.; Rosenthal, J. *J. Chem. Phys.* **1964**, *40*, 3378.

[13] Compton, R. N.; Reinhardt, P. W.; Copper, C. D. *J. Chem. Phys.* **1975**, *63*, 3821.

Table VII. Measured Infrared Frequencies (cm^{-1}) for $MM'CO_3$ and $MM'^{13}CO_3$ in N_2 Matrix

symmetry	MM'	$MM'CO_3$	$MM'^{13}CO_3$
B_2	Cs_2	1460.8	1420.1
	KCs	1469.0	1427.7
	K_2	1471.2	1430.2
A_1	Cs_2	1319.0	1283.7
	KCs	1319.0	1283.7
	K_2	1317.1	1282.4

and oxygen atom has the highest value for the CO_2^{2-} valence-bond angle.

Only two frequencies have been measured for K_2CO_2 (C_s) and Cs_2CO_2 (C_s) isotopomers, and they have been assigned to C–O stretching modes due to their large carbon-13 and oxygen-18 isotopic shifts. A list of these frequencies is given in Table V. The lower value of the C–O stretching frequency is consistent with the idea that one of the metal atoms is bridging the two oxygens while the other is bridging one oxygen and one carbon atom.

IV. Bonding and Structure of K_nCO_2. Table VI lists measured frequencies assigned to the asymmetric stretching mode of CO_2^- in K_nCO_2, $K_n{}^{13}CO_2$, $K_nC^{18}O_2$, and $K_nC^{18}O^{16}O$. A large bond angle has been calculated for CO_2^- in this molecule. This result suggests that very little electron transfer is taking place between the potassium cluster and the carbon dioxide molecule. It is hard to predict the number of potassium atoms present in this cluster, but since molecules like Li_3, Na_3, and K_3 are known to exist,[14] one would assume that $n = 3$ in this species is likely.

V. Bonding and Structure of M_2CO_3. Ogden and coworkers[8] have recently studied the infrared spectra of matrix-isolated cesium, rubidium, and potassium carbonates. They have concluded that the alkali-metal carbonate has a C_{2v} geometry in which the CO_3 group coordinates in a bidentate fashion to one of the alkali-metal atoms and in a monodentate fashion to the other. These conclusions were based on an extensive oxygen-18 enrichment study.

In this section we report frequencies measured for $K_2{}^{13}CO_3$, $KCs^{13}CO_3$, and $Cs_2{}^{13}CO_3$ in nitrogen matrices. These frequencies are listed in Table VII along with those measured for the carbon-12 analogue, which are in excellent agreement with the values previously reported.[8]

VI. Concluding Remarks. 1. Reaction of carbon dioxide with Li, Na, K, and Cs in inert-gas and nitrogen matrices leads to the formation of $LiCO_2$ (C_s) and MCO_2 (C_{2v}) (where M = Li, Na, K, Cs).

2. The CO_2^- valence-bond angles have been calculated for $LiCO_2$, KCO_2, and $CsCO_2$. The value of the calculated bond angle is a function of the matrix used. Both the ionization potential of the alkali metal as well as its ionic radius appear to affect the size of the CO_2^- valence-bond angle.

3. Under high metal concentrations, M_2CO_2 (C_{2v}) molecules are also formed (where M = K, Cs). They are photolytically converted to M_2CO_2 (C_s) by infrared radiation. In the case of Li, only the most stable isomer, Li_2CO_2 (C_s), has been isolated. This observation leads us to conclude that M_2CO_2 (C_{2v}) is formed via the reaction between M_2 and CO_2 as opposed to M_2CO_2 (C_s), which is produced from the addition of M to MCO_2 (C_{2v}), i.e., the sequential addition of metal atoms.

4. CO_2^{2-} valence-bond angles of 125.9 and 123.2° have also been calculated for K_2CO_2 (C_{2v}) and Cs_2CO_2 (C_2v), respectively.

5. In highly concentrated matrices, the formation of potassium and cesium carbonates was more favored over that of their oxalate counterparts whereas, in the cases of lithium and sodium, formation of the oxalates was favored. The latter decompose to metal carbonate and carbon monoxide when the matrix block is raised to room temperature.

Acknowledgment. Grants from the National Science Foundation and the Robert A. Welch Foundation have supported this study. We also acknowledge useful conversations with Professor K. Jordan about metal atom reactions.

Registry No. CO_2, 124-38-9; Na, 7440-23-5; K, 7440-09-7; Cs, 7440-46-2; $NaCO_2$, 80480-96-2; KCO_2, 88057-30-1; $CsCO_2$, 88057-31-2; K_2CO_2, 88057-32-3; Cs_2CO_2, 88057-33-4; Na_2CO_2, 88057-34-5.

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[14] Lindsay, D. M.; Garland, D.; Tischler, F.; Thompson, G. A. "Metal Bonding and Interactions in High Temperature Systems"; American Chemical Society: Washington, DC, 1982; ACS Symp. Ser. No. 179, p 69.