Matrix Isolation Studies on the Lithium-induced Reductive Coupling of Carbon Dioxide

By ROBERT H. HAUGE,* JOHN L. MARGRAVE, JAMES W. KAUFFMAN, NANCY A. RAO, MARK M. KONARSKI, JOHN P. BELL, and W. EDWARD BILLUPS*
(*Department of Chemistry, Rice University, Houston, Texas* 77001)

Summary Both the anion and dianion of CO_2 have been detected by i.r. matrix isolation spectroscopy as reactive intermediates in the reductive coupling of CO_2 by lithium atoms to give lithium oxalate.

The successful exploitation of CO_2 as a carbon resource requires a detailed knowledge of the ways in which this substance can be activated.[1] Electron transfer to yield the radical ion CO_2^- provides one form of activated CO_2. This species has been postulated in several studies including the decomposition of oxalates in the presence of metal ions[2–6] and in electrochemical[5,6] and chemical reductions.[7–16] Electron transfer to CO_2 has also been observed when CO_2 is irradiated on a metal surface.[17] Several C_1—C_3 products have been isolated from the reduction of CO_2 with amalgams[9] and model studies for the reductive coupling of CO_2 to oxalic acid *via* metal-promoted C–C bond formation have been reported recently.[18]

Direct evidence for CO_2^- is found in i.r. [19–21] matrix studies where the anion is part of a contact ion pair with sodium, potassium, and caesium ions. Studies of the interaction of lithium atoms with CO_2 provide a useful extension of existing studies and offer some advantages, since inter-ionic modes will occur at higher frequencies and exhibit pronounced lithium isotope effects. Thus one can hope to evaluate the nature of the cation–anion interactions.

The high mobility of lithium atoms[22] during the co-condensation process favours formation of new dilithium species. At moderate CO_2/Xe concentrations (1/50) it is also possible to study the bond-forming steps between the C_1 units.[9] We report here a study of the stepwise reductive coupling of carbon dioxide by lithium atoms leading to lithium oxalate.

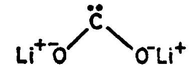
Three groups of peaks (labelled A, B, and C) were observed (Table) when lithium atoms were co-condensed with CO_2 in a xenon matrix. The set of peaks labelled A persists at the lowest concentrations of lithium and CO_2 and is thus assigned to $Li^+CO_2^-$. The peaks labelled B are favoured by high concentrations of both lithium and CO_2 and are assigned to $Li_2C_2O_4$, lithium oxalate. Isotopic ^{13}C and ^6Li frequency shifts indicate that the peaks assigned to $Li^+CO_2^-$ ('A' peaks) at 1564, 1324, and 792 cm^{-1} are intra-ionic modes of CO_2^- and that the 539 cm^{-1} peak is an inter-ionic mode. The doubling of the peaks is apparently caused by a second matrix site. The mixed carbon isotope and lithium isotope experiments (Table) further support the assignment of the peaks labelled A to a species containing one carbon and one lithium atom.

Table. Product band positions/cm^{-1} for $Li^+CO_2^-$, $Li_2C_2O_4$, and $Li^+{}_2CO_2^{2-}$ of various isotopic compositions in a xenon matrix at 15 K.[a]

Peaks A				Peaks B				Peaks C			
$^6Li^{12}C^{16}O_2$	$^6Li^{13}C^{16}O_2$	$^7Li^{12}C^{16}O_2$	$^7Li^{13}C^{16}O_2$	$^6Li_2{}^{12}C_2{}^{16}O_4$	$^6Li_2{}^{13}C_2{}^{16}O_4$	$^7Li_2{}^{12}C_2{}^{16}O_4$	$^7Li_2{}^{13}C_2{}^{16}O_4$	$^6Li_2{}^{12}C^{16}O_2$	$^6Li_2{}^{13}C^{16}O_2$	$^7Li_2{}^{12}C^{16}O_2$	$^7Li_2{}^{13}C^{16}O_2$
1564·5	1524·2	1563·1	1523·7	1656·4	1612·0	1656·1	1611·9	1429·8	1397·9	1428·0	1393·4
1562·6	1522·6		1522·2	1653·8	1609·8	1653·6	1609·5				
								995·4	975·4	991·0	974·0
1324·3	1300·3	1320·0	1299·4	1307·9	1283·2	1307·2	1282·6	990·8	970·6	987·1	964·0
1316·7	1295·7		1298·2		1278·2						
								592·2	591·5	555·5	555·3
792·4	785·7	792·1	782·4	809·5	803·5		796·9				
788·0	782·7		779·5	806·2							
				804·2	799·2		789·4				
539·3	538·4	506·0	505·2								
526·5	526·0	495·4	494·8	497	487		483				

[a] The apparatus has been described previously: NBS Spec. Publ. (U.S.) 561, Proceedings of the 10th Materials Research Symposium on Characterization of High Temperature Vapors and Gases held at NBS, Gaithersburg, MD, September 18—22, 1978. Lithium metal was vaporized from 350—480 °C and co-condensed with variable amounts of CO_2 and xenon.

The peaks labelled C are assigned to $Li^+{}_2CO_2^{2-}$, represented as (**1**). The lower frequencies of the 1428 and 987 cm^{-1} peaks relative to those of CO_2^- are reasonable, since CO_2^{2-} would contain two carbon-oxygen single bonds, whereas the average bond order for each bond in CO_2^- is 1·5.



(1)

The $Li^+CO_2^-$ and $Li_2C_2O_4$ species are also detected when lithium atoms are co-condensed with pure CO_2. As the temperature of the matrix is warmed from 15 to 613 K, bands assigned to $Li^+CO_2^-$ at 1572·3 and 1328·2 cm^{-1} disappear along with the excess of CO_2. At 200 K only lithium oxalate remains. The observed frequencies which are assigned to lithium oxalate were confirmed by comparison with known absorptions of lithium oxalate. By the time 613 K is reached, the oxalate has completely decomposed to lithium carbonate as expected.

Several conclusions can be drawn from these results regarding the mechanism of the dimerization process which leads to oxalate. First, the presence of $Li^+CO_2^-$ and lack of evidence for $Li^+C_2O_4^-$ suggests that CO_2^- does not react with another CO_2, eliminating Scheme 1 as the source of $Li_2C_2O_4$. Secondly, the large amount of $Li_2C_2O_4$ and the absence of $Li^+{}_2CO_2^{2-}$ (in the CO_2 matrix) support Scheme 2 as the origin of $Li_2C_2O_4$; however, the dimerization of two $Li^+CO_2^-$ species in adjacent sites could also produce the oxalate.

$$\begin{gathered} Li + CO_2 \rightarrow Li^+CO_2^- \\ Li^+CO_2^- + CO_2 \rightarrow Li^+C_2O_4^- \\ Li^+C_2O_4^- + Li \rightarrow Li_2C_2O_4 \end{gathered}$$

Scheme 1

$$\begin{gathered} Li + CO_2 \rightarrow Li^+CO_2^- \\ Li^+CO_2^- + Li \rightarrow Li^+{}_2CO_2^{2-} \\ Li^+{}_2CO_2^{2-} + CO_2 \rightarrow Li_2C_2O_4 \end{gathered}$$

Scheme 2

Finally, the matrix experiments suggested that oxalate could be derived on a macroscale basis by the co-condensation of CO_2 with lithium atoms. This was confirmed when lithium atoms were co-condensed with CO_2 to yield lithium oxalate in $>90\%$ yield based on consumed lithium. Similar results were observed when sodium or calcium atoms and CO_2 were co-condensed.

We gratefully acknowledge Dow Chemical U.S.A. for support of this work. Acknowledgment is made to the Robert A. Welch Foundation and the National Science Foundation for partial support.

(*Received*, 23*rd July* 1981; *Com.* 890.)

[1] Reviews: M. E. Volpin and I. S. Kolomnikov, 'Organometallic Reactions,' Vol. 5, Wiley-Interscience, New York, 1975, pp. 313—386; I. S. Kolomnikov and M. Kh. Grigoryan, *Russ. Chem. Rev.*, 1978, **47**, 334; R. P. A. Sneeden, *L'Actualite Chimique*, 22nd February, 1979.
[2] J. A. Brivati, N. Keen, M. C. R. Symons, and P. A. Trevalian, *Proc. Chem. Soc., London*, 1961, 66.
[3] P. C. Mathur and O. P. Bansal, *J. Indian Chem. Soc.*, 1965, **42**, 863.
[4] A. J. Kalb and T. L. Allen, *J. Am. Chem. Soc.*, 1964, **86**, 5107.
[5] A. Bewick and G. P. Greener, *Tetrahedron Lett.*, 1969, 4623.
[6] S. Meshitsubra, M. Ichikawa, and K. Tamura, *J. Chem. Soc., Chem. Commun.*, 1974, 158.
[7] L. Paoloni, *Gazz. Chim. Ital.*, 1963, **93**, 1605.
[8] F. A. Henglein and H. Sontheimer, *Z. Anorg. Chem.*, 1952, **267**, 181.
[9] R. M. Miller, H. V. Knorr, H. J. Eichel, C. M. Meyer, and H. A. Tanner, *J. Org. Chem.*, 1962, **27**, 2646.
[10] V. A. Tushnalobova, V. A. Smirnov, and V. D. Semchenko, *Zh. Prikl. Khim.*, 1968, **41**, 275.
[11] V. A. Smirnov, V. D. Semchenko, D. P. Semchenko, and L. I. Andropov, *Zh. Prikl. Khim.*, 1967, **40**, 2345.
[12] C. H. Bamford and V. J. Robinson, *Polymer*, 1966, **7**, 573.
[13] N. Getoff, G. Scholes, and J. Weiss, *Tetrahedron Lett.*, 1960, 17.
[14] J. T. Allan, N. Getoff, H. D. Lehman, K. E. Nixon, G. Scholes, and N. Simic, *J. Inorg. Nucl. Chem.*, 1961, **19**, 204.
[15] N. Getoff, *Nature*, 1966, **211**, 408.
[16] M. Z. Hoffman and M. Simic, *Inorg. Chem.*, 1973, **12**, 2471.
[17] J. H. Lunsford and J. P. Jayne, *J. Phys. Chem.*, 1965, **69**, 2182.
[18] M. Pasquali, C. Floriani, A. Chiesi-Villa, and C. Guastini, *J. Am. Chem. Soc.*, 1979, **101**, 4740; M. Pasquali, C. Floriani, A. Chiesi-Villa, and C. Guastini, *Inorg. Chem.*, 1981, **20**, 349 and references therein.
[19] M. E. Jacox and D. E. Milligan, *Chem. Phys. Lett.*, 1974, **28**, 163.
[20] J. E. Bennett, S. C. Graham, and B. Mile, *Spectrochim. Acta*, 1973, **29A**, 375.
[21] K. O. Hartman and I. C. Hisatsune, *J. Chem. Phys.*, 1966, **44**, 1913.
[22] L. Andrews and G. C. Pimentel, *J. Chem. Phys.*, 1967, **47**, 2905.