The Chemistry of Metal Carbonato and Carbon Dioxide Complexes

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I. Introduction

A general review[1] of the chemistry of metal carbonato complexes appeared in the literature in 1969, and in the same year a detailed review devoted entirely to cobalt(III) complexes was also published.[2] Since this time the field has undergone tremendous growth, with abundant new data available on the physical properties of these compounds. Changes have occurred in how the mechanisms of metal carbonato formation reactions are perceived and the entire discipline of metal carbon dioxide complexes (organometallic chemistry) has virtually been created.[3] Certainly the environmental impact of the industrial CO_2 output and the growing shortage of strategic materials, and the problems associated with nuclear waste storage have led to a greater interest by environmental chemists, geochemists, oceanographers, and biologists in the applied aspects of metal carbonate chemistry.

In compiling the material for this presentation we have surveyed the literature in *Chemical Abstracts* from 1969 to 1981 and have attempted to include the most relevant publications appearing in 1982. In many cases it was found necessary to include data prior to 1969, although we have avoided duplicating material already covered by Krishnamurthy, Harris, and Sastri[1] where possible. As we cataloged in excess of 1400 references within this 11-year period, some of these studies that did not bear directly on the subject matter had to be deleted. For example, the role of CO_2 in the atmosphere will not be treated in this text.[4-10]

To break down briefly the sequence of topics treated here, we first deal with the physical properties, aqueous equilibria, and kinetics of CO_2(aq) and its hydrolysis products in order to provide some background for the subsequent sections. The metal carbonato complexes are then introduced by tabulating their preparative procedures, spectral characteristics, and X-ray crystallographic structures. As will be seen, a large number of natural minerals are included in the latter that could have otherwise been included in the later geochemical section. However, in keeping with our policy throughout the review, we have tried to centralize such material in the appropriate specific section to make comparisons easier and to avoid unnecessary duplication of discussion. Solid-state thermal reactions are then discussed in the light of their potential for producing certain carbonato complexes and with the intention of using the decomposition temperatures as rough fingerprints

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Donald A. Palmer received his B.Sc. and Ph.D. (1970) degrees from the School of Chemistry at the University of Western Australia. His Ph.D. work dealt with inorganic reaction kinetics in aprotic solvents and was supervised by Professor D. W. Watts. After 1 year at the Australian National University in the research group of the late Professor A. J. Parker, he joined Professor G. M. Harris as a postdoctorate at the State University of New York at Buffalo for 2 years. He then moved to the University of Frankfurt, F.R.G., where he became involved in studying the kinetics of inorganic reactions under high pressures in cooperation with Professor H. Kelm (1973–1979). He is currently a member of the staff of the Chemistry Division of ORNL and is concerned with basic studies of the thermodynamics and kinetics of aqueous solutions at high temperatures and pressures.

Rudi van Eldik was born (1945) in Amsterdam, Holland. His parents emigrated to South Africa (1952), where he received his B.Sc. (1966), M.Sc. (1968), and D.Sc. (1971) degrees from Potchefstroom University. He spent a year (1972) with Prof. Gordon M. Harris at SUNY at Buffalo (U.S.A.) after which he returned to Potchefstroom University as Senior Lecturer in Physical Chemistry. A fellowship from the Alexander von Humboldt Foundation enabled him to spend a year (1977) with Prof. Hartwig Kelm at the Institute for Physical Chemistry, University of Frankfurt (F.R.G.). During 1978 he was a Senior Research Associate of Prof. Gordon M. Harris (SUNY at Buffalo) after which he returned to Potchefstroom University (1979) as Professor of Chemistry. In the same year he was awarded the Raikes Medal by the South African Chemical Institute. He joined the staff of the University of Frankfurt in 1980 where he completed his Habilitation in Physical Chemistry in 1982. His research interests are in the general area of inorganic reaction mechanisms with special emphasis on the application of high pressure techniques in the study of fast reactions.

of such carbonato complexes. The equilibrium section serves mainly to list current values of stability constants, ion-pair formation constants and solubility data, and the related thermodynamic data, for metal carbonato complexes. The section on kinetics gives a detailed discussion of the individual modes of reaction with present-day concepts of the mechanisms involved in these processes and how the data for each type of reaction can be correlated. The relatively new field involving metal–carbon dioxide complexes is divided into three sections which describe the preparation and characterization of these species, followed by discussions of CO_2 fixation and insertion reactions, with again much of the data being presented in tabular form. Finally, the applied sections on geochemistry, oceanography, and biochemistry are not meant to provide researchers active in these areas with a comprehensive review of the literature, but rather to give research chemists an insight into some of the applied aspects and implications of carbonato metal chemistry in these areas.

There are still minor topics within this framework that are difficult to qualify precisely. It is hoped that a significant degree of cross referencing will help eleviate this problem. Furthermore, during the literature survey we discovered numerous papers that dealt with chemical systems in which CO_2 is produced as a product. Although such systems were not reported to involve the direct participation of metal carbonato or metal–CO_2 complexes, this possibility cannot be ruled out completely. Carbon dioxide is usually one of the main products during the thermal or photochemical oxidation of carboxylic acids in the presence of metal ions. Many papers describe the oxidation of oxalic acid and oxalate bound to metal centers.[11-15] The radical, CO_2^-, usually participates in such processes, and much chemistry has been developed around this species,[16] especially in cases where it is produced via the radiolysis of formic acid[17-23] and oxalate complexes.[24] Similarly, the uranyl-sensitized photolysis of carboxylic acids also produces CO_2 via the CO_2^- radical.[25-28] Alternative systems involve the application of photocatalytic, photosynthetic, or radiolytic techniques.[29-33] Reduction of CO_2 and subsequent reactions must also be considered during thermal and photochemical activation[34-36] and radiolysis.[37]

Finally, it is also the intention of this review to bring the large body of data on metal carbonato and metal carbon dioxide systems to the attention of other research workers who are concerned with other or closely related aspects of this general topic.

The Chemistry of Carbonates

II. Physical Properties of Carbonates

In this section we present a compact summary of the physical properties of CO_2, HCO_3^-, and CO_3^{2-}. This includes the various spectroscopic characterization data and electrochemical analytical methods; structural information; solubility in aqueous salt and mixed solvent solutions; thermodynamic data; miscellaneous physical properties; and thermal decomposition properties.

A. Spectroscopic Characterization

IR and Raman spectroscopy are among the methods adopted most commonly for the characterization of the different carbon dioxide/carbonate species. The CO_2 molecule ($D_{\infty h}$) in the gas phase has three normal vibrational modes,[38] the symmetric stretching mode ν_1, the bending mode ν_2, and the antisymmetric stretching mode ν_3. ν_1 is Raman active while ν_2 and ν_3 are infrared active and typical values are summarized in Table I. Information on the rotational structure of these bands for CO_2 gas has been published[39-43] and the pressure dependence up to 12 GPa has also been investigated.[38,44,45] It was found that the stretching modes stiffen and the bending mode softens with pressure.[38] Until recently, spectroscopy could not show the existence of H_2CO_3 molecules in aqueous solutions of CO_2.[46,47]

TABLE I. IR and Raman Spectra Data on CO_2

		frequencies, cm^{-1}				
phase	spectra	ν_1	ν_2	ν_3	comments	ref
gas	IR	1337	667	2349		70
				2326	studied up to 3.2 MPa	45
				2326		42
		1333	667	2349		38
	R	1388	1285^a		10-20 °C, 4.5 MPa	47
		1388, 1409	1265, 1285^a			46
		1390, 1411	1266, 1386^a		500 kPa	46
		1388	1286^a			*b*
aq soln	R	1381	1274^a		12-18 °C, 4-176 MPa	44
		1386-1388			−56-10 °C, 4.5 MPa	47
		1384	1280^a		in D_2O, 4.5 MPa	47
		1383	1274^a		in H_2O, 4.5 MPa	47
		1386, 1405	1279^a		in D_2O	46
		1384	1276^a		in H_2O	46
solid	IR, R	1352, 1347	660, 655	2354	0.6-12 GPa	38
			639		$^{13}C^{16}O_2$	38

[a] $2\nu_2$. [b] Fenner, W. R.; Hyatt, H. A.; Kellam, J. M.; Porto, S. P. S. *J. Opt. Soc. Am.* 1973, *63*, 173.

However, in a high temperature, high-pressure study, Kruse and Franck[48] recently reported a band at 1017 cm^{-1} in the Raman spectrum of a CO_2 solution and ascribed this to the C–OH stretching vibration of H_2CO_3.

In aqueous solution, carbonic acid deprotonates to produce HCO_3^- and CO_3^{2-} (see section III). In addition to the spectral information included as a comparison in section V, a number of studies have reported the IR and Raman bands of these species.[48-54] Note that in aqueous solution (H_2O and D_2O) the IR and Raman bands of the alkali metal carbonates (Li–Cs)[49] correspond closely to those observed in the solid state, D_{3h} point group, except that the ν_3 band is consistently split by ca. 55 cm^{-1} for which carbonate–water interaction is believed responsible. For example, in 2 M solutions bands are found at: 1060 (ν_1); 880 (ν_2); 1425 and 1370 cm^{-1} (ν_3) in the IR; 1066 (ν_1), 1435 and 1380 (ν_3), 686 cm^{-1} (ν_4) in the Raman spectrum. The Raman inactive band does appear at very high concentrations of >6 M at 880 cm^{-1}, in keeping with the general observation that all the peak intensities increase linearly with concentration. No splitting of the weak ν_4 band in the Raman spectra was observed, indicating that ion pairing is probably not substantial, despite the high concentrations of up to 8 M employed in this study.[49] The lack of any significant dependence of the spectra on the nature of the cation tends to support this view.

For the alkali metal bicarbonate salts in solution (H_2O and D_2O), again no positive evidence for ion-pair formation was observed[46,49] and the positions of the bands appeared independent of the nature of the metal ion. In accordance with the C_s symmetry for the HCO_3^- ion, the following assignments were made: 1630 R, 1620 IR (ν_2) asymmetric C–O stretch; 1360 R, 1355 IR (ν_3) symmetric C–O stretch; 1302 R, 1300 IR (ν_4) COH bend; 1017 R, 1000 IR (ν_5) C–OH stretch; 841 R, 840 IR (ν_8) CO_3 out-of-plane deformation; 672 R (ν_6) CO_2 bend; 632 cm^{-1} R (ν_7) (OH)CO bend.[46]

The UV absorption characteristics of CO_2(aq), HCO_3^-, and CO_3^{2-} form the basis of a spectrophotometric titration method.[55,56] A detailed review of the electronic spectra of CO_2 has also been published.[57] Additional spectroscopic characterization methods include: ^{13}C NMR,[54,58] ^{17}O NMR,[59] mass spectrometry,[60,61] EPR,[62] photoelectron emission spectroscopy,[63] and X-ray techniques.[64] A number of electrodes have been developed for the selective identification of carbonate species in solution.[65,68]

Structural studies[69] indicate that CO_2 is a symmetrical linear molecule with no dipole moment and a C–O distance of 1.159 Å. In the case of the carbonate ion, the distance is 1.32 Å and the bond angle 120°.[70] (See section VB.) In addition, a recent report[64] reviews the stereochemical aspects of 34 well-known carbonate groups.

B. Solubility Characteristics

The solubility of CO_2 in aqueous solutions depends strongly on the temperature and applied CO_2 pressure. Various research groups have studied solubility phenomena, and a summary of the most recent work is presented in Table II. In a quite recent review paper[71] it was demonstrated that the mole fraction (x) of dissolved CO_2 at 1 atm partial pressure of CO_2 can be expressed as

$$R \ln x = A + BT^{-1} + C \ln (T/K) + DT \qquad (1)$$

over the temperature range 273–353 K with $A = -1327.8$ J K^{-1} mol^{-1}, $B = 72611.6$ J mol^{-1}, $C = 179.99$ J K^{-1} mol^{-1}, and $D = -0.009159$ J K^{-2} mol^{-1} for water as solvent. The corresponding values for D_2O as solvent over the temperature range 298–353 °C are −1256.2, 71255.6, and 167.75 for A, B, and C, respectively. Malinin[72] developed a general equation for the salting out of CO_2 in aqueous solutions of NaCl and $CaCl_2$ over a wide temperature range (25–300 °C) and chloride concentration range (up to 5–7 M):

$$\log \frac{x^L_{CO_2}}{x^L_{CO_{2,s}}} = K^m_{sh}m + K_x \Delta x^L_{CO_2} + K_v(P - P_s{}^\circ) \qquad (2)$$

where K^m_{sh} = salting-out coefficient corrected for the activity of CO_2 in solution; $x^L_{CO_2}$ = solubility of CO_2 in the pure liquid phase (mole fraction); $x^L_{CO_{2,s}} = x^L_{CO_2}$ for the electrolyte solution; $\Delta x^L_{CO_2} = x^L_{CO_{2,s}} - x^L_{CO_2}$; P = overall pressure; $P_s{}^\circ$ = saturated vapor pressure of the electrolyte solution; and K_x, K_v = constants which are functions of temperature. Typical values for K^m_{sh}, K_x, and K_v are 0.07, 2.9, and 0.0, respectively, for the solubility of CO_2 in a 3 M NaCl solution at 150 °C.

TABLE II. Solubility Measurements of CO_2 in Aqueous Solution

authors	soln composition	temp range, °C	P_{CO_2} range, MPa	ref
Matous et al. (1969)	pure H_2O	30-80	0.1-4	*a*
Stewart and Mungal (1970)	pure H_2O, synthetic seawater	−5-25	1-4.5	*b*
Mungal and Stewart (1971)	pure H_2O, seawater	−5-25	0.1-4.5	*c*
Malinin and Savelyeva (1972)	0.4 M NaCl, 0.4-3.4 M $CaCl_2$	25-75	~5	*d*
Krestov and Nedelko (1972)	0.5-6 M various electrolytes	15-25	0.1	*e*
Malinin and Kurovskaya (1975)	0-6 M NaCl	25-150	~5	*f*
	1-6 M $CaCl_2$	100-150		
Yasunishi and Yoshida (1979)	16 electrolytes	15-35	~0.1	*g*
Sada and Yasunishi (1980)	7 binary salt solutions	25	~0.1	*h*
Sada et al. (1981)	molten alkali halides and nitrates	300-1000	0.1	*i*
Zawisza and Malesinska (1981)	pure H_2O	50-200	0.2-5.0	*j*
Drummond (1981)	0-6 M NaCl	50-400	3.0-15.0	118

[a] Matous, J.; Sobr, J.; Novak, J. P.; *J. Collect. Czech. Chem. Commun.* 1969, *34*, 3982. [b] Stewart, P. B.; Mungal, P. K. *J. Chem. Eng. Data* 1970, *15*, 67. [c] Mungal, P. B.; Stewart, P. B. *J. Chem. Eng. Data* 1971, *16*, 170. [d] Malinin, S. D.; Savelyeva, N. I. *Geokhimiya* 1972, 643. [e] Krestov, G. A.; Nedel'ko, B. E. *Tr. Ivanov. Khim.-Tekhnol. Inst.* 1972, 32. [f] Malinin, S. D.; Kurovskaya, N. A. *Geokhimya* 1975, 547. [g] Yasunishi, A. *Kenkyu Hokoku-Asahi Garasu Kogyo Gijutsu Shoreikai* 1980, *36*, 25; *Chem. Abstr.* 1982, *95*, 226522v. [h] Sada, E.; Yasunishi, A.; *Kenkyu Hokoku-Asahi Garasu Kogyo Gijutsu Shoreikai* 1980, *36*, 25; *Chem. Abstr.* 1982, *95*, 226522v. [i] Sada, E.; Katoh, S.; Yoshii, H.; Takemoto, I.; Shiomi, N. *J. Chem. Eng. Data* 1981, *26*, 279. [j] Zawisza, A.; Malesinska, B. *J. Chem. Eng. Data* 1981, *26*, 388.

TABLE III. Thermodynamic and Related Properties

substance	properties	temp range, °C	pressure range, MPa	ref
CO_2	ΔH_{sub}	−80 to −233	<0.1	*a*
	PVT	−50 to 1000	0.1-1000	80
	PVT	−50 to 50	<250	*b*
	PVT, γ	<500	<3000	*c*
	PVT	0 to 600	0-15	89
	PVT	0 to 1030	0.1-100	*d*
	$\Delta H_f°$, $S°$	25	0.1	81
	γ	450 to 800	0-50	*e*
	f	180 to 1030	0.1-1000	*f*
	f, G	50 to 1000	2.5-140	*g*
	C_p	0 to 6000	0.01-100	*h*
	C_p, H, G, S	0-1230, 600-5700, 5700-20 000		*i*
	vapor/liquid distribution const	100-340		521
$NaHCO_3$	C_p	25	0.1	108
	$\Delta H_f°$, $S°$	25	0.1	81
	γ	25	0.1	91, *j*
	γ, ϕ	25	0.1	84
Na_2CO_3	γ, ϕ	25	0.1	79
	γ	25	0.1	91
	$\Delta H_f°$, $S°$	25	0.1	81
	C_p	25	0.1	108
	C_p, a, ϕ, γ	25	0.1	82
K_2CO_3	γ, ϕ	25	0.1	83

[a] Angus, S.; Armstrong, B.; de Reuck, K. M. IUPAC International Thermodynamic Tables of the Fluid State Carbon Dioxide; Pergamon Press: New York, 1976; Vol. 3, p 3, 380. [b] Vasserman, A. A.; Golovskii, E. A.; Tsymarnyi, V. A. *Inzh.-Fiz. Zh.* 1971, *20*, 734. [c] Lentz, H.; Franck, E. U. "High Pressure Science and Technology"; Timmerhaus, K. D., Barber, M. S., Eds.; Plenum Press: New York, 1977; Vol. 1 p 539. [d] Altunin, V. V.; Gadetskii, O. G. *Tr. Mosk. Energ. Inst.* 1970, 3. [e] Greenwood, H. J. *Am. J. Sci.* 1973, *273*, 561. [f] Shmulovich, K. I.; Schmonov, V. M. *Geochem. Int.* 1975, 202. [g] Majumdar, A. J.; Roy, R. *Geochim, Cosmochim. Acta* 1956, *10*, 311. [h] Kessel'man, P. M.; Afanas'ev, M. M.; Bestukhev, A. S.; Blank, Yu. I.; Gorykin, S. F.; Kotlyarevskii, P. A.; Chernyshev, S. K.; Shchekatolina, S. A. *Teplo-Massoperenos, Dokl. Vses. Soveshch., 3rd* 1968, 7, 142; *Chem. Abstr.* 1971, *74*, 16343c. [i] Maslov, P. G. *Termodin, Termokhim. Konstanty* 1970, 235, *Chem. Abstr.* 1971, *74*, 16302p. [j] Pitzer, K. S.; Pelper, J. C. *J. Phys. Chem.* 1980, *84*, 2396.

The solubility of CO_2 has also been measured for aqueous solutions of ethanol,[73,74] propanol,[74,75] glycol,[76] glycerol,[76] 1,5-pentanediol,[76] ethylene carbonate,[77] ethylene oxide,[77] diethylene glycol,[76] ethanolamine;[76] binary mixed solvents including CCl_4, various alcohols, and formamide,[74] and a series of heavy hydrocarbons.[78] Finally the solubility of Na_2CO_3 in water at 25 °C was found to be 2.767 mol kg^{-1},[79] which is in good agreement with a series of values dating back as far as 1911.[79]

C. Thermodynamic and Related Properties

A variety of thermodynamic and related properties of CO_2, HCO_3^-, and CO_3^{2-} have been investigated. A summary of the most recent studies is given in Table III. These properties include heat of sublimation (ΔH_{sub}), heat of formation ($\Delta H_f°$), free energy (G), entropy (S), heat capacity (C_p), activity coefficient (γ), fugacity coefficient (f), and osmotic coefficient (ϕ). In this respect we would like to draw attention to a number of recent papers in which the mentioned properties are reviewed in detail.[80-84] Other properties that have been reported include diffusion coefficient,[74,85] thermal conductivity,[86] refractive index,[87] viscosity,[88] compressibility,[89,90] ion-pair formation,[91] thermal expansion coefficients in the solid state,[92] and critical properties.[93-95] Some of the important physical constants for

CO_2 can be summarized as follows:[95] molecular mass, 44.009 g mol^{-1}; ΔH_{sub} at 0 K, 26 250 J mol^{-1}; critical temperature, 304.21 K; critical pressure, 7.3825 MPa; critical density, 0.010 59 mol cm^{-3}; triple-point temperature, 216.58 K; triple-point pressure, 518.5 kPa.

The molar volume of $CO_2(g)$ has been determined in a number of ways as a function of temperature and pressure.[96–98] The partial molar volume of dissolved CO_2 was reported to vary between 31.3 and 37.6 cm^3 mol^{-1} at 25 °C.[99–106] The effect of temperature up to 400 °C and pressure up to 700 MPa on $\bar{V}(CO_2)$ has also been studied.[106,107] Similar data have been reported for the molar volumes of $NaHCO_3$, $KHCO_3$, Na_2CO_3, and K_2CO_3.[100,108,109]

D. Thermal Decomposition of CO_2

The thermal decomposition of CO_2 to CO and O has been studied by various groups.[110–112] Theoretical calculations[112] have predicted Arrhenius parameters for the dissociation and recombination of CO_2 up to 6000 K which are in good agreement with those measured experimentally.[110,111,113] Typical activation energies are 535 and 13 kJ mol^{-1} for the dissociation and recombination of CO_2 at 1500 K, respectively.[112] Lietzke and Mullins[114] described the thermal decomposition in terms of the following mechanism:

$$CO_2 \rightleftarrows CO + {}^1/_2O_2$$
$$2CO \rightleftarrows CO_2 + C$$
$$C + O_2 \rightleftarrows CO_2 \qquad (3)$$

The equilibrium constants were calculated over a wide range of temperature and pressure, using the relationship

$$\ln K_i = a_i/T + b_i + c_iT + d_iT^2 \qquad (4)$$

for which the various constants a_i, b_i, c_i, and d_i were reported.[114]

III. Carbonic Acid, Bicarbonate, and Carbonate Hydrolysis Equilibria

Equilibrium constants referred to here are in molality units unless stated otherwise.

A. Carbon Dioxide Dissolution Equilibria

Any consideration of the "carbonate" equilibria must deal with the Henry's law constants for the equilibration of gaseous CO_2 with $CO_2'(aq)$. We refer to $CO_2'(aq)$ as the total dissolved carbon dioxide which is the sum of $CO_2(aq)$ and H_2CO_3, but does not include the ionized forms, HCO_3^- and CO_3^{2-}. Thus, the solubility equilibrium can simply be represented by

$$CO_2(g) \xrightleftharpoons{K_s} CO_2'(aq) \qquad (5)$$

The numerous studies of this equilibrium have been thoroughly appraised by Berg and Vanderzee[115] who, in some cases, applied corrections to the reported constants, and arrived at a mean value for $K_s°$ of (0.034 16 ± 0.000 15) mol kg^{-1} atm^{-1} and a $\Delta\bar{H}_s° = -(19.74 \pm 0.17)$ kJ mol^{-1} at 25 °C and 101.325 kPa (1 atm). Note that Hu et al.[116] selected a $K_s°$ value of 0.034 16 mol dm^{-3} atm^{-1}. From their previous calorimetric measurements,[117] which should generally be more reliable, these same authors[115] calculated a remarkably similar value for $\Delta\bar{H}_s°$ of $-(19.75 \pm 0.17)$ kJ mol^{-1}. Moreover, Wilhelm et al.[71] earlier reviewed a narrower range of data and reported a value for $\Delta\bar{H}_s°$ of −19.79 kJ mol^{-1}. The maximum temperature considered in any of these treatments was about 80 °C. Drummond[118] has since extended the temperature range of these measurements to 400 °C using PVT methods.

The solubility of $CO_2(g)$ in seawater has been determined in terms of the apparent equilibrium constant, $K_s' = [CO_2'(aq)]/p_{CO_2}$, calculated[119] as a function of temperature and ionic strength using the data of Harned and Davis:[120]

$$pK_s' = -2385.73/T + 14.0184 - 0.0152642T + I(0.28596 - 6.167 \times 10^{-4}T) \qquad (6)$$

where the ionic strength of seawater can be represented as a function of chlorinity, Cl, by the equation

$$I = 0.00147 + 0.03592\ Cl + 6.8 \times 10^{-5}\ Cl^2 \qquad (7)$$

For comparison of K_s' values, correction may be needed depending on how the standard state for the original potentiometric measurements is defined.[119] Edmond and Gieskes also acknowledged the criticism[121] that seawater would have a different salting-out effect than those of pure NaCl solutions. This restriction notwithstanding, eq 6 represents a good first-order approximation of seawater.

B. Carbonic Acid Ionization

Although expressed as carbonic acid ionization, the majority of studies consider the first ionization constant in the following form:

$$CO_2'(aq) + H_2O \xrightleftharpoons{K_1} H^+ + HCO_3^- \qquad (8)$$

The distinction will be readdressed in the subsequent section on the kinetics of these processes where a consideration of the actual rate-determining step is critical to the elucidation of the reaction mechanism. Patterson and co-workers[122,123] determined the true ionization constant for H_2CO_3 by high field conductivity methods in accordance with eq 9. The $K_0°$ value at 25 °C was determined to be (1.72 ± 0.05) × 10^{-4} mol kg^{-1} {cf. 1.6 × 10^{-4} mol kg^{-1} evaluated at 25 °C and ca. 0.01 ionic strength by the pressure jump, conductometric technique;[124] and (2.5 ± 0.3) × 10^{-4} mol kg^{-1} at 0 °C in the presence of NaCl, by a flow thermoelectric method[125]}. Of the techniques mentioned, the conductivity method of Wissburn, French, and Patterson[122] must be considered as the most precise. They measured the temperature dependence of $K_0°$ over the range 5–45 °C and found a small trend in the values with a maximum at ca. 17 °C. This allowed them to calculate $\Delta\bar{H}°$ values which ranged from 2.4 kJ mol^{-1} at 0 °C to −3.7 kJ mol^{-1} at 37 °C. However, in the light of results presented later in this section,[126] if log $(K_0°/K_w°)$ is plotted against $1/T$, where $K_w°$ is the dissociation constant of water, a straight line results with a slope of (2.98 ± 0.04) × 10^3 and intercept of 0.25 ± 0.13 (correlation coefficient = 0.999 65). This is equivalent to writing eq 9 in the form:

$$H_2CO_3 \xrightleftharpoons{K_0} H^+ + HCO_3^- \qquad (9)$$

$$H_2CO_3 + OH^- \rightleftarrows HCO_3^- + H_2O \qquad (10)$$

As has been demonstrated by Patterson et al.,[126] this behavior is typical of acid and base dissociation equilibria. Thus, rearranging the equations into their anionic and cationic forms and thereby equalizing the charges on both sides of the equation, reduces $\Delta\bar{C}_p$ to ca. 0. This allows for a more exact linear extrapolation of the temperature dependence data.

This result may be applied to the equilibrium

$$CO_2(aq) + H_2O \xrightleftharpoons{K_H^\circ} H_2CO_3 \qquad (11)$$

which has been likened to a hydration reaction. The equilibrium constant can be determined from the quotient K_1°/K_0°. Thus, at 25 °C, $K_H^\circ = (4.48 \times 10^{-7})/(1.74 \times 10^{-4}) = 2.58 \times 10^{-3}$, while at 300 °C, $K_H^\circ = (3.18 \times 10^{-9})/(1.38 \times 10^{-3}) = 2.31 \times 10^{-3}$ (the values used for each numerator came from ref 126), so that despite the length of the extrapolation it is clear that K_H° varies only slightly with temperature as would be expected for a hydration reaction. This finding justifies the use of eq 8 to describe the overall behavior of $CO_2(aq) + H_2CO_3$ over a wide range of temperature. Raman spectroscopy[46,47,54] had confirmed that the only detectable species in such aqueous solutions at ambient conditions is the linear symmetrical CO_2 molecule. However, Kruse and Franck[48] have now reported a small band at 1017 cm^{-1} in the Raman spectrum of $CO_2'(aq)$ attributable to the C–OH stretching vibration of H_2CO_3 or HCO_3^-. This band was observed at <40 °C and up to 200 MPa, indicating about 2–3% H_2CO_3 was present at room temperature and 100 MPa. Bar and Sasson[58] reported an analysis of the ^{13}C NMR spectra of HCO_3^-/CO_3^{2-} solutions indicating the existence of both H_2CO_3 and dissolved CO_2 at virtually negligible levels at 31 °C. Abbott and co-workers[54] could not detect either species by this technique.

C. Aqueous Carbon Dioxide Ionization

Considerable attention has been paid to the exact measurements of K_1° at ambient conditions using mainly potentiometric techniques,[120,127-132] with perhaps the study of Harned and Davis[120] being the most noticeable. Berg and Vanderzee[115] combined three sets of emf data[120,130,131] to obtain the thermodynamic parameters for the hydrolysis of $CO_2(g)$ to form $H^+(aq)$ and $HCO_3^-(aq)$. This calculation depended on a knowledge of the standard enthalpy for the reaction

$$CO_2(g) + NaOH(aq) \rightleftarrows NaHCO_3(aq) \qquad (12)$$

i.e., $\Delta\bar{H}^\circ = -(66.40 \pm 0.14)$ kJ mol^{-1}, which was determined by calorimetry, as well as the standard enthalpy for the ionization of water $-(55.81 \pm 0.42)$ kJ mol^{-1}. Combination of these parameters resulted in a pK_1° value of 6.351 (cf. the model of Peiper and Pitzer,[133] $pK_1^\circ = 6.355$, which incorporated very recent emf measurements by Roy et al.[132] at high concentration levels), a $\Delta\bar{H}_1^\circ$ of 9.155 ± 0.063 kJ mol^{-1}, and $\Delta\bar{S}_1^\circ$ of $-(90.9 \pm 0.3)$ J K^{-1} mol^{-1} at 25 °C. Note that Millero[134] has since reanalyzed the data base and arrived at a similar value of $\Delta\bar{H}_1^\circ$ of 9.33 kJ mol^{-1}. The pK_1° value reported by Berg and Vanderzee is very close to the original values of Harned and Davis[120] (6.352) and MacInnes and Belcher[131] (6.343) who each used their own measured values of K_s°. Two sets of conductance measurements resulted in pK_1°'s of 6.365[102] and 6.382.[135] Slightly more recent conductance measurements,[136] which extended the conditions to 101.325 MPa and 300 °C, diverged substantially from the above parameters at 25 °C and 101.325 kPa, e.g., $pK_1^\circ = 6.37$, $\Delta\bar{H}_1^\circ = 6.78$ kJ mol^{-1}, and $\Delta\bar{S}_1^\circ = -382$ J K^{-1} mol^{-1}, and even greater discrepancies at 300 °C,[126] cast doubt on the validity of these results.[136]

TABLE IV. Partial Molar Volume Changes for the Dissociation of "Carbonic Acid" at 101.325 kPa

method	temp, °C	$-\Delta\bar{V}_1^\circ$, cm^3 mol^{-1}	ref
glass electrode	22.0	25.4 (buffered)	129
	22.0	25.5 (buffered)	*a*
	22.0	26.6 (unbuffered)	*a*
conductance	25.0	26.5 (27.7)[b]	138
	25.0	27.6	102
density	25.0	29.0	137

[a] Distèche, A.; Distèche, S. *J. Electrochem. Soc.*, 1965, *112*, 350. [b] Recalculated by Read[102] from Ellis's original data.[138]

The heat capacity data are based on the free-energy measurements, and therefore subjected to possible error as discussed later in this section. The original $\Delta\bar{C}_p^\circ$ value of Harned and Davis[120] is -374 J K^{-1} mol^{-1} compared to recent interpolated values of -377 J K^{-1} mol^{-1} [134] and -388 ± 27 J K^{-1} mol^{-1} [126] at 25 °C and 101.325 kPa.

The partial molal volume change associated with eq 8 has been determined by a number of methods, with again the preponderance involving emf measurements. The results summarized in Table IV are generally in good agreement, except for the early density measurements of Owen and Brinkley.[137] The observation by Ellis[138] that $\Delta\bar{V}_1$ increases with increasing pressure ($\Delta\bar{V}_1^\circ = -20.7$ cm^3 mol^{-1} at 303.975 MPa and 25 °C) was substantiated by Read.[102] However, Read[102] investigated the temperature dependence of K_1° over a much larger temperature range of 25.0–250.1 °C and found that $\Delta\bar{V}_1^\circ$ *decreases* markedly with increasing temperature at constant pressure ($\Delta\bar{V}_1^\circ = -88$ cm^3 mol^{-1} at 250 °C and 303.975 MPa), so that obviously no evidence for a maximum as suggested by Ellis[138] was observed. Typical of other weak acids and bases, such as acetic acid,[139] a linear relationship exists between $\Delta\bar{V}_1^\circ$ and $\Delta\chi_1^\circ$, the standard partial molar compressibility change, at constant pressure up to 250 °C, and the slopes of these isobars become less with increasing pressure.[102] Contributing somewhat to this temperature dependence of $\Delta\bar{V}_1^\circ$, the partial molar volume of $CO_2'(aq)$ was calculated to increase from 34.3 (33.2[101]) to 47.4 cm^3 mol^{-1} over the range 25–200 °C.[102] Note, however, that literature values for $\bar{V}^\circ$ ($CO_2(aq)$) at 25 °C vary sharply. Millero and Berner[140] proposed that $\bar{V}^\circ(H_2CO_3) = \bar{V}^\circ(CO_2(aq)) = 31.3$ cm^3 mol^{-1}.

The discussion of reaction 8 has been limited to this point to results extrapolated to infinite dilution. Patterson et al.[126] recently reported the results of a potentiometric study of this reaction in NaCl media, up to 5 *m*, and to temperatures of 300 °C at the saturated vapor pressures of these solutions. These data are of more practical interest. Two sets of equations were presented to model these data as well as the results of some previous research.[102,117,130,131,138] Both models have in common a Bronsted–Guggenheim expression for ionic activity coefficients to calculate the activity coefficient quotient for eq 8. The difference in the two models is that one is based on the expression

$$\partial^2 \ln K/(\partial T \partial(1/T))p_{sat} = a_1 + a_2 T + a_3/T^2 \qquad (13)$$

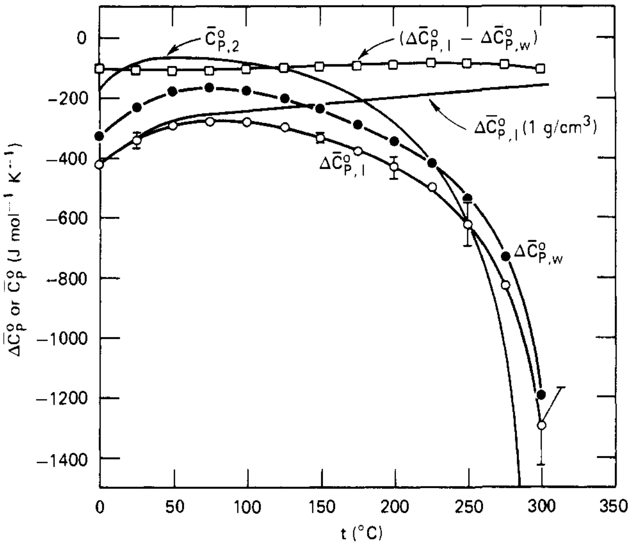


Figure 1. Heat capacity functions at infinite dilution along the saturation vapor pressure curve and at unit density: $\Delta\bar{C}_{p,1}°$, the change in heat capacity for the first ionization of aqueous carbon dioxide; $\Delta\bar{C}_{p,w}°$, the change in heat capacity for the ionization of water; $\bar{C}_{p,2}°$, the partial molar heat capacity of sodium chloride in water. Reprinted with permission from ref 126. Copyright 1982, Pergamon Press Ltd.

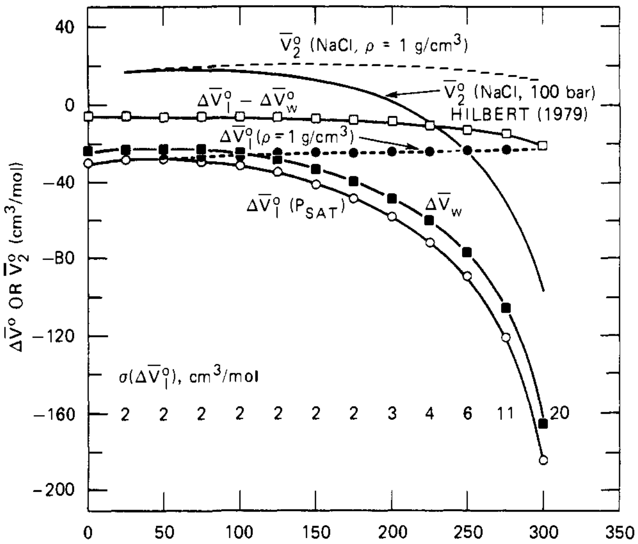


Figure 2. Volume functions along the saturation vapor pressure curve and at unit density; subscripts as in Figure 1. Uncertainties (3σ) are shown by the row of numbers across the figure. Reprinted with permission from ref 126. Copyright 1982, Pergamon Press Ltd.

whereas the basic assumption in the other involves the partial molal volumes of ions

$$\bar{V}_1° = b_{1,i} - b_{2,i}\beta + b_{3,i}\bar{V}_w° \qquad (14)$$

where β is the compressibility coefficient and $\bar{V}_w°$ is the molar volume of water. As a check of the models, the $\Delta\bar{H}_1°$ value obtained from an analysis of all these data is 9.06 ± 0.12 kJ mol^{-1} at 25 °C, which compares favorably with the value of Berg and Vanderzee[115] shown above. As alluded to earlier in this section, the values of $\Delta\bar{C}_p°$ and $\Delta\bar{V}_1°$ decrease dramatically as the temperature approaches 300 °C along the saturation vapor pressure curve. This behavior, which is illustrated in Figures 1 and 2, was said to stem from the temperature dependencies of the first and second derivatives of the dielectric constant of water with respect to T.[126] In keeping with this explanation, the heat capacity and volume changes were virtually constant over the same temperature range when calculated at unit density. Alternatively, when eq 8 is written in its anionic form

$$CO_2'(aq) + OH^- \rightleftarrows HCO_3^- \qquad (15)$$

which essentially removes the contributions to $\Delta\bar{C}_p°$ and $\Delta\bar{V}_1°$ from the ionization of water, both parameters are substantially less dependent on temperature and salt concentration. In fact, $\Delta\bar{C}_p \simeq -100$ J K^{-1} mol^{-1} over the entire range, while $\Delta\bar{V} \simeq -7$ cm^3 mol^{-1} up to 100 °C, then decreases to −20 cm^3 mol^{-1} at $I = 0$ and 300 °C, and to −60 cm^3 mol^{-1} at 5 m at 300 °C. The authors[126] tabulate the parameters of log K_1, $\Delta\bar{G}_1$, $\Delta\bar{H}_1$, $\Delta\bar{S}_1$, $\Delta\bar{C}_p$, and $\Delta\bar{V}_1$, based on model I, at 25 °C intervals over the range 0–300 °C, at ionic strengths of 0, 0.1, 0.5, 1.0, 3.0, and 5.0. The immediate conclusion of this work is that "carbonic acid" becomes weaker with increasing temperature and decreasing pressure or salt concentration.

A further practical aspect of eq 8 concerns the role played by this reaction in seawater. Potentiometric studies[121,129,141-144] have dealt with this problem directly. For comparison, $I = 0.75$ (NaCl), which corresponds approximately to the ionic strength of seawater at a chlorinity of 20.0‰, Distèche and Distèche[129] reported a pK_1^c of 5.995 at 22 °C and 101.325 kPa (K_1^c, concentrations in units of molarity). In natural seawater, the effects of the divalent ions Mg^{2+}, Ca^{2+}, and SO_4^{2-} must be considered as well as the additional buffering capacity of boric acid. Millero[134] treats the additional complication of the different standards used to calibrate the pH electrodes, namely the NBS and Tris pH scales, with the latter preferred by Hansson[143] as it maintains a continuity of medium because the standardizing buffer solution is made up in seawater. Millero[134] concluded in favor of the NBS system. An apparent dissociation constant, K_1', is defined as $a_{H^+}[HCO_3^-]_{total}/[CO_2'(aq)]_{total}$, where [ ] refers to concentrations in molarity units. Some typical values of pK_1' at 25 °C, atmospheric pressure, and 20‰ chlorinity are: 5.93,[143] 6.000,[141] 6.06,[144] 6.08,[121] and 6.00 (22 °C),[129] where the first value was measured on the Tris scale which indeed reads lower (e.g., 25 °C and Cl = 19.4‰, ΔpH = 0.144).[134] At 100 MPa, Cl = 20‰ and 22 °C, pK_1' = 5.663[129] so that it is clear that increasing chlorinity[143] and pressure cause "carbonic acid" to become a stronger acid in seawater, thus complying with the behavior in "pure" water. However, over the narrow temperature range investigated (5–35 °C), which is of relevance to the seawater system, *increasing* temperature increases the strength of "carbonic acid" in seawater.

On a more quantitative basis, Edmond and Gieskes[119] combined earlier results[121,129,130,144] in the following empirical equation using the temperature dependence established for $K_1°$.[130]

$$pK_1' = 3404.71/T + 0.032786T - 14.7122 - 0.19178Cl^{1/3} \qquad (16)$$

Millero[134] used a somewhat different equation to fit previous data over the range 0–50 °C and 0 ≤ Sl ≤ 40‰ with the generalized equation

$$\ln K_1' - \ln K_w = (a_0 + a_1/T + a_2 \ln T)Sl^{1/2} + b_0Cl \qquad (17)$$

where a_0, a_1, a_2, and b_0 are constants ($a_2 = 0$ in this case), and $\ln K_w$ is determined from a similar equation, and Sl is the salinity of the seawater and is equivalent to 1.806 55 (Cl ‰).

A general equation[145] to rigorously describe the pressure dependence of K_1' in seawater is

$$\ln (K_i^p/K_i^0) = -(\Delta\bar{V}_i/RT)P + (0.5\Delta\bar{\kappa}_1/RT)P^2 \quad (18)$$

where $\Delta\bar{V}_i$ and $\Delta\bar{\kappa}_i$ are the changes in the volumes and compressibilities for ionization. The values of $\Delta\bar{V}_1'$ and $\Delta\bar{\kappa}_1'$ are obtained from the following:

$$-\Delta\bar{V}_1' = 25.50 + 0.151(\mathrm{Sl} - 34.8) - 0.1271t \quad (19)$$

$$-10^3\Delta\bar{\kappa}_1' = 3.08 + 0.578(\mathrm{Sl} - 34.8) - 0.0877t \quad (20)$$

At $t = 25$ °C and Cl = 19.26‰, $\Delta\bar{V}_1' = -22.3$ cm^3 mol^{-1} and $\Delta\bar{\kappa}_1' = 9 \times 10^{-4}$ cm^3 mol^{-1} atm^{-1}. Based on the partial molal volumes of the individual species,[140] $\Delta\bar{V}_1 = -21.7$ cm^3 mol^{-1}, which assumes $\bar{V}\{\mathrm{H^+(aq)}\} = -3.7$ cm^3 mol^{-1}, $\bar{V}\{\mathrm{CO_2'(aq)}\} = 31.3$ cm^3 mol^{-1}. By ignoring the effects of change in salinity and by considering the solvated species to be incompressible, a simple expression for $\Delta\bar{V}_1$ can be presented, viz.[119]

$$\Delta\bar{V}_1' = -(24.2 - 0.085t) \quad (21)$$

which at $t = 25$ °C results in a $\Delta\bar{V}_1' = -22.1$ cm^3 mol^{-1}. Note eq 19 gives a value of -20.1 cm^3 mol^{-1} at the lower chlorinity of 11.1‰, so that eq 21 represents at least a good first-order approximation of $\Delta\bar{V}_1'$. These values appear preferable to -18.8 cm^3 mol^{-1} derived[119,140] from the pressure study of Distèche and Distèche[129] at Cl = 20‰ and 22 °C.

It is often assumed that divalent metal ions can form ion pairs with carbonate ions at ambient conditions, an assumption of particular importance in modeling seawater equilibria. However, their existence and more particularly those of alkali metal carbonate and bicarbonate ion pairs under these conditions is disputable. Nevertheless, Nakayama[127,146] recalculated the original results of Harned and Davis[120] by allowing for the formation of $\mathrm{NaHCO_3^0}$ ion pairs in the mass and charge balance equations. The pK_1 value was only slightly affected (6.356 at 25 °C) and, as expected, the association constant proved to be very small, viz. 1.5 ± 0.2. Independent potentiometric measurements by Butler and Huston[91] gave similarly small values for the formation of $\mathrm{NaHCO_3^0}$ ion pairs of 0.5 and 0.8. Although, as these authors[91] point out, these data can be equally well or better fitted to the conventional model which does not include ion pairs. This important, general statement is appropriate to all the ion pairs at ambient conditions discussed here, such that until a more precise solution theory is developed to prove otherwise, such apparent effects are better described by conventional activity coefficients of the individual ionic species.

D. Bicarbonate Ion Ionization

The most generally accepted[115,147] equilibrium constant for this reaction (eq 22) was determined potentiometrically by Harned and Scholes[148] to be 4.69×10^{-11} (4.60×10^{-11}[133] and 4.68×10^{-11}[134]) at 25 °C and atmospheric pressure. This is reasonably close to previous work of MacInnes and Belcher[131] who reported a value of 5.61×10^{-11} for the potassium rather than the sodium salt, but in the main their values over the temperature range 0–50 °C are lower than previously reported. However, there is excellent agreement with the conductivity data of Ryzhenko,[135] $K_2° = 4.70 \times 10^{-11}$. Again a recalculation of Harned's value[148] by Nakayama[127,146] led to an ion-pair association constant for $\mathrm{NaCO_3^-}$ of 3.6 which compares to 8 ± 2 derived by Butler and Huston.[91]

$$\mathrm{HCO_3^-} \overset{K_2}{\rightleftharpoons} \mathrm{H^+} + \mathrm{CO_3^{2-}} \quad (22)$$

It is noteworthy that Plummer and Busenberg[149] have also reevaluated the data for $K_s°$, $K_1°$, and $K_2°$ and report these values in the general form

$$\log K° = A + BT + C/T + D \log T + E/T^2 \quad (23)$$

and claim validity for this expression to 250 °C at the appropriate vapor pressure for water. They also derived similar expressions for the association constants of the ion pairs $\mathrm{CaHCO_3^+}$ and $\mathrm{CaCO_3^0}$ as a function of pressure, except that $E = 0$ in these equations (see section VII for more details), but again these values are too small to definitely establish their existence.

Berg and Vanderzee[115,117] recorded a standard enthalpy of ionization of (14.70 ± 0.10) kJ mol^{-1} with a corresponding entropy of -148.4 ± 0.4 J K^{-1} mol^{-1} at 25 °C and 101.325 kPa. Millero's[134] treatment of the earlier data[148] yielded 15.1 kJ mol^{-1} for $\Delta\bar{H}_2°$.

Flow calorimetric measurements by Larson and coworkers[147] were used to derive a $\Delta\bar{C}_p°$ value of -247 ± 8 J K^{-1} mol^{-1} at 25 °C. Earlier estimates were based on the double differentiation of $\log K = f(T)$ with respect to T by Harned and Scholes[148] and others,[134] resulting in a range of values, -272,[148] -280, and -213 J K^{-1} mol^{-1}.[134] However, the latter method can give rise to large uncertainties in $\Delta\bar{C}_p$ in those cases where the parameters in the equation of $\log K = f(T)$ are strongly correlated.[150,151] Therefore, the calorimetric measurements are intrinsically more reliable. Larson et al.[147] recalculated the results of a previous calorimetric study of Perron, Desnoyers, and Millero[108] to obtain a corrected $\Delta\bar{C}_p°$ of -249 J K^{-1} mol^{-1}.

Larson, Zeeb, and Hepler[147] measured a $\Delta\bar{V}_2°$ at 25 °C of $-(29.2 \pm 1.2)$ cm^3 mol^{-1} from density measurements of $\mathrm{NaHCO_3/Na_2CO_3}$ buffers. Much earlier less negative values of 27.7 and 25.6 cm^3 mol^{-1} were reported from density[152] and potentiometric methods.[129] The partial molar volumes reported for $\mathrm{NaHCO_3}$ and $\mathrm{Na_2CO_3}$ would result in a $\Delta\bar{V}_2° = -28.4$ cm^3 mol^{-1} assuming $\bar{V}°\{\mathrm{H^+(aq)}\} = 0$ and $\bar{V}°\{\mathrm{Na^+(aq)}\} = -1.2$ cm^3 mol^{-1}. In summary, Larson et al.[147] combined their results with selected values in the literature[108] to give preferred values of $\Delta\bar{C}_p° = -250$ J K^{-1} mol^{-1} and $\Delta\bar{V}_2° = -28.7$ cm^3 mol^{-1} at 25 °C and 101.325 kPa. Their experimental values for the individual ions are: $\phi_c° = -55$ $\{\mathrm{HCO_3^-(aq)}\}$ and -302 J K^{-1} mol^{-1} $\{\mathrm{CO_3^{2-}(aq)}\}$; and $\phi_v° = 24.8$ and -4.4 cm^3 mol^{-1}, respectively, based on the assumption $\phi°$ $\{\mathrm{H^+(aq)}\} = 0$.

Potentiometric measurements of the dissociation of $\mathrm{DCO_3^-}$ in $\mathrm{D_2O}$ over the range 5–50 °C led to the constants shown in Table V.[153] The preferred parameters for eq 22 are also listed for comparison. It is interesting that in comparison with other acids such as acetic, acetic-d_3, and $\mathrm{H_2PO_4^-}$ the differences in $\Delta\bar{S}°$ ($\mathrm{D_2O}$) $-$ $\Delta\bar{S}°$ ($\mathrm{H_2O}$) and $\Delta\bar{C}_p°$ ($\mathrm{D_2O}$) $-$ $\Delta\bar{C}_p°$ ($\mathrm{H_2O}$) are all small and the values are equal within the experimental un-

TABLE V. Comparison of the Standard Thermodynamic Constants for the Dissociation of HCO_3- in water and DCO_3- in Deuterium Oxide[153] at 25 °C and 101.325 kPa

constant	HCO_3-	DCO_3-
pK_2°	10.329	11.076 (11.00,[a] 10.85[b])
$\Delta\overline{H}_2^\circ$ (kJ mol^{-1})	14.70	17.62 ± 0.03
$\Delta\overline{S}_2^\circ$ (J K^{-1} mol^{-1})	−148.4	−153.0 ± 0.1
$\Delta\overline{C}_p^\circ$ (J K^{-1} mol^{-1})	−250	−257 ± 4
$\Delta\overline{V}_2^\circ$ (cm^3 mol^{-1})	−28.7	

[a] Glasoe, P. K.; Schaleger, L. L.; Long, F. A. *J. Am. Chem. Soc.* 1964, *86*, 1. [b] Curry, J.; Hugus, Z. Z. *J. Am. Chem. Soc.* 1944, *66*, 653.

certainties. The equivalent term for $\Delta\bar{H}^\circ$ is considerably greater than HCO_3^-.

Empirical equations were again proposed by Edmond and Gieskes,[119] and Millero[134] to quantify these relationships. The former equation is as follows:

$$pK_2' = 2902.39/T + 0.02379T - 6.4710 - 0.4693Cl^{1/3} \quad (24)$$

while Millero's equation again takes the form of eq 17 with $a_2 = 0$. Mehrbach and co-workers[141] have proposed a much more elaborate equation involving the independent variables T and Sl, leading to a pK_2' value of 9.115 at 25 °C and Sl = 35‰.

The partial molar volume changes are also calculated in the same two ways described for carbonic acid, viz.[119,134]

$$\Delta\bar{V}_2' = -(16.4 - 0.04t) \quad (25)$$

$$-\Delta\bar{V}_2' = 15.82 - 0.321(\mathrm{Sl} - 334.8) + 0.0219t \quad (26)$$

Thus, at 25 °C and Sl = 35‰, $\Delta\bar{V}_2' = -15.4$ cm^3 mol^{-1} [119] and −16.4 cm^3 mol^{-1}.[134] From partial molal volume data of the individual ions, $\Delta\bar{V}_2' = -15.9$ cm^3 mol^{-1},[140] assuming $\bar{V}_2\{CO_3^{2-}(aq)\} = 19.2$ cm^3 mol^{-1}.[134] These values are in marked disagreement with the $\Delta\bar{V}_2'$ value of −10.8 cm^3 mol^{-1} at 22 °C and Sl = 35‰. Note also that eq 25 and 26 predict opposite temperature effects, but the absolute changes are small in both cases, i.e., ≤0.8 cm^3 mol^{-1} for 15–35 °C. The dominant effect is the salinity; thus, at lower values, i.e., Sl = 20‰, $\Delta\bar{V}_2'$ according to eq 26 becomes −21.1 cm^3 mol^{-1} at 25 °C leading to larger discrepancies between eq 25 and 26.

E. Isotopic Exchange Equilibria

These equilibria have been represented by Oliver and Davis[49] as follows:

$$H_2O + D_2O \overset{K_3}{\rightleftharpoons} 2HOD$$

$$HCO_3^- + D_2O \overset{K_4}{\rightleftharpoons} DCO_3^- + HOD$$

$$HCO_3^- + HOD \overset{K_5}{\rightleftharpoons} DCO_3^- + H_2O \quad (27)$$

They used Raman spectroscopy to monitor the 1017-cm^{-1} band associated with HCO_3^- and then obtained a quantitative measure of the DCO_3^- concentration after subtracting the HCO_3^- contribution from the band centered at 1030 cm^{-1}, which is attributable to DCO_3^-. From the known value for K_3 of 3.8 at 25 °C, values for K_4 and K_5 were estimated at 1.9 ± 0.2 and 0.50 ± 0.05, respectively, for 1 M $NaHCO_3$ solutions. Similar values were obtained for 2.9 M $KHCO_3$ solutions.

IV. Kinetics of Carbon Dioxide Hydrolysis and Carbonic Acid Dehydration

The rates of the reactions within this system have been studied extensively by many researchers using a wide variety of techniques.[69,154,155] The history of these endeavors up until 1960 has been particularly well documented by Kern,[154] who gave a critical evaluation of the experimental methods. The inordinate depth of these kinetic data is primarily due to their importance in biological and environmental sciences, and partially to the fact that they are convenient for examining new rapid-response techniques and improvisations. Note that the biological aspects of these reactions, involving mainly enzyme catalysis, are discussed in section XIII.

The following set of equations adequately describes the entire "uncatalyzed" system:

$$CO_2(aq) + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2CO_3 \quad (28)$$

$$CO_2(aq) + OH^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} HCO_3^- \quad (29)$$

$$CO_2(aq) + CO_3^{2-} + H_2O \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} 2HCO_3^- \quad (30)$$

$$H_2CO_3 \overset{K_0}{\rightleftharpoons} HCO_3^- + H^+ \quad (31)$$

$$HCO_3^- \overset{K_2}{\rightleftharpoons} CO_3^{2-} + H^+ \quad (32)$$

Below a pH of ca. 7.4, coincidentally the pH of blood, eq 28 and 31 dominate. Indeed, carbonic acid never represents more than 1% of the total dissolved CO_2 because $k_{-1} >> k_1$. In addition, calculations based on Coulombic interactions for diffusion-controlled processes yield[156] a value for the rate of protonation of HCO_3^- of ca. 6.5×10^{10} M^{-1} s^{-1}, in good agreement with the value reported by Eigen[157] of 4.7×10^{10} M^{-1} s^{-1} which he obtained from an electrical-jump relaxation technique. This emphasizes the speed of reaction 31, and by inference eq 32, and permits the estimation of the rate constant for the protolytic dissociation of carbonic acid (1.5×10^7 s^{-1}) when coupled with the value of K_0. Thus H_2CO_3 acts as an intermediate in the net reaction

$$CO_2(aq) + H_2O \overset{K_1}{\rightleftharpoons} HCO_3^- + H^+ \quad (33)$$

with K_1 being referred to as the "apparent" acid dissociation constant.

Kern[154] has cataloged the problems in the interpretation of the pioneer work in this field and declared that it was not until the meticulous study of Faurholt[158] in 1924 that a meaningful value for k_{-1} was reported. A summary of the subsequent rate data is given in Table VI.

Of the principal methods utilized, spectrophotometric measurements invariably involved the use of indicators to transpose the change in pH associated with reaction 33 into a spectral signal. Conductivity provides a direct response to the decrease in charge accompanying reaction 33. It is significant that the applicability of oxygen-exchange studies relies on the slow rate of oxygen exchange between either HCO_3^- or CO_3^{2-} with

TABLE VI. Summary of Kinetic Data for the Dehydration of Carbonic Acid at 25 °C

year	k_{-1}, s^{-1}	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J K^{-1} mol^{-1}	method	ref
1924	29.3[a,b]			quenching	158
1927	17.4[b]			H_2-electrode and conductometric	*c*
1933	21.7			manometric and spectrophotometric	*d*
1941	27.1[b]	68.1	11	flow thermometric	125
1953	24.4[b]	68.2	10	flow spectrophotometric	*e*
1957	24.4[a]	68.2	10	stopped-flow glass electrode	*f*
1958	23.0[b]	62.9	−8	flow spectrophotometric	*g*
1961	15.1			temperature-jump spectrophotometric	*h*
1969	22.2			stopped-flow calorimetric	*i*
1970	27.9[b]	60.8	−13	stopped-flow spectrophotometric	*j*
1972	16.7			stopped-flow spectrophotometric	*k*
1973	22.1	52.7	−42	concentration-jump spectrophotometric	155
1973	29.4	51.4	−46	pressure-jump conductometric	155
1973	21.0	55.2	−35	stopped-flow spectrophotometric	155
1978	12.4[l]			rapid mixing-pH statt	161
1979	25.1	73.4	28	stopped-flow spectrophotometric	*m*
1980	28.0			pressure-jump conductometric	156
1981	25.7[n]			stopped-flow calorimetric	*o*
1982	18.7			stopped-flow spectrophotometric	163

[a] Corrected by the factor 2.3 as described.[154] [b] Interpolated from the temperature dependence of k_{-1}. [c] Saal, R. N. J. *Recl. Trav. Chim. Pay-Bas* 1928, *47*, 264. [d] Brinkman, R.; Margaria, R.; Roughton, F. J. W. *Philos. Trans. Soc. London* 1933, *A232*, 65. [e] Dalziel, K. *Biochem. J.* 1953, *55*, 79. [f] Sirs, J. A. *Trans. Faraday Soc.* 1958, *54*, 207. [g] Scheurer, P. G.; Brownell, R. M.; Lu Valle, J. E. *J. Phys. Chem.* 1958, *62*, 809. [h] Eigen, M.; Kustin, K.; Maass, G. *Z. Phys. Chem. (Wiesbaden)* 1961, *30*, 130. [i] Balko, B.; Berger, R. L.; Friauf, W. *Anal. Chem.* 1969, *41*, 1506. [j] Soerensen P. E.; Jensen, A. *Acta. Chem. Scand.* 1970, *24*, 1483. [k] Lal, L. C.; Maren, T. H. *Biochim. Biophys. Acta.* 1972, *261*, 70. [l] Calculated by assuming $K_1 = 2.49 \times 10^{-4}$ at 25 °C,[122] corrected to an ionic strength of 0.1. [m] Morelli, B. *Anal. Chim. Acta.* 1979, *106*, 73. [n] 24 °C. [o] Balko, B.; Bowen, P.; Berger, R. L. *J. Biochem. Biophys. Methods* 1981, *4*, 1.

TABLE VII. Summary of Kinetic Data for the "Acid" Hydrolysis of CO_2 at 25 °C and $I = 0$

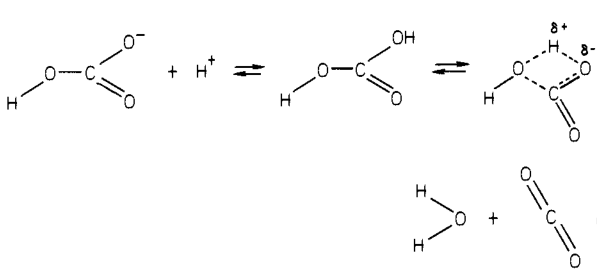
year	$10^2 k_1$, s^{-1}	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J K^{-1} mol^{-1}	method	ref
1940	2.75	67.9	−46	^{13}C and ^{18}O exchange	*a*
1951/1956	2.57	61.1[b]	−71[b]	manometric	165, 166
1967	2.70[c]	71.1[c]	−36[c]	^{18}O exchange	159
1969	3.13[d]	67.8	−46	^{18}O exchange	167
1969	5.00[b]			manometric	173
1977	2.6[e]			quenching, titration	162
1982	3.7			pH statt	558

[a] Mills, G. A; Urey, H. C. *J. Am. Chem. Soc.* 1940, *62*, 1019. [b] Recalculation[166] of original results[165] led to $\Delta H^{\ddagger}$ being temperature dependent with the resulting empirical equation: $\log k_1 = 329.85 - 110.541 \ln T - 17265.4/T$; cf. $\log k_1 = 195.3 - 63.590 \ln T - 11715.8/T$.[173] [c] $I = 1.5$ M. [d] Interpolated to 25 °C. [e] $I = 1.0$ M.

water, such that the rate of hydrolysis through CO_2 is rate-determining. Manometric methods take advantage of the rapid transfer of $CO_2(gas) \rightleftarrows CO_2(aq)$ from well-stirred solutions to provide a discernible pressure change during the reaction. Considering the diversity of techniques and their degrees of sophistication, the agreement between the k_{-1} values in Table VI is quite remarkable. This comparison can be more freely made with the knowledge that k_{-1} is relatively insensitive to variations in ionic strength, as demonstrated by Atkinson et al.[155] for ionic strengths from 5×10^{-3} to 3 M NaCl or NaBr, for which $\Delta G^{\ddagger}$ remained constant at ca. 66 kJ mol^{-1}. A fit of the combined data in Table VI gave the activation parameters, $\Delta H^{\ddagger} = 60.7 \pm 1.8$ kJ mol^{-1} and $\Delta S^{\ddagger} = -15 \pm 6$ J K^{-1} mol^{-1}, while k_{-1} at 25 °C was interpolated at 23.7 s^{-1}.

In the majority of cases, the hydration rate constant, k_1, was determined from the relationship $k_1 = k_{-1}K_H$, where K_H is the hydrolysis equilibrium constant (28). A typical K_H value at 25 °C and zero ionic strength is 2.6×10^{-3},[122] leading to an average value of k_1 of 6.2×10^{-2} s^{-1} under these conditions. However, there are three examples where hydration was studied directly, and these data are shown in Table VII. In contrast to dehydration, hydration rate constants are greatly affected by variations in ionic strength,[155,159] despite the fact that the reactants are neutral species. The combined data[155,159] show an approximate linear decrease in k_1 with increasing ionic strength over the range 0.005 to 3.0 M, with the relationship being: $k_1 = \{-(8 \pm 3) \times 10^{-3} I + (3.9 \pm 0.5) \times 10^{-2}\}$ s^{-1}. As will be shown for k_2, the ionic strength effect remains somewhat controversial as Dennard and Williams[160] observed no change in k_1 at 0 °C within an overall uncertainty of ± 4.7% up to $I = 1$ M (KCl) at different pH values. The rate of CO_2 hydration has been compared to the hydration rates of some carbonyl compounds and shown to be not only slower, but also not strongly acid catalyzed. These effects were attributed to the unique linear structure of the CO_2 molecule.

On a mechanistic level, the dehydration (dehydrolysis, decarboxylation, or decomposition) rate of HCO_3^- in H_2O and D_2O at 25 °C was compared with the corresponding reaction of the alkyl carbonates, $CH_3OCO_2^-$, $C_2H_5OCO_2^-$, and *sec*-$C_4H_9OCO_2^-$, based on pH-statt data.[161] For the acid-catalyzed reaction analogous to reaction 33, $k_{-1}(H_3O^+)/k_{-1}(D_3O^+)$ averaged 0.6[161,162] which, when coupled with the observed acid-catalysis effect, implied a mechanism intermediate between a preequilibrium proton transfer and the other extreme of a rate-determining proton-transfer step. Therefore, the mechanistic form of eq 33 becomes



(34)

where H would be replaced by an alkyl group in the case of the alkyl carbonates.

A study[163] of the effect of pressure on k_{-1} yielded an activation volume of +6.4 ± 0.4 cm^3 mol^{-1} (25 °C and $I = 0.5$ M). This is considered as direct evidence for a dissociative mechanism with the volume increase mainly reflecting the elongation of the C–O bond as shown in eq 34. When an interpolated value for $\Delta\bar{V}$ (eq 28) of −17.2 ± 1.5 cm^3 mol^{-1} (25 °C and $I = 0.5$ M) was used, a $\Delta V^{\ddagger}$ for the hydrolysis reaction was calculated as −10.8 ± 1.9 cm^3 mol^{-1}, which is also compatible with the overriding effect of C–O bond formation in the transition state. Secondary contributions to $\Delta V^{\ddagger}$ from proton transfer, where bonds are partially formed and broken, will tend to cancel out, while electrostriction increases due to partial charge separation are small and negative in both directions.

The value of k_{-1} was also measured as a function of the alcohol content of the solution.[164] In both mixtures of water/methanol and water/*tert*-butyl alcohol, maxima in $\Delta H^{\ddagger}$ with increasing alcohol content were observed. On the other hand, $\Delta S^{\ddagger}$ increased monotonically in the former [$x(CH_3OH)$, 0–0.8], but showed a maximum in the latter at $x(BuOH) = 0.06$. Based on similarities to organic solvolysis reactions, these results were construed as evidence for a decrease in polarity and hydrogen bonding as the initial state, H_2CO_3, rearranges to the transition state. This interpretation is also compatible with the formulation in eq 34.

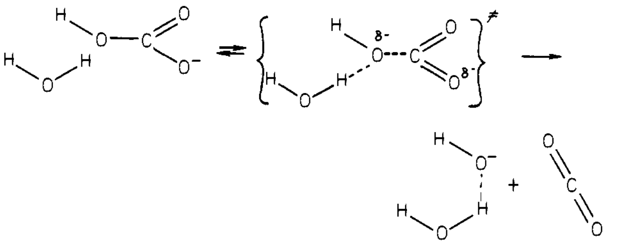
In the general pH range 7–10, eq 28–32 contribute to the dynamics of aqueous CO_2 chemistry, while beyond a pH of 10, eq 29, 30, and 32 are alone responsible. The kinetic parameters associated with eq 29 are presented in Table VIII. Combining all these data leads to the activation parameters: $\Delta H^{\ddagger} = 54.4 \pm 2.4$ kJ mol^{-1} and $\Delta S^{\ddagger} = 12 \pm 8$ J K^{-1} mol^{-1}. It appears generally accepted that the most reliable set of data is that reported by Pinsent et al.[165,166] They[166] also present the most extensive results on the ionic strength dependence of k_2, although there is considerable discrepancy as to the magnitude, and even the sign, of the dependence.[159] The combined results[166] for NaCl, KCl, and Na_2CO_3 as the inert salts can be fitted to a quadratic equation of the form

$$\log k_2 = 3.773 + (0.213 \pm 0.013)I - (0.0214 \pm 0.0028)I^2 \quad (35)$$

Specific catalysis by certain salts can modify this relationship. This aspect is discussed in more detail in this section.

Welch et al.[167] reported a value for k_{-2} of 2.25×10^{-4} s^{-1} at 25 °C, corrected for the contribution of k_{-1} in the pH range 8.5 to 9.3, based on the exchange rate of oxygen-15 between CO_2 and water. Good agreement was obtained with the k_{-2} value of 2.91×10^{-4} s^{-1} derived from the mean k_2 value from Table VIII (7740 M^{-1} s^{-1} at 25 °C), and the equilibrium constant for eq 29 of 2.66×10^7 M^{-1}. Activation parameters were determined from the values of k_{-2} at three temperatures: $\Delta H^{\ddagger} = 93 \pm 9$ kJ mol^{-1} and $\Delta S^{\ddagger} = 0 \pm 29$ J K^{-1} mol^{-1}.

A study[161] of the deuterium isotope effect on the respective rate constants k_2 and k_{-2} has established a $k(H_2O)/k(D_2O)$ ratio of 0.6 and 1.8, where the latter was derived by analogy to the "water-catalyzed" decarboxylation of alkyl carbonates. Atkinson et al.[155] report a range of values from 1.4 to 2.0 over the temperature range 3.5–38.5 °C which they ascribe to $k_{-1}(H_2O)/k_{-1}(D_2O)$; whereas, as discussed earlier, a value of 0.6 was assigned to the ratio $k_{-1}(H_3O^+)/k_{-1}(D_3O^+)$.[161] However, both groups agree that ca. 1.8 is in keeping with the predicted secondary-isotope effect for the removal of an –OH vs. an –OD group from a molecule (theoretical 2.02).[155] In other words, these results are compatible with reaction 29 and the proposed mechanism:[161]



(36)

Logically, the presence of excess carbonate in solution would lead to the increasing importance of eq 30 in the overall scheme. However, some authors[160,168] have concluded that the contribution from such a path, also referred to as carbonate catalysis, is negligible; a position that is substantiated by Pinsent et al.[166] in their ionic strength dependence study described earlier. Nevertheless, Poulton and Baldwin[159] argue that the uncertainties of the manometric method[160,168] are large enough to mask such small catalytic effects which could be quantitatively assessed from their oxygen-18 exchange data. They went on to assign a value to k_3 (eq 30) of ca. 1.2 M^{-1} s^{-1} at 25 °C [this value represents the average of three values at ionic strengths of 0.5, 1.5, and 2.5 M (NaCl)]. Moreover, two more reactions involving other permutations of carbonate species were proposed[159]

$$CO_2(aq) + CO_3^{2-} + OH^- \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} HCO_3^- + CO_3^{2-} \quad (37)$$

$$CO_2(aq) + HCO_3^- + H_2O \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} HCO_3^- + H_2CO_3 \quad (38)$$

for which the average values (25 °C, $I = 0.5$–2.5 M) of k_4 and k_5 are 1.4×10^5 M^{-2} s^{-1} and 4.7×10^{-2} M^{-1} s^{-1}, respectively. Therefore, unless a "carbonate" buffer is used, these three reactions would provide negligible contributions to the established rate expressions for reactions 28 and 29. This subject will be treated again later in this section.

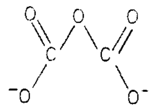
More recent investigations by Silverman et al.[169,170] have brought these processes more into perspective by fixing the rate of intermolecular exchange between $CO_2(aq)$ and CO_3^{2-} in slightly alkaline solution using both ^{18}O-labeled and ^{13}C-enriched carbonate. The exchange rate constant at 25 °C is 114 ± 11 M^{-1} s^{-1} which, although slower than the rate of exchange via eq 29 at higher pH values, is considerably faster than the re-

TABLE VIII. Summary of Rate Data for the Base Hydrolysis of CO_2 at 25 °C

year	I, M	k_2, M^{-1} s^{-1}	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J K^{-1} mol^{-1}	method	ref
1924	.22/.11	4563[a,b]			quenching, titration	158
1928	0.01	3700 (13.7 °C)			conductometric	*c*
1933	<0.21	2820[a]			gas evolution spectrophotometric	*d*
1951	0	6771[a]			manometric	165
1956	0	8430[e]	52.8	7	thermal method	
	0	8500[f]	52.7	7	manometric	166
1958	<0.01	7610[e]	61.2	35	photoelectric	
		7515[e]	49.4	−5	conductometric	*g*
1963	0	8100 (25.1 °C)			gas absorption: ^{14}C tracer	178
1966	0	1100 (0 °C)[h]			manometric	160
1967	1.5	8000	48.1	−9	mass spectroscopy, ^{18}O tracer	159
1973	0	8049	43.3	−25	manometric	*i*
1982	0	7043			pH statt	558

[a] Interpolated from two data points. [b] Data corrected by a factor of 2.303 and using more recent values for K_2[148] and K_W at 0 °C and 18 °C (Marshall, W. L.; Franck, E. U. "Water and Steam"; Pergamon Press: New York, 1980, p 506). [c] Saal, R. N. J. *Recl. Trav. Chim. Pays-Bas* 1928, *47*, 264. [d] Brinkman, R.; Margaria, R.; Roughton, F. J. W. *Philos. Trans. R. Soc.* 1933, *A232*, 65. [e] Interpolated to 25.0 °C. [f] Appendix to ref 166 by E. Meda. [g] Sirs, J. A. *Trans. Faraday Soc.* 1958, *54*, 201. [h] Equilibrium constant values for K_1 and K_2 at 25 °C were used. [i] Pohorecki, R.; Moniuk, W. *Pr. Inst. Inz. Chem. Politech. Warszaw* 1972, *1*, 69; *Chem. Abstr.* 1973, *79*, 35528m.

maining hydrolysis reactions. Albeit bicarbonate ion does not enter into the intermolecular exchange process, it still undergoes oxygen exchange with water.[169] A labile dimeric intermediate with the structure



was considered as one possible intermediate in the exchange for which an activation energy of 63 kJ mol^{-1} was recorded.[170]

Catalysis of the hydration reactions of $CO_2(aq)$ is of obvious interest to industry. Nonenzymatic catalysis has been studied by a considerable number of workers (ref 69,160,162,165,168,171–174) using mainly manometric techniques. A general relationship for the observed rate constant for CO_2 hydrolysis can be expressed in terms of the contributions of the concentrations of base B and its conjugate acid, HB.[160,162]

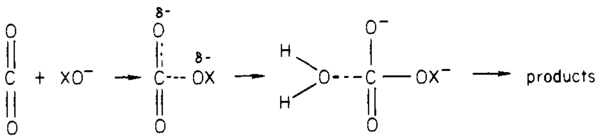
$$k_{obs} = k_1 + k_2[OH^-] + k_{HB}[HB] + k_B[B] \quad (39)$$

For example, for HB = $H_2PO_4^-$, $k_{HPO_4^{2-}} = 0.3$ M^{-1} s^{-1}, $k_{H_2PO_4^-} \simeq 0$ at $I = 1.0$ and 25 °C,[162] whereby HPO_4^{2-} is considered a weak catalyst.[160]

Despite the wide range of bases investigated by Sharma and Danckwerts,[174] their finding that the Bronsted relationship holds for certain bases which have in common a high degree of localized negative charge on an oxygen atom has been criticized[160] because the pH range chosen was too low relative to the pK_a values of the conjugate acids. However, the general classification of bases according to their catalytic effect and structure was substantiated.[160] In addition, strong acid anions, as well as carbonate, cyanide, and hydrogen sulfide, are not effective catalysts, a fact which validates the ionic strength effects discussed previously and eq 35 in particular. Dennard and Williams[160] laid down the following criteria for bases to be good catalysts:

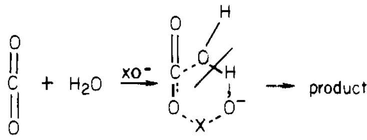
(1) For oxyanions with the nonmetal in its highest oxidation state there can be no resonant form for the basic oxygen atom, i.e., $[OTe(OH)_5]^-$, $[OGe(OH)_3]^-$, and $[OSi(OH)_3]^-$ are good catalysts, while HPO_4^- and $HAsO_4^-$ are only weak catalysts despite the similar basicity of all five.

(2) The oxyanions of nonmetals in lower oxidation states with at least one lone pair of electrons are the best catalysts, e.g., SO_3^{2-}, AsO_2^-, ClO^-, and BrO^-. The authors[160] point out that these rules can be related to specific properties of the bases. For the majority of cases, the nucleophilicity and ability of the anion to act as a leaving group are paramount and consistent with the favored mechanism:[160]



(40)

Furthermore, certain oxyanions with lower oxidation state centers, class 2, can act as electrophilic agents (e.g., SO_3^{2-} or ClO^-), compliant with the following mechanism:



(41)

McLachlan's work[172] on the catalysis of reaction 28 by $As(OH)_2O^-$ and ClO^- in carbonate buffers bears directly on the general topic of catalysis, as well as "carbonate" catalysis in the form of eq 37.[159] Using gas absorption techniques he was able to demonstrate that catalysis under these conditions obeys a third-order rate law which is first order with respect to the base B^-, $[As(OH)_2O^-]$, or $[ClO^-]$, and $[CO_3^{2-}]$. A linear least-squares fit of McLachlan's results for $k[B^-]$ vs. $[CO_3^{2-}]$ yielded the rate constants: $k_{As(OH)_2O^-} = 393 \pm 13$ M^{-2} s^{-1} (25 °C and I = 1.4–5.1) and $k_{ClO^-} = 7300 \pm 400$ M^{-2} s^{-1} (25 °C and I = 0.45–5.03 M). These constants are obviously insensitive to ionic strength and bicarbonate concentration, albeit the latter increases sharply in the presence of chloride ion which most likely reflects a change in the oxidation state of ClO^-. Note also that $k_{As(OH)_2O^-}$ values could be calculated from two earlier measurements of Danckwerts et al. and gave a fair fit to the third-order model, whereas the value of 6670 M^{-1} s^{-1} reported[171] for ClO^- catalysis in mixtures of 1 M

$KHCO_3$/1 M K_2CO_3 at 25 °C is in excellent agreement with the calculated k_{ClO^-} value. These authors[171] also report a second-order rate constant for BrO^- under the same conditions of 6×10^5 M^{-1} s^{-1}.

Of direct application to the earlier discussion on carbonate catalysis is McLachlan's[172] plot of k_{obsd} vs. $[CO_3^{2-}]^2/[HCO_3^-]$ which includes the results of five other investigators[175-177] who used potassium or sodium carbonate buffers, but no other catalysts. A good straight line results and translates into a slope of 0.99 ± 0.03 M^{-2} s^{-1} (25 °C and $I = 1.0$–6.4 M), which, in turn, gives a third-order rate constant for reaction 37 of $(4.7 \pm 0.1) \times 10^3$ M^{-2} s^{-1} (K_2 and K_w values at $I = 0$, 25 °C were used). This value is 2 orders of magnitudes greater than reported by Poulton and Baldwin,[159] but must be considered more accurate as it was determined directly. It is difficult to speculate on what role carbonate plays in the detailed mechanisms 40 and 41, although it appears logical that it involves interaction of either carbonate or B^- with the type of intermediate (viz., $C_2O_5^{2-}$) proposed for intermolecular oxygen exchange, which is first-order in both $[CO_2]$ and $[CO_3^{2-}]$, and is also independent of $[HCO_3^-]$.

Catalysis by coordinated metal ions is well documented and is discussed in section VIII.

A brief mention of the rate of CO_2 absorption into solution should be made as it is technologically important and central to many of the hydrolysis studies discussed here. In alkaline solutions the rate of absorption of gaseous CO_2 is given by the following equation in units of mol cm^{-2} s^{-1},

$$\text{rate} = [CO_2(aq)](k_L^2 + Dk_2[OH^-])^{1/2} \qquad (42)$$

where k_L represents the individual mass-transfer coefficient for CO_2 in solution and D is the diffusivity of CO_2 in solution with typical values ranging from 1×10^{-5} to 2×10^{-5} cm^2 s^{-1} at 25 °C. Depletion of $[OH^-]$ from the surface layer can present a problem at high rates of absorption or low agitation rates as the reaction proceeds. Notwithstanding this retardation effect, in eq 29 k_2 is generally considered to be rate-determining. Numerous investigations have been reported on this subject.[175-185] However, note that in view of the exchange studies of Silverman et al.[169,170] and the abovementioned rapid equilibration of $CO_2(gas) \rightleftarrows CO_2(aq)$, the recently reported[185] relaxation time of ca. 13.4 min (15–18 °C) for ^{13}C exchange for this process appears much too slow, even at pH values of 8.5. This discrepancy can probably be traced to the aforementioned diffusion problems in the solution. However, Szaran and Zuk[185] did determine the equilibrium fractionation factor δ ^{13}C for CO_2(gas) vs. mainly HCO_3^- over the temperature range 0–52 °C. The fractionation factor proved to be a linear function of temperature, t(°C), e.g., $\delta\ ^{13}C = 10.2 \pm 0.1 - (0.090 \pm 0.006)t$ (‰); an equation which is consistent with previous work.[186]

As a final comment, the rate of dissolution of calcium carbonate in relatively neutral solutions (pH 6.5–8) is apparently diffusion controlled;[187,188] i.e., the overall hydrolysis reaction (eq 43) in this case is faster than the

$$CaCO_3(s) + CO_2(aq) + H_2O \rightleftarrows Ca^{2+} + 2HCO_3^- \qquad (43)$$

rate of diffusion of $CO_2(aq)$, or more explicitly the proposed reactant H_2CO_3, to the surface of the crystal.

The Chemistry of Metal Carbonato Complexes

V. Preparation and Characterization

A. Preparation and Spectroscopic Data

The preparative techniques have been described in some detail in previous reviews.[1,2] Conventional solution methods basically rely on carbon dioxide uptake by the hydroxo form of the parent transition-metal compound[189] (the mechanism of which is explained in section VIII), or involve using the carbonato complex as the starting materials, as in the case of $Co(CO_3)_3^{3-}$,[190] and substituting other ligands into such species. High pressures of CO_2 and high temperatures are generally required for solid-state conversions to form carbonates (see section VI).

We have attemped to summarize the spectroscopic properties of metal carbonato complexes in Tables IX–XIII with particular emphasis on the most recent results. The preparative methods are referenced in these Tables and, in a number of cases, represent only one of a number of published techniques.

The spectroscopic data can serve most readily to fingerprint the species. The visible and UV spectra are particularly useful for this purpose, but will not be discussed further in this review except to point out that a practical test for the existence and, to certain extent, the purity of a soluble carbonato complex is to acidify an aqueous solution containing the suspected complex and then compare the spectrum of the generated aquo species with the known spectrum of the aquo complex obtained directly.

The infrared and Raman spectra have more general application and will therefore be discussed in more detail.

(1) **Infrared and Raman Spectroscopy.** Infrared and Raman spectroscopy are the traditional means of ascertaining the bonding modes of coordinated carbonates. As the free ion, carbonate has a D_{3h} symmetry and four bands may be assigned to the following vibrational modes: ν_1, the C–O symmetrical stretch at $\sim$1065 cm^{-1}; ν_2, the CO_3 out-of-plane deformation at $\sim$880 cm^{-1}; ν_3, the C–O asymmetrical stretch at $\sim$1400 cm^{-1}; and ν_4, the CO_3 in-plane deformation (or rocking) mode at $\sim$685 cm^{-1}. The ν_2 mode should be inactive in the Raman. On this basis, the spectral data in Table XIV for the alkali metal carbonates confirm that the ν_2 mode is absent from the Raman spectrum; however, the ν_1 mode is generally of medium to weak intensity in the IR which may indicate a lowering of the D_{3h} symmetry. It can also be seen that the range of frequencies cited in Table XIV embrace the values quoted above, viz. the mean values are 1064 (20), 861 (22), 1417 (33), and 696 (19) cm^{-1}, respectively. Temperature affects the energy of these transitions slightly, whereas the degree of hydration generally has a much stronger effect.

As was observed in the spectra of alkali metal carbonates in aqueous solution,[49] the D_{3h} symmetry is also lowered in the molten state.[191] This is thought to be due largely to the anisotropic nature of the melt.

The IR and Raman spectra of a series of compounds with calcite and aragonite structures led Donoghue et

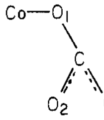
TABLE IX. Spectroscopic Properties of Monodentate Carbonato Complexes

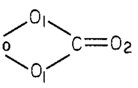
compd	prepn ref	vis/UV, nm (M^{-1} cm^{-1})	ref	IR, cm^{-1}	ref	comments
trans-$K_2[Co(H_2O)_4CO_3]$	*a*					
$[Co(NH_3)_5CO_3]NO_3 \cdot 1.5H_2O$	*b*	505 (94), 237 (13 800)	333	1482, 1365, 1052, 856, 738, 690	195	
				1453, 1373	340	
cis-$[Co(en)_2(NH_3)CO_3]Br \cdot 0.5H_2O$	189					
trans-$[Co(en)_2(NH_3)CO_3]ClO_4$	189					
trans-$[Co(NH_3)_4(CN)CO_3]$	*c*	458 (109)	*c*			
trans-$[Co(en)_2(Cl)CO_3] \cdot H_2O$	353	~578 (~74), ~450 (~25)	353			
trans-$[Co(en)_2(Cl)(CO_3H)]^+$	*d*	510 (21.2)	*d*			
cis-$[Co(en)_2(OH)CO_3]$	353	~512 (~114), ~361 (~110)	353			
trans-$[Co(en)_2(OH)CO_3]$	353	532 (~81)	353			
trans-$[Co(en)_2(HCO_3)_2]^+$	*d*	510 (65.1)	*d*			
cis-$\alpha\beta$S-$[Co(tetren)CO_3]ClO_4 \cdot 3H_2O$	189	500 (198)	327	1458, 1340	327	
cis-$[Co(tren)(OH)(HCO_3)]^{+}$[e]	352	530 (120), 430 (20)	352			
cis-$[Co(tren)(OH)CO_3]$	352	515 (155), ~350 (130 sh)	352			
		520 (144), 367 (117 sh)	328			
cis-$[Co(cyclam)(OH)(CO_3H)]^{+}$[e]	314	~525 (~222), ~365 (~194 sh)	314			
trans-$[Co(cyclam)(OH)(CO_3H]^{+}$[e]	314	~555 (~45), ~438 (~33)	314			
trans-$[Co(cyclam)(OH)CO_3]$	314	~562 (~50), ~453 (~29)	314			
$[Cu(NH_3)_2(CO_3H)_2]$	480					
$[Cu(PEt_3)_3(CO_3H)]$	*f*			1612	*f*	^1H NMR data
cis-$[Mo(dmpe)_2(CO)_2CO_3]$	*g*			1625	*g*	zwitterionic
$[RhH_2\{P(i\text{-}Pr)_3\}_2(CO_3H)]$	403			2650 m, 1587 s, 1338 s, 792 m	403	^1H NMR spectrum
$[RhH_2\{PPh(t\text{-}Bu)_2\}_2(CO_3H)]$	403			2660 m, 1583 s, 1340 s, 802 m	403	^1H NMR spectrum
$[RhH_2\{P(c\text{-}C_6H_{11})_3\}_2(CO_3H)]$	403			2640 m, 1585 s, 1340 s, 790 m	403	
$[Rh(CO)\{P(c\text{-}C_6H_{11})_3\}_2(CO_3H)]$	403			2650 w, 1608 s, 1420 s, 1355 s, 821 m	403	mp = 169-172 °C
$[Rh(CO)\{P(i\text{-}Pr)_3\}_2(CO_3H)]$	403			2600 w, 1615 s, 1413 s, 1350 s, 823 m	403	^1H NMR spectrum
$[Rh(NH_3)_5CO_3]ClO_4$	*h*	325 (178)	*h*	1455	*h*	
cis-$[Rh(en)_2(H_2O)CO_3]^+$	*i*	332 (224)	*i*			
trans-$[Rh(en)_2(CO_3)_2]^-$	322	347 (146)	322			
trans-$[Rh(en)_2(H_2O)CO_3]ClO_4$	322	345 (101)	322			
trans-$[Rh(en)_2(OH)CO_3]$	322	346 (121)	322			
trans-$[Rh(en)_2(Cl)CO_3]$	315	376 (118)	315			
trans-$[Rh(en)_2(Br)CO_3]$	315	384 (141)	315			
trans-$[Rh(en)_2(I)CO_3]$	315	456 (232), 415 (216)	315			
trans-$[Pd(PPh_3)_2(Me)(CO_3H)]$	*j*			1634 s, 1353 s, 830 m	*j*	
$[Ir(NH_3)_5CO_3]ClO_4$	*h*	262 (125)	*h*	1370	*h*	

[a] Reynolds, W. C. *J. Chem. Soc. Trans.* 1898, *73*, 262. [b] Lamb, A. B.; Mysels, K. J. *J. Am. Chem. Soc.* 1945, *67*, 468. [c] Krishnamoorthy, C. R.; Palmer, D. A.; van Eldik, R.; Harris, G. M. *Inorg. Chim. Acta* 1979, *35*, L361. [d] Jackson, W. G.; Sargeson, A. M. *Inorg. Chem.* 1978, *17*, 1348. [e] As mentioned in the discussion, we prefer the form, $ML_4(H_2O)CO_3^+$. [f] Tsuda, T.; Chujo, Y.; Saegusa, T. *J. Am. Chem. Soc.* 1980, *102*, 431. [g] Connor, J. A.; Riley, P. I. *J. Chem. Soc., Dalton Trans.* 1979, 1231. [h] Palmer, D. A.; Harris, G. M. *Inorg. Chem.* 1974, *13*, 965. [i] Palmer, D. A.; van Eldik, R.; Kelm, H.; Harris, G. M. *Inorg. Chem.* 1980, *19*, 1009. [j] Crutchley, R. J.; Powell, J.; Faggiani, R.; Lock, C. J. L. *Inorg. Chim. Acta* 1977, *24*, L15.

al.[192] to favor a C_3 symmetry for these carbonates. They list the positions of the bands for the ν_1, ν_2, and ν_4 modes of these compounds in the calcite form where M = Mg, Ca, Mn, Zn, Cd: ν_1 = 1074 (10) IR, 1091 (4) R; ν_2 = 872 (9), 845 (7) IR; ν_3 = 730 (13) IR, 720 (8) cm^{-1} R; and in the aragonite form where M = Ca, Sr, Ba, Pb: ν_1 = 1065 (14) IR, 1065 (9) R; ν_2 = 851 (7), 839 (10) IR; ν_4 = 697 (14), 686 (7) IR, 690 (11) cm^{-1} R. Note that the ν_4 band is split in some cases. Donoghue et al.[192] suggest that the second peak at the ν_2 frequency could be due to a combination with a lattice mode. Coincidently, the lower energy band corresponds exactly to that reported by Sterzel[193] for the ν_2 ^{13}C absorption such that for calcite $\Delta\nu_2$ (^{12}C–^{13}C) = 27 cm^{-1} and 11 cm^{-1} for aragonite.

Coordination lowers the symmetry of the carbonate further from D_{3h} to C_{2v}, or possibly C_s, for monodentate coordination and thereby results in the splitting of each of the degenerate ν_3 and ν_4 modes into two. Gatehouse, Livingstone, and Nyholm[194] catagorize six fundamental frequencies associated with C_{2v} symmetry: ν_4, asym stretch, 1577–1493 cm^{-1}; ν_1, CO_2 sym stretch, 1338–1260 cm^{-1}; ν_2, CO stretch, 1082–1055 and 1050–1021 cm^{-1}; ν_6, nonplanar rock, 889–824 cm^{-1}; ν_3, CO_2 bend, and ν_5, planar rock, 809–738 cm^{-1}, all of which are both IR and Raman active. Fujita, Martell, and Nakamoto[195] used the normal coordination treatment to calculate the theoretical band assignments and force constants for cobalt(III) carbonato complexes. Although they obtained a satisfactory agreement for the C_{2v} symmetry in both the monodentate and bidentate cases, the C_s model gave better agreement for the ν_4 frequency in the former case. The notation derived by Fujita et al.[195] is different from that described above,[194] and is shown in Table XV along with the calculated frequencies and the experimental values for the examples of mono- and bidentate coordination. The authors adopted the following reference structures (see Tables XVIII and XIV for bond lengths and angles):





The magnitude of the split between the ν_1 and ν_5 modes is a function of the carbonato ligand polarization and the M–O bond strength, and is greater for bidentate bonding than for monodentate bonding, given that the two first mentioned independent variables are constant.[196] The examples cited in Table XV attest to the validity of this postulate. Other more subtle distinctions exist between the spectra resulting from these two forms of coordination.[196] These criteria are generally met for all the compounds listed in Tables IX and X. Similar bidentate characteristics are expected to be observed for the bridged carbonato complexes in Table XI. From the limited data available it can be seen that the splitting of the degenerate ν_3 is ambiguous in many cases with $|\Delta(\nu_1 - \nu_5)|$ values lying between the extremes quoted in Table XV. Note the example of the $[\{Co(diars)_2HCO_3\}_2(\mu\text{-}CO_3H)]^{3+}$ cation is complicated by the presence of monodentate carbonate.[197]

The majority of the lanthanide and actinide complexes shown in Tables XII and XIII exhibit complex spectra associated with mixed mono- and bidentate ligands. Although Caro et al.[198] favor monodentate bonding in the series of complexes, $Ln_2(CO_3)_x(OH)_{2(3-x)}\cdot nH_2O$, Ln = Pr, Nd, Sm, Tb, Dy, and Nd·Tb, on the basis of their IR spectra which closely resemble that of $[Co(NH_3)_5CO_3]Br$, with modifications due to the existence of two crystallographic sites for the two rare earth atoms. This lanthanide formula also raises the point that in some of the complexes found in Tables XII and XIII, the participation of one or more "waters of crystallization" in the first coordination sphere of the metal ion cannot always be ruled out. On the other hand, the IR spectra of the sodium pentacarbonatothorate(IV) hydrates suggest strongly that only bidentate coordination is present.[199] The same is true for $Na_4[UO_2(CO_3)_3]$ for which the ν_3 splitting is strong (1560–1342, 1630–1358 cm^{-1}).[200]

A matrix isolation IR spectroscopic study[201] of the vaporization of the alkali metal carbonates $Cs_2(CO_3)$, $Rb_2(CO_3)$, and $K_2(CO_3)$ showed evidence for molecular carbonates with the C_{2v} symmetry discussed above for bidentate complexes.

(2) Other Methods. ^{1}H and ^{13}C NMR spectroscopy provide a more exact description of the configuration of ligands around the metal center and have been used for this purpose for carbonato metal complexes (see Tables IX–XI). Similarly ESR, magnetic, and conductometric properties have been recorded and ORD and CD measurements made where appropriate. These properties are referred to in Tables IX–XI and XIII.

However, as these properties are generally associated with the molecule as a whole, we feel they are outside the immediate scope of this review so that we have limited ourselves to merely indicating in the tables where such data are available.

B. Structure

The unit cell parameters determined from X-ray crystallography for a wide range of carbonato complexes, including a number of naturally occurring minerals, are listed in Table XVI. The corresponding bond lengths and angles for these complexes are given in Tables XVII–XXIV, with the main emphasis on the carbonato ligand itself. Obviously space does not permit a complete breakdown of these structures in terms of bond lengths and angles, but it is hoped that where just mean values for these measurements are given this will convey the degree of distortion, if any, as reflected by the standard deviation. In other words, even though average values are listed, this is not meant to imply equality.

For ease of comparison, the structures of the bicarbonate and carbonate salts of the alkali and alkaline earth metals are given separately in Table XVII. They warrant a brief clarification because the sodium and potassium (rubidium) salts exhibit different structures.

Sass and Scheuerman[202] determined the CO_3 group in $NaHCO_3$ to have a C_{2v} symmetry (planar within 0.01 Å) with two oxygens hydrogen bonded; viz., O_3 covalently and O_2 electrostatically. Thus, in this classical picture, the C–O_3 bond has approximately 14% double bond character (cf. the expected bond length for a single C–O bond of 1.43 Å), while the remaining two C–O bonds have ca. 50% double bond character, based on an estimate for a double bond length of 1.255 Å.

The structure of potassium bicarbonate is different in that it consists of H-bonded dimers reminiscent of

TABLE X. Spectroscopic Properties of Bidentate Carbonato Complexes

compd	prepn ref	vis/UV, nm (M^{-1} cm^{-1})	ref	IR, cm^{-1}	ref	comments
$K_2[Co(CO_3)_2]\cdot 4H_2O$	*a*			1338 m, 1082 m, 1049 m, 884 m, 799 s, 766 m	194	
$[Co(HDPA)(H_2O)_2CO_3]\cdot 0.5H_2O$	*b*			1065 sh, 1277, 842	*b*	1320, 1110, 535, 488, 395, 347 nm, diffuse reflectance spectrum
$Na_3[Co(CO_3)_3]\cdot 3H_2O$	190	635 (154), 440 (166), 260 (10^5)	364			
		640 (162), 440 (173)	367			
		645 (155), 439 (166)	*c*			
$K_3[Co(CO_3)_3]\cdot 3H_2O$	364			1600, 1495, 1335	358	optically resolved
				1527 s, 1330 s, 1080 w, 1037, 851 m, 809 m	194	
$[(NH_3)_4Co(\mu\text{-}NH_2)(\mu\text{-}OH)Co(CO_3)_2]\cdot 5H_2O$	*d*			1585 s, 1265 s	*d*	
$Li(-)_{589}[Co(NH_3)_2(CO_3)_2]$	*e*					$\tilde{\nu}_{max}$ = 17.8 (−2.32)
cis-$K[Co(NH_3)_2(CO_3)_2]$ (blue)	362	578, 394	362	1623, 1597, 1265, 1026, 839, 763, 744, 673	195	
		574 (138), 390 (251)	359	1370, 970, 740, 690	362	
$K[Co(NH_3)_2(CO_3)_2]\cdot H_2O$ (violet)	362	540 (63), 374 (110), 234 (13 800)	359			
cis-$K[Co(py)_2(CO_3)_2]\cdot 0.5H_2O$	364	561 (165), 388 (232)	364			
cis-$K[Co(py)_2(CO_3)_2]\cdot 2H_2O$		562 (156), 391 (197)	*f*			spectrum taken in 0.1 M pyridine
cis-$K[Co(py)_2(CO_3)_2]\cdot 3H_2O$	366	568 (178), 392 (251)	366			
trans-$K[Co(py)_2(CO_3)_2]\cdot 3H_2O$	366	549 (100), 417 sh, 372 (107)	366			
		549 (89.1), 426 (36.3), 375 (72.4)	*g*			
$K[Co(bpy)(CO_3)_2]\cdot 2H_2O$	*h*	562 (151), 391 (240 sh)	*h*			$\tilde{\nu}_{max}$ = 17.7 (+5.93)
$K[Co(phen)(CO_3)_2]\cdot H_2O$	*h*	568 (151), 394 (251 sh)	*h*			$\tilde{\nu}_{max}$ = 17.5 (−7.72)
$K_2[Co(picol)(CO_3)_2]\cdot 0.5H_2O$	*i*	588 (145), 415 (191)	*i*			
$[Co(en)_3]$-*cis*-$[Co(CN)_2(CO_3)_2]\cdot 2H_2O$	*j*	546 (91), 444 (107), 363 (158)	*j*			corrected for contribution of cation
cis-$Na[Co(en)(CO_3)_2]\cdot H_2O$	*k*	568 (154), 395 (173)	*k*			
cis-$K[Co(en)(CO_3)_2]\cdot H_2O$	31	570 (148), 390 (214)	365			
	359	570 (148), 390 (214), 239 (28 800)	359			
	220	567 (159), 394 (164)	220			
cis-$[Co(NH_3)_4CO_3]NO_3\cdot 0.5H_2O$	*l*	520 (104)	334	1598, 1035, 765	334	
cis-$[Co(NH_3)_4CO_3]Cl$				1593, 1265, 1030, 834, 760, 673	195	
cis,cis-$[Co(NH_3)_2(py)_2CO_3]Cl\cdot H_2O$	*m*	515 (115), 362 (117)	*m*			$\tilde{\nu}_{max}$ = 18.1 (−0.59), 20.3 (+0.92), 27.8 (−0.28)
cis-$[Co(en)(py)_2CO_3]Cl\cdot H_2O$	*m*	513 (123), 362 (123)	*m*			$\tilde{\nu}_{max}$ = 20.0 (+1.87), 27.4 (−0.36)
cis-$[Co(py)_2(H_2O)_2CO_3]^+$	*n*	536 (~89), 388 (~111)	*n*			
	f	536 (87), 388 (107)	*f*			
mer-$[Co(py)_3(Cl)CO_3]$	*o*	577 (125), 409 (150)	*o*	1675 br, 1640 s, 1245 s	*o*	ϵ values multiplied by 2.5
		582 (113), 401 (142)	*p*			
$[Co(py)_3(H_2O)CO_3]ClO_4\cdot H_2O$	*p*	540 (119), 380 (138)	*p*	1650 s, 1625 br, 1250 s	*p*	
cis-$[Co(py)_4CO_3]ClO_4\cdot H_2O$	*o*	530 (170), 378 (189)	342	1680 br, 1640 s, 1240 sh	*o*	
		530 (172), 379 (187)	*o*			
cis-$[Co(NH_3)_2(bpy)CO_3]Cl\cdot 2H_2O$	*m*	513 (117)	*m*			$\tilde{\nu}_{max}$ = 19.0 (+2.03), 25.3 (+0.25), 29.2 (−0.66)
cis-$[Co(bpy)_2CO_3]Cl\cdot 3H_2O$	*q*	504 (116)	321			^{13}C NMR spectrum[321]
		504 (110), 380 (sh), 305 (30 000)	*r*			
$[Co(terpy)(OH)CO_3]\cdot 4H_2O$	*s*			1605, 1270	*s*	
$[Co(HDPA)_2CO_3]ClO_4$	*b*		*b*	1626, 1259, 830, 678	*b*	510, 400 (sh), 342 nm, diffuse reflectance spectrum
cis,cis-$Na[Co(NH_3)_2(CN)_2CO_3]\cdot 2H_2O$	*t*	483 (91.2), 426 (105)	*t*			$\tilde{\nu}_{max}$ = 20.9 (+0.98), 24.1 (−1.11), 29.7 (+0.245)
		499 (91), 431 (105), 336 (sh)	*c*			
mer(*N*)-$[Co(NH_3)_3(CN)CO_3]\cdot H_2O$	*u*	485 (112), 347 (112)	*u*			

fac(*N*)-[Co(NH$_3$)$_3$(CN)CO$_3$]	*u*	495 (107), 345 (158), 377 (sh)	*u*			
K[Co(NH$_3$)(NO$_2$)$_3$CO$_3$]·H$_2$O	360	472 (219), 347 (7410), 259 (25 700)	360			
cis-[Co(en)$_2$CO$_3$]ClO$_4$	*v*	511 (133), 359 (122)	336	1643, 1285, 1267, 833, 757, 673	195	$[\alpha]^{25}{}_{D}$ −1331°(H$_2$O)^{w}
cis-[Co(en)$_2$CO$_3$]Cl	*v*			1577 s, 1290 sh, 1278 s, 1055 m, 1034 m, 824 s, 756 m	194	
cis-$(+)_{546}$[Co(en)CO$_3$]$^+$		515 (145), 361 (132)	*m*			$\tilde{\nu}_{max}$ = 18.7 (+3.70), 25.6 (+0.27), 27.5 (−0.10), 29.1 (+0.15)
cis-$(+)_{589}$[Co(NH$_3$)$_2$(en)CO$_3$]Cl·H$_2$O	*m*	515 (120), 358 (120)	*m*			$\tilde{\nu}_{max}$ = 18.8 (+1.53), 25.5 (+1.30), 27.4 (−0.05), 30.1 (+0.11)
cis-[Co(NH$_3$)$_2$(en)CO$_3$]ClO$_4$·2H$_2$O	355	504 (125), 347 (148)	355			
		500 (125)	326			
trans-[Co(NH$_3$)$_2$(en)CO$_3$]Cl·H$_2$O	355	512 (95), 356 (103)	355			
		520 (95)	326			
μ-*fac*(*N*)-[Co(NH$_3$)(en)(CN)CO$_3$]·H$_2$O	*u*	485 (117), 345 (145), 377 (sh)	*u*			
mer(*N*)-[Co(NH$_3$)(en)(CN)CO$_3$]·H$_2$O	*u*	485 (115), 347 (120)	*u*			
trans-[Co(NH$_3$)$_2$(tn)CO$_3$]Cl·H$_2$O	355					
cis-[Co(phen)$_2$CO$_3$]Cl·3H$_2$O	38	509 (109)	38			^{13}C NMR spectrum[38]
K$(+)_{589}$[Co(NH$_3$)$_2$(ox)CO$_3$]·H$_2$O	*x*	565 (123), 389 (151)	*m*			$\tilde{\nu}_{max}$ = 17.3 (+1.74), 23.6 (+0.22), 25.8 (0.11), 28.3 (+0.09)
$\Lambda(+)_{589}$[Co(en)$_3$][Co(NH$_3$)$_2$(ox)CO$_3$]·H$_2$O	*y*	535 (79), 435 (117), 356 (178)	*y*			$\tilde{\nu}_{max}$ = 19.3 (−1.74), 22.9 (2.17), 28.4 (−0.57)
cis-K[Co(NH$_3$)$_2$(ox)CO$_3$]·H$_2$O	*z*	565 (123), 388 (151)	*c*			
K[Co(en)(ox)CO$_3$]·H$_2$O	*z*	560 (148), 382 (200)	*c*			
K$(-)_{589}$[Co(en)(ox)CO$_3$]·H$_2$O	*x*	552 (145), 391 (178)	*m*			$\tilde{\nu}_{max}$ = 17.2 (+3.43), 23.9 (+0.33), 25.9 (−0.07), 28.3 (+0.21)
cis-K$_3$[Co(ox)(NO$_2$)$_2$CO$_3$]	*c*	535 (182)	c			
cis-[Co(en)$_2$(NO$_2$)$_2$]*cis*$(+)_{589}$[Co(py)$_2$(ox)CO$_3$]·2H$_2$O	*m*	556 (138), 391 (191)	*m*			$\tilde{\nu}_{max}$ = 18.4 (+0.87), 25.9 (−0.10)
trans-K[Co(py)$_2$(ox)CO$_3$]·2.5H$_2$O	*g*	549 (66.1), ~420, 374 (63.1)	*g*			
Na$(+)_{589}$[Co(tn)(ox)CO$_3$]	*m*	562 (120), 388 (195)	*m*			$\tilde{\nu}_{max}$ = 18.3 (+1.27), 23.8 (+0.09), 25.8 (−0.06)
[Co(en)$_2$ox]$(+)_{589}$[Co(NH$_3$)$_2$(mal)CO$_3$]·2H$_2$O	*x*	562 (100), 389 (138)	*x*			$\tilde{\nu}_{max}$ = 16.5 (−1.21), 18.4 (+0.81), 23.9 (−0.28), 27.2 (−0.26)
trans(*N*)-[Co(picol)$_2$CO$_3$]$^-$	*i*	549, 397	*i*			
C_1-*cis*(*N*)-K[Co(picol)$_2$CO$_3$]·2H$_2$O	*i*	549 (155), 395 (186)	*i*			
C_2-*cis*(*N*)-K[Co(picol)$_2$CO$_3$]·1.5H$_2$O	*i*	543 (115), 397 (200)	*i*			
mer,cis(NH$_3$)-[Co(NH$_3$)$_2$(picol)CO$_3$]	*i*	546 (105), 373 (182)	*i*			
mer,trans(NH$_3$)-[Co(NH$_3$)$_2$(picol)CO$_3$]·2H$_2$O	*i*	521 (110), 400 (sh)	i			
fac-[Co(NH$_3$)$_2$(picol)CO$_3$]·H$_2$O	*i*	529 (117), 372 (170)	*i*			
cis-K$_2$[Co(acac)(NO$_2$)$_2$CO$_3$]·H$_2$O	*c*	534 (151)	*c*			
K$_2$[Co(NH$_3$)(NO$_2$)$_3$CO$_3$]·H$_2$O	*c*	471 (135)	*c*			
mer,cis(NH$_3$)-[Co(NH$_3$)$_2$(gly)CO$_3$]	*aa*	530 (85.1), 401 (39.8), 367 (70.8)	*aa*			^{1}H NMR and IR spectra
mer,trans(NH$_3$)-[Co(NH$_3$)$_2$(gly)CO$_3$]	*aa*	553 (107), 377 (178)	*aa*			^{1}H NMR and IR spectra
fac-[Co(NH$_3$)$_2$(gly)CO$_3$]	*aa*	533 (110), 374 (135)	*aa*			^{1}H NMR and IR spectra
		533 (144), 374 (166)	*bb*			
cis,cis-[Co(NH$_3$)$_2$(CN)$_2$CO$_3$]$^-$	*c*	499 (91), 431 (105), 336 (sh)	*c*			
cis-K[Co(gly)$_2$CO$_3$]·H$_2$O	*cc*	556 (147), 391 (163)	*cc*			
cis-Ag$_3$[Co(L-asp)$_2$CO$_3$]·4H$_2$O	*c*					
β-*mer*(*N*)-[Co(adao)CO$_3$]·H$_2$O	*dd*	526 (162), 379 (177)	*dd*			^{1}H NMR spectrum
β-*fac*(*N*)-[Co(adao)CO$_3$]·2H$_2$O	*dd*	526 (206), 369 (160)	*dd*			^{1}H NMR spectrum
mer(*N*)-[Co(i-dtma)CO$_3$]	*ee*	516 (132), 364 (95.5)	*ee*			^{1}H NMR spectrum
fac(*N*)-[Co(i-dtma)CO$_3$]	*ee*	517 (162), 368 (129)	*ee*			^{1}H NMR spectrum
mer,cis(NH$_3$)-[Co(NH$_3$)$_2$(val)CO$_3$]	*bb*	555 (93.3), 373 (120)	*bb*			^{1}H NMR spectrum
mer,trans(NH$_3$)-[Co(NH$_3$)$_2$(val)CO$_3$]·0.5H$_2$O	*bb*	532 (79.4), 416 (sh), 366 (63.1)	*bb*			^{1}H NMR spectrum

TABLE X (*Continued*)

compd	prepn ref	vis/UV nm (M^{-1} cm^{-1})	ref	IR, cm^{-1}	ref	comments
fac-$[Co(NH_3)_2(val)CO_3]$	*bb*	532 (110), 371 (135)	*bb*			^1H NMR spectrum
D(+)*cis*(*N*),*cis*(*O*)-$K[Co(\text{L-val})_2CO_3]\cdot 3.5H_2O$	*cc*	552 (172), 392 (163)	*cc*	1595	*cc*	$\tilde{\nu}_{max}$ = 17.9 (+3.55)
mer,cis(NH_3)-$[Co(NH_3)_2(\alpha\text{-ala})CO_3]\cdot H_2O$	*bb*	550 (93.3), 378 (129)	*bb*			^1H NMR spectrum
mer,trans(NH_3)-$[Co(NH_3)_2(\alpha\text{-ala})CO_3]$	*bb*	531 (100), 414 (sh), 366 (110)	*bb*			^1H NMR spectrum
fac-$[Co(NH_3)_2(\alpha\text{-ala})CO_3]$	*bb*	533 (141), 369 (158)	*bb*			^1H NMR spectrum
fac-$[Co(NH_3)_2(\beta\text{-ala})CO_3]$	*bb*	537 (148), 375 (151)	*bb*			^1H NMR spectrum
mer,cis(NH_3)-$[Co(NH_3)_2(\beta\text{-ala})CO_3]$	*bb*	555 (97.7), 375 (126)	*bb*	1600, 1270, 1030, 760	*bb*	^1H NMR spectrum
mer,trans(NH_3)-$[Co(NH_3)_2(\beta\text{-ala})CO_3]\cdot 0.5H_2O$	*bb*	547 (129), 372 (141)	*bb*			^1H NMR spectrum
cis-$K[Co(\text{L-ala})_2CO_3]\cdot 3H_2O$	*cc*					
$[Co(DH)_2(py)_2]$*cis*-$[Co(DH)_2CO_3]$	363					
$[Co(DH)_2(\beta\text{-picoline})]$*cis*-$[Co(DH)_2CO_3]$	363					
$[Co(DH)_2(PhNH_2)]$*cis*-$[Co(DH)_2CO_3]$	363					
$[Co(DH)_2(p\text{-}ClC_6H_4NH_2)]$*cis*-$[Co(DH)_2CO_3]$	363					
$[Co(DH)_2(p\text{-}BrC_6H_4NH_2)]$*cis*-$[Co(DH)_2CO_3]$	363					
trans(*N*)-$K[Co(mda)(NH_3)CO_3]\cdot 2.5H_2O$	*u*	543 (115), 379 (98), 418 (sh)	*u*			
cis-$K_2[Co(nta)CO_3]\cdot H_2O$	*ff*	~571 (~146), ~378 (~128)	*ff*	1670 sh, 1605 s, 1010, 765	*ff*	
Δ-*cis*-α-$Na[Co(pren)CO_3]\cdot 3H_2O$	*gg*	570 (109), 520 (90 sh), 385 (150)	*gg*			^{13}C NMR spectrum; $\tilde{\nu}_{max}$ = 17.2 (−3.04), 24.0 (−0.31), 26.0 (+0.10)
α-*cis*-$K[Co(edda)CO_3]\cdot 4H_2O$	*hh*	565 (114), 382 (128)	*hh*			^1H NMR and CD spectra
		545 (96), 385 (138)	359			
β-*cis*-$K[Co(edda)CO_3]\cdot H_2O$	*hh*	533 (234), 390 (182)	*hh*			^1H NMR and CD spectra
		540 (214)	359			
S-fac(*N*)-$[Co(dien)(CN)CO_3]$	*u*	481 (162), 345 (182), 377 (sh)	*u*			
mer(*N*)-$[Co(dien)(CN)CO_3]$	*u*	490 (151), 350 (158)	*u*			
cis-$[Co(tren)CO_3]ClO_4\cdot H_2O$	*ii*	504 (130), 354 (110)	325			
	320	505 (132), 354 (111)	328			
		503 (134), ~354 (~112)	320			
		504 (132)	326			
α-*cis*-$[Co(trien)CO_3]ClO_4\cdot H_2O$	*jj*	503 (124)	326			CD spectrum[kk]
β-*cis*-$[Co(trien)CO_3]ClO_4\cdot H_2O$	*jj*	503 (180)	326			CD spectrum[kk]
$(+)_{589}$*cis*-β-$[Co(3,8\text{-dimetrien})CO_3]ClO_4$	214					
α-*cis*-$[Co(dmtr)CO_3]ClO_4$	343					
β-*cis*-$[Co(dmtr)CO_3]ClO_4\cdot H_2O$	343					
Λ-*cis*-α-$[Co(S,S\text{-pyhn})CO_3]$	11					CD spectrum
cis-$[Co(cyclen)CO_3]Cl\cdot 2H_2O$	*mm*	530 (280), 368 (210)	*mm*			
cis-$[Co([13]aneN_4)CO_3]ClO_4$	*nn*	501 (178), 356 (133)	*nn*	1653 s, 1605 br, 831 m, 752 m, 676 m	*nn*	Λ = 81 cm^2 ohm^{-1} mol^{-1} (H_2O)
cis-$[Co(Me_2[14]dieneN_4)CO_3]ClO_4\cdot 1.5H_2O$	*oo*	504 (133), 360 (167), 244 (18 000), 233 (16 000 sh)	338	1660 vs, 1630 vs, 1250 m, 810 m, 755 m	*oo*	
cis-$[Co(cyclam)CO_3]Cl$	*pp*	~517 (~204), ~360 (~183)	314			
		520 (154), 365 (140)	*nn*			
cis-$[Co(trans[14]dieneN_4)CO_3]ClO_4$	*qq*	500 (121), 350 (135), 243 (16 000), 192 (~10 000)	*rr*	1660 vs, 1630 vs, 1220 m, 820 m, 750 ms	*rr*	^1H NMR spectrum[ss]
cis-$[Co(Me_4[14]diene)CO_3]ClO_4\cdot 2H_2O$	*tt*	506 (126), 364 (176)	*tt*	1630, 830, 755, 675	*tt*	
cis-$[Co(Me_6[14]diene)CO_3]ClO_4$	351	500 (121), 350 (135), 243 (16 000), 192 (10 000)	*rr*	1665	131	
cis-$[Co([15]aneN_4)CO_3]ClO_4\cdot 1.5H_2O$	*nn*	528 (138), 366 (182)	*nn*	1662 s, 1621 br, 828 m, 750 m, 676 m	*nn*	Λ = 90 cm^2 ohm^{-1} mol^{-1} (H_2O)

cis-[Co([16]aneN$_4$)CO$_3$]ClO$_4$	*nn*	540 (146), 375 (197)	*nn*	1656 s, 1613 br, 828 m, 752 m, 672 m	*nn*	$\Lambda = 95$ cm^2 ohm^{-1} mol^{-1} (H$_2$O)
Λ-β-[Co(5*R*,7*R*-Me$_2$-2,3,2-tet)CO$_3$]Cl·1.5 H$_2$O	*uu*	515 (158), 360 (132)	*uu*			$\tilde{\nu}_{\mathrm{max}} = 18.35$ (+2.47), 20.49 (−1.51), 25.51 (+2.47), 28.57 (+0.41); ^{1}H NMR spectrum
Λ-β-[Co(1,5*R*,7*R*,11-Me$_4$-2,3,2-tet)CO$_3$]ClO$_4$·H$_2$O	*uu*	530 (174), 372 (148)	*uu*			$\tilde{\nu}_{\mathrm{max}} = 18.05$ (+2.19), 20.37 (−0.46), 25.13 (+0.55), 28.01 (+0.42); ^{1}H NMR spectrum
cis-[Co(3,2,3-tet)CO$_3$]ClO$_4$	*vv*	520 (127), 360 (125)	*vv*			$\Lambda = 90$ cm^2 ohm^{-1} mol^{-1} (H$_2$O)
α-*cis*-[Co(tetb)CO$_3$]ClO$_4$	*ww*	554 (200), ~387 (~185)	*ww*			
β-*cis*-[Co(tetb)CO$_3$]ClO$_4$	*ww*	551 (184), ~381 (~180)	*ww*			
cis-[Co(tetd)CO$_3$]ClO$_4$	*ww*	~553 (~188), ~385 (~171)				
(+)-Δ-*cis*-β-*R*,*R*:*S*,*S*-[Co(3,2,3-tet)CO$_3$]ClO$_4$·MeOH	*xx*					$[\alpha]_{\mathrm{D}}$ 21° (0.01 M H$_2$O)
cis-β-*R*,*R*:*S*,*S*-[Co(*R*,*S*,*S*,*R*:*S*,*R*,*R*,*S*-ch-3,2,3-tet)CO$_3$]ClO$_4$	*yy*					$\Lambda_{\mathrm{M}} = 85$ cm^2 ohm^{-1} mol^{-1} (H$_2$O)
cis-β-*R*,*R*:*S*,*S*-[Co(*R*,*S*,*R*,*S*-ch-3,2,3-tet)CO$_3$]Cl	*yy*					$\Lambda_{\mathrm{M}} = 73$ cm^2 ohm^{-1} mol^{-1} (H$_2$O) $[\alpha]_{\mathrm{D}}$ +92° (0.002 M, H$_2$O)
(+)-Λ-*cis*-β-*R*,*R*-[Co(*R*,*S*,*R*,*S*-ch-3,2,3-tet)CO$_3$]BPh$_4$	*yy*					$[\alpha]_{\mathrm{D}}$ +63° (0.001 M, MeOH)
cis-β-*R*,*R*:*S*,*S*-[Co(*R*,*S*,*R*,*S*-ch-3,2,3-tet)CO$_3$]ClO$_4$	*yy*					not active
(−)-Δ-*cis*-β-*S*,*S*-[Co(*S*,*R*,*R*,*S*-ch-3,2,3-tet)CO$_3$]ClO$_4$·H$_2$O	*yy*	~526 (~145), ~364 (~138)	*yy*			$[\alpha]_{\mathrm{D}}$ −320° (0.005 M, H$_2$O)
cis-[Co(diars)$_2$CO$_3$]PF$_6$	197			1675 s, 1190 m, 982 w, 890 sh, 732 m, 665 m, 449 m	197	mp 142°; ^{1}NMR spectrum
cis-[Co(diars)$_2$CO$_3$]ClO$_4$·CH$_2$Cl$_2$	*zz*					*cis*-(+) isomer resolved
cis-β-[Co(*R*,*R*:*S*,*S*-tetars)CO$_3$]ClO$_4$	*aaa*					$\Lambda = 77$ cm^2 ohm^{-1} mol^{-1} (MeOH)
cis-α-[Co(*R*,*R*:*S*,*S*-tetars)CO$_3$]ClO$_4$	*aaa*					$\Lambda = 75$ cm^2 ohm^{-1} mol^{-1} (MeOH)
Δ-*cis*-β-[Co(*R*,*R*-tetars)CO$_3$]ClO$_4$	*aaa*					$[\alpha]_{\mathrm{D}}$ −87 (±40)°, $[\alpha]_{436}$ +308 (±30)° (MeOH)
Λ-*cis*-α-[Co(*R*,*R*-tetars)CO$_3$]ClO$_4$	*aaa*					$[\alpha]_{\mathrm{D}}$ +284 (±25)°, $[\alpha]_{578}$ +328 (±30)°, $[\alpha]_{546}$ +425 (±40)°, MeOH
cis-β-[Co(*R*,*S*-qars)CO$_3$]ClO$_4$	*bbb*					
cis-β-[Co(*R*,*S*-fars)CO$_3$]ClO$_4$·0.25NaClO$_4$	*bbb*					
cis-β-[Co(dtnd)CO$_3$]ClO$_4$	*ccc*	524 (387), 368 (485 sh)	*ccc*	1655 s, 1630 vs, 1610 vs, 823	*ccc*	
K$_3$[VO(O$_2$)$_2$CO$_3$]	232			1575 vs, 1358 s, 1337 s, 1048 m, 690 w	232	
cis-K[Cr(ox)$_2$CO$_3$]·3H$_2$O	350	577 (69), 415 (108), 265 (1040 sh)	350	1025	350	
K$_6$[{Fe(OH)}$_2$(CO$_3$)$_5$]·H$_2$O	*ddd*			1515 s, 1380 s, 1080 s, 858 s, 835 s, 707 m	*ddd*	
Na$_2$[Fe$_3$O$_2$(OH)$_3$(CO$_3$)$_2$]	*ddd*			1517 s, 1340 s, 1058 s, 840 s	*ddd*	
K[Co(NH$_3$)$_6$][Fe$_3$(OH)$_4$(CO$_3$)$_6$]	*ddd*			1340 s, 1085 s, 837 s, 700 w	*ddd*	
K$_5$[Co(NH$_3$)$_6$][Fe$_3$(OH)$_4$(CO$_3$)$_6$]$_2$	*ddd*			1335 s, 1070 w, 853 m	*ddd*	
K[Co(NH$_3$)$_6$][Fe$_2$(OH)$_4$(CO$_3$)$_3$]	*ddd*			1600 s, 1340 sh, 1068 w, 696 m	*ddd*	
NH$_4$[Co(NH$_3$)$_6$][Fe$_2$(OH)$_4$(CO$_3$)$_3$]	*ddd*			1350 s, 1090 s, 855 s	*ddd*	
CuCO$_3$	*eee*			1460 s, 1420 s, 1090 w, 860 m, 760 w, 743 w	*eee*	
Na$_2$[Cu(CO$_3$)$_2$]·3H$_2$O	*fff*			1525 s, 1385 s, 1355 s, 1330 s, 1070 m, 1055 m, 855 s, 750 s, 700 m, 645 w	*fff*	Raman: 1523, 1395, 1330, 1071, 766, 750, 697 (cm^{-1})
[Cu(NH$_3$)$_2$CO$_3$]	*ggg*	635	*ggg*	282 {ν (Cu–O)}	*ggg*	
[C(NH$_2$)$_3$]$_2$[Cu(CO$_3$)$_2$]	*hhh*			1518 vs, 1022 w, 860 vs, 747 s, 708 s	*hhh*	
NH$_4$[Ga(OH)$_2$CO$_3$]	*iii*			1540, 1470, 1380, 1100, 860, 770, 725	*iii*	
K$_4$[Zr(CO$_3$)$_4$]·2H$_2$O	*jjj*			1040, 1012, 860, 755	*kkk*	CO$_3$ bands only

TABLE X (*Continued*)

compd	prepn ref	vis/UV nm (M^{-1} cm^{-1})	ref	IR, cm^{-1}	ref	comments
$K_4[Zr(ox)_2F_2CO_3]\cdot 5H_2O$	*kkk*			1052, 848, 770	*kkk*	CO_3 bands only
$K_4[Hf(ox)_2F_2CO_3]\cdot 5H_2O$	*kkk*			1053, 848, 770	*kkk*	CO_3 bands only
$[Ru(phen)_2CO_3]$	*lll*	571 (9770)	*lll*	1563, 1255, 385, 301	*lll*	vis spectrum in CH_2Cl_2
$[Ru(phen)_2CO_3]\cdot 5H_2O$	*lll*			1563, 1300, 377, 298	*lll*	
$[Ru(bpy)_2CO_3]$	*lll*	585 (9770), 391 (10 200)	*lll*	1565, 1225, 381, 300	*lll*	vis spectrum in CH_2Cl_2
$[Ru(bpy)_2CO_3]$	*lll*			1563, 1300, 377, 298	*lll*	
cis-$[Rh(en)_2CO_3]ClO_4$	*mmm*	327 (312)	*mmm*			
$[Pt(diphos)_2CO_3]$	502			1665 w, 1175 s, 972 sh, 815 s, 352 m	502	
$[Pt(PPh_3)_2CO_3]$	502			1685 vs, 1185 s, 980 s, 815 s, 675 sh, 409 m, 363 vs	502	
	nnn			1680 vs, 1180 w, 980 w, 815 w, 760 m	*nnn* *ooo*	mp = 202-205 °C; ^1H NMR spectrum[nnn,ooo]
$[Pd(PPh_3)_2CO_3]$	502			1655 vs, 1630 vs, 1200 vs, 989 s, 817 s, 667 sh, 402 s, 370 vs	502	
$[Pd(PPh_3)_2CO_3]$	*nnn*					mp = 202-205 °C
$[Pt(PEt_3)_2CO_3]$	382			1660, 1635, 1613	382	mp = 160-170 °C; ^1H NMR spectrum
$[Pt(PMe_2Ph)_2CO_3]$	382			1660, 1635, 1615	382	mp = 160 °C; ^1H NMR spectrum
$[Pt(PMePh_2)_2CO_3]$	*ppp*			1670 vs, 1630 m, 1290 s, 985 m 820 m	*ppp*	mp = 206-208 °C
$[Pt(AsPh_3)_2CO_3]$	502			1693 vs, 1187 s, 975 s, 810 s, 678 s, 427 m, 344 vs		
$PbCl_2\cdot PbCO_3$	*qqq*			1512, 1344, 1062, 837, 760, 650	*rrr*	Raman: 1417.5, 1326.5, 1062, 834, 666.5 cm^{-1}

[a] Preparation the same as for $Na_2[Cu(CO_3)_2]\cdot 3H_2O$: Applebey, M. P.; Lane, K. W. *J. Chem. Soc.* 1918, *113*, 609. [b] Johnson, W. L.; Geldard, J. F. *Inorg. Chem.* 1979, *18*, 664. [c] Shibata, M. *Proc. Jpn. Acad.* 1974, *50*, 779. [d] Churchill, M. R.; Harris, G. M.; Lashewycz, R. A.; Dasgupta, T. P.; Koshy, K. *Inorg. Chem.* 1979, *18*, 2290. [e] Muramoto, S.; Shibata, M. *Chem. Lett.* 1977, 1499. [f] Hyde, K. E.; Hyde, E. W.; Moryl, J.; Baltus, R.; Harris, G. M. *Inorg. Chem.* 1980, *19*, 1603. [g] Ida, Y.; Fujinami, S.; Shibata, M. *Bull. Chem. Soc. Jpn.* 1977, *50*, 2665. [h] Ida, Y.; Imai, K.; Shibata, M. *Ibid.* 1978, *51*, 2741. [i] Ida, Y.; Sakai, M.; Shibata, M. *Ibid.* 1977, *50*, 2807. [j] Fujinami, S.; Shibata, M. *Chem. Lett.* 1972, 219. [k] Coddington, P. M.; Hyde, K. E. *Inorg. Chem.*, in press. [l] Schlessinger, G. *Inorg. Synth.* 1960, *6*, 173. [m] Tsuji, K.; Fujinami, S.; Shibata, M. *Bull. Chem. Soc. Jpn.* 1981, *54*, 1531. [n] Glenister, J. 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acetic acid in the vapor phase. More recent X-ray and neutron diffraction data[203,204] led to a refinement of this structure with the hydrogen atoms, or deuterium atoms, occupying two possible sites with an approximate probability ratio of 4:1. This gives rise to a degree of disorder in the dimer, $(HCO_3)_2^{2-}$.[204] The authors[204] did point out, however, that the degree of disorder may be specimen dependent. Note that $RbHCO_3$ also has this dimeric structure.[205]

Sodium carbonate monohydrate consists of sheets of CO_3^{2-} groups with H bonding between the layers of the O_1 and O_3 oxygen atoms.[206] These oxygens are also bound to sodium atoms, whereas the O_2 oxygen is bound only to four sodiums in an approximate planar configuration. Anhydrous K_2CO_3 is symmetrical and planar with a D_{3h} symmetry.

Consideration of the various magnesium, calcium, strontium, and barium carbonates in Table XVII shows the carbonate to be, or very close to, planar and trigonal, with C–O bond lengths that vary only slightly. In fact, for the majority of carbonates and bicarbonates considered up to this point in the discussion, the average C–O bond length is (1.285 ± 0.021) Å and the average O–C–O angle is (120.0 ± 2.1)°, which compares almost exactly with the mean values computed by Zemann[64] for 34 carbonates of (1.284 ± 0.018) Å and (120.0 ± 2.1)°. From these two values, an average O–O distance within the carbonate of (2.22 ± 0.17) Å can be derived.

A more detailed examination of these data in Table XVII reveals that in dolomite, for example, the carbonate group has a slight pyramidal shape with the carbon atom 0.018 Å out from the plane of the oxygen atoms,[207] whereas fairchildite exhibits a somewhat larger deviation of 0.038 (9) Å.[208] Another finer aspect of these structures is that the arrangement of six oxygen atoms around the Mg^{2+} ion has a more exact octahedral symmetry than for the larger Ca^{2+} ion. Moreover, in our example of dolomite, the Mg–O bond lengths are shorter than they are in magnesite, while the Ca–O bond lengths are longer than in calcite. In the other example of fairchildite, $K_2Ca(CO_3)_2$[209] is in fact a double salt of potassium and calcium carbonate which therefore contains two distinct carbonate groups as shown in Table XVII.

Pauling[210] used measurements of the diamagnetic anisotropy of the minerals calcite, aragonite, strontianite, and witherite to estimate the degree of covalency within the metal–oxygen bonds, amounting to 20.6, 20.6, 15.4, and 14.2%, respectively. This allowed him to further calculate the resultant charge on the metal atoms.

All three monodentate carbonato complexes shown in Table XVIII are involved in extensive hydrogen bonding. For the Pd(II) complex, intermolecular H bonding between O_2 and O_3 of a pair of such complexes leads to a structure similar to that of $KHCO_3$. Intramolecular H bonding for the two cobalt complexes is observed between the carbonate oxygens, O_2, and the protons on the axial ligands. Of particular interest is the trans effect of the carbonate ligand in the $[Co(NH_3)_5CO_3]^+$ moiety, where the trans Co–NH_3 bond is weakened to 1.98 (3) Å compared to 1.96 (2) Å for the four cis ligands.[211] Some distortion of octahedral symmetry occurs in this case with the O_1CoN_{cis} angle being 89.9 (1.2)°.

From the data listed in Table XIX it can be seen that the bidentate carbonate creates the largest distortion in the symmetry of the metal ion by imposing such a narrow O_1MO_2 angle. It is therefore somewhat surprising that the O_1MO_2 angle and, for that matter, the MO_1C angle remain so constant for metal complexes with coördination numbers 4 through 6, i.e., mean values for these two angles are 68.0 (18)° and 90.3 (8)°, respectively. The origin of this consistency can be easily traced to the O_1CO_2 angle that is not reduced below 108° for any of the complexes listed in Table XIX. In fact, for the larger central metal ions with their longer M–O_1 distances (such as W^{IV}–$O_{1,2}$) the O_1MO_2 angle becomes quite narrow at ca. 53° while maintaining an O_1CO_2 angle of ca. 114°. The narrowest O_1CO_2 angle in this group is reported for $[Co(phen)_2CO_3]Cl\cdot 3H_2O$ where the strain due to the planar phenanthroline ligands is quite acute leading to two distinct phen ligands and large differences in the C–O_1, C–O_2 bond lengths.[212] Note that these two bonds are generally almost equal except where the remaining ligands are asymmetrical, such as in the example of $K[Co(L\text{-}val)_2CO_3]\cdot 2H_2O$.[213] In this particular case, the cis(*N*)-cis(*O*) configuration could in fact be inferred from this inequality. Complexes in this group with coordination numbers 5 and 6 all have longer C–O_1, C–O_2 bonds (1.315 (15), 1.312 (18) Å) relative to their C–O_3 bonds (1.234 (20) Å) as a direct result of M–$O_{1,2}$ bonding, with the exception of the aforementioned valinato complex. In other words, this reflects the enhanced double bond character of the C–O_3 bond. For most of the remaining complexes of higher coordination number, hydrogen bonding tends to cloud this picture.

Distortion of the symmetry of the complex at the metal center is manifested in the angle of twist of the MCO_3 plane. For the cobalt(III) complexes this can be measured relative to the plane of the ML_1L_2 plane, where L_1 and L_2 are the ligands trans to O_1 and O_2. The angle of twist may be as great as 4.3° as in the case of *cis*-*β*-$[Co(3,8\text{-}Me_2trien)CO_3]ClO_4$.[214] However, no elongation of the M–$L_{1,2}$ bonds due to the trans effect of the oxygen atoms, O_1 and O_2, was observed. In general, the coordinated bidentate amine ligands, phen, bpy, tn, etc., are asymmetrical. In the particular example of *cis*-$[Co(tn)_2CO_3]ClO_4$, the two six-membered CoN_2C_3 rings adopt their configurations, with one flatter than the other.[215]

Little comment can be made concerning the bonding in the remaining bridged carbonato complexes summarized in Tables XXI–XXIV, except one is immediately struck by the incredible diversity of the carbonate ligand as it displays such a range of bonding modes. The complexes in Table XXI establish that the bonding angle, MO_1C, of the bridge in this particular group is close to 120°, especially where M–M bonding is involved, e.g., in the Cr(II) and two Rh(III) complexes. Where metal–metal bonding does not occur, this MO_1C angle is extended to ca. 127°. In addition, the carbonate group has close to trigonal symmetry and the C–$O_{1,2}$, C–O_3 bonds are similar to those recorded for mononuclear bidentate complexes (viz., 1.301 (15), 1.260 (17) Å).

A comparison of the structure of $[\{Rh(H_2O)\}_2(\mu\text{-}CH_3CO_2)_4]$[216] with that of $Cs_4[\{Rh(H_2O)\}_2(\mu\text{-}CO_3)_4]\cdot 6H_2O$ shown in Table XXI establishes the close similarity of

Table XI. Spectroscopic Properties of Bridged Carbonato Complexes

compd	prepn ref	vis/UV, nm (M^{-1} cm^{-1})	ref	IR, cm^{-1}	ref	comments
$[\{Ti(cp)_2\}_2(\mu\text{-}CO_3)]_2$	402			1475 ms, 1425 vs	402	
$[\{Cr([9]aneN_3)\}_2(\mu\text{-}OH)_2(\mu\text{-}CO_3)](ClO_4)_2\cdot 3H_2O$	345	510 (101), 373 (84), 335 (41 sh)	345			$I_2\cdot 3H_2O$ salt also prepared
$[Cr_2(CO_3)_3]^{3-}$		590, 407, 353	*a*			
$[\{Co(NH_3)_3\}_2(\mu\text{-}OH)_2(\mu\text{-}CO_3)]SO_4\cdot 5H_2O$	347	~520 (~122), ~294 (~3200 sh)	347	1600, 1480, 1270, 825	347	
$[\{Co(NH_3)_5\}_2(\mu\text{-}CO_3)](SO_4)_2\cdot 4H_2O$	*b*	505 (151), 350 (170)	*c*	1480, 1340, 1030, 830, 760, 670	*c*	
	d	505 (138), 350 (sh), 255	*d*			
		510 (151)	*e*			
ΛΛ-*cis*(*N*),*trans*(*O*)-$[(S\text{-}pra)_2Co(\mu\text{-}CO_3)(\mu\text{-}OH)\text{-}Co(S\text{-}pra)(S\text{-}praH)]\cdot 2H_2O$	*f*					vis, IR, and CD spectra
ΛΛ-*cis*(*N*),*cis*(*O*)-$[(S\text{-}pra)_2Co(\mu\text{-}CO_3)(\mu\text{-}OH)\text{-}Co(S\text{-}pra)(S\text{-}praH)]$	*f*					vis, IR, and CD spectra
ΛΛ-*cis*(*N*),*trans*(*O*)-$[\{(S\text{-}pra)(S\text{-}praH)Co\}_2\text{-}(\mu\text{-}CO_3)_2]\cdot 2NaHCO_3\cdot 2H_2O$	*f*					vis, IR, and CD spectra
$[\{Co(diars)_2(CO_3H)\}_2(\mu\text{-}CO_3H)](BF_4)_3$	197			1669 s, 1633 m, 1220 mw, 821 m, 767 m, 744 m, 670 w	197	^1H NMR spectrum
$[\{Co(diars)_2(CO_3H)\}_2(\mu\text{-}CO_3H)](ClO_4)_3$	197			1665 s, 1630 ms, 1215 mw, 1000 w, 820 m, 764 m	197	mp = 216 °C; ^1H spectrum
$[\{Ni(dla)\}_2(\mu\text{-}CO_3)](ClO_4)_2\cdot 2DMF$	*g*			1587 vs, 1459 s, 1375 s, 1342 vs, 834, 733	*g*	the $Me_2CO\cdot 3H_2O$ solvate also isolated
$[\{Cu(PPh_3)_2\}_2(\mu\text{-}CO_3)]$	*h*			1475 s, 1340 s, 830 m	*h*	^1H NMR spectrum
$[\{Cu(dla)\}_2(\mu\text{-}CO_3)](ClO_4)_2\cdot DMF$	*i*	1053 (50), 645 (300), 373 (5100)	*i*	1570, 1350, 830, 730	*i*	
$[\{Cu(dla)\}_2(\mu\text{-}CO_3)](ClO_4)_2\cdot H_2O$	*g*			1560 vs, 1454 s, 1370 sh, 1354 vs, 829, 733	*g*	the $1.5Me_2O\cdot 1.5H_2O$ solvate also isolated
$[\{Cu(teed)Cl\}_2(\mu\text{-}CO_3)]$	*j*	760 (285), 300 (6700)	*j*	1530, 840	*j*	magnetic, ESR, emf properties
$[\{Cu(tmed)Cl\}_2(\mu\text{-}CO_3)]$	*j*	750 (570), 375 (2500 sh), 287 (9770)	*j*	1520, 1380, 810, 745, 515	*j*	magnetic, ESR, emf properties
$[\{Cu(teed)Br\}_2(\mu\text{-}CO_3)]$	*j*	713 (320), 492 (360 sh), 320 (5400), 270 (4560)	*j*	1535, 830, 510	*j*	magnetic, ESR properties
$[\{Cu(tmtd)Br\}_2(\mu\text{-}CO_3)]$	*j*	744 (590), 380 (5880), 330 (4400), 275 (5060)	*j*	1560, 1380, 890, 735, 505	*j*	diamagnetic
$[\{Cu(tmtd)(NO_3)\}_2(\mu\text{-}CO_3)]$	*j*	720 (33), 290 (5630), 265 (5125)	*j*	1580, 1390, 895, 740, 505	*j*	diamagnetic
$[\{Cu(tmtd)Cl\}_2(\mu\text{-}CO_3)]$	*k*	775 (450), 375 (4475), 300 (5080), 255 (5140)	*k*	1560 s, 1380 s, 895 m, 730 m	*k*	mp = 124-126 °C
$[\{Cu(tpam)Cl\}_2(\mu\text{-}CO_3)]$	*j*	719 (156), 294 (33 600), 265 (28 000)	*j*	1600, 1490	*j*	magnetic, ESR, emf properties
$[\{Cu(tpam)(OAc)\}_2(\mu\text{-}CO_3)]$	*j*	750 (570), 375 (2500 sh), 287 (9770)	*j*			magnetic, ESR properties
$[\{Cu(tpam)Br\}_2(\mu\text{-}CO_3)]$	*j*	684 (95), 293 (29 200), 266 (23 750)	*j*	1600, 1490	*j*	magnetic, ESR properties

$\{Cu(pip)(H_2O)\}_3(\mu\text{-}CO_3)](NO_3)_4$	*l*			1460, 840, 752	*l*	$(ClO_4)_4$ salt also isolated
$[\{Cu(mdpt)\}_3(\mu\text{-}CO_3)](ClO_4)_4$	*g*			1474 s, 1425 vs, 838, 774, 672	*g*	$\mu_{eff} = 1.91$ BM
$[\{Cu(dpt)\}_3(\mu\text{-}CO_3)](ClO_4)_4 \cdot 2H_2O$	*m*			1475, 1425, 837, 782, 672	*m*	$\mu_{eff} = 1.87$ BM (20 °C)
$[\{Cu(dpt)\}_4(\mu\text{-}CO_3)]Cl_6 \cdot 8H_2O$	*m*			1540, 1365, 818, 740	*m*	$\mu_{eff} = 1.67$ BM (20 °C)
$[Rh_2(PPh_3)_5(\mu\text{-}CO_3)] \cdot C_6H_6$	500			1485 s, 1460 vs, 1360 m, 1350 m, 820 w, 500 w	500	Raman: 1660 m, 1300 s (cm^{-1}); ^{31}P, ^1H NMR spectra
$[\{Rh(P(i\text{-}Pr)_3)_2(CO)\}_2(\mu\text{-}CO_3]$	403			1533 s, 1300 s, 1275 s, 829 w	403	mp = 145 °C
$Cs_4Na_2[\{RhCl\}_2(\mu\text{-}CO_3)_4] \cdot 8H_2O$	*n*					
$Cs_4[\{Rh(H_2O)\}_2(\mu\text{-}CO_3)_4] \cdot 6H_2O$	*n*					
$[\{Rh([9]aneN_3)\}_2(\mu\text{-}OH)_2(\mu\text{-}CO_3)]$	346	339 (430)	346			
$[Mo_2(PMe_2Ph)_6(CO)_2(\mu\text{-}CO_3)_2]$	445			1835	500	
$[(PPh_3)_2(Me)Pd(\mu\text{-}CO_3)Pd(PPh_3)(Me)]$	*o*			1475 s, 1360 m, 820 w	*o*	^1H, ^{31}P NMR data
$[\{Tl(8\text{-hydroxyquinoline})\}_2(\mu\text{-}CO_3)]$	*p*			1690, 1580, 1300, 1260, 1020	*p*	
$[Ce_3Cl(CO_3)_4]$	*q*			1540 s, 1460 s, 1380 s, 1095 w, 859 s, 826 s, 743 w, 714 m, 675 w	*q*	
$[Ce_4Cl(OH)_3(CO_3)_4]$	*q*			1520 s, 1425 s, 1395 sh, 1065 w, 869 m, 840 m, 775 m, 725 sh, 705 m, 680 w	*q*	

[a] Tandon, S. P.; Sule, K. K.; Surana, S. S. L. *Phys. Status Solidi* 1973, *20*, K65. [b] Kranig, J. *Ann. Chim. Paris* 1929, *41*, 87. [c] Kremer, E.; Mac-Coll, C. R. P. *Inorg. Chem.* 1971, *10*, 2182. [d] Abedini, M. *Ibid.* 1976, *15*, 2945. [e] Mac-Coll, C. R. P. *Rev. Roum. Chim.* 1979, *24*, 575. [f] Nishide, T.; Saito, K. *Bull. Chem. Soc. Jpn.* 1977, *50*, 2618. [g] Martin, J. W. L.; Curtis, N. L. *Aust. J. Chem.* 1980, *33*, 1241. [h] Yamamoto, T.; Kubota, M.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* 1980, *53*, 680. [i] Davis, A. R.; Einstein, F. W. B.; Curtis, N. F.; Martin, J. W. L. *J. Am. Chem. Soc.* 1978, *100*, 6258. [j] Churchill, M. R.; Davies, G.; El-Sayed, M. A.; El-Shazly, M. F.; Hutchinson, J. P.; Rupich, M. W. *Inorg. Chem.* 1980, *19*, 201. [k] Churchill, M. R.; Davies, G.; El-Sayed, M. A.; El-Shazly, M. F.; Hutchinson, J. P.; Rupich, M. W.; Watkins, K. O. *Ibid.* 1979, *18*, 2296. [l] Kolks, G.; Lippard, S. J.; Waszczak, J. V. *J. Am. Chem. Soc.* 1980, *102*, 4832. [m] Curtis, N. F.; Hay, R. W.; Curtis, Y. M. *J. Chem. Soc. A* 1968, 182. [n] Cotton, F. A.; Felthouse, T. R. *Inorg. Chem.* 1980, *19*, 320. [o] Ozawa, F.; Ito, T.; Yamamoto, A. *Chem. Lett.* 1979, 735. [p] Singh, N. B.; Singh, R. P.; Singh, J.; Singh, H. C. *J. Solid State Chem.* 1980, *33*, 391. [q] Peterson, E. J.; Onstott, E. I. *J. Inorg. Nucl. Chem.* 1979, *41*, 517.

the bonding parameters, e.g., $Rh\text{-}O_2CCH_3 = 2.039$ (8) Å, C–O = 1.269 (4) Å, Rh–Rh = 2.39 (8) Å, and the $O_1\text{-}C\text{-}O_2$ angle = 1.248 (3)°, and the $Rh\text{-}O_1\text{-}C$ angle = 119.5 (3) Å. A similarly close relationship is expected for the corresponding formato rhodium(II) complex[217] and has been established between the Cr(II) complexes, $(NH_4)_4[\{Cr(H_2O)\}_2(\mu\text{-}CO_3)_4] \cdot H_2O$ (see Table XXI) and $[\{Cr(py)\}_2(\mu\text{-}CHO_2)_4]$,[218] e.g., $Cr\text{-}O_2CH = 2.019$ (6) Å, C–O = 1.254 (9) Å, $O_1\text{-}C\text{-}O_2 = 126.0$ (7)°, and $Cr\text{-}O_1\text{-}C$ = 120.3 (3)°. The structures of the complexes involved in "bidentate" and "monodentate" carbonate bridging (Table XXII) reflect the angles and bond lengths observed for the individual species, Tables XVIII and XIX, respectively. Although it is not immediately obvious, the same pattern exists for the multinuclear compounds in Tables XXIII and XIV, with the exception of $[(dpf)_4Cu_4(\mu\text{-}CO_3)(\mu\text{-}Cl)_2]Cl_4 \cdot 7.5H_2O$ where bonding of two Cu(II) atoms to O_1 apparently causes the C–O bond to be exceptionally long.[219] This effect is not observed for malachite, $Cu_2(OH)_2CO_3$, which has a continuous structure with no discrete units.

Finally, the metal–oxygen bond lengths for the carbonate ligands vary from 1.909 (13) Å for the bidentate cobalt(III) complex to 2.81 (11) Å for $BaCO_3$. No definite trend could be detected between the relative lengths of monodentate vs. bidentate M–O bonds, but this may well be due to the large experimental uncertainties in the former for which only a limited number of examples are available. The effect of increased charge on the metal decreasing the M–O bond length is quite apparent in every case.

VI. Solid-State Thermal Decomposition

Solid carbonato complexes, with few exceptions, decompose on heating. Consequently, the melting points of these solids are generally not available as an intrinsic property. However, thermal decomposition does provide a "fingerprint" of the solid which may not be precise, but is nevertheless appropriate to this section. Furthermore, numerous examples are to be found where new carbonato complexes have been isolated, and/or characterized, or at least their composition inferred from the decomposition products of similar complexes.

Table XXV lists the abbreviated results of thermolytic studies, the more complicated of which are discussed in the body of this text. In those cases where various heating rates were used, the results of the slowest were chosen. Obviously the heating rate strongly influences the recorded temperature range over which species appear to be stable. The compounds listed under "products" in Table XXV do not necessarily represent all of the residue formed in that particular temperature range. We have not attempted to establish whether the thermal transitions are endo- or exothermic in this brief synopsis. Moreover, the dehydration reactions are not treated, unless they are coupled with a change in coordination of the central metal.

Many reactions that may appear simple from a cursory look at the data in Table XXV involve more complicated mechanisms, as exemplified by the thermal decomposition of $MgCO_3 \cdot 3H_2O$.[220] Magnesium carbonate trihydrate can be better represented as containing a bicarbonato and a hydroxo ligand coupled together to form a dimer. Thermolysis results in polymerization

TABLE XII. Infrared Spectral Data of Lanthanide Carbonato Complexes

compd	hydrate	prepn ref	IR, cm^{-1}	ref
$Na[La(CO_3)_2]$	0	250	1500, 1480, 1440, 1088, 1080, 882, 873, 868, 854, 747, 727, 690, 684, (275)[a]	250
	2		1470 vs, 1370 vs, 1080 vw, 850 m, 750 m, 680 vw, (280 m)	*b*
	6		1470 vs, 1410 vs, 1350 vs, 1090 vw, 1065 vw, 875 sh, 860 s, 750 m, 720 vw, 700 sh, 680 vw, (315 s, 250 vw)	*b*
$K[La(CO_3)_2]$	2		1470 vs, 1410 vs, 1360 vs, 1085 vw, 1060 w, 870 sh, 850 s, 760 sh, 735 m, 700 m, 670 m, (280 s)	*b*
	3		1470 vs, 1410 vs, 1360 vs, 1090 vw, 1060 sh, 870 sh, 850 s, 760 w, 735 m, 700 m, 670 w, (280 m)	*b*
$[C(NH_2)_3]_5[La(ox)_2(CO_3)_2]$	*x*		1440, 1370, 1060, 870, 720, 675	*c*
$[La_2(CO_3)_3]$	8	*d–f*	1460 s, 1360 s, 1330 m, 1075 m, 860 w, 850 s, 743 m, 675 m	198
	8		1470 vs, 1370 vs, 1085 vw, 1075 vw, 875 w, 850 s, 750 vs, 680 vw, (290 m, 225 sh)	*b*
$Na[Sc(CO_3)_2]$	1		1500 vs, 1490 vs, 1410 vs, 1100 m, 1060 sh, 840 s, 770 w, 700 w, (370 s, 280 s)	*b*
$K[Sc(CO_3)_2]$	2		1500 vs, 1400 vs, 1085 m, 1050 sh, 865 s, 855 vs, 780 s, 685 w, (380 s, 310 m, 250 w)	*b*
$Na_5[Sc(CO_3)_4]$	0		1550 vs, 1365 vs, 1060 m, 880 s, 860 s, 740 s, 700 w, (370 m)	*b*
	2		1550 vs, 1415 s, 1350 vs, 1060 m, 870 m, 745 m, 700 w, (360 s, 260 m)	*b*
	2		1550, 1420, 1360, 1062, 870, 740, 680 (360, 250)	253
	11		1565 vs, 1410 s, 1355 s, 1060 s, 870 s, 750 s, 710 m, (370 s, 260 m)	*b*
$Na[Ce(CO_3)_2]$	0	250	1500, 1480, 1440, 1089, 1080, 882, 873, 867, 853, 749, 728, 689, 683, 661 (275)	250
$[Ce(OH)CO_3]$ (A form)	0		1485 s, 1410 s, 1071 m, 850 m, 800 m, 710 sh, 692 m	*g*
$[Ce(OH)CO_3]$ (B form)	0		1490 s, 1440 s, 1405 s, 1095 w, 1080 w, 872 m, 848 m, 795 w, 780 w, 739 w, 729 w, 705 m, 690 w	*g*
$[Ce(Cl)CO_3]$	3		1480 s, 1450 s, 1405 s, 1089 w, 860 sh, 851 m, 829 w, 770 w, 748 m, 715 sh, 692 m	*g*
$[Ce_2(CO_3)_3]$	8	*f*	1470 s, 1370 s, 1340 sh, 1075 w, 845 m, 745 m, 673 w	*g*
$Na[Pr(CO_3)_2]$	0	250	1500, 1485, 1440, 1092, 1081, 883, 874, 867, 854, 753, 730, 691, 683, 661 (275)	250
	6		1550 sh, 1460 vs, 1405 vs, 1355 vs, 1090 vw, 1060 w, 875 sh, 860 s, 755 m, 720 vw, 685 vw, 670 vw, 660 vw, (320 m, 260 vw)	*b*
$[Pr_2(CO_3)_3]$	5		1550, 1500, 1085, 860, 750, 690	*h*
	8		1460 s, 1360 s, 845 s, 745 m	198
	10		1655, 1380, 1335, 810, 725, 503	*h*
$Na[Nd(CO_3)_2]$	0	250	1510, 1495, 1450, 1098, 1087, 888, 878, 872, 858, 760, 735, 693, 687, 665, (280)	250
	6		1550 sh, 1460 vs, 1405 vs, 1355 vs, 1090 vw, 1060 w, 880 s, 875 sh, 760 vw, 750 sh, 730 vw, 710 vw, 690 vw, 670 vw, (320 m, 255 vw)	*b*
$[Nd(OH)CO_3]$	0		1495, 1425, 1078, 856, 810, 723, 712	310
$[Nd_2(CO_3)_3]$	2	*e*	1480 s, 1410 s, 1070 m, 863 m, 834 s, 782 w, 761 m, 730 w, 685 m	198
	5		1520, 1090, 860, 750, 695	*h*
	8	*d*	1470 s, 1370 s, 1340 s, 1080 m, 847 s, 748, 675	198
	10		1650, 1370, 1340, 812, 750, 497	*h*
$Na[Sm(CO_3)_2]$	0	250	1525, 1465, 1099, 1087, 887, 876, 870, 857, 761, 734, 690, 685, 663, (300)	250
	6		1550 sh, 1460 vs, 1400 vs, 1350 vs, 1090 vs, 1060 w, 875 sh, 860 s, 760 vw, 750 sh, 730 vw, 710 vw, 685 vw, 670 vw, (300 sh, 270 m, 240 vw)	*b*
$K_5[Sm(ox)_2(CO_3)_2]$	5		1480, 1380, 1060, 865, 710, 670	*c*
$[C(NH_2)_3]_5[Sm(ox)_2(CO_3)_2]$	2		1485, 1365, 1050, 868, 730, 685	*c*
$Na_3[Sm(CO_3)_3]$	6		1490 vs, 1390 vs, 1060 m, 880 s, 720 s, 690 s, (260 m)	*b*
$Na(Eu(CO_3)_2]$	0		1500 vs, 1380 vs, 1070 m, 850 s, 740 m, 700 w, (280 sh)	*b*
	0	250	1515, 1465, 1101, 1089, 887, 877, 872, 857, 763, 735, 690, 685, 663, (300)	250
	6		1500 vs, 1380 vs, 1090 vw, 1065 w, 875 sh, 860 s, 780 sh, 750 vw, 730 vw, 710 vw, 690 vw, 680 vw, (300 sh, 265 m)	*b*
$EuCO_3$	0		1457, 1440, 1067.5, 852,[i] 700.5, 695	*j*
$Na_3[Eu(CO_3)_3]$	6		1490 vs, 1380 vs, 1060 m, 880 s, 720 s, 690 s, (265 m)	*b*
$Na[Gd(CO_3)_2]$	0	250	1520, 1470, 1101, 1090, 885, 876, 867, 857, 765, 738, 692, 686, 663, (300)	250
	6		1500 vs, 1360 vs, 1070 w, 890 sh, 860 s, 760 vw, 750 vw, 730 vw, 710 vw, 690 vw, 670 vw, (300 sh, 270 m)	*b*
	6		1520, 1500, 1360, 1116, 1069, 763, 725	253
$Na_3[Gd(CO_3)_3]$	6		1500 vs, 1385 vs, 1060 m, 880 s, 720 s, 690 s, (265 m)	*b*
$[Gd_2(CO_3)_3]$	5	*d*	1550, 1530, 1095, 862, 750, 690	*h*
	10	*f*	1665, 1380, 1340, 815, 760, 497	*h*
$Na[Tb(CO_3)_2]$	0	250	1560, 1520, 1430, 1415, 1395, 1107, 1092, 857, 768, 758, 692, 688, (330, 300)	250
	6		1500 vs, 1370 vs, 1060 w, 880 sh, 855 s, 760 vs, 750 vw, 730 vw, 710 vw, 690 vw, 670 vw, (280 sh, 260 w)	*b*

TABLE XII (*Continued*)

compd	hydrate	prepn ref	IR, cm^{-1}	ref
$Na_3[Tb(CO_3)_3]$	6		1495 vs, 1385 vs, 1060 m, 880 s, 720 s, 690 s, (270 m)	*b*
$Na[Dy(CO_3)_2]$	0	250	1560, 1540, 1435, 1415, 1390, 1112, 1097, 862, 773, 766, 687, 682, (330, 300)	250
	6		1500 vs, 1370 vs, 1060 w, 890 sh, 855 s, 760 vw, 690 vw, 670 vw, (290 w, 260 w)	*b*
$Na_3[Dy(CO_3)_3]$	6		1495 vs, 1390 vs, 1065 m, 880 s, 720 s, 690 s, (270 m)	*b*
$Na[Ho(CO_3)_2]$	0	250	1565, 1540, 1435, 1410, 1380, 1115, 1095, 860, 773, 765, 685, 680, (330, 300)	250
$Na_3[Ho(CO_3)_3]$	6		1510 vs, 1380 vw, 1060 m, 880 s, 720 s, 690 s, (270 m)	*b*
$Na[Y(CO_3)_2]$	0	250	1545, 1445, 1420, 1400, 1115, 1100, 862, 765, 757, 688, 682, (370, 330, 300)	250
	6		1500 vs, 1370 vs, 1100 vw, 1055 w, 900 vw, 765 vw, 740 vw, 670 vw, (290 w)	*b*
$Na_3[Y(CO_3)_3]$	6		1510 vs, 1400 vs, 1070 m, 880 s, 710 sh, 690 s, (265 m)	*b*
$[Y_2(CO_3)_3]$	2	*d*, *f*	1540 w, 1500 s, 1450 sh, 1420 sh, 1087 w, 1062 w, 862 m, 846 s, 835 s, 760 s, 683 s	198
$Na[Er(CO_3)_2]$	0	250	1570, 1550, 1435, 1415, 1385, 1110, 1090, 859, 773, 765, 682, 677, (335, 300)	250
	6		1530, 1370, 1110, 1060, 855, 760, 740, 680, (290, 260)	253
	6		1530 vs, 1370 vs, 1110 w, 1060 w, 930 sh, 855 s, 760 vs, 740 vw, 680 vw	*b*
$Na_3[Er(CO_3)_3]$	6		1500 vs, 1390 vs, 1070 m, 880 s, 720 s, 690 s, (260 m)	*b*
	6		1500 vs, 1390 vs, 1070, 1064, 880, 860, (260)	253
$Na_5[Er(CO_3)_3]$	9		1490 vs, 1390 vs, 1070 m, 900 sh, 870 s, 760 w, 720 m, 690 m, (260)	*b*
$Na[Tm(CO_3)_2]$	0	250	1550, 1435, 1415, 1380, 1110, 1090, 856, 771, 763, 680, 675, (330, 300)	250
	6		1530 vs, 1360 vs, 1105 vw, 1060 w, 930 sh, 850 s, 770 vw, 760 vw, 690 vw, (290 w, 260 w)	*b*
$Na_3[Tm(CO_3)_3]$	6		1490 vs, 1380 vs, 1070 m, 880 s, 710 sh, 690 s, (260 w)	*b*
$Na_5[Tm(CO_3)_4]$	2		1550 vs, 1380 vs, 1340 vs, 1050 s, 870 s, 740 s, 700 m, 680 w, (300 m, 250 m)	*b*
$[Tm_2(CO_3)_3]$	0		1535 vs, 1385 vs, 1085 w, 850 m, 770 w, 690 w, (300 sh)	*b*
	3		1520 vs, 1420 vs, 1090 vw, 1070 vw, 845 s, 835 s, 765 w, 690 w, (290 m, 220 sh)	*b*
$Na[Yb(CO_3)_2]$	0	250	1550, 1440, 1420, 1385, 1112, 1095, 860, 776, 768, 682, 678, (335, 300)	250
	0		1530 vs, 1380 vs, 1070 m, 850 s, 755 m, 700 w, (300 sh)	*b*
	6		1530 vs, 1360 vs, 1100 vw, 1050 w, 850 s, 770 sh, 760 vw, 690 w, (300 w, 260 sh)	*b*
$Na_3[Yb(CO_3)_3]$	6		1500 vs, 1400 vs, 1070 m, 880 s, 710 sh, 690 s, (265 m)	*b*
$[Yb_2(CO_3)_3]$	0		1550 vs, 1360 vs, 1085 w, 830 s, 770 m, 700 vw, (300 sh)	*b*
	6		1550 vs, 1430 sh, 1360 vs, 1100 vs, 1080 w, 1060 vw, 860 w, 850 s, 840 s, 770 w, 700 w, (350 sh, 300 m, 260 sh)	*b*
$Na[Lu(CO_3)_2]$	0		1550, 1445, 1410, 1385, 1117, 1095, 860, 780, 771, 686, 680, (335, 300)	250
$Na_3[Lu(CO_3)_3]$	6		1490 vs, 1390 vs, 1060 m, 880 s, 715 s, 690 s, (275 m)	*b*

[a] Frequencies in parentheses assigned to ν(Ln-O) stretch. [b] Taravel, B.; Fromage, F.; Delorme, P.; Lorenzelli, V. *J. Chim. Phys. Physicochim. Biol.* 1971, *68*, 715. [c] Thomas, Y.; Taravel, B.; Dumonceau, J.; Fromge, F.; Lorenzelli, V. *J. Mol. Struct.* 1978, *43*, 159. [d] Wakita, H.; Nagashima, K. *Bull. Chem. Soc. Jpn.* 1972, *45*, 2476. [e] Salutsky, M. L.; Quill, L. L. *J. Am. Chem. Soc.* 1950, *72*, 3306. [f] Nagashima, K.; Wakita, H.; Mochizuki, A. *Bull. Chem. Soc. Jpn.* 1973, *46*, 152. [g] Peterson, E. J.; Onstott, E. I. *J. Inorg. Nucl. Chem.* 1979, *41*, 517. [h] Karyakin, A. V.; Davitashvili, E. G.; Kublashvili, Zh. Sh. *Bull. Acad. Sci. Georhian SSR* 1969, *55*, 297; *Chem. Abstr.* 1969, *71*, 117990. [i] $\nu_2(^{13}C) = 837$ and $\nu_2(^{14}C) = 818.8$ cm^{-1}. [j] Sterzel, W.; Schnee, W.-D. *Z. Naturforsch.* 1971, *26*, 615.

through the carbonate ligands, followed by partial dehydration and eventually the formation of additional Mg–O–Mg bridges which are characterized by a band at 780 cm^{-1} in the IR spectrum. Decomposition of the polymer occurs in the range 315–380 °C.[221]

Alkaline earth metal carbonates can also undergo phase rearrangements at elevated temperatures. One such example involved heating $SrCO_3$ and $BaCO_3$ to form the solid solution, γ-(Sr,Ba)CO_3 at 500 °C, with another phase change at 800 °C corresponding to the formation of β-(Sr,Ba)CO_3, given a reasonably slow heating rate.[222]

The importance of the presence of CO_2 in the prevailing atmosphere of certain thermolysis processes is clearly illustrated by the decomposition of cerussite, $PbCO_3$.[223] Using TG and DTA, combined with X-ray diffraction and SEM of the products, Yamaguchi et al.[223] established that for CO_2 pressures less than 1 atm only one intermediate exists

$$3PbCO_3 \xrightarrow{200\ ^\circ C} PbCO_3{\cdot}2PbO + 2CO_2(\uparrow) \xrightarrow{310\ ^\circ C} 3PbO + CO_2(\uparrow) \quad (44)$$

whereas at ca. 1 atm of CO_2, two intermediates are observed

$$2PbCO_3 \xrightarrow{300\ ^\circ C} PbCO_3{\cdot}PbO + CO_2(\uparrow) \xrightarrow[+PbCO_3]{330\ ^\circ C} PbCO_3{\cdot}2PbO + CO_2(\uparrow) \xrightarrow{440\ ^\circ C} 3PbO + CO_2(\uparrow) \quad (45)$$

These two reaction paths were also proposed by Ball and Casson,[224,225] although higher temperatures were generally reported (e.g., reaction 45, 365, 412, and 472 °C, respectively). These authors[224] found white lead, $PbCO_3{\cdot}Pb(OH)_2$, behaved similarly with three/four

TABLE XIII. Spectroscopic Properties of Actinide Carbonato Complexes

compd	prepn. ref	vis/UV, nm (M^{-1} cm^{-1})	ref	IR, cm^{-1}	ref	comments
$[Th(OH)_2CO_3]\cdot 2H_2O$	*a*			1535, 1460, 1380, 1070, 840, 730	199	bi- and unidentate
$Na_6[Th(CO_3)_5]\cdot 3H_2O$	*a*			1570, 1375, 1350, 1046, 856, 718	199	bidentate
$Na_6[Th(CO_3)_5]\cdot 12H_2O$	*a*			1535, 1378, 1340, 1067, 1054, 1050 sh, 867, 735, 725	199	bidentate
$[C(NH_2)_3]_6[Th(CO_3)_5]$	*a*			1590, 1485, 1350, 1059, 1047, 859, 723	199	bi- and unidentate
$[UO_2(CO_3)]$	266	424				
$[UO_2(CO_3)_2]^{2-}$		466 (13.7), 451 (19.1), 437 (19.9), 424 (18.9)	268			
$Na_4[UO_2(CO_3)_3]$	266	463 (19.0), 449 (27.0), 435 (24.4), 423 (21.1)	266	1560 br, 1460 br, 1340 br, 1070 s, 850 vs, 830 vs, 735, 710	*b*	luminescence spectrum; 19 931, 19 590, 19 341, 19 202 cm^{-1} [c]
		460, 445, 435, 420	*d*	1560, 1342, 1062, 821, 732, 700	*c*	Raman: 1630, 1358, 1077, 737, 697 cm^{-1} [c]
$K_4[UO_2(CO_3)_3]$	*e*			1600 m, 1550 m, 1358 sh, 1338 m, 1054 sh, 1049 m, 1045 m, 882 s, 855 w, 847 w, 719 s, 694 m	*e*	Raman: 1065 sh, 1055 m, 1046 sh, 879 vw, 863 vw, 806 vs, 785 vw, 725 m, 719 w, 693 w, cm^{-1} [e]
$[UO_2(CDMBA)(CO_3)_3]$	*f*			1610, 1551, 1385, 1352	*f*	
$[(UO_2)_3(CO_3)_6]^{6-}$		459 (29.9), 445 (44.8)	270			
$(NH_4)_2[UO_2(neocupferron)_2CO_3]\cdot H_2O$	*g*, *h*	470 (417)	*g*	1565, 1535	*g*	vis spectrum in Me_2CO
		470 (274), 370 (2540 sh), 365 (2560 sh), 283 (32 730)	*h*			Λ = 54.6 (DMF), 134.3 (CH_3CN) cm^2 ohm^{-1} mol^{-1}
$Na_4[(Np)_2(CO_3)_3]$	*i*					
$[Pu(OH)CO_3]\cdot xH_2O$	*j*			1620, 1508, 1435, 1370	*j*	

[a] Chernyaev, I. I.; Golovnya, V. A.; Molodkin, A. K. *Zh. Neorg. Khim.* 1958, *3*, 2671. Chernyaev, I. I.; Molodkin, A. K. *Ibid.* 1961, *6*, 587, 809. [b] Novikov, Yu. P.; Gliva, V. B.; Komarevskii, V. M.; Akhmanova, M. V. *Radiokhimiya* 1977, *19*, 546. [c] Koglin, E.; Schenk, H. J.; Schwochau, K. *Spectrochim. Acta, Part A* 1979, *35A*, 641. [d] Gao, H.-C.; Zhang, M.-L.; Pen, Q.-X.; Pen, L.-E.; Wang, W.-Q. *Heh Hua Hsueh Yu Fang She Hua Hsueh* 1981, *3*, 88; *Chem. Abstr.* 1981, *95*, 194031r. [e] Anderson, A.; Chieh, C.; Irish, D. E.; Tong, J. P. K. *Can. J. Chem.* 1980, *58*, 1651. [f] Vera Palomino, J.; Galiano Sedano, J. A.; Parellada Bellod, R.; Bellido Gonzalez, A. *Junta Energ. Nucl., JEN* (*Spain*) 1975, *306*, 1. [g] Kundu, P. C.; Bera, A. K. *Indian J. Chem.* 1979, *18A*, 62. [h] Kundu, P. C.; Roy, P. S.; Banerjee, R. K. *J. Inorg. Nucl. Chem.* 1980, *42*, 851. [i] Dzyubenko, V. I.; Karavaev, S. A.; Peretrukhin, V. F.; Krot, N. N. *Dokl. Akad. Nauk. SSSR* 1979, *248*, 1362. [j] Hagan, P. G.; Navratil, J. D.; Cichorz, R. S. *J. Inorg. Nucl. Chem.* 1981, *43*, 1054.

decomposition steps in a CO_2 atmosphere but only three in nitrogen (see Table XXV). For CO_2 pressures exceeding 4 atm (405.3 kPa), three intermediates were detected and the temperatures of these transformations increased with increasing pressure:[223]

$$3PbCO_3 \rightarrow 2PbCO_3{\cdot}PbO + CO_2(\uparrow) \xrightarrow[-PbO]{} PbCO_3{\cdot}PbO + CO_2(\uparrow) \xrightarrow[+PbCO_3]{} PbCO_3{\cdot}2PbO + CO_2(\uparrow) \rightarrow 3PbO + CO_2(\uparrow) \quad (46)$$

An equally detailed study[226] of the thermal decomposition of hydrocerussite, $2PbCO_3{\cdot}Pb(OH)_2$, at four pressures revealed a similar reaction sequence at $p(CO_2)$ of 0.304–2.533 MPa with $PbCO_3$ as the common intermediate. The complete reactions are as follows:

in air

$$2PbCO_3{\cdot}Pb(OH)_2 \xrightarrow[-PbO]{\sim 200\ ^\circ C} PbCO_3{\cdot}PbO + CO_2(\uparrow) + H_2O(\uparrow) \xrightarrow{\sim 300\ ^\circ C} 2PbO + CO_2(\uparrow) \quad (47)$$

$p(CO_2) = 304$ kPa

$$2PbCO_3{\cdot}Pb(OH)_2 \xrightarrow[+CO_2]{\sim 200\ ^\circ C} 3PbCO_3 + H_2O(\uparrow) \xrightarrow{\sim 330\ ^\circ C} PbCO_3{\cdot}PbO + PbCO_3 + CO_2(\uparrow) \xrightarrow{\sim 400\ ^\circ C} PbCO_3{\cdot}2PbO + CO_2(\uparrow) \xrightarrow{\sim 410\ ^\circ C} 3PbO + CO_2(\uparrow) \quad (48)$$

$p(CO_2) = 912$ kPa

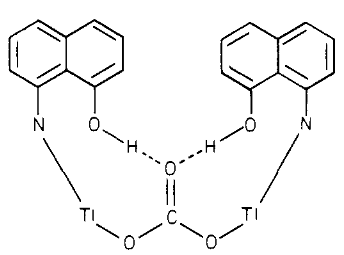
$$2PbCO_3{\cdot}Pb(OH)_2 \xrightarrow[+CO_2]{\sim 190\ ^\circ C} 3PbCO_3 + H_2O(\uparrow) \xrightarrow{\sim 340\ ^\circ C} 2PbCO_3{\cdot}PbO + CO_2(\uparrow) \xrightarrow[-PbO]{\sim 360\ ^\circ C} PbCO_3{\cdot}PbO + CO_2(\uparrow) \xrightarrow[+PbCO_3]{\sim 410\ ^\circ C} PbCO_3{\cdot}2PbO + CO_2(\uparrow) \xrightarrow{\sim 550\ ^\circ C} 3PbO + CO_2(\uparrow) \quad (49)$$

$p(CO_2) = 2.533$ MPa

$$2PbCO_3{\cdot}Pb(OH)_2 \xrightarrow[+CO_2]{\sim 190\ ^\circ C} \{?\} + H_2O(\uparrow) \xrightarrow{\sim 250\ ^\circ C} 3PbCO_3 + CO_2(\uparrow) \xrightarrow{\sim 370\ ^\circ C} 2PbCO_3{\cdot}PbO + CO_2(\uparrow) \xrightarrow[-PbO]{\sim 420\ ^\circ C} PbCO_3{\cdot}PbO + CO_2(\uparrow) \xrightarrow[+PbCO_3]{\sim 460\ ^\circ C} PbCO_3{\cdot}2PbO + CO_2(\uparrow) \xrightarrow{\sim 620\ ^\circ C} 3PbO + CO_2(\uparrow) \quad (50)$$

Kato and Mizutani[226] concluded that lead carbonates, together with some of the rare earth carbonates, exhibit the common behavior of losing all of the H_2O and some CO_2 initially, with the loss of CO_2 being dependent on the partial pressure of CO_2. Other basic carbonates may lose all the H_2O and CO_2 at one temperature, e.g., those of Co, Ni, and Cu. As discussed earlier, magnesium carbonates behave in a more complicated manner with the loss of CO_2 drastically affected by $p(CO_2)$.

A rather unique solid-state reaction was reported by Singh et al.[226a] who reacted thallous carbonate with 8-hydroxyquinoline at temperatures of 40–55 °C to produce a yellow product which analyzed as $[(Tl(C_{10}H_6NOH))_2CO_3]$. X-ray and IR data (3200 br, H-bonded OH; ~1270, ν(C–OH); 1690, ν(C=O); 1580, 1300, ν_3; 1020 cm^{-1}, ν_1) of the solid material and conductivity measurements in nitrobenzene indicate the following structure with a bidentate, H-bonded carbonate bridge.



However, the thermal stabilities of transition-metal carbonates, particularly those of the lanthanides and actinides, are of greater interest within the mandate of this review. The discussion of these processes will be subdivided into individual subsections according to the nature of the central metal.

A. Transition-Metal Complexes

The decomposition of $A[Sc(CO_3)_2]{\cdot}nH_2O$ (A = K, NH_4, Rb, or Cs; $n = 1$ and 2) was studied in dry air and the reaction products characterized by IR, X-ray diffraction, and GC.[227] For the alkali metals the complex maintains its anionic form when heated and yields yet another carbonate, the tetrameric form.

$$4A[Sc(CO_3)_2]{\cdot}H_2O + 2O_2 \xrightarrow{320\text{–}400\ ^\circ C} A_4[Sc_4O_4(H_2O)_2(CO_3)_4] + 4CO_2 + 4H_2O \quad (51)$$

This reaction is manifested in the IR by a shift in the strong band at 1540 cm^{-1} to 1665 cm^{-1} (carbonate) and the appearance of a band at 635 cm^{-1} that can be related to Sc–O–Sc bonding in the tetramer. Subsequent heating produces another carbonato species which then decomposes.

$$A_4[Sc_4O_4(H_2O)_2(CO_3)_4] \xrightarrow{400\text{–}450\ ^\circ C} A_4[Sc_4O_5(H_2O)(CO_3)_3] + CO_2 + H_2O \quad (52)$$

$$A_4[Sc_4O_5(H_2O)(CO_3)_3] \xrightarrow{>450\ ^\circ C} 2Sc_2O_3 + 2A_2CO_3 + CO_2 + H_2O \quad (53)$$

The behavior of the ammonium salt is anomalous in that it decomposes as follows:

$$NH_4[Sc(CO_3)_2]{\cdot}2H_2O \xrightarrow{180\ ^\circ C} NH_4[Sc(CO_3)_2]{\cdot}H_2O \xrightarrow{220\ ^\circ C} NH_4[Sc_4O_{2.5}(OH)_4(CO_3)] \xrightarrow{280\ ^\circ C} (NH_4)_{0.5}[Sc_4O_4(OH)_2CO_3] \rightarrow Sc_2O_3 \quad (54)$$

The stoichiometry of these reactions is difficult to rationalize. The coordinated carbonate in this tetramer exhibits two strong bands in the IR at 1410 and 1535 cm^{-1}.

It was further suggested[227] that $Na_5[Sc(CO_3)_4]{\cdot}11H_2O$ decomposes at 250 °C through a similarly coordinated carbonato tetrameric intermediate $[Sc_4O(CO_3)_5(H_2O)]$ or $[Sc_4(OH)_2(CO_3)_5]$. Moreover, the authors[227] observed that heating $Sc(OH)_3{\cdot}nH_2O$ to 300 °C in the presence of CO_2 yielded another tetramer, namely $[Sc_4O_3(OH)_4CO_3]$ which decomposed to Sc_2O_3 at 420 °C.

Carbonato complexes are commonly formed during the thermolysis of carboxylato metal complexes. Within this group, oxalato complexes provide the main thermal source of carbonate complexes. One such mechanism involves complexes of the general formula, $A[MO(C_2O_4)_2]{\cdot}xH_2O$, where M = V(IV), A = Ba ($x = 4$) or Sr

TABLE XIV. Infrared and Raman Spectra of Alkali Metal Bicarbonates and Carbonates at Room Temperature[j]

salts	spectra[j]	ν_6	$\nu_5{}^+$ (δ_{OH})	ν_1	ν_2	ν_4	ν_3	ref
			Bicarbonate					
$NaHCO_3$	IR	1655 s, 1617 s	1452 s, 1398 s, 1300 vs	1045 m, 1032 s	836 vs	694 vs	656 s	*a*
	R	1623 vw	1459 w, 1437 w	1047 vs	834 vw	699 w, 687 m	660 w	*a*
$NaDCO_3$	IR	1620 sh, 1598 vs	1326 vs	1040 sh, 990 m	835 s	686 vs	626 s	*a*
	R	1597 w	1319 br	1036 vs, 995 vw	835 vw	678 s	627 vw	*a*

salt	spectra	ν_3	ν_1	ν_2	ν_4	ref
			Carbonate			
Li_2CO_3	IR	1495 vs, 1437 vs	1088 m	866 s, 846 w[b]	741 w, 712 w	*c*
		1420	1088	859 m, 847 w[b]	740 m,[d] 713 w	*e*
	R	1459	1091	n.o.[f]	748, 711	*e*
Na_2CO_3	IR	1451 vs	1079 vw	881 s, 855 w,[b] 851 w[b]	701 w, 694 w, 691 m	*c*
	R	1431, 1422	1083, 1079	n.o.[f]	702, 698	*e*
K_2CO_3	IR	1480 sh, 1400 br	1063	880, 854[b]	690, 685, 683	*g*
	R	1418, 1408, 1400	1063, 1043	n.o.[f]	694, 691, 686, 684	*g*
Rb_2CO_3	IR	1445 sh, 1380 br	1053 vw	879, 852[b]	688, 684, 681	*g*
	R	1405, 1395, 1384	1053, 1033[h]	n.o.[f]	690, 688, 682, 680	*g*
Cs_2CO_3	IR	1367 m	1041 m	878 s, 851[b]	679 s, 674 s	*i*
	R	1391 w, 1381 w	1042 vw, 1020 vw[h]	n.o.[f]	680 m, 674 m	*i*

[a] Bertoluzza, A.; Monti, P.; Morelli, M. A.; Battaglia, M. A. *J. Mol. Struct.* 1981, *73*, 19. [b] Generally assigned to $^{13}CO_3{}^{2-}$ ν_2 frequency. [c] Buijs, K.; Schutte, C. J. H. *Spectrochim. Acta* 1961, *17*, 927. [d] Not assigned. [e] Brooker, M. H.; Bates, J. B. *J. Chem. Phys.* 1971, *54*, 4788. [f] Not observed. [g] Brooker, M. H.; Bates, J. B. *Spectrochim. Acta Part A* 1974, *30A*, 2211. [h] Assigned to $C^{16}O_2{}^{18}O^{2-}$ ν_1 frequency. [i] Hase, Y. *An. Acad. Brasil. Cienc.* 1980, *52*, 521. [j] In cm^{-1}.

TABLE XV. Calculated and Experimental Carbonate Infrared Frequencies[a]

	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8
				Monodentate Carbonate				
C_s (calcd)	1373	1039	765	369	1483	711	82	
C_{2v} (calcd)	1376	1069	772	303	1483	676	92	
(assignment)	ν (C-O_2) + ν (C-O_1)	ν (C-O_1) + ν (C-O_2)	δ (O_2CO_2)	ν (C-O_1)	ν (C-O_2)	P_r (O_2CO_2)	δ (CoO_1CO_2)	π
$(Co(NH_3)_5CO_3)Br$	1373	1070	756	362	1453	678	*b*	850
				Bidentate Carbonate				
C_{2v} (calcd)	1595	1038	771	370	1282	669	429	
(assignment)	ν (C-O_2)	ν (C-O_1)	ring deformation + ν (Co-O_1)	ν (Co-O_1) + ring deformation	ν (C-O_1) + δ (O_1CO_2)	δ (O_1CO_2) + ν (Co-O_1)	ν (C-O_1)	π
$(Co(NH_3)_4CO_3)Cl$	1593	1038	760	395	1265	673	430	834

[a] Reference 195, frequency in cm^{-1}. [b] Outside CsBr range.

($x = 4$); M = Zr(IV), A = Ca ($x = 7$) or Sr ($x = 4$). They all undergo dehydration during the initial heating stage (up to ca. 200 °C), but then their chemistries are different in that only in the case of $Sr[Zr(C_2O_4)_2]$ was a mixed carbonato–oxalato complex detected, although not isolated, i.e., $Sr_2[Zr_2O_2(C_2O_4)_3CO_3]$.[228] The oxalato and carbonato ligands were characterized by IR bands at 1650 and 1320 cm^{-1}, respectively, but no band was found at ca. 2350 cm^{-1} which would have indicated the presence of CO_2 trapped in the residue. The mixed complex yielded $Sr_2[Zr_2O_5CO_3]$ on further heating (375–500 °C). Reddy and Mehrotra[229] had previously not observed the mixed complex and reported the direct transformation of the dehydrated oxalato host over a similar temperature range of 325–475 °C to the $Sr_2[Zr_2O_5CO_3]\cdot(CO_2)$ species in which the CO_2 is trapped within the lattice as evidenced by an IR band at 2310 cm^{-1}. The anhydrous calcium analogue, on the other hand, initially forms $Ca[Zr_2O_4(CO_3)_2]$ at 225–375 °C containing both uni- and bidentate carbonate, then rearranges at 375–500 °C to the common form, $Ca_2[Zr_2O_5CO_3]$, in which the carbonate is ionic.[228]

In oxidizing media, the barium and strontium salts of the anhydrous bis(oxalato)vanadium complex decompose at 280 and 300 °C, respectively, to produce the monodentate vanadium(V) carbonato complex according to the following equation:[230]

$$2A[VO(C_2O_4)_2] + {}^1/_2O_2 \rightarrow A_2[V_2O_{7-x}(CO_3)_x] + 4CO + (4 - x)CO_2 \quad (55)$$

Conversely, under nonoxidizing conditions at 400 °C, the mononuclear bidentate vanadium(IV) complex is formed, viz. $A[VO_2CO_3]$, which in turn converts at 500 °C to $A[V_2O_5CO_3]$, which is the analogue of the zirconium species.[230]

Stable vanadium oxycarbonato complexes can also be synthesized by the interaction of vanadium oxide with gaseous CO_2:[231]

$$K_4[V_2O_3(O_2)_4]\cdot 2H_2O + CO_2 \rightarrow K_3[VO(O_2)_2CO_3] + KVO_3 + O_2 + 2H_2O \quad (56)$$

$$2K_3[HV_2O_3(O_2)_4]\cdot H_2O + CO_2 \rightarrow K_3[VO(O_2)_2CO_3] + 2KVO_3 + 3O_2 + 3H_2O \quad (57)$$

The rates of these reactions were monitored by IR spectroscopy and below 100 °C proved to be dependent on such factors as air humidity, CO_2 partial pressure, sample surface area, etc., whereas the stoichiometry of the products is independent of such factors. The mechanism for CO_2 uptake parallels the reaction in aqueous solution with CO_2 combining with the terminal OH group formed by O_2 release, H_2O addition, and subsequent proton transfer. Note that $K_3[VO(O_2)_2CO_3]$ can be more conveniently prepared from aqueous solutions.[232]

A group of oxalato complexes of mainly the first transition series (viz., $K_3[M(C_2O_4)_3]\cdot xH_2O$ for M = Al, V, Cr, Mn, Fe, Co, Rh; $K_2[M(C_2O_4)_2]\cdot xH_2O$ for M = Cu, Zn, Pd, Pt) was investigated up to 600 °C by EGA (evolved gas analysis)[233] and the liberated gases were CO and CO_2. No evidence for the formation of intermediate carbonato complexes was presented. On the other hand, oxalato complexes of the form $[MC_2O_4]\cdot 2H_2O$, where M = Mn, Fe, Co, Ni, Cu, Zn, and Cd, did yield the corresponding carbonato complexes when heated in a CO_2 atmosphere,[234] although the Cu^{II} transformation required the presence of an oxidizing agent. These reactions are outlined in Table XXVI and as intimated, $VC_2O_4\cdot 2H_2O$ and $CrC_2O_4\cdot 0.4H_2O$ decomposed directly to their oxides with no evidence for carbonate formation. Most of these carbonates can be prepared by an alternative thermolytic route, namely by heating solutions of the metal hydroxide or oxide under CO_2 pressure.[235] These results are summarized in Table XXVII together with the appropriate IR information, which suggests a common calcite structure for Mn–Zn.

As an interesting side issue Moreau[236] established a linear relationship between the carbonate absorption bands in the IR of the complexes, $MnCO_3$, $FeCO_3$, $CoCO_3$, and $NiCO_3$, and the radius of their cations.[236] A linear relationship also exists between the cationic radius and the coefficients of thermal expansion in the planes containing the carbonate anions up to temperatures where decomposition begins.

Other carboxylate complexes, such as the iron and cobalt caprylate soaps also decompose on heating in air to form $[Fe_2(CO_3)_3]$ at 200–300 °C and $CoCO_3$ at 390–480 °C, although these observations appear to be based solely on the thermogravimetric record.[237]

Another aspect of the solid-state conversion of carbonato complexes is that they can provide a source for other complexes via substitution. For example, heating $[Co(en)_2CO_3]NO_3$ or $[Co(en)_2CO_3]Cl$ to 165 °C for 1–4 h in the presence of NH_4Cl produces *cis*- and *trans*-$[Co(en)_2Cl_2]^+$ as the main products.[238] In the absence of NH_4Cl no reaction occurred at this temperature over 24 h. Another example is the solid-state reaction between thallous carbonate, Tl_2CO_3, and tungstic oxide at 550 °C to give thallous tungstate, Tl_2WO_4.[239]

B. Lanthanide Complexes

At least over the past decade, the thermal chemistry of these complexes has attracted the most interest.

To begin with, consider the stepwise decomposition of the carbonato complexes themselves. The thermolysis of $[La_2(CO_3)_3]\cdot 8H_2O$ gives rise to $La_2O_2CO_3$.[240] These authors[240] were careful to point out that the transition temperatures are strongly influenced by the gas-phase composition (i.e., CO_2 content, presence of oxidizing gases, vacuo, etc.) depending on the stoichiometry and reversibility of the transition. The kinetics of this process can also be affected. In addition, Prodan et al.[241] showed that for this particular reaction the specific surface changes, which occur during the two steps of this reaction (i.e., the formation and decomposition of $La_2O_2CO_3$), are modified considerably in the presence of CO_2.

In their review of the thermal decomposition of lanthanide carbonates, $Ln_2(CO_3)_3\cdot xH_2O$, including yttrium carbonate, Sharov and Bezdenezhnykh[242] demonstrated that the thermal stability of this series of complexes increases with increasing atomic number, e.g., $[La_2(CO_3)_3]$ begins to decompose at 495 °C, while $Er_2(CO_3)_3$ first decomposes at 770 °C. Consistent with the example of $[La_2(CO_3)_3]\cdot 8H_2O$ cited above,[240] all the lanthanides degenerate following dehydration into $Ln_2O_2CO_3$ in its tetragonal form.[242] Given a slow heating rate of 0.6 °C h^{-1}, there is then a phase change to $Ln_2O_2CO_3$ (hexagonal) for Ln = La–Pr. For Na and Sm–Gd, this phase change does not reach completion before thermal decomposition to Ln_2O_3 begins. The hexagonal form is not encountered for lanthanides smaller than Gd^{3+}, but now the initial phase may be either the tetragonal or monoclinic form. Within this group of heavy lanthanides, the thermal stability of either form of $Ln_2O_2CO_3$ decreases markedly from Tb to Lu and is a reflection of a weakening of the $Ln–CO_3$ bond with increasing atomic number. Sharov and Bezdenezhnykh[242] also cite numerous publications[243] supporting the existence of $Ln_2O(CO_3)_2$ for the light lanthanides as an intermediate prior to the formation of $Ln_2O_2CO_3$. The fact that this intermediate only becomes apparent for light lanthanides is consistent with the concept of $Ln–CO_3$ bond strength decreasing as a function of atomic number. Indeed, it was suggested that decomposition of carbonates of heavy lanthanides and yttrium is accompanied by the formation of $Ln_2O_3\cdot 2CO_2$ as well as $Ln_2O_2CO_3$.

Peterson et al.[244] examined the thermal decomposition of both $[Ce_2(CO_3)_3]\cdot 8H_2O$ and $[Ce(OH)CO_3]\cdot xH_2O$ in vacuo within sealed tubes and were able to establish that the anhydrous form of the latter is an intermediate in the dehydration of the former at 573 °C. $[Ce(OH)CO_3]$ decomposes at 773 °C to the familiar $Ce_2O_2CO_3$ form which in turn converts to CeO_2 at 873 °C.

It is worthwhile mentioning at this point that hydroxo carbonates $[Ln(OH)CO_3]$, where Ln = La, Gd, Er, and "Y", can be produced by heating solutions of the appropriate tris(carbonato) complex in the presence of ca. 6 M ammonium or potassium salts of chloride or carbonate at 250–500 °C, 100–200 MPa, and over time periods of 27–58 days.[245] In addition to $[Ln(OH)CO_3]$, the familiar species $Y_2O_2CO_3$, $Gd_2O_2CO_3$, and $Er_2O_2CO_3$ were formed under various combinations of these conditions. Although $La_2O_2CO_3$ was not observed at all, the complex $[La_3Cl(CO_3)_4]$ was detected along with the hydroxo carbonate in the presence of NH_4Cl. SEM photomicrographs established that well-developed crystals were obtained by this method and tentative phase diagrams were also constructed for the systems Ln_2O_3–H_2O–CO_2 at temperatures ranging from 100 to 900 °C.

Thermal decomposition of $[Ln_2(C_2O_4)_3]\cdot xH_2O$ occurs with the usual initial dehydration step at low temperatures followed by the formation of $[Ln_2(CO_3)_3]$, followed again by the chemistry outlined immediately above.[242] The appearance of mixed carbonato–oxalato complexes has been confirmed for the lighter lanthanides. For the heavier lanthanides, when heated in va-

TABLE XVI. Summary of Crystal Data Describing the Unit Cell of Metal Carbonate Compounds

compd	cryst syst,[uuuu] space grp	obsd[a]	a_0, Å	b_0, Å	c_0, Å	β, deg	Z	vol, Å^3	d,[b] g cm^{-3}		ref
									measd	calcd	
$NaHCO_3$	monoc, $P2_1/c$	319 (0.108)	3.51 (1)	9.71 (1)	8.05 (1)	111.85	4	255	2.22	2.19	202
$KHCO_3$	monoc, $P2_1/c$		15.11	5.67	3.71	103.75					*c*
	monoc, $P2_1/c$		15.1725 (11)	5.6283 (5)	3.7110 (4)	104.631	4	306.62	2.169		203, 204
$KDCO_3$	monoc, $P2_1/a$		15.1948 (9)	5.6307 (3)	3.7107 (3)	104.567	4	307.27	2.186		203, 204
$RbHCO_3$	monoc, $C2\text{-}C2^3$		15.05	5.83	4.02	107	4				205
Li_2CO_3	monoc, $C2/c$	291 (0.043)	8.3593 (36)	4.9725 (11)	6.1975 (21)	114.83 (3)	4	233.8	2.086	2.094	*d*
$\gamma\text{-}Na_2CO_3$	monoc, $C2/m$	313 (0.128)	8.90	5.24	6.04	101.2	4				*e*
$Na_2CO_3 \cdot H_2O$	ortho, $P2_1ab$	1231 (0.034)	6.474 (2)	10.724 (3)	5.259 (2)		4	365.1	2.255	2.256	206
K_2CO_3	monoc, $P2_1/c$	316 (0.129)	5.64 (3)	9.80 (4)	6.88 (3)	98.8 (5)	4	375.78	2.428	2.44	*f*
$KNa_{22}[Cl(CO_3)_2(SO_4)_9]$ (hanksite)[b]	hex, $P6_3/m$	1535 (0.034)	10.490 (1)		21.240 (1)		2				*g*
$MgCO_3$ (magnesite)[k]	trig, $R\bar{3}(2/c)$	253 (0.020)	4.6328 (2)		15.0129 (5)		6	279.05 (3)			207
$MgCO_3$ (magnesite)[l]	trig		4.6330		15.016						*h*
$MgCO_3$ (magnesite)[l]	trig, $R\bar{3}c$	234 (0.037)	4.637 (1)		15.023 (3)		6				*i*
$MgCO_3 \cdot 3H_2O$ (nesquehonite)[l]	monoc, $P2_1/n$	595 (0.124)	7.7053 (11)	5.3673 (6)	12.1212 (11)	90.451 (13)	4	497	1.85		*j*
$Mg_5(CO_3)_4(OH)_2(H_2O)_4$ (hydromagnesite)[k]	monoc, $P2_1/c$	2598 (0.052)	10.105 (5)	8.954 (2)	8.378 (4)	114.44 (5)	2	690	2.25	2.25	*m*
$Na_2Mg(CO_3)_2$ (eitelite)[l]	trig, $R\bar{3}$		4.942 (2)		16.406 (7)				2.737 (10)		*n*
	trig, $R\bar{3}$	210 (0.045)	4.946 (2)		16.422 (4)		3	347.9 (4)			*o*
$Na_3Mg(CO_3)_2Cl$ (northupite)[k]	isom, $Fd3$	401 (0.023)	14.069 (2)				16	2785	2.380	2.374	*p*
$K_2Mg(CO_3)_2 \cdot 4H_2O$ (baylissite)[l]	monoc, $P2_1/n$	1153 (0.045)	11.404 (4)	6.228 (2)	6.826 (2)	99.66 (2)	2	477.9 (3)	2.04		*q*
$KHCO_3 \cdot MgCO_3 \cdot 4H_2O$	tric, $\sim P\bar{1}$	860 (0.075)	6.713 (3)	7.337 (3)	5.364 (1)	108.92 (3)	1	213.6	1.99		*r*
$CaCO_3$ (aragonite)[k]	ortho, $Pmcn$	(0.031)	4.9614 (3)	7.9671 (4)	5.7404 (4)		4				*s*
	ortho, $Pmcn$	271 (0.022)	4.9616 (2)	7.9705 (6)	5.7394 (4)						*t*
$CaCO_3$ (calcite)[l]	trig, $R\bar{3}c$		4.9900 (2)		17.002 (1)						*u*
			4.9899		17.064						*h*
$CaCO_3$ (calcite)[k]	trig, $R\bar{3}(2/c)$	340 (0.022)	4.9896 (2)		17.0610 (11)		6	367.85 (5)			207
$Ca_{10}(PO_4)_6CO_3$ "apatite"[l]	monoc, Pb		9.557 (3)	19.114	6.872 (2)	120.36 (4)					*v*
$Na_2Ca(CO_3)_2 \cdot 2H_2O$ (pirssonite)[l]	ortho, $Fdd2$	1079 (0.044)	11.340 (4)	20.096 (5)	6.034 (2)		8	1368	2.35	2.35	*w*

$Na_2Ca(CO_3)_2 \cdot 5H_2O$ (gaylussite)[l]	monoc, $C2/c$	2632 (0.054)	14.361 (2)	7.781 (1)	11.209 (2)	127.84 (1)	4	988	1.99	1.99	*w*
$Na_2Ca_2(CO_3)_3$ (shortite)[k]	ortho, $Amm2$	684 (0.020)	4.947 (1)	11.032 (2)	7.108 (1)		2	387.9	2.629	2.620	208
$K_2Ca(CO_3)_2$ (buetschliite),[l] low temp form	trig, $R\bar{3}2/m$		5.38		18.12		3			2.61	*x*
	trig, $R\bar{3}m$	173 (0.052)	5.387 (2)		18.16 (1)		3	456.4 (6)			*o*
$K_2Ca(CO_3)_2$ (fairchildite),[l] high temp form	hex, $P6_3/mmc$	197 (0.10)	5.294 (1)		13.355 (2)						209
$MgCa(CO_3)_2$ (dolomite)[k]	trig, $R\bar{3}$	596 (0.021)	4.812 (1)		16.020 (3)		3	321.06 (9)		2.86	207
		178 (0.045)	4.8033 (9)		15.984 (4)			319.3 (1)			215
$MgCa(CO_3)_2$(dolomite)[l]	trig, $R\bar{3}$	501 (0.0925)	4.815		16.119						*y*
	trig, $R\bar{3}$		4.8079		16.010						*h*
$Mg_3Ca(CO_3)_4$ (huntite)[k]	trig		9.505		7.821						*z*
$Ca_2F_2CO_3$ (brenkite)[k]	ortho, $Pbcn$	840 (0.023)	7.650 (2)	7.550 (2)	6.548 (2)		4	378	3.10 (4)	3.126	*aa*
$SrCO_3$ (strontianite)[k]	ortho, $P2_1cn$	(0.031)	5.090 (2)	8.358 (2)	5.997 (4)		4				*s*
$SrCO_3$ (strontianite)[l]			5.108	8.420	6.040						*bb*
$Sr_{10}(PO_4)_6CO_3$	monoc, $P2_1/b$		9.88 (2)	19.72 (5)	7.23 (9)	119.4 (3)					*cc*
$BaCO_3$ (witherite)[k]	ortho, $P2_1cn$	(0.033)	5.3126 (5)	8.8958 (5)	6.4284 (5)		4				*s*
$BaCO_3$ (witherite)[l]			5.309	8.889	6.401						*bb*
$BaMg(CO_3)$ (norsethite)[k]	trig, $R32$		5.020 (5)		16.75 (2)		3	365.6	3.837 (5)	3.840	*dd*
$BaMg(CO_3)$ (norsethite)[l]	trig, $R32$		5.017 (1)		16.77 (1)		3	365.54	3.796	3.838	*dd*
$BaCa(CO_3)_2$ (barytocalcite)[k]	monoc, $P2_1/m$	1652 (0.023)	8.092 (1)	5.2344 (6)	6.544 (1)	106.05 (1)	2	266.4	3.71	3.72	*ee*
$BaCa(CO_3)_2$ (paralstonite)[k]	trig, $P321$	725 (0.053)	8.692 (3)		6.148 (4)		3				*ff*
$Ba_6Ca_6Mg(CO_3)_{13}$ (benstonite)	trig, $R\bar{3}$	964 (0.062)	18.289 (9)		8.652 (8)		3		3.596	3.695	*gg*
$NaAl(OH)_2CO_3$ (dawsonite)[k]	ortho, $Imma$	488 (0.058)	6.759 (1)	5.585 (1)	10.425 (1)		4	393.53	2.436 (4)	2.431	*hh*
$NH_4[Ga(OH)_2CO_3]$	ortho, $Pbcu$		6.608	12.06	5.882		4		2.47	2.575	*ii*
$Na_8Al_6Ge_6O_{24}(CO_3) \cdot 2H_2O$	hex, $P6_3mc$		12.913 (2)		10.493 (3)						*jj, kk*
$[Sb(C_6H_5)_4(\mu\text{-}OCO_2)\text{-}(C_6H_5)_4Sb]$	tric, $P\bar{1}$	2394 (0.049)	10.108 (5)	14.018 (7)	15.702 (8)	79.84 (4), (α = 73.92 (4), γ = 74.39 (4))	2	2046	1.48	1.49	*ll*
Tl_2CO_3	monoc, $C2/m$	655 (0.051)	12.486 (3)	5.382 (2)	7.530 (2)	122.35 (2)	4	425.4	7.25	7.32	*mm*
$PbCO_3$[l]			5.176	8.511	6.137						*bb*
$PbMg(CO_3)_2$	trig, $R32$		4.924 (1)		16.56 (1)		3				*dd*
				Transition-Metal Complexes							
$[\{Ti(Cp)_2\}_2(\mu\text{-}CO_3)]_2$	ortho, $Cmca$	1508 (0.058)	11.282 (1)	16.038 (1)	19.729 (2)		4			1.548	402
$MnCO_3$ (rhodochrosite)[k]	trig, $R\bar{3}(2/c)$	288 (0.015)	4.7682 (2)		15.6354 (8)		6	307.86 (4)			207
$MnCO_3$ (rhodochrosite)[l]	trig		4.7771		15.664						*h*
$FeCO_3$ (siderite)[k]	trig, $R\bar{3}(2/c)$	274 (0.013)	4.6916 (4)		15.3796 (16)		6	293.17 (8)			207
$FeCO_3$ (siderite)[l]	trig		4.6887		15.373						*h*
$CoCO_3$	trig		4.6581		14.958						*h*
trans-$K_2[Co^{II}(H_2O)_4(CO_3)_2]$	monoc, $P2_1/n$	2514 (0.024)	11.450 (1)	6.184 (1)	6.817 (1)	99.46 (1)	2	476.1	2.293	2.296	*nn*

TABLE XVI (*Continued*)

compd	cryst syst,[uuuu] space grp	obsd[a]	a_0, Å	b_0, Å	c_0, Å	β, deg	Z	vol, Å^3	d,[b] g cm^{-3}		ref
									measd	calcd	
$[Co(NH_3)_5CO_3]Br\cdot H_2O$	ortho, $Pna2_1$	956 (0.095)	12.370 (3)	12.144 (3)	6.433 (6)		4	966.4	2.08	2.075	211
$[Co(NH_3)_4CO_3]Br$	ortho, $Pcmn$	459 (0.12)	6.760 (5)	7.629 (5)	16.886 (10)		4	870.8	2.028	2.036	*oo*
$[Co(py)_4CO_3]ClO_4\cdot H_2O$	monoc, $P2_1/c$	3302 (0.049)	9.457 (3)	16.333 (6)	15.582 (11)	97.93 (4)	4	2384	1.547	1.540	*pp*
$[Co(en)_2CO_3]I\cdot 2H_2O$	monoc, $C2/c$	1485 (0.030)	8.362 (2)	15.327 (8)	10.223 (8)	93.34 (3)	4	1308 (1)	2.009	2.042	*qq*
$[Co(tn)_2CO_3]ClO_4$	monoc, $P2_1/c$	1904 (0.092)	9.51 (2)	13.22 (3)	12.03 (3)	111.17 (10)	4	1410	1.73 (1)	1.726	*rr*
$[Co(phen)_2CO_3)]Cl\cdot 3H_2O$	monoc, $P2_1/c$	1332 (0.089)	12.512 (2)	19.172 (4)	10.075 (2)	96.32 (2)	4		1.49	1.50	212
$[Co(phen)_2CO_3]Br\cdot 4H_2O$	tric, $P\bar{1}$	2958 (0.062)	16.411 (8)	7.858 (4)	10.601 (3)	108.3 (2), (α = 89.1 (2), γ = 76.0 (1))	2	1253.1	1.68		*ss*
$Na[Co(pren)CO_3]\cdot 3H_2O$	monoc, $P2_1$	2463 (0.059)	7.845 (4)	7.760 (2)	14.922 (10)	106.51 (2)	2	871 (1)	1.71 (3)	1.717	*tt*
$\Lambda(+)$-*cis*(*N*)-*cis*(*O*)-$K[Co(\text{L-val})_2CO_3]\cdot 2H_2O$	ortho, $P2_12_12_1$	996 (0.087)	21.41 (4)	14.68 (3)	5.76 (1)		4	1810	1.54	1.56	213
$[Co(cyclen)CO_3]ClO_4\cdot H_2O$	ortho, $P2_12_12_1$	940 (0.067)	13.68 (3)	13.32 (3)	8.92 (2)		4		1.69 (1)	1.669 (7)	*uu*
$(+)_{589}$-*cis*-β-$[Co(3,8\text{-dimetrien})CO_3]ClO_4$	ortho, $P2_12_12_1$	1894 (0.053)	12.284 (2)	17.913 (8)	7.179 (3)		4	1579.9	1.65	1.65	214
$[Co(terpy)(CO_3)(OH)]\cdot 4H_2O$	tric, $P\bar{1}$	1354 (0.075)	11.407 (6)	10.566 (6)	8.445 (4)	107.35 (5), (α = 100.21 (5), γ = 102.18 (5))	2	917 (1)	1.60 (1)	1.60	*vv*
$[(NH_3)_4Co(\mu\text{-}NH_2)(\mu\text{-}OH)\text{-}Co(CO_3)_2]\cdot 5H_2O$	monoc, $P2_1/c$	3435 (0.044)	9.5572 (15)	15.8477 (29)	9.8036 (20)	90.305 (14)	4	1484.8 (5)	1.864 (13)	1.919	*ww*
$[(NH_3)_6Co_2(\mu\text{-}OH)_2\text{-}(\mu\text{-}CO_3)]SO_4\cdot 5H_2O$	tric, $P\bar{1}$	2258 (0.029)	6.6914 (14)	11.2847 (18)	11.8251 (23)	99.096 (15), (α = 92.766 (14), γ = 101.496 (15))	2	861.1 (3)		1.929	491
$Tl[Cr(CO_3)_2]$	monoc, $P2_1/c$		19.917 (7)	8.605 (3)	19.138 (5)	104.79 (3)	24	3169.3	4.65	4.73	*xx*
$[([9]aneN_3)_2Cr_2(\mu\text{-}OH)_2\text{-}(\mu\text{-}CO_3)]I_2\cdot H_2O$	ortho, $Pbnm$	2545 (0.072)	8.577 (3)	14.169 (5)	21.805 (6)		4	2650		1.806	345
$(NH_4)_4[(H_2O)_2Cr^{II}{}_2\text{-}(\mu\text{-}CO_3)_4]\cdot H_2O$	monoc, $P2_1/c$	1511 (0.033)	6.949 (2)	16.112 (4)	7.737 (2)	108.14 (2)	2	823.2 (7)	1.90		*yy*
$NiCO_3$	trig		4.5975		14.723						*h*
$CuCO_3$	monoc		6.092	4.493	7.030	101.34	4	188.7	4.18	4.35	*zz*
$Na_2[Cu(CO_3)_2]$	monoc, $P2_1/a$	286 (0.115)	6.18 (2)	8.19 (2)	5.64 (2)	116.2 (2)	2	256	3.1 (1)	2.98	*aaa*
$Na_2[Cu(CO_3)_2]\cdot 3H_2O$ (chalconatronite)[l]	monoc, $P2_1/c$	2373 (0.042)	9.961 (2)	6.091 (1)	17.111 (3)	126.40 (1)	4	813.0	2.314	2.317	*bbb*
	monoc, $P2_1/n$	2487 (0.042)	9.696 (2)	6.101 (2)	13.779 (3)	91.83 (2)	4	814.6	2.29 (2)	2.312	*ccc*
	monoc, $P2_1/n$	995 (0.13)	13.81 (2)	6.10 (1)	9.70 (1)	91.7 (2)	4	817	2.28 (2)	2.31	*ddd*
$Rb_2[Cu(CO_3)_2]\cdot H_2O$	monoc, $P2_1/a$	714 (0.11)	6.574 (5)	16.081 (5)	7.697 (5)	92.5 (1)	4	762.4	3.06	3.24	*eee*
$Tl_2[Cu(CO_3)_2]$	monoc, $P2_1/c$	1883 (0.112)	7.583 (1)	9.799 (1)	9.119 (1)	111.51 (1)	4	630.4	6.07	6.21	*xx*

$[Cu(NH_3)_2CO_3]$	monoc, $P2_1/c$	934 (0.032)	5.640 (2)	10.579 (3)	7.462 (3)	97.82 (1)	4	441.32	2.35	2.372	*fff*
$[Cu_2(OH)_2CO_3]$ (malachite)[k]	monoc, $P2_1/a$	579 (0.063)	9.502	11.974	3.24	98.75	4				*ggg*
	monoc, $P2_1/a$	635 (0.021)	9.502	11.974	3.240	98.75					*hhh*
$[Cu_3(OH)_2(CO_3)_2]$ (azurite)[k]	monoc, $P2_1/c$		5.00 (2)	5.85 (2)	10.35 (2)	92.33 (33)			3.773 (3)	3.78	*iii*
	monoc, $P2_1/c$	482 (0.024)	5.0109 (5)	5.8485 (6)	10.345 (2)	92.43 (3)					*jjj*
$[Cu_8Mg_8(CO_3)_4(OH)_{24}]\cdot 8H_2O$ (callaghanite)[k]	monoc	2690 (0.038)	10.0060 (7)	11.7520 (8)	8.2132 (7)	107.38					*kkk*
	monoc, $C2/c$	(0.183)	8.24 (3)	11.80 (3)	10.06 (4)	107.30	4		2.71	2.65	*lll*
$K_{0.4}[Cu_{0.9}HCO_3)_2(OH)_2]\cdot 1.66H_2O$	trig, $P3c1$	466 (0.085)	11.664		9.615		6	1132.8	2.70		*mmm*
$[(teed)_2Cu_2Cl_2(\mu\text{-}CO_3)]$	monoc, Cc	4963 (0.035)	18.9001 (26)	12.1728 (16)	13.7210 (22)	117.43 (1)	4	2801.8		1.43	*nnn*
$[(tmtn)_2Cu_2Cl_2(\mu\text{-}CO_3)]$	ortho, $P22_12_1$	2232 (0.029)	8.0832 (15)	11.6855 (14)	11.9301 (17)		2	1126.9		1.528	*ooo*
$[LCu_2(\mu\text{-}CO_3)L](ClO_4)_2\cdot DMF^{tttt}$	ortho, $Iba2$	1230 (0.052)	16.19 (1)	16.67 (1)	15.43 (1)		4	4164	1.35 (2)	1.34	*ppp*, *qqq*
$[\{Cu(pip)H_2O\}_3CO_3](NO_3)_4$	hex, $P\bar{6}2c$	926 (0.054)	13.414 (3)		16.024 (2)		2		1.585	1.578	*rrr*
$[Cu_4(dpt)_4(\mu\text{-}CO_3)(\mu\text{-}Cl)_2]Cl_4\cdot 7.5H_2O$	tric, $P\bar{1}$	4950 (0.053)	9.246 (3)	13.957 (3)	25.898 (6)	106.82 (1), (α = 121.87 (1), γ = 96.02 (1))	2	2576.9	1.53	1.529	219
$ZnCO_3$ (smithonite)[k]	trig, $R3(2/c)$		4.6526 (7)		15.0257		6	281.68 (13)			207
	trig		4.6887		15.373						*h*
$Cs_4[Rh_2(H_2O)_2(\mu\text{-}CO_3)_4]\cdot 6H_2O$	monoc, $P2_1/c$	1991 (0.052)	7.867 (1)	7.963 (1)	18.211 (2)	91.83 (1)	2	1140.2 (3)		3.27	*sss*
$Cs_4Na_2[Rh_2Cl_2(\mu\text{-}CO_3)_4]\cdot 8H_2O$	monoc, $P2_1/c$	1409 (0.037)	9.798 (2)	10.753 (2)	12.906 (3)	107.98 (2)	2	1293.2 (4)		3.18	*sss*
$[Rh(PPh_3)_3(\mu\text{-}CO_3)(PPh_3)_2Rh]\cdot C_6H_6$	tric, $P\bar{1}$	12330 (0.079)	22.518 (9)	28.051 (12)	12.841 (7)	97.91 (3), (α = 96.12 (3), γ = 92.66 (3))	4	7972	1.39	1.38	500
$[Rh\{P(i\text{-}Pr)_3\}_2H_2(CO_3H)]$	monoc, $P2_1/c$	5844 (0.028)	15.82 (1)	10.88 (1)	15.49 (1)	114.5 (1)	4	2428	1.28	1.33	403
trans-$[Pd(PEt_3)_2(CH_3)CO_3H]$	tric, $P\bar{1}$	1308 (0.075)	7.713 (5)	9.014 (5)	15.339 (8)	94.80 (5), (α = 111.35 (4), γ = 90.77 (5))	2			1.407	*ttt*
$K[AgCO_3]$	ortho, $Ibca$		20.23 (10)	5.75 (3)	5.95 (3)		8		3.77	3.94	*uuu*
	ortho, $Ibca$		20.50 (20)	5.82 (6)	6.00 (6)		8	716	3.77	3.94	*vvv*
$CdCO_3$	trig		4.9204		16.298						*h*
$CdMg(CO_3)$	trig		4.7770 (9)		15.641 (3)						*h*
$[Pt(PPh_3)_2CO_3]$	tric, $P\bar{1}$	1200 (0.057)	12.49	15.70	10.56	70.0, (α = 110.9, γ = 98.1)					*www*
Lanthanide Complexes											
$Na[La(CO_3)_2]$	ortho		6.436	5.161	7.217		2	239.1	3.86	3.91	250
$[La_2(CO_3)_3]\cdot 8H_2O$	ortho, $Pccn$	705 (0.061)	8.984 (4)	9.580 (4)	17.00 (1)		4		2.72 (2)	2.732	*xxx*
	ortho, $Pccn$		8.991 (5)	9.573 (5)	17.019 (8)		4			2.729	198
$Na[Ce(CO_3)_2]$	ortho		6.405	5.140	7.163		2	235.8		3.99	250

TABLE XVI (*Continued*)

compd	cryst syst,[uuuu] space grp	obsd[a]	a_0, Å	b_0, Å	c_0, Å	β, deg	Z	vol, Å^3	d,[b] g cm^{-3} measd	d,[b] g cm^{-3} calcd	ref
$Na_6[Ce(CO_3)_5]\cdot 12H_2O$	tric, $P\bar{1}$	7157 (0.051)	9.53 (2)	9.84 (2)	13.58 (3)	104.50 (21), (α = 90.46 (18), γ = 95.42 (19))	2	1226	2.13	2.10	*yyy*
$[C(NH_2)_3]_6[Ce(CO_3)_5]\cdot 4H_2O$	monoc, *Bb*	7092 (0.072)	16.05 (3)	16.63 (3)	13.14 (3)	108.10 (22)	4	3397	1.63	1.69	*zzz*
$[Ce_4Cl(OH)_3(CO_3)_4]$	hex, $P\bar{6}$		12.53 (2)		9.96 (2)						*aaaa*
$[Ce_3Cl(CO_3)_4]$	trig, *R*3*m*		9.934 (7)		8.826 (9)						*aaaa*
$Na[Pr(CO_3)_2]$	ortho		6.381	5.125	7.136		2	233.4		4.04	250
$[Pr_2(CO_3)_3]\cdot 8H_2O$	ortho, *Pccn*		8.914 (5)	9.485 (5)	16.932 (9)		4		2.80	2.811	198
$Na[Nd(CO_3)_2]$	ortho		6.346	5.097	7.068		2	228.6		4.17	250
$Na[Nd(CO_3)_2]\cdot 6H_2O$	tetrag, *P*4		13.11		9.93		8	1706.7			251
$[Nd_2(CO_3)_3]\cdot 7.93H_2O$	ortho, *Pccn*		8.890 (5)	9.444 (5)	16.902 (9)		4			2.867	198
$Na[Sm(CO_3)_2]$	ortho		6.324	5.079	7.026		2	225.7		4.32	250
$Na[Sm(CO_3)_2]\cdot 6H_2O$	tetrag, *P*4		13.05		9.85		8	1677.5			251
$Na[Gd(CO_3)_2]\cdot 6H_2O$	tetrag, *P*4		12.99		9.77		8	1648.6			251
$[Gd(HCO_3)_3(H_2O)_4]\cdot H_2O$	monoc, $P2_1/a$	1906 (0.117)	6.877 (1)	9.575 (2)	18.871 (2)	102.61 (2)	4	1212.6		2.37	*bbbb*
$Na[Tb(CO_3)_2]$	monoc		6.268	13.186	6.169	102.89	4	497.0		4.04	250
$Na[Dy(CO_3)_2)]$	monoc		6.238	13.146	6.151	102.82	4	491.8		4.13	250
$Na[Dy(CO_3)_2]\cdot 6H_2O$	tetrag, *P*4		12.93		9.69		8	1620.0			251
$Na[Ho(CO_3)_2]$	monoc		6.224	13.100	6.138	102.73	4	488.2	4.11	4.19	250
$[Ho_2(CO_3)_3)]\cdot 2.25H_2O$			15.056	9.165	6.065						*cccc*
$Na[Y(CO_3)_2]$	monoc		6.222	13.106	6.140	102.70	4	488.4		3.15	250
$Na[Y(CO_3)_2]\cdot 6H_2O$	tetrag, *P*4		12.90		9.65		8	1605.8	2.31		251
$[Y_2(CO_3)_3]\cdot 2\text{–}3H_2O$	ortho		9.20 (2)	11.32 (2)	7.59 (1)		4		3.2 (1)		*dddd*
$Na[Er(CO_3)_2]$	monoc		6.206	13.065	6.124	102.68	4	484.4		4.25	250
$[Er_2(CO_3)_3]\cdot 2.25H_2O$	ortho		6.05 (1)	9.13 (1)	15.00 (1)						198
$Na[Tm(CO_3)_2]$	monoc		6.186	13.020	6.114	102.65	4	480.5		4.31	250
$Na[Yb(CO_3)_2]$	monoc		6.160	12.978	6.100	102.58	4	476.0		4.41	250
$Na[Lu(CO_3)_2]$	monoc		6.150	12.941	6.089	102.46	4	474.2		4.46	250
$(Na,Ca)[Ln,Sr,Ca,Mg](CO_3)_2$ (carbocernaite)[k]	- - -, $Pb2_1m$		6.41 (3)	7.30 (3)	5.23 (2)		2				*eeee*
$(Na,Ca)_3[Ca,Sr,Ba,Ln]_3(CO_3)$ (berbankite)[k]	hex, $P6_3mc$		10.52 (4)		6.51 (2)		2		3.58		*ffff*
Actinide Complexes											
$Na_6[Th(CO_3)_5]\cdot 12H_2O$	tric, $P\bar{1}$	4806 (0.060)	9.60 (2)	9.92 (2)	13.64 (3)	104.38 (21), (α = 90.47 (18), γ = 95.52 (19))	2	1248	2.31	2.35	*gggg*
$[C(NH_2)_3]_6[Th(CO_3)_5]\cdot 4H_2O$	monoc, *Bb*	11601 (0.062)	16.15 (3)	16.70 (3)	13.23 (3)	108.41 (22)	4	3418	1.94	1.92	*hhhh*
$[UO_2(CO_3)]$ (rutherfordine)[c]		(0.073)	4.85 (1)	9.22 (2)	4.30 (1)						*iiii*
$[UO_2(CO_3)]$ (rutherfordine)[b]	ortho, $Pm2_1n$/ *Pmmm*		4.845 (10)	9.205 (8)	4.296 (6)				5.7	5.724	*jjjj*
$[C(NH_2)_3]_4[UO_2(O_2)(CO_3)_2]\cdot 2H_2O$	ortho, $Pca2_1$	1447 (0.07)	15.883 (1)	8.788 (2)	16.155 (1)		4		2.02		*kkkk*

$K_4[UO_2(CO_3)_3]$	monoc, *C*2/*c*	1693 (0.038)	10.247 (3)	9.202 (2)	12.226 (3)	95.11 (2)	4		3.5	3.507	*llll*
$[NH_4]_4[UO_2(CO_3)_3]$	monoc, *C*2/*c*	1833 (0.076)	10.68 (1)	9.38 (1)	12.85 (1)	96.45 (8)	4	1279		2.71	*mmmm*
$Ca_2[UO_2(CO_3)_3]\cdot 10\text{-}11H_2O$ (liebigite)[c]	ortho, *Bba*2		16.74	17.54	13.72		8				*nnnn*
$NaK_3[UO_2(CO_3)_3]$	hex, $P\bar{6}2c$		9.29		8.26		2				*oooo*
$Na[NpO_2CO_3]$	hex		3.915		17.68						*pppp*
$Na_3[NpO_2(CO_3)_2)]\cdot nH_2O$	monoc		5.070 (5)	8.78 (1)	8.00 (1)	92.5 (2)	2	356.6		4.53	*qqqq*, *rrrr*
$K_3[NpO_2(CO_3)_2)]\cdot nH_2O$	ortho		5.31	9.12	8.95		2	433.4		4.10	*qqqq*
$Rb_3[NpO_2(CO_3)_2]\cdot nH_2O$	hex		5.410 (5)	9.37 (1)	9.37 (1)		2	475.0		4.71	*qqqq*
$KPuO_2CO_3$	hex, *C*6/*mmc*		5.09 (1)		9.83 (2)		2	221		5.57	*ssss*
$NH_4PuO_2CO_3$	hex, *C*6/*mmc*		5.09 (1)		10.39 (2)		2	233		4.99	*ssss*
$K_3[PuO_2(CO_3)_2]\cdot nH_2O$	ortho		5.29	9.09	8.90		2	428.0		4.21	*qqqq*
$RbAmO_2CO_3$	hex, *C*6/*mmc*		5.12 (1)		10.46 (4)		2	237		6.06	*ssss*
$K_3[AmO_2(CO_3)_2]\cdot nH_2O$	ortho		5.29	9.11	8.83		2	425.5		4.22	*qqqq*

[a] Obsd. generally refers to the total number of independent reflections measured with the unweighted reliability index given in parentheses. [b] *d* is density. [c] Koo, C. H. *Acta Crystallogr.* 1952, *5*, 292. [d] Effenberger, H.; Zemann, J. *Z. Kristallogr.* 1979, *150*, 133. [e] Dubbeldam, G. C.; de Wolf, P. M. *Acta Crystallogr., Sect. B*, 1969, *B25*, 2665. [f] Gatehouse, B. M.; Lloyd, D. J. *J. Chem. Soc., Dalton Trans.* 1973, 70. [g] Kato, K.; Saalfeld, H. *Acta Crystallogr., Sect. B* 1972, *B28*, 3614. [h] Graf, D. L. *Am. Min.* 1961, *46*, 1283. [i] Oh, K. D.; Morikawa, H.; Iwai, S.; Aoki, H. *Ibid.* 1973, *58*, 1029. [j] Stephan, G. W.; MacGillavry, C. H. *Acta Crystallogr., Sect. B* 1972, *B28*, 1031. [k] Natural mineral sample. [l] Synthetic mineral sample. [m] Akao, M.; Iwai, S. *Acta Crystallogr., Sect. B* 1977, *B33*, 1273. [n] Pabst, A. *Am. Min.* 1973, *58*, 211. [o] Knobloch, D.; Pertlik, F.; Zemann, J. *N. Jb. Miner. Mh.* 1980, 230. 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Table XVI (*Continued*)

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TABLE XVII. Bond Lengths (Å) and Angles (deg) in Alkali Metal and Alkaline Earth Metal Carbonates (X-ray Diffraction)

compd	M-O (M-$O_{1,2}$)	C_1-O_1	C_1-O_2	C_1-O_3	$O_1C_1O_2$	$O_1C_1O_3$	O_2CO_3	ref
			Bicarbonates					
$NaHCO_3$	2.438	1.346[dd]	1.263	1.264	116.27	118.77	124.97	202
	2.44 (3)	1.345[dd]	1.275	1.249	114.6	119.9	125.5	202, *a*
$KHCO_3$	2.85 (15)	1.32[dd]	1.33[dd]	1.28	119.5	122	118.5	*b*
	2.84 (10)	1.274 (2)[dd]	1.337 (2)[dd]	1.240 (3)	118.14 (18)	124.12 (17)	117.74 (16)	203
c	2.84 (10)	1.274 (1)[dd]	1.332 (1)[dd]	1.244 (1)	118.35 (6)	123.75 (6)	117.89 (6)	204
$KDCO_3$	2.84 (11)	1.266 (3)[dd]	1.346 (3)[dd]	1.239 (3)	118.12 (20)	125.05 (20)	116.82 (19)	203
c	2.85 (11)	1.268 (2)[dd]	1.337 (2)[dd]	1.243 (1)	118.18 (11)	124.62 (12)	117.19 (12)	204
$RbHCO_3$	2.97 (11)	1.33	1.32	1.32	119.75	119.75	120.50	205
			Carbonates					
Li_2CO_3	1.96 (5)	1.270 (3)	1.286 (2)	1.286 (2)	120.0 (1)	120.1 (2)	120.0 (1)	*d*
$Na_2CO_3 \cdot H_2O$	2.48 (16)	1.299 (3)[dd]	1.274 (2)	1.285 (2)[dd]	119.6 (2)	119.2 (2)	121.2 (2)	206
K_2CO_3	2.85 (18)	1.28 (2)	1.32 (2)	1.28 (2)	118.0 (23)	122.0	120.1	*e*
$KNa_{22}[Cl(CO_3)_2(SO_4)_9]$	2.46 (18) (Na) (Na)	1.287 (3)						*f*
	2.03 (14) (K)							
$MgCO_3$	2.1018 (4)	1.2852 (4)						207
	2.105 (1)	1.283 (1)			120			*g*
$MgCO_3 \cdot 3H_2O$	2.08 (5)	1.275 (13)	1.273 (10)	1.284 (12)	122.6 (9)	114.1 (9)	123.3 (8)	*h*
$Mg_5(CO_3)_4(OH)_2(H_2O)_4$	2.08 (4)	1.254 (4)[dd]	1.262[dd]	1.299 (3)	118.4 (3)	121.8 (3)	119.8 (3)	*i*
$Na_2Mg(CO_3)_2$	2.074 (2) (Mg)	1.284 (2)	1.284 (2)	1.284 (2)				*j*
	2.63 (30) (Na)							
$Na_3Mg(CO_3)_2Cl$	2.073 (1) (Mg)	1.284 (1)	1.284 (1)	1.284 (1)	120.0 (1)	120.0 (1)	120.0 (1)	*k*
	2.424 (12) (Na)							
$K_2Mg(CO_3)_2 \cdot 4H_2O$	2.09 (3) (Mg)	1.282 (3)[dd]	1.298 (3)[dd]	1.282 (4)	119.6 (3)	120.0 (2)	120.4 (2)	*l*
$(K_2CO_3 \cdot MgCO_3 \cdot 4H_2O)$	2.78 (6) (K)							
$KHCO_3 \cdot MgCO_3 \cdot 4H_2O$	2.07 (2) (Mg)	1.275 (4) (Mg)			118.0 (5)	118.3 (5)	123.5 (5)	*m*
	3.09 (20) (K)		1.309 (4)	1.266 (4)				
$Cu_8Mg_8(CO_3)_4(OH)_{24} \cdot 8H_2O$[n]	2.03 (Mg)	1.41	1.41	1.29[dd]	114	122	122	*o*
	2.061 (Mg)	1.282 (1)	1.282 (1)	1.284 (3)	121.3 (2)	119.35 (9)	119.35 (9)	*p*
$CaCO_3$ (aragonite)	2.53 (13)	1.279 (5)	1.284 (3)	1.284 (3)	120.19 (18)	120.19 (18)	119.55 (37)	*q*
	2.52 (10)	1.287	1.280	1.287	120.70	120.70	118.47	*t*
$CaCO_3$ (calcite)		1.283 (2)						*s*
	2.3598 (6)	1.2815 (6)						207
$Na_2Ca(CO_3)_2 \cdot 2H_2O$	2.46 (6)	1.300 (12)[dd]	1.276 (14)	1.281 (14)	120.5 (11)	120.1 (11)	119.4 (9)	*t*
	2.47 (21) (Na)							
$Na_2Ca(CO_3)_2 \cdot 5H_2O$	2.47 (8)	1.280 (3)[dd]	1.291 (2)[dd]	1.293 (3)	121.8 (2)	120.1 (2)	118.1 (2)	*t*
	2.43 (10) (Na)							
$Na_2Ca_2(CO_3)_2$	2.50 (6) (Ca)	1.273 (3)	1.286 (2)	1.286 (2)	119.6 (1)	119.6 (1)	120.9 (2)	208
	2.46 (20) (Na)	1.306 (4)	1.273 (3)	1.273 (3)	118.7 (2)	118.7 (2)	122.7 (3)	

$K_2Ca(CO_3)_2$ (buetschliite)	2.34 (Ca)							*u*
	2.80 (K)							
	2.326 (3) (Ca)	1.285 (2)	1.285 (2)	1.285 (20)				*j*
	2.91 (11) (Na)							
$K_2Ca(CO_3)_2$ (fairchildite)	2.76^{v}	1.29 (1)	1.29 (1)	1.29 (1)	120	120	120	209
	2.61^{v}	1.31 (3)	1.31 (3)	1.26 (1)	116 (2)	116 (2)	124 (1)	
$MgCa(CO_3)_2$	2.3822 (5) (Ca)	1.2853 (4)						207
	2.0877 (4) (Mg)							
	2.378 (1) (Ca)	1.2835 (15)			119.95 (1)			215
	2.081 (1) (Mg)							
	2.390 (Ca)	1.283						*u*
	2.095 (Mg)							
$Mg_3Ca(CO_3)_4$	2.35	1.28						*x*
	2.10 (Mg)							
$Ca_2F_2CO_3$	2.43 (9)	1.297 (2)	1.279 (2)	1.279 (2)	119.4 (2)	119.4 (2)	121.2 (2)	*y*
$SrCO_3$	2.64 (12)	1.269 (10)	1.293 (6)	1.293 (6)	120.28 (40)	120.28 (40)	119.43 (79)	*q*
$BaCO_3$	2.81 (11)	1.282 (12)	1.289 (7)	1.289 (7)	120.28 (46)	120.28 (46)	119.43 (93)	*z*
$BaMg(CO_3)_2$	2.094 (2) (Mg)							
	2.94 (22) (Ba)							
$BaCa(CO_3)_2$ (barytocalcite)	2.39 (9) (Ca)	1.275 (4)	1.286 (2)	1.286 (2)	120.3 (2)	120.3 (2)	119.3 (2)	
	2.91 (13) (Ba)	1.259 (4)	1.294 (2)	1.294 (2)	121.6 (1)	121.6 (1)	116.6 (3)	*aa*
$BaCa(CO_3)_2$ (paralstonite)	2.50 (10) (Ca)	1.29 (6)	1.29 (6)	1.29 (6)	120 (1)	120 (1)	120 (1)	*bb*
	2.81 (3) (Ba)							
$Ba_6Ca_6Mg(CO_3)_{13}$	2.07 (2) (Mg)	1.27 (2)	1.29 (2)	1.32 (2)	121.7 (12)	119.2 (17)	119.0 (14)	*cc*
	2.48 (15) (Ca)	1.32 (2)	1.27 (3)	1.25 (2)	117.9 (12)	118.9 (17)	122.8 (16)	
	2.83 (12) (Ba)							
$PbMg(CO_3)_2$	2.095 (1) (Mg)	1.281 (1)	1.281 (1)	1.281 (1)	120	120	120	*z*
	2.67 (12) (Pb)							

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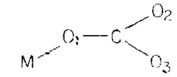
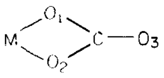
TABLE XVIII. Bond Lengths (Å) and Angles (deg) for Monodentate, Mononuclear Carbonato Complexes



complex	CN[d]	$M-O_1$	$C-O_1$	$C-O_2$	$C-O_3$	$M-O_1-C$	O_1-C-O_2	O_1CO_3	O_2CO_3	O_1ML_{cis}	ref
trans-$[Pd^{II}(PEt_3)_2(CH_3)CO_3H]$	4	2.13 (2)	1.27 (4)	1.31 (3)	1.28 (3)	131 (1)	121 (3)	119 (2)	120 (3)	89.2 (1.3)[a]	*b*
trans-$K_2[Co^{II}(H_2O)_4(CO_3)_2]$	6	2.068 (1)	1.291 (1)	1.284 (1)	1.291 (1)		119.4 (1)	120.6 (1)	120.1 (1)	87.8 (4.6)[a]	*c*
$[Co^{III}(NH_3)_5CO_3]Br\cdot H_2O$	6	1.93 (3)	1.31 (5)	1.29 (5)	1.20 (5)		117.9 (3.4)	122.7 (3.4)	117.2 (3.4)		211

[a] In these cases, the calculated mean value has a standard deviation considerably greater than the largest standard deviation in the individual values. [b] Crutchley, R. J.; Powell, H.; Faggiani, R.; Lock, C. J. L. *Inorg. Chim. Acta* 1977, *24*, L15. [c] Harlow, R. L.; Simonsen, S. H. *Acta. Crystallogr., Sect. B* 1976. *B32*, 466. [d] Coordination number.

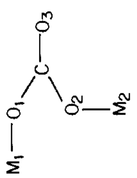
TABLE XIX. Bond Lengths (Å) and Angles (deg) for Bidentate, Mononuclear Carbonato Complexes



complex	CN	$M-O_1$	$C-O_1$	$C-O_2$	$C-O_3$	MO_1C	O_1MO_2	O_1CO_2	O_1CO_3	O_2CO_3	ref
$[Pt(PPh_3)_2CO_3]$	4	2.07	1.28	1.28	1.28		64.0				*a*
$Na_2Cu(CO_3)_2\cdot 3H_2O$	5	1.993 (10)[b]	1.302 (5)	1.299 (5)	1.261 (5)	90.5 (6)	66.0 (1)	113.1 (3)	124.3 (4)	122.6 (4)	*c*
	5	1.999 (12)[b]	1.317 (5)	1.295 (5)	1.251 (5)	90.6 (10)[b]	65.9 (1)	112.8 (4)	123.5 (4)	123.6 (4)	*d*
	5	1.99 (2)	1.29 (2)	1.30 (2)	1.27 (2)	91.5 (11)	65.3 (4)	111.7 (13)	124.2 (14)	124.1 (14)	*e*
$[Rh[P(i\text{-}Pr)_3]_2H_2(CO_3H)]$	5	2.293 (16)	1.261 (3)	1.284 (3)	1.329 (3)		57.91 (7)	121.5 (2)	118.7 (2)	119.8 (2)	403
$[Co(NH_3)_4CO_3]Br$	6	1.905 (11)	1.336 (18)	1.336 (18)	1.237 (20)	89.5 (8)	70.5 (5)	110.4 (1.3)	124.8 (1.4)	124.8 (1.4)	*f*
	6	1.93 (2)	1.34 (3)	1.34 (3)	1.24 (4)	88.5 (8)	70.5 (6)	112.7 (1.4)	123.9 (1.5)	123.9 (1.5)	*g*
$[Co(py)_4CO_3]ClO_4\cdot H_2O$	6	1.894 (5)	1.330 (6)	1.319 (5)	1.210 (3)	91.0 (5)	69.28 (12)	108.7 (3)	125.5 (4)	125.8 (4)	*h*
$[Co(en)_2CO_3]I\cdot 2H_2O$	6	1.907 (2)	1.306 (3)	1.306 (3)	1.234 (6)	90.9 (1)	68.2 (1)	109.9 (2)	125.0 (1)	125.0 (1)	*i*
$[Co(tn)_2CO_3]ClO_4$	6	1.92 (4)[b]	1.32 (2)	1.32 (2)	1.22 (2)	90.2 (2)[b]	68.8 (5)	110.4 (7)			*j*
$[Co(phen)_2CO_3]Cl\cdot 3H_2O$	6	1.883 (12)	1.331 (22)	1.284 (23)	1.198 (21)		68.4 (5)	108.1 (1.1)	122.2 (1.2)	129.7 (1.2)	212
$[Co(phen)_2CO_3]Br\cdot 4H_2O$	6	1.892 (7)	1.315 (8)	1.332 (8)	1.213 (8)		69.3 (2)	108.7 (6)	126.3 (7)	125.0 (7)	*k*
$Na[Co(pren)CO_3]\cdot 3H_2O$	6	1.907 (6)	1.305 (8)	1.329 (7)	1.225 (8)	90.1 (8)	69.1 (2)	110.5 (5)	125.0 (6)	124.5 (6)	*l*
Λ-(+)-cis(*N*)-cis(O)-$K[Co(l\text{-}val)_2CO_3]\cdot 2H_2O$	6	1.914 (27)[b]	1.26 (3)	1.33 (3)	1.29 (3)						213
$[Co(cyclen)CO_3]ClO_4\cdot H_2O$	6	1.917 (18)	1.308 (16)	1.324 (15)	1.219 (16)	90.5 (9)	68.4 (4)	110.0 (11)	125.7 (12)	123.3 (12)	*m*
(+)-*cis*-β-$[Co(3,8\text{-}dimetrien)CO_3]ClO_4$	6	1.915 (18)[b]	1.314	1.296 (8)	1.236 (8)	89.9 (1.3)[b]	68.6 (2)	111.6 (5)	123.1 (6)	125.3 (6)	214
$[Co(terpy)(CO_3)(OH)]\cdot 4H_2O$	6	1.918 (9)	1.29 (2)	1.29 (2)	1.26 (2)		68.0 (4)	113 (1)	123 (2)	124 (1)	*n*
$[(NH_3)_4Co(\mu\text{-}NH_2)(\mu\text{-}OH)Co(CO_3)_2]\cdot 5H_2O$[o]	6	1.918 (5) (1.963 (2))[q]	1.314 (8)	1.314 (8)	1.237 (5)	90.0 (1.1)	68.5 (4)				*p*
$[C(NH_2)_3][UO_2(O_2)(CO_3)_2]\cdot 2H_2O$	8	2.42 (1)	1.34 (3) 1.30 (3)	1.24 (3) 1.23 (3)	1.27 (3) 1.28 (3)		53 (1) 52 (1)	114 (2) 115 (2)	119 (2) 119 (2)	127 (2) 125 (2)	*r*
$K_4[UO_2(CO_3)_3]$	8	2.430 (5)	1.32	1.30	1.24	95.8 (6)	53.7 (4)	113.9 (13)	123.2 (7)	123.2 (7)	*s*
$(NH_4)_4[UO_2(CO_3)_3]$	8	2.45 (1)	1.34 (2)	1.29 (2)	1.25 (3)	95 (1)	54.1 (1.1)	115 (3)	123 (2)	122 (2)	*t*
$[La_2(CO_3)_3]\cdot 8H_2O$	10	2.54 (10)	1.27 (2)	1.27 (2)	1.27 (2)			119.8 (46)[b]			*u*
$Na_6[Ce(CO_3)_5]\cdot 12H_2O$	10	2.437 (48)[b]	1.284 (24)[b]	1.283 (25)[b]	1.280 (30)[b]			119.4 (47)[b]	120.1 (48)[b]	120.5 (40)[b]	*v*
$[C(NH_2)_3]_6[Ce(CO_3)_5]\cdot 4H_2O$	10	2.448 (35)[b]	1.38 (16)[b]	1.21 (10)[b]	1.27 (8)[b]			117.3 (62)[b]	118 (4)[b]	124 (6)[b]	*w*
$[Gd(HCO_3)_3(H_2O)_4]\cdot H_2O$	10	2.54 (11)[b]	1.26 (3)	1.28 (3)	1.30 (13)[b]						*x*
$Na_6[Th(CO_3)_5]\cdot 12H_2O$	10	2.505 (43)[b]	1.29 (3)[b]	1.28 (4)[b]	1.30 (3)[b]			119.3 (49)[b]	119.9 (52)[b]	120.8 (40)[b]	*y*
$[C(NH_2)_3]_6[Th(CO_3)_5]\cdot 4H_2O$	10	2.493 (35)[b]	1.34 (8)[b]	1.26 (5)[b]	1.28 (5)[b]			117.8 (72)[b]	117.5 (49)[b]	123 (10)[b]	*z*

[a] Cariata, F.; Mason, R.; Robertson, G. B.; Ugo, R. *J. Chem. Soc., Chem. Commun.* 1967, 408. [b] See *a*, Table XVIII. [c] Harlow, R. L.; Simonsen, S. H. *Acta Crystallogr., Sect. B* 1975, *B31*, 1313. [d] Mosset, A.; Bonnet, J.-J.; Galy, J. *Z. Kristallogr.* 1978, *148*, 165. [e] Brotherton, P. D.; White, A. H. *J. Chem. Soc., Dalton Trans.* 1973, 2338. [f] Barclay, G. A.; Hoskins, B. F. *J. Chem. Soc.* 1962, 586. [g] Snow, M. R. *Aust. J. Chem.* 1972, *25*, 1307. [h] Kaas, K.; Sørensen, A. M. *Acta Crystallogr., Sect. B* 1973, *B29*, 113. [i] Bigoli, F.; Lanfranchi, M.; Leporati, E.; Pellinghelli, M. A. *Cryst. Struct. Comm.* 1980, *9*, 1261. [j] Geue, R. J.; Snow, M. R. *J. Chem. Soc. A* 1971, 2981. [k] Hennig, H.; Sieler, J.; Benedix, R.; Kaiser, J.; Sjoelin, L.; Lindqvist, O. *Z. Anorg. Allg. Chem.* 1980, *464*, 151. [l] Woon, T. C.; Mackay, M. F.; O'Connor, M. J. *Acta Crystallogr., Sect B* 1980, *B36*, 2033. [m] Loehlin, J. H.; Fleischer, E. B. *Ibid* 1976, *B32*, 3063. [n] Kucharski, E. S.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* 1978, *31*, 47. [o] Note that no carbonate bridging is involved here. [p] Churchill, M. R.; Harris, G. M.; Lashewycz, R. S.; Dasgupta, T. P.; Koshy, K. *Inorg. Chem.* 1979, *18*, 2290. [q] Note that this M-CO_3 bond is substantially longer than the other three. [r] Mikhailov, Yu. N.; Lobanova, G. M.; Shchelokov, R. N. *Zh. Neorg. Khim.* 1981, *26*, 718. [s] Anderson, A.; Chieh, C.; Irish, D. E.; Tong, J. P. K. *Can. J. Chem.* 1980, *58*, 1651. [t] Graziani, R.; Bombieri, G.; Forsellini, E. *J. Chem. Soc., Dalton Trans.* 1972, 2059. [u] Shinn, D. B.; Eick, H. A. *Inorg. Chem.* 1968, *7*, 1340. [v] Voliotis, S.; Rimsky, A. *Acta Crstallogr., Sect. B* 1975, *B31*, 2620. [w] Voliotis, S.; Rimsky, A.; Faucherre, J. *Ibid.* 1975, *B31*, 2607. [x] Furmanova, N. G.; Soboleva, L. V.; Belyaev, L. M. *Kristallogr.* 1981, *26*, 312. [y] Voliotis, S.; Rimsky, A. *Acta Crystallogr., Sect. B* 1975, *B31*, 2615. [z] Voliotis, S.; Rimsky, A. *Ibid.* 1975, *B31*, 2612.

TABLE XX. Bond Lengths (Å) and Angles (deg) for Monodentate, Binuclear Asymmetric Carbonato Complexes



complex	CN	M-O	C-O$_1$	C-O$_2$	C-O$_3$	M$_1$O$_1$C	M$_2$O$_2$C	O$_1$CO$_2$	O$_1$CO$_3$	O$_2$CO$_3$	ref
$Na_2Cu(CO_3)_2$	4	1.93 (4)[a]	1.29 (2)	1.36 (2)	1.22 (2)	111.4 (5)	117.1 (5)	117.5 (16)	123.8 (16)	118.7 (16)	b
$Na_2Cu(CO_3)_2 \cdot 3H_2O$	5	1.946 (9)[a]	1.304 (5)	1.295 (5)	1.264 (5)	107.9 (3)	78.3 (2)	115.6 (4)	121.1 (4)	123.3 (4)	c
	5	1.953 (9)[a]	1.296 (5)	1.294 (5)	1.261 (5)	107.8 (3)	88.6 (1)	115.9 (4)	121.3 (4)	122.8 (4)	d
	5	1.97 (1)	1.27 (2)	1.32 (2)	1.28 (2)	108.6 (9)	132.0 (10)	116.9 (13)	121.7 (13)	121.3 (13)	e

[a] See *a*, Table XVIII. [b] Healy, P. C.; White, A. H. *J. Chem. Soc., Dalton Trans.* 1972, 1913. [c] Harlow, R. L.; Simonsen, S. H. *Acta. Crystallogr., Sect. B* 1975, *B31*, 1313. [d] Brotherton, P. D.; White, A. H. *J. Chem. Soc., Dalton Trans.* 1973, 2338.

cuo, air, CO_2 or N_2, the only commonly reported intermediate in the decomposition of $[Ln_2(C_2O_4)_3]$ to Ln_2O_3 is $Ln_2O_2CO_3$.

Similarly, formate complexes, $[M(HCO_2)_3] \cdot xH_2O$, of the rare earth elements lanthanum,[246] europium, terbium, and lutecium[247] first dehydrate, then decompose with increasing temperature to form the binuclear complex $M_2O_2CO_3$ which eventually degrades to M_2O_3. However, the route taken to yield $M_2O_2CO_3$ varies according to the metal. The most recent studies indicate that the bidentate intermediate $EuCO_3$ is formed following dehydration,[247] while the binuclear intermediate $M_2O(CO_3)_2$ is formed at this stage for M = Lu[247] and La[246] with the lanthanum complex stemming from yet another intermediate, viz. $[La_2(C_2O_4)_3]$. Note also that the decomposition of $EuCO_3$ to $Eu_2O_2CO_3$ was studied separately by Dobrovol'skii[248] who observed this transition in both an oxygen and an argon atmosphere. He attributed oxidation of Eu(II) to Eu(IV) in argon to the "acid residue".

Under different conditions, the oxalato complexes, $[Ln_2(C_2O_4)_3] \cdot xH_2O$, provide a source of lanthanum carbonates of a different kind, namely the lithium bis(carbonato) complexes, $Li[Ln(CO_3)_2]$ where Ln = La to Lu. The conditions involved heating the oxalato complex to 500 °C in the presence of Li_2CO_3 under 200 MPa CO_2.[249] These bis(carbonato) salts were well characterized and thereby shown to fall into two distinct groups. The first group includes the lanthanides, La through Gd, which exhibit the averaged properties: lattice constants, $a_0 = 8.30$, $b_0 = 7.73$, $c_0 = 6.82$ Å—each decreases monotonically with increasing atomic number over a narrow range, i.e., ≤ 0.21 Å; densities in the range, 3.89 to 4.50 g cm^{-3}; and volumes of the unit cell, 453.0–419.2 Å^3. Infrared bands were observed as follows: 1100 cm^{-1} (symmetric valence frequency); 1410, 1505, and 1565 cm^{-1} (asymmetric valence frequency); 660, 690, 738, and 750 (bending frequency); 860 cm^{-1} (deformation frequency); Li–O vibrations at 385, 435, and 585 cm^{-1}; Ln–O vibrations at 280 cm^{-1}. The second group, terbium through lutetium, plus yttrium, demonstrated the corresponding properties: $a_0 = 6.63$, $b_0 = 13.63$, $c_0 = 10.37$ Å, with the same trend when Y follows Ho in the series, $\pm \leq 0.21$ Å; densities, 4.13–4.56 g cm^{-3} (for yttrium, 3.17 g cm^{-3}); and volumes 917.7–876.2 Å^3.

The thermal decomposition of two examples from the first group, namely La and Nd, and one from the second, Yb, was investigated in a streaming nitrogen atmosphere.[249] Both $Li[La(CO_3)_2]$ and $Li[Nd(CO_3)_2]$ behaved similarly in the following manner (presumably this is symptomatic of the whole group):

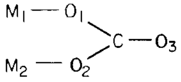
$$2Li[Ln(CO_3)_2] \xrightarrow{400\text{–}510\ ^\circ C} Li_2CO_3 + Ln_2O_2CO_3 + 2CO_2 \quad (58)$$

$$Li_2CO_3 + Ln_2O_2CO_3 \xrightarrow{510\text{–}820\ ^\circ C} Li_2O + Ln_2O_2CO_3 + CO_2 \quad (59)$$

$$Li_2O + Ln_2O_2CO_3 \xrightarrow{820\text{–}1100\ ^\circ C} Li_2O + Ln_2O_3 + CO_2 \quad (60)$$

Note that Li_2O melts at ~700 °C so that part of reaction 59 and all of reaction 60 take place within this melt. Moreover, the same binuclear intermediate $Ln_2O_2CO_3$ is observed again, but $Li[LnOCO_3]$ was not seen (see

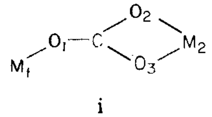
TABLE XXI. Bond Lengths (Å) and Angles (deg) for Monodentate, Binuclear Symmetric Carbonato Complexes



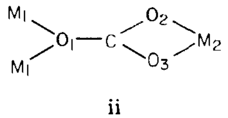
complex	CN	M-O	C-O_1	C-O_2	C-O_3	M_1-M_2	MOC	O_1CO_2	O_1CO_3	O_2CO_3	ref
$KAgCO_3$	2	2.09 (4)	1.33 (7)	1.33 (7)	1.24 (6)		126.5 (15)	121.0 (15)	119.5 (15)	119.5 (15)	*a*
$NaAl(OH_2)_2CO_3$ (dawsonite)	6	1.939 (1) (Al)	1.308 (3)	1.308 (3)	1.250 (5)			119.79 (34)	120.91 (18)	120.91 (18)	*b*
$[(NH_3)_6Co^{III}_2(\mu\text{-}OH)_2(\mu\text{-}CO_3)]SO_4\cdot5H_2O$	6	1.901 (4)	1.286 (3)	1.303 (3)	1.262 (3)	2.817 (1)	126.9 (6)[c]	122.4 (3)	119.7 (3)	118.0 (3)	347
$[([9]aneN_3)_2Cr^{III}_2(\mu\text{-}OH)_2(\mu\text{-}CO_3)]I_2\cdot H_2O$	6	1.976 (7)	1.286 (9)	1.286 (9)	1.244 (16)	2.898 (2)	126.9 (7)	122.5 (11)	118.7 (6)	118.7 (6)	345
$(NH_4)_4[(H_2O)_2Cr^{II}_2(\mu\text{-}CO_3)_4]\cdot H_2O$	6	2.012 (3)	1.297 (8)	1.292 (12)[c]	1.261 (9)[c]	2.214 (1)	120.3 (9)	119.1 (6)	120.2 (4)	120.8 (7)	*d*
$Cs_4[(H_2O)_2Rh^{II}_2(\mu\text{-}CO_3)_4]\cdot6H_2O$	6	2.033 (4)	1.301 (16)	1.276 (19)[c]	1.283 (21)[c]	2.378 (1)	120.3 (7)[c]	122.7 (14)[c]	118.1 (15)[c]	119.3 (8)	*e*
$Na_2Cs_4[Cl_2Rh^{II}_2(\mu\text{-}CO_3)_4]\cdot8H_2O$	6	2.043 (5)	1.31 (3)	1.30 (3)	1.28 (2)	2.380 (2)	120.2 (13)[c]	123 (2)	119 (2)	121 (3)	*e*

[a] Barclay, G. A.; Hoskins, B. F. *J. Chem. Soc.* 1963, 2807. [b] Corazza, E.; Sabelli, C.; Vannucci, S. *N. Jb. Miner. Mh.* 1977, 381. [c] See *a*, Table XVIII. [d] Cotton, F. A.; Rice, G. W. *Inorg. Chem.* 1978, *17*, 2004. [e] Cotton, F. A.; Felthouse, T. R. *Ibid.* 1980, *19*, 320.

TABLE XXII. Bond Lengths (Å) and Angles (deg) for Mono/bidentate, Binuclear Asymmetrical Carbonato Complexes



i

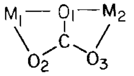


ii

complex	CN	M-O_1	M-$O_{2,3}$	C-O_1	C-O_2	C-O_3	M_1O_1C	$M_2O_{2,3}C$	$O_2M_2O_3$	O_1CO_2	O_1CO_3	O_2CO_3	ref
					Structure i								
$[Cu(NH_3)_2CO_3]$	5	2.303 (2)	1.988 (4)	1.245 (3)	1.307 (3)	1.299 (3)			66.38 (8)	123.12 (23)	123.6 (2)	113.3 (2)	*a*
$[(PPh_3)_5Rh_2(\mu\text{-}CO_3)]\cdot C_6H_6$	4	2.109	2.119	1.29 (2)	1.29 (2)	1.29 (2)	121.1 (8)	90.8 (17)	62.6 (6)	123.9 (9)	120.1 (11)	115.9 (20)	500
$[(C_6H_5)_8Sb_2(\mu\text{-}CO_3)]$	5/6	2.257 (7)	2.325 (7) 2.185 (7)	1.275 (13)	1.293 (13)	1.308 (13)	124.3 (6)	89.8 (6)	58.5 (3)	123.9 (10)	120.0 (10)	116.1 (10)	*b*
$[(Me_2PhP)_6(CO)_2Mo_2(\mu\text{-}CO_3)_2]$[c]	7	2.32 (11)	2.20 (11)	1.28 (3)	1.27 (3)	1.28 (3)			49.5 (1)				445
					Structure ii								
$[\{Ti(Cp)_2\}_2(\mu\text{-}CO_3)]_2$	4	2.183 (2)	2.128 (3)	1.301 (6)	1.268 (4)	1.268 (4)	124.5 (1)	90.5 (2)	61.3 (1)	117.7 (5)	121.2 (3)	121.3 (3)	402

[a] Meyer, M. H.; Singh, P.; Hatfield, W. E.; Hodgson, D. J. *Acta Crystallogr., Sect. B* 1972, *B28*, 1607. [b] Harlow, R. L.; Simonsen, S. H. *Ibid.* 1975, *B31*, 1313. [c] Asymmetrical, with two oppositely oriented carbonate bridges.

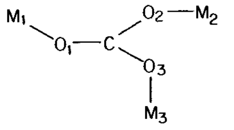
TABLE XXIII. Bond Lengths (Å) and Angles (deg) for Bidentate, Binuclear Symmetrical Carbonato Complexes



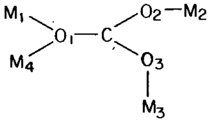
complex	CN	M-O_1	M-$O_{2,3}$	C-O_1	C-O_2	C-O_3	$M_1O_1M_2$	MO_1C	$MO_{2,3}C$	O_1MO_2	O_1CO_2	O_1CO_3	O_2CO_3	ref
$[(dla)_2Cu^{II}_2(\mu\text{-}CO_3)](ClO_4)_2\cdot DMF$	5	2.041 (1)	2.028 (5)	1.32 (1)	1.27 (1)	1.27 (1)	176.6 (2)	88.3 (5)	90.3 (4)	65.3 (3)	116.1 (5)	116.1 (5)	128 (1)	*a* *b*
$[(tmtn)_2Cl_2Cu^{II}_2(\mu\text{-}CO_3)]$	5	2.1527 (4)	1.978 (2)	1.299 (5)	1.270 (3)	1.270 (3)	170.26 (13)	85.13 (7)		63.96 (9)	117.2 (2)	117.2 (2)	125.6 (4)	*c*
$[(teed)_2Cl_2Cu^{II}_2(\mu\text{-}CO_3)]$	5	2.093 (2) 2.412 (2)	1.962 (16)	1.300 (4)	1.277 (4)	1.255 (4)	165.97 (13)	86.90 (20)	92.81 (21)	64.73 (10)	115.5 (3)	119.9 (3)	124.6 (3)	*d*

[a] Davis, A. R.; Einstein, F. W. B. *Inorg. Chem.* 1980, *19*, 1203. [b] Davis, A. R.; Einstein, F. W. R.; Curtis, N. F.; Martin, J. W. L. *J. Am. Chem. Soc.* 1978, *100*, 6258. [c] Churchill, M. R.; Davies, G.; El-Sayed, M. A.; El-Shazly, M. F.; Hutchinson, J. P.; Rupich, M. W.; Watkins, K. O. *Inorg. Chem.* 1979, *18*, 2296. [d] Churchill, M. R.; Davies, G.; El-Sayed, M. A.; El-Shazly, M. F.; Hutchinson, J. P.; Rupich, M. W. *Ibid.* 1980, *19*, 201.

TABLE XXIV. Bond Lengths (Å) and Angles (deg) for Monodentate, Trinuclear Symmetrical (i) and Tetranuclear Asymmetrical (ii) Carbonato Complexes



i



ii

complex	CN	M–O	C–O$_1$	C–O$_2$	C–O$_3$	M$_1$–M$_2$	MO$_1$C	O$_1$CO$_2$	O$_1$CO$_3$	O$_2$CO$_3$	ref
				Structure i							
$Cu_3(OH)_2(CO_3)_2$	4	1.88 (5)	1.30 (5)	1.27 (5)	1.24 (5)		116.1	113.5	121.9	126.1	*a*
	4	1.930 (1)	1.283 (2)	1.286 (1)	1.277 (1)			119.5 (1)	119.6 (1)	120.9 (2)	*b*
$Tl_2Cu(CO_3)$	5 (Cu)	2.01 (10)	1.288	1.331	1.324	2.583		122.79	123.09	114.07	*c*
	7 (Tl)[d]	2.94 (27)[d]	1.309	1.288	1.283	3.78 (18)		122.29	117.30	120.40	
				Structure ii							
$Cu_2(OH)_2CO_3$[f]	4/6	2.06 (5)	1.30	1.27	1.29						*e*
		2.05 (5)	1.308 (1)	1.266 (1)	1.287 (1)			119.55 (7)	119.00 (7)	121.44 (8)	*g*
$[(dpf)_4Cu_4(\mu\text{-}CO_3)(\mu\text{-}Cl)_2]Cl_4\cdot 7.5H_2O$	5	2.058 (21)	1.411 (18)	1.237 (26)	1.212 (11)		117.5 (8)	111.8 (17)	113.4 (10)	134.8 (13)	219

[a] Gattow, G.; Zemann, J. *Acta. Crystallogr.* 1958, *11*, 866. [b] Zigan, F.; Schuster, H. D. *Z. Kristallogr.* 1972, *135*, 416. [c] Ehrhardt, H.; Lemor, R.; Seidel, H. *Z. Anorg. Allg. Chem.* 1981, 477, 183. [d] Bonding between M$_1$ and O$_2$ exits to give resulting coordination number of 7. [e] Süsse, P. *Naturwissenschaft* 1966, *53*, 80. [f] Neutron diffraction. [g] Zigan, F.; Joswig, W.; Schuster, H. D.; Mason, S. A. *Z. Kristallogr.* 1977, *145*, 412.

next paragraph). Ytterbium carbonate decomposes directly to the oxide with subsequent decomposition of Li_2CO_3 to Li_2O, as shown in reaction 61.

$$2Li[Yb(CO_3)_2] \xrightarrow{350\text{–}540\ °C} Li_2CO_3 + Yb_2O_3 + 3CO_2 \quad (61)$$

The analogous sodium bis(carbonato) complexes $Na[Ln(CO_3)_2]$, where Ln = La through Lu, plus Y, were similarly synthesized either by the reaction of $[Ln_2(C_2O_4)_3]\cdot xH_2O$ with Na_2CO_3 at 350–500 °C and 300 MPa of CO_2, or by dehydration of $Na[Ln(CO_3)_2]\cdot xH_2O$.[250] Again the same two structural groups were characterized, but all thermally decomposed by the same mechanism corresponding to eq 58. The three examples cited in the original paper[250] are listed in Table XXV. Conflicting results were published by Mochizuki et al.[251] and Oda[252] who claim decomposition of $Na[Nd(CO_3)_2]$, $Na[Y(CO_3)_2]\cdot H_2O$, and $Na[Gd(CO_3)_2]\cdot H_2O$ yields $Na[NdO(CO_3)]$, $Na[YO(CO_3)]$, and $Na[GdO(CO_3)]$ at 650–680, 580, and 400–600 °C, respectively, although the conditions are not specified. Taravel et al.[253] report the direct decomposition of $Na[Er(CO_3)_2]$ to Er_2O_3 under unspecified conditions using only TG as a monitor.

By applying about one-tenth the CO_2 pressure when heating $[Ln_2(C_2O_4)_3]\cdot H_2O$, where Ln = Sm to Lu, plus Y, to 500–550 °C results in the formation of $Li[LnOCO_3]$ as evidenced by IR and X-ray spectroscopy.[249] The IR spectra are all similar, consistent with a common structure. The symmetrical vibration frequency is represented by two bands at 1090 and 1120 cm^{-1}, while the asymmetrical vibration occurs at 1445 and 1515 cm^{-1}. The low energy bands in the 400–600 cm^{-1} range increase in energy with decreasing radius of the Ln^{3+} ion (i.e., Sm through Lu). From the X-ray data the lattice parameters decrease from Sm through Lu as follows: a_0 = 3.49–3.36; b_0 = 7.71–7.44; c_0 = 7.56–7.28 Å. The densities vary systematically over the range 3.91–4.82 g cm^{-3}, with the exception of $Li[YOCO_3]$ (3.06 g cm^{-3}). The TG and DTA curves, which monitored the thermal decomposition of these carbonates in a N_2 environment, are reminiscent of those obtained for the second group of $LiLn(CO_3)_2$ complexes. Equation 62 is given for $Li[YbOCO_3]$.[249]

$$2[LiYbOCO_3] \xrightarrow{515\text{–}600\ °C} Li_2CO_3 + Yb_2O_3 + CO_2 \quad (62)$$

C. Actinide Complexes

The thermal decomposition of americium(III) oxalate, formate, and carbonate has been investigated in some detail.[254] The initial dehydration of $[Am_2(C_2O_4)_3]\cdot 10H_2O$ involved the immediate formation of the hexahydrate. Complete dehydration involved an additional four stages over the range 50–340 °C. Subsequent transformation to $[Am_2(CO_3)_3]$ occurred at 390–430 °C. The thermolysis of this anhydrous carbonate behaved in a similar fashion to the lighter lanthanides with conversion to $[Am_2O(CO_3)_2]$ occurring at 430–470 °C, succeeded by the familiar form $Am_2O_2CO_3$ at 470–520 °C. Decomposition to Am_2O_3 took place at 520–610 °C.

It is somewhat confusing, however, that following the dehydration of $[Am_2(CO_3)_3]\cdot 2H_2O$ at 50–310 °C, only $Am_2O_2CO_3$ was clearly observable.[254] The thermolysis of $[Am(HCO_2)_3]\cdot 0.2H_2O$ also yielded $Am_2O_2CO_3$ directly

TABLE XXV. Representative Sample of the Data on the Thermal Decomposition of Metal Carbonato Complexes

initial complex	medium	temp., °C	products	technique[a]	ref
$KHCO_3$	<100 torr	145-200	$K_2CO_3 + H_2O + CO_2$	manometric	*b*
$CaCO_3$	vacuo	700 max	$CaO + CO_2$	dielectrometry	*c*
$SrCO_3$	vacuo	850 max	$SrO + CO_2$	dielectrometry	*c*
$BaCO_3$	vacuo	950 max	$BaO + CO_2$	dielectrometry	*c*
$NaAl(OH)_2CO_3$ (synthetic dawsonite)	air	320	$Na_2O + Al_2O_3 + H_2O + CO_2$	TG, DTA, IR, X-ray	*d*
	air	300-650	$NaAlO_2 + H_2O + CO_2$	TG, IR, X-ray	*e*
$Na_5[Sc(CO_3)_4]$		210-400	$Sc_2O_3 + Na_2CO_3 + CO_2$	TG, IR	253
(Ba or Sr)$_2V_2O_5CO_3$	vacuo	600	(Ba or Sr)$VO_3 + CO_2$	TG, DTA, IR, X-ray	230
$MnCO_3 \cdot 0.3H_2O$	air, N_2	400	$MnO + H_2O + CO_2$	TG, DTA, DTG, TGT, DTGT, DT, DTD	*f*
$CoCO_3$	vacuo	300-400	$CoO + CO_2$	manometric	*b*
	air	390-480	$CoO + CO_2$	TG	237
$2CoCO_3 \cdot 3Co(OH)_2 \cdot nH_2O$	vacuo	200-230	$Co_3O_4 + H_2O + CO_2$	TG, magnetic susceptibility	*g*
$FeCO_3$ (siderite)	vacuo	480-580	FeO (wustite) + CO_2	TG, GC, EGA, TM, X-ray	*h*
	N_2	~400-550	Fe_3O_4 (magnetite) + CO_2	TG, GC, EGA, TM, X-ray	*h*
	O_2	~420-590	Fe_2O_3 (hematite) + CO_2	TG, GC, EGA, TM, X-ray	*h*
$Fe_2(CO_3)_3$	air	360-460	$Fe_2O_3 + CO_2$	TG	237
$NiCO_3$	vacuo	360-460	$NiO + CO_2$	manometric	*b*
$Ca_2[Zr_2O_5CO_3]$	air	550-650	$CaZrO_3 + CO_2$	TG, DTA, IR, X-ray	228
$Sr_2[Zr_2O_5CO_3]$	air	550-725	$SrZrO_3 + CO_2$	TG, DTA, IR, X-ray	228
$K_4[Zr(C_2O_4)_2CO_3F_2]$	air	250-565	$ZrO_2 + K_2CO_3 + KF + CO + CO_2$	TG, IR, X-ray	*i*
$K_4[Hf(C_2O_4)_2CO_3F_2]$	air	250-565	$HfO_2 + K_2CO_3 + KF + CO + CO_2$	TE, IR, X-ray	*i*
$[La_2(CO_3)_3] \cdot 0.25H_2O$	vacuo	430-580	$La_2O_2CO_3 + H_2O + CO_2$	TG	240
$Na[La(CO_3)_2]$	Ar, N_2	400-540	$La_2O_2CO_3 + Na_2CO_3 + CO_2$	TG, DTA	250
$La_2O_2CO_3$	vacuo	590-760	$La_2O_3 + CO_2$	TG	240
		700-820	$La_2O_3 + CO_2$	TG, DTA, IR	*j*
$[La_2O(CO_3)_2]$	air	530	$La_2O_3 \cdot 0.8CO_2$	TG, DTA, DTG	*k*, 243
$[Ce_3Cl(CO_3)_4]$	vacuo	600	$CeOCl + CeO_2 + CO_2 + CO$	X-ray, GC	*l*
$[Ce_4Cl(OH)_3(CO_3)_4]$	vacuo	600	$CeOCl + CeO_2 + CO_2 + CO + H_2O$	X-ray, GC	*l*
$Na[Ce(CO_3)_2]$	Ar, N_2	380-500	$Ce_2O_2CO_3 + Na_2CO_3 + CO_2$	TG, DTA	250
$Ce_2O_2CO_3$	Ar, N_2	500-570	$Ce_2O_3 + CO_2$	TG, DTA	250
$[Nd_2O(CO_3)_2] \cdot 1.5H_2O$	air	500	$Nd_2O_3 \cdot 0.9CO_2$	TG, DTA, DTG	*k*, 243
$EuCO_3$	air	360-540	$Eu_2O_2CO_3 + CO_2$	DTA	247, 248
	Ar	600-670	$Eu_2O_2CO_3 + CO$	DTA	248
$Eu_2O_2CO_3$	air	610-810	$Eu_2O_2 + CO_2$	DTA	248
$Tb_2(CO_3)_3$	air	490	$Tb_2O_2CO_3 + CO_2$	TG, IR	*m*
$Tb_2O_2CO_3$	air	560-880	$Tb_4O_7 + CO_2$	DTA	248
		690	$Tb_4O_7 + CO_2$	TG, IR	*m*
$Na[Ho(CO_3)_2]$	Ar, N_2	350-480	$Ho_2O_2CO_3 + Na_2CO_3 + CO_2$	TG, DTA	250
$Ho_2O_2CO_3$	Ar, N_2	350-480	$Ho_2O_3 + CO_2$	TG, DTA	250
$Na_5[Er(CO_3)_4]$		350-500	$Er_2O_2 + Na_2CO_3 + CO_2$	TG, IR	253
$Na_3[Er(CO_3)_3]$		200-500	$Er_2O_3 + Na_2CO_3 + CO_2$	TG, IR	253
$Na[Er(CO_3)_2]$		330-500	$Er_2O_3 + Na_2CO_3 + CO_2$	TG, IR	253
$[Tm_2(CO_3)_3]$	air	460	$Tm_2O_2CO_3$	TG, IR	*m*
$Tm_2O_2CO_3$	air	640	Tm_2O_3	TG, IR	*m*
$[Lu_2O(CO_3)_2]$	air	350-360	$Lu_2O_2CO_3 + CO_2$	DTA	248
	air	440	$Lu_2O_2CO_3 + CO_2$	TG, IR	*m*
$Lu_2O_2CO_3$	air	620-800	$Lu_2O_3 + CO_2$	DTA	248
	air	610	$Lu_2O_3 + CO_2$	TG, IR	*m*
$PbCO_3 \cdot Pb(OH)_2$	N_2	503	$PbCO_3 \cdot PbO + CO_2$	calorimetry	224
$PbCO_3 \cdot PbO$	N_2	588	$PbO + CO_2$	calorimetry	224
$PbCO_3 \cdot Pb(OH)_2$	CO_2	508	$PbCO_3 \cdot PbO + CO_2$	calorimetry	224

$2PbCO_3{\cdot}PbO$	CO_2	500	$PbCO_3{\cdot}PbO + CO_2$	calorimetry	224
$(NH_4)_2[UO_2(cupferron)CO_3]$[b]	air	285	$UO_2CO_3 + \ldots$	TG, DTA, IR	*n*, *o*
$[UO_2CO_3]$	air	620	$U_3O_8 + \ldots$	TG, DTA	*n*, *o*
$[Co(NH_3)_6][Np(CO_3)_5]$	air	100	$CoCO_3 + NpO_2$ or Np_3O_8	DTA, TGA, X-ray	*p*

[a] TG = thermogravimetric; DTA = differential thermoanalysis; DTG = derivative thermogravimetric; DTD = derivative thermodilatation; TGT = thermo-gas-titrimetric; TD = thermodilatation; DTGT = derivative thermo-gas-titrimetric; EGA = evolved gas analysis; TM = thermomagnetometric; GC = gas chromatographic. [b] Wendlant, W. W. *Thermochim. Acta.* 1974, *9*, 7. [c] Mikheev, V. N.; Brovikov, V. N.; Grinevich, V. I. *Izv. Akad. Nauk SSSR, Neorg. Mater.* 1975, *11*, 1895. [d] Szczepanik, M.; Rudnicki, R. *Pol. J. Chem.* 1978, *52*, 439. [e] Huggins, C. W.; Green, T. E. *Am. Min.* 1973, *58*, 548. [f] Paulik, F.; Paulik, J. *Thermochim. Acta* 1971, *3*, 17. [g] Mehandjiev, D.; Nikolova, E. *Ibid.* 1978, *23*, 117. [h] Gallagher, P. K.; Warne, S. S. J. *Ibid.* 1981, *43*, 253. [i] Medkov, M. A.; Davidovich, R. L. *Izv. Akad. Nauk SSSR, Ser. Khim.* 1978, 270. [j] Petru, F.; Kutek, F.; Satava, J. *Coll. Czech. Chem. Commun.* 1966, *31*, 4459. [k] Nagashima, K.; Wakita, H.; Mochizuki, A. *Bull Chem. Soc. Jpn.* 1973, *46*, 152. [l] Peterson, E. J.; Onstott, E. I. *J. Inorg. Nucl. Chem.* 1979, *41*, 517. [m] Deineka, G. F.; Tselik, I. N.; Il'inskaya, E. P. *Zh. Neorg. Khim.* 1972, *17*, 1291. [n] Kundu, P. C.; Roy, P. S.; Banerjee, R. K. *J. Inorg. Nucl. Chem.* 1980, *42*, 851. [o] Kundu, P. C.; Roy, P. S. *Ibid.* 1981, *43*, 186. [p] Saito, A.; Ueno, K. *Ibid.* 1980, *42*, 1301.

at 420–540 °C with emission of CO_2, CO, H_2, and H_2O as determined by mass spectroscopy. An intermediate in this reaction was postulated to be $[AmO(HCO_2)]$. The apparent discrepancy in the decomposition paths of the oxalato and carbonato complexes was not rationalized.

A thermogravimetric analysis of $Tl_6[Th(CO_3)_5]{\cdot}2H_2O$ was made in an attempt to elucidate the structure of this compound.[255] After dehydration at 50–180 °C, 2 mol of CO_2 are generated per mole of compound over the temperature range 180–380 °C, with final decomposition to Tl_2O_3 and ThO_2 at 380–510 °C. The observation of the initial loss of two-fifths of the total carbonate led Karkhanavala and Daroowalla[255] to suggest that the original complex is really the double salt $3Tl_2CO_3{\cdot}[Th(CO_3)_2(H_2O)_2]$ with the thorium coordinated to two bidentate carbonates and two water molecules, and thus it is these two carbonates that are lost initially. A previous infrared study[256] of the sodium analogue implied the existence of both ionic (1080 w, 865 s, 855 m, 700–705 vw) and coordinated carbonate (1055 m, 725 m) (N.B. these authors[256] write the formula, $Na_4[Th(CO_3)_4]{\cdot}Na_2CO_3$), in agreement with the notion of a double salt. Furthermore, Tl_2CO_3 was shown to decompose at the higher temperature range of 335–445 °C.[255]

$[Th(CO_3)_2]{\cdot}xH_2O$ can be thermolytically synthesized from aqueous $Th(OH)_4$ at temperatures ranging from 100–150 °C, CO_2 pressures of 182.4–344.5 MPa, and reaction times of 36–720 h.[235] These conditions are inversely correlated. The partially dehydrated product, $[Th(CO_3)_2]{\cdot}0.5H_2O$, was characterized by its IR absorption spectrum: 1085 (ν_1); 830 (ν_2); 1350, 1550 (ν_3); 680, 752 (ν_4), and 3400 cm^{-1} ($\nu_3 - H_2O$).

Finally, many publications have appeared in the literature dealing with the kinetics of thermal decomposition.[257-265] However, as this information does not serve to characterize a solid in a unique sense, it will not be presented in this review.

VII. Equilibria

In this section a compilation of the available stability constants for carbonate species, complexes, and ion pairs in solution, and solubility constants for various carbonate salts is presented. A detailed discussion of the various methods employed in the determination of such stability constants was presented in the earlier review on carbonato complexes.[1] Methods used to determine the stability constants reported in Table XXVIII include spectrophotometry,[266-272] polarography,[273,274] potentiometry,[275-284] pH measurements,[285,286] solvent extraction,[287,288] solubility measurements,[267,289-296] ion exchange,[297,298] ^1H NMR,[299] and kinetic methods.[271,300] The notation adopted in the compilation of stability and solubility constants in Table XXVIII is in agreement with that used in standard reference texts on such data.[301]

The stability constants in Table XXVIII differ in some exceptional cases by as much as 3 orders of magnitude.[282,300] In general, the agreement between the various reported constants is fairly good, and in many cases only one or two data points really fall out of the series. The scatter in the $\Delta H/\Delta S$ data is more severe and could partially be associated with the different equations adopted to fit the temperature dependencies

TABLE XXVI. Thermolysis Reactions Yielding Transition-Metal Carbonato Compounds of the Form MCO_3[234]

starting material	temp, °C	$^{p}CO_2$, MPa	time, h	product[a]
$[MnC_2O_4]\cdot 2H_2O$	410-420	250	24	$MnCO_3$ (colorless)
$[FeC_2O_4]\cdot 2H_2O$	415-470	350	24	$FeCO_3$ (light blue)
$[CoC_2O_4]\cdot 2H_2O$	400-430	250	72	$CoCO_3$ (purple, violet)
$[NiC_2O_4]\cdot 2H_2O$	390-435	400	24	$NiCO_3$ (light gray)
$[ZnC_2O_4]\cdot 2H_2O$	400	300	24	$ZnCO_3$ (colorless)
$[CdC_2O_4]\cdot 2H_2O$	400	250	24	$CdCO_3$ (light gray)
$[CuC_2O_4]\cdot 2H_2O$[b]	260-290	270-310	24	$CuCO_3$ (green)
$[VCO_3]\cdot 2H_2O$	240	350	48	$VCO_3\cdot 0.5H_2O$ (grey brown)
	265	390	48	V_2O_3 (black)
$[Cr(CO)_6]$	280	300	48	$CrCO_3$:Cr_2O_3 (2:3) (green)
	300	320	24	Cr_2O_3

[a] Compounds were characterized from IR and X-ray diffraction. [b] Occurs only in the presence of the oxidizing agent NH_4NO_3.

TABLE XXVII. Thermolysis Reactions in Aqueous Media Yielding Transition-Metal Carbonato Compounds[235]

starting material	temp, °C	$^{p}CO_2$, MPa	time, h	product	IR bands,[a] cm^{-1}
$Mn(OH)_2$	160	243.2	40	$MnCO_3$ (pale pink)	210, 280, 360, 728, 867, 1085, 1440, 1805, 2500
$Fe(OH)_2$	150	253.3	30	$FeCO_3$ (ca. colorless)	215, 320, 370, 739, 866, –, 1425, 1820, 2520
$Co(OH)_2$	160	273.6	60	$CoCO_3$ (purple, violet)	225, 320, 360, 745, 865, 1080, 1465, 1820, 2510
$Ni(OH)_2$	160	192.5	24	$NiCO_3$ (light green)	240, 335, 370, 758, 869, 1080, 1445, 1830, 2510
$Zn(OH)_2\cdot xH_2O$	160	283.7	30	$ZnCO_3$ (colorless)	210, 310, 370, 744, 870, –, 1430, 1820, 2500
$ZrO_2(aq)$	150	405.3	24	$ZrOCO_3\cdot 2H_2O$	450,[b] 650, 840, 1050, 1350, 1410, 1545, 1625,[c] 3390[c]

[a] Cf. $CaCO_3$ (228, 310, 325, 712 (ν_4), 875 (ν_2) – (ν_1), 1430 (ν_3), 1810, 2520 cm^{-1}). [b] Zr-O. [c] ν_2 and ν_3 (H_2O).

of the stability constants. The equations used will in turn depend to a large extent on the temperature ranges over which these measurements were made. A recent review[302] covered the various expressions used to describe the temperature dependence of stability constants. For the data in Table XXVIII, expressions of the form

$$\log K = A + BT + CT^2 \text{ (ref 282)}$$

$$\log K = A + BT + C/T \text{ (ref 282, 284, 296)}$$

$$\log K = A + B \log T + C/T \text{ (ref 281, 282)}$$

$$\log K = A + BT + C/T + D \log T \text{ (ref 149)} \qquad (63)$$

were adopted. Similar expressions have also been applied to solubility constant data.[149,303] Some deprotonation/protonation constants of metal bicarbonato/carbonato complexes are included in Table XXVIII. A more complete series of such data is given in Table XXXIII (section VIII), which deals with kinetically determined acid dissociation constants of unstable bicarbonato complexes. The data in Table XXVIII fall within the range of values reported in section VIII and are close to the first acid dissociation constant of carbonic acid, which illustrates the similarity in the nature in the O–H bond in $HOCO_2$–H and $MOCO_2$–H.

The data in Table XXVIII illustrate that much work has been done on the carbonate species of Mg^{2+}, Ca^{2+}, Pb^{2+}, UO_2^{2+}, and PuO_2^{2+}. In this respect it is interesting to note that $Na_4UO_2(CO_3)_3$ had been prepared and identified as early as 1842.[304,305] The interest in the mentioned species mainly comes from biologically and environmentally orientated investigations. The modelling of biological processes, natural waters, seawater, and geochemical processes strongly depends on the availability of such data.[272,274,306-308] In addition to the species summarized in Table XXVIII, evidence for the formation and presence of a large number of carbonate species has been reported during the time covered by this review, and a compact summary is given in Table XXIX. These species were not included in Table XXVIII due to an absence of data on their stability or solubility constants. In some cases solubility data were reported for some of these and closely related species.[309-311]

Many papers deal with thermodynamic data for various metal carbonato species. We, however, feel that a presentation and discussion of such data lies beyond the scope of this review, and therefore we only present a summary of the references where such data can be found (see Table XXX).

VIII. Kinetics and Mechanisms

This section deals with the kinetics and mechanisms of the formation, aquation, substitution, exchange, isomerization, redox, radiochemical, and photochemical reactions of metal carbonato complexes. Significant progress has especially been made in the understanding of such processes during the period covered by this review. Our own contributions in some of these areas motivated us to present a complete and critical coverage of the appropriate subsections. The various types of reactions are treated in different subsections, and differentiation between the various bonding modes of the carbonate ligand, viz., monodentate, bidentate, or bridged, is emphasized throughout.

A. Formation Reactions

Various reaction routes exist for the formation of carbonato complexes in aqueous solution. When $CO_2(g)$ is dissolved in aqueous solution, the reactions/equilibria in eq 64 and 65 set in (see sections III and IV). As

$$CO_2(aq) + H_2O \rightleftarrows H_2CO_3 \rightleftarrows HCO_3^- + H^+ \qquad K_1 \tag{64}$$

$$HCO_3^- \rightleftarrows CO_3^{2-} + H^+ \qquad K_2 \tag{65}$$

discussed in section IV, the hydration rate constant of $CO_2(aq)$ and the dehydration rate constant of H_2CO_3 are such that the $CO_2(aq)/H_2CO_3$ equilibrium lies to the left and more than 99% of CO_2 in water exists as dissolved CO_2 (less than 1% as true H_2CO_3[155]). Typical values for the overall equilibrium constants are $pK_1 = 6.03$ and $pK_2 = 9.8$ at 25 °C and ionic strength 0.5 M[312] (see section III). It follows that there are actually four potentially reactive species in solution, viz., $CO_2(aq)$, H_2CO_3, HCO_3^-, and CO_3^{2-}, which can in principle produce carbonato complexes during their reaction with metal aquo/hydroxo species. Water coordinated to a metal ion is quite acidic such that the pK (on a molarity scale) of a typical transition-metal aquo complex ion is close to 7 as compared to a value of about 16 for solvent water molecules.[313] In a near neutral or weakly basic solution it is thus possible to have appreciable quantities of the hydroxo species present, which could react in a completely different manner than the corresponding aquo species (eq 66). The values of K_3 are usually

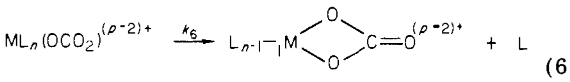
$$ML_n(OH_2)^{p+} \rightleftarrows ML_n(OH)^{(p-1)+} + H^+ \qquad K_3 \tag{66}$$

known from conventional pH or spectrophotometric titrations.

It follows that the different species present in both the carbonate and metal complex systems (eq 64–65) can result in various reaction routes for the formation of metal carbonato complexes, and these possibilities will be explored in some detail in the following subsections.

(1) **Via Carbon Dioxide Uptake.** In a series of papers (see references quoted in Table XXXI) Harris and co-workers demonstrated that metal hydroxo complexes can in general react with dissolved CO_2 to produce carbonato complexes according to the overall process shown in eq 67. This is a reversible pH-controlled CO_2 uptake/decarboxylation process. The produced monodentate carbonato species may, depending on the nature of L, undergo a ring-closing reaction to produce a bidentate carbonato species.

$$ML_n(OH)^{(p-1)+} + CO_2(aq) \rightleftarrows ML_n(OCO_2)^{(p-2)+} + H^+ \qquad K_4 \tag{67}$$



(68)

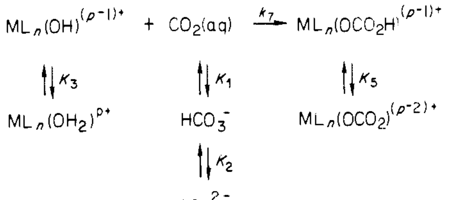
The kinetics of CO_2 uptake reactions can be studied by following two different procedures;[312] viz., (i) the equilibration method and (ii) acidification method. In method (i), the metal aquo complex under investigation is dissolved in an appropriate buffer solution in which the ionic strength has been adjusted to a preset value and then rapidly mixed in a stopped-flow instrument with a 0.1 M $NaHCO_3$ solution of similar ionic strength. The $[CO_2(aq)]$ can be calculated from eq 69. At higher

$$[CO_2(aq)] = [H^+]^2[\text{total carbonate}]/\{[H^+]^2 + K_1[H^+] + K_1K_2\} \tag{69}$$

pH, where the equilibrium concentration of $CO_2(aq)$ is not in considerable excess over the complex ion concentration, micromolar quantities of carbonic anhydrase were introduced into the complex solution in order to ensure the rapid maintenance of the CO_2/HCO_3^- equilibrium (see section XIIIA).

In method (ii), buffered solutions of the metal aquo species are prepared in the same way as in method (i). The second reactant is usually a 0.02 M $NaHCO_3$ solution (in an appropriate ionic strength controlled medium) which has been carefully acidified with $HClO_4$ to pH ~3 on a pH meter. After temperature equilibriation, these solutions are mixed rapidly in the stopped-flow system and the final pH of the mixture measured immediately after mixing. The $[CO_2(aq)]$ of such a mixture is then 0.01 M, and no carbonic anhydrase is employed in this method since CO_2 hydrolysis must be kept as slow as possible during measurements, i.e., the uncatalyzed rate of CO_2 hydrolysis is considerably slower than the rate of reaction under investigation. In most of the quoted studies (Table XXXI), method (ii) was employed.

The CO_2 uptake reactions were all found to proceed according to the general mechanism:[312]



(70)

Protons are omitted from this scheme for the sake of simplicity, k_7 is the rate-determining CO_2 uptake rate constant, and K_1, K_2, K_3, and K_5 are acid-dissociation constants. An important aspect of this mechanism is the fact that only the metal hydroxo species are capable of taking up CO_2. This was verified by an analysis of the kinetic data. For the mechanism outlined in (70)

$$k_{\text{obsd}} = k_7\left[\frac{K_3}{[H^+] + K_3}\right][CO_2(aq)] \tag{71}$$

and substituting for $[CO_2(aq)]$ from eq 69 results in

$$k_{\text{obsd}} = \frac{k_7K_3[H^+]^2[\text{total carbonate}]}{([H^+] + K_3)([H^+]^2 + K_1[H^+] + K_1K_2)} \tag{72}$$

During the kinetic measurements k_{obsd} was studied as a function of pH and $[CO_2(aq)]$ (acidification method) or [total carbonate] (equilibration method). The validity of the suggested mechanism required a pH and $[CO_2(aq)]$ or [total carbonate] independent value for k_7. This was found to be the case for all the uptake reactions studied.

A summary of the available rate and activation parameters for a series of CO_2 uptake reactions along with the pK_3 values of the corresponding aquo complexes is given in Table XXXI. It was found[313-315] that log k_7 increases linearly with pK_3 as shown in Figure 3. This correlation is in agreement with the suggestion that the rate of CO_2 uptake depends on the nucleophilicity of the bound hydroxide ion which in turn depends on the strength of the O–H bond of the corresponding aquo complex as reflected by the pK_3 value. The plot in Figure 3 has a slope of 0.15 ± 0.04 and an intercept of 1.2 ± 0.3,[315] which is in close agreement with that reported for a limited number of systems.[314] The very

TABLE XXVIII. Equilibrium Constants for Metal Bicarbonate and Carbonate Species, $HL = HCO_3^-$; $L = CO_3^{2-}$; M = Metal Ion

metal ion	equilibrium	temp, °C	ionic strength, M	log *K*	ΔH, kJ mol^{-1}	ΔS, J K^{-1} mol^{-1}	ref
Mg^{2+}	$ML/M\cdot L$	25	1.0	0.544			271
		25	-	3.11 ± 0.22^a			*b*
		25	-	2.98 ± 0.03	8.44	85.5	*b*
		90	-	3.41 ± 0.07			*b*
		20	0	3.26			280
		25	-	2.88 ± 0.05	13.5		284
		25	0.72	2.05			*c*
		25	-	3.20 ± 0.22^a			306
		20	0.1	2.18 ± 0.05			279
		25	0	5.30	28.4	196	271
		25	0	2.88	12.5	84	301
	$MHL/M\cdot HL$	25	-	1.07	3.26		281
		25	-	1.07			*d*
		25	-	1.27			*e*
		25	-	1.05 ± 0.18^a			*d*
		25	-	1.07 ± 0.03	4.99	37.2	*d*
		90	-	1.34 ± 0.03			*d*
		20	0	0.84			280
		25	0.72	0.21			*c*
		25	-	1.01 ± 0.19^a			*f*
		25	-	1.07			*f*
		25	-	1.14 ± 0.13^a			306
		22	0.15	0.77			285
		25	0	4.85	28.0	186	271
		25	0	0.95			301
	$M_2L/M^2\cdot L$	25	0.72	2.59			*c*
	$MHL/ML\cdot H$	25	0.15	8.5			285
		20	0	7.99			280
	$M\cdot L/ML(s)$	25	0	−7.46	20.9	−84	301
	$M\cdot L$/magnesite(s)	25	-	−8.1			290
Ca^{2+}	$ML/M\cdot L$	25	-	3.22 ± 0.14			149
		25	-	3.2			559
		25	-	3.15 ± 0.08	16.8	-	284
		25	0.72	2.21			*c*
		25	-	3.34 ± 0.39^a			306
		25	0	3.15 ± 0.05	16.7	125	301
		22	0.15	3.00			301
		25	0	3.10			*g*
	$MHL/M\cdot HL$	25	-	1.23	0.89		289
		25			2.63		*h*
		25	-	1.17 ± 0.11^a			*i*
		25	-	1.11 ± 0.07			149
		0	-	0.7			559
		25	-	1.0			559
		50	-	1.35			559
		25	0.72	0.29			*c*
		25	-	1.08 ± 0.17^a			*f*
		25	-	1.23	1.96		*f*
		25	-	1.19 ± 0.11^a			306
		22	0.15	0.79			285
		25	0	1.0 ± 0.0			301
		25	0	1.24			*g*
	$MHL/ML\cdot H$	22	0.15	7.9			285
	$M\cdot L/ML(s)$	22	0.15	−8.01			285
		25	0	−8.33			*g*
	$M\cdot L/ML(s)$ calcite	25	-	-8.48 ± 0.02			149
		25	0	-8.35 ± 0.1	8.4	−125	301
	$M\cdot L/ML(s)$ calcite	25	-	−8.42	−10.1	−195	559
	$M\cdot L/ML(s)$ calcite	25	-	−8.47	−10.8	−198	559
	$M\cdot L/ML(s)$ aragonite	25	-	−8.34			149
	$M\cdot L/ML(s)$ vatenite	25	-	−7.91			149
Sr^{2+}	$MHL/M\cdot HL$	25	-	1.25			306
	$ML/M\cdot L$	25	-	3.92			306
	$M\cdot L/ML(s)$	25	0	−9.03			301
Ba^{2+}	$ML/M\cdot L$	25	0	2.78			301
		25	-	3.78			*j*
	$M\cdot L/ML(s)$	25	0	-8.30 ± 0.01			301
		25	0.01	−5.48			*j*
$Cr(en)_3^{3+}$	$ML/M\cdot L$	25	3	−0.046	19.2	63.5	289
	$ML_2/M\cdot L^2$	25	3	−0.071	13.8	45.0	289
Mn^{2+}	$ML/M\cdot L$	25	0	4.90			*k*
	$MHL/M\cdot HL$	25	0	1.95			*k*
		25	0	1.80			301
		25	-	1.28			281

TABLE XXVIII (*Continued*)

metal ion	equilibrium	temp, °C	ionic strength, M	log *K*	Δ*H*, kJ mol⁻¹	Δ*S*, J K⁻¹ mol⁻¹	ref
		25		1.27	4.1	38.1	282
		25		1.04			300
Mn^{2+}	$M(HL)_2/MHL\cdot HL$	25	-	0.57			300
	$M\cdot L/ML(s)$	25	0	−9.3			301
		25	0	−10.4			*g*
Fe^{2+}	$MHL/M\cdot HL$	25	-	1-1.5			283
	$M\cdot L/ML(s)$	25	0	−10.7			301
Co^{2+}	$M\cdot L/ML(s)$	25	0	−9.98			301
Co^{3+}	$ML_3/M\cdot L^3$	25	1	29			277
$Co(en)_3{}^{3+}$	$ML/M\cdot L$	25	0	3.33 ± 0.05			*l*
		25	0-0.5	-	1.05	57.3	*m*
	$ML_2/M\cdot L^2$	25	0	5.1 ± 0.2			*l*
		25	0-0.5	-	−2.9	21	*m*
	$ML_3/M\cdot L^3$	25	0-0.5	-	0.4	17	*m*
$Co(pn)_3{}^{3+}$	$ML/M\cdot L$	25	0	3.27 ± 0.05			*l*
	$ML_2/M\cdot L^2$	25	0	4.9 ± 0.2			*l*
	$ML_3/M\cdot L^3$	25	0	4.3 ± 0.2			*l*
$Co(NH_3)_6{}^{3+}$	$ML/M\cdot L$	25	0	3.47 ± 0.05			*l*
	$ML_2/M\cdot L^2$	25	0	3.3 ± 0.2			*l*
$Co(NH_3)_5NO_2{}^{2+}$	$ML/M\cdot L$	25	3	-	4.0	21	*n*
	$ML_2/M\cdot L^2$	25	3	-	5.8	29	*n*
	$ML_3/M\cdot L^3$	25	3	-	6.5	33	*n*
	$ML_4/M\cdot L^4$	25	3	-	4.8	33	*n*
	$ML_5/M\cdot L^5$	25	3	-	8.4	46	*n*
$Co(NH_3)_5Cl^{2+}$	$ML/M\cdot L$	25	0	2.88			*o*
	$ML_2/M\cdot L^2$	25	0	3.9			*o*
	$ML_3/M\cdot L^3$	25	0	3.6			*o*
cis-$Co(en)_2(NH_3)Cl^{2+}$	$ML/M\cdot L$	25	0	2.6			*o*
	$ML_2/M\cdot L^2$	25	0	3.9			*o*
	$ML_3/M\cdot L^3$	25	0	3.6			*o*
trans-$Co(en)_2(NH_3)Cl^{2+}$	$ML/M\cdot L$	25	0	2.5			*o*
	$ML_2/M\cdot L^2$	25	0	4.1			*o*
	$ML_3/M\cdot L^3$	25	0	4.0			*o*
Ni^{2+}	$M\cdot L/ML(s)$	25	0	−6.87			301
Cu^{2+}	$ML/M\cdot L$	25	0.1	6.8			298
		25	0	6.78			278
		25	0	6.75 ± 0.02			301
	$ML_2/M\cdot L^2$	25	0	10.24			278
		25	0	9.92 ± 0.09			301
		18	1.7	8.6			301
	$MHL/M\cdot HL$	25	-	2.08	23.4		281
		25	-	-	20.9		*p*
	$M\cdot L/ML(s)$	25	0	−9.63			301
Zn^{2+}	$ML/M\cdot L$	25	0	5.3			*k*
	$MHL/M\cdot HL$	25	0	2.1			*k*
		25	-	1.4			281
		25	-	-	7.3		*q*
		25	-	1.4	3.5	39	*q*
		25	-	1.4			*f*
	$M\cdot L/ML(s)$	25	0	−9.84			*t*
		25	0.2	−10.79			*t*
		25	0	−10.00			301
	$M^5\cdot OH^6\cdot L^2/M_5OH_6L_2(s)$	25	0.2	−14.01			*q*
		25	0	−14.86			*q*
Ag^{+}	$M^2\cdot L/M_2L(s)$	25	0	−11.09			301
Cd^{2+}	$ML/M\cdot L$	25	0	5.4			*s*
	$MHL/M\cdot HL$	25	3	2.1			*g*
	$M\cdot L/ML(s)$	25	0	−13.74			301
$Hg_2{}^{2+}$	$M\cdot L/ML(s)$	25	0	−16.05			301
Pb^{2+}	$ML/M\cdot L$	25	-	7			296
		200		10.9			296
		25	0.7	5.36			76
		25	0	5.59			76
		25	seawater	5.62			76
		25	0.1-1.0	6.4[a]			303
		25	0.3	5.4 ± 0.1			292
		25	0	7.5			*s*
	$ML_2/M\cdot L^2$	18	1.7	8.2			301
		25	0.1-1.0	9.4[a]			303
		25	-	9.0			296
		200	-	12.3			296
		25	0.7	8.6			76
		25	0	9.08			76
		25	seawater	8.8			*t*
		25	0.3	8.86 ± 0.1			292
	$MHL/M\cdot HL$	25	0	2.9			*s*

TABLE XXVIII (*Continued*)

metal ion	equilibrium	temp, °C	ionic strength, M	log *K*	Δ*H*, kJ mol^{-1}	Δ*S*, J K^{-1} mol^{-1}	ref
	$M\cdot L/ML(s)$	25	0	−13.1			303
		25	0	−13.1			301
		25	1	−11.0			301
		25	0.3	−12.1			292
	$M^3\cdot L^2\cdot OH^2/ML\text{-}MOH_2(s)$	25	0.3	−44.1 ± 0.06			292
		25	0.1	−44.8 ± 0.2			292
	$ML/ML(s)$	25	0.3	−6.4 ± 0.1			292
	$ML_2/ML(s)\cdot L$	25	0.3	−3.1 ± 0.2			292
$Pb(CH_3)_3^+$	$ML/M\cdot L$	25	0.3	2.6 ± 0.1			299
Y^{3+}	$M^2\cdot L^3/M_2L_3(s)$	25	0	−30.6			301
La^{3+}	$M^2\cdot L^3/M_2L_3(s)$	25	0	−33.4			301
	$ML_4/M\cdot L^4$	25	2.5	13.24 ± 0.11			288
Ce^{4+}	$M\cdot L^5/ML_5$	25	2.25-3	−0.02			*u, v*
Pr^{3+}	$ML_4/M\cdot L^4$	25	2.5	13.78 ± 0.06			288
Nd^{3+}	$ML_4/M\cdot L^4$	25	2.5	14.03 ± 0.08			288
	$M^2\cdot L^3/M_2L_3(s)$	25	0	−33.0			301
Sm^{3+}	$ML_4/M\cdot L^4$	25	2.5	14.20 ± 0.01			288
	$M^2\cdot L^3/M_2L_3(s)$	25	0	−32.5			301
Eu^{3+}	$ML_4/M\cdot L^4$	25	2.5	14.33 ± 0.09			288
Gd^{3+}	$ML_4/M\cdot L^4$	25	2.5	14.31 ± 0.10			288
	$M^2\cdot L^3/M_2L_3(s)$	25	0	−32.2			301
Tb^{3+}	$ML_4/M\cdot L^4$	25	2.5	15.03 ± 0.12			288
Dy^{3+}	$ML_4/M\cdot L^4$	25	2.5	15.32 ± 0.16			288
	$M^2\cdot L^3/M_2L_3(s)$	25	0	−31.5			301
Ho^{3+}	$ML_4/M\cdot L^4$	25	2.5	15.55 ± 0.11			288
Er^{3+}	$ML_4/M\cdot L^4$	25	2.5	15.69 ± 0.08			288
Tm^{3+}	$ML_4/M\cdot L^4$	25	2.5	15.71 ± 0.09			288
Yb^{3+}	$ML_4/M\cdot L^4$	25	2.5	15.84 ± 0.09			288
	$M^2\cdot L^3/M_2L_3(s)$	25	0	−31.1			301
Lu^{3+}	$ML_4/M\cdot L^4$	25	2.5	15.83 ± 0.13			288
Th^{4+}	$M\cdot L^5/ML_5(s)$	2.25-3		0.14			*u, v*
UO_2^{2+}	$ML/M\cdot L$	25	0.22-0.36	2.78			273
		25	0.40-0.53	2.23			273
		25	-	9.87			*w*
		25	3	9.02			275
	$ML_2/M\cdot L^2$	25	0.03-0.18	4.03			373
		25	0.2	15.57			293
		20	0.1	16.2			268
		25	-	14.7; 16.7			*w*
		25	0	14.6			269
		25	0.1	16.16			286
	ML_3/ML^3	25	0.1-0.29	7.71			373
		20	0.1	21.54			287
		25	0.2	20.7			293
		25	-	18.3			267, 269
		25	0.5	23.0			297
		25	1	22.8			294
		20	-	21.4			*w*
		25	0.1	21.57			286
	$ML_2/ML\cdot HL$	25	0	1.4			269
	$ML_3/ML_2\cdot L$	25	2	3.5			266
		25	-	3.77			267
		20	0.1	5.48			268
	$ML_3/ML_2\cdot HL$	25	0	1.8			269
	$MOHL\cdot H/M\cdot L$	25	0.1	4.1			286
	$M_3OH_3L/M^3\cdot OH^3\cdot L$	25	3	16.34			275
	$(ML_3)^3/M_3OH_5\cdot L^9$	25	-	80.4			*z*
	$(ML_3)^3H^6/M_3L_6\cdot(CO_2)^3$	25	3	−41.5 ± 0.1			270
	$(ML_3)^3(CO_2)^3/M_3L_6\cdot(HL)^6$	25	3	6.4 ± 0.1			276
	$M\cdot L^3/ML_3(s)$	26	1	−1.16			266
Pu^{2+}	$ML/M\cdot L$	20	10	47			*g*
Pu(VI)	$ML_3/M\cdot L^3$	25	0.15	6.24			*y*
PuO_2^{2+}	$ML/M\cdot L$	25	0	23.0			291
		25	0	23.8			291
		25	1	12.0			*g*
	$ML_2/M\cdot L^2$	25	0	15.1			291
		25	0	15.04			*z*
		25	0.1	13.1			272
	$ML_3/M\cdot L^3$	25	1	2.09			*h*
	$MLOH/M\cdot L\cdot OH$	25	0	23.85			*z, aa*
	$MLOH_2/M\cdot L\cdot OH^2$	25	0	23.0			*z*
	$MHL/M\cdot HL$	25	0.1	2.7 ± 0.1	6		272
	$M(HL)_2/M\cdot HL^2$	25	0.1	4.36			272
	$M\cdot L/ML(s)$	25	1	−12.77			*g*
	$M\cdot L^2/ML_2(s)$	25	1	−1.33			*g*

[a] Mean value of quoted literature data in this reference. [b] Siebert, R. M.; Hostetler, P. B. *Am. J. Sci.* 1977, *277*, 716. [c] Pytkowicz, R. M.; Hawley, J. E. *Limnol. Oceanogr.* 1974, *19*, 223. [d] Siebert, R. M.; Hostetler, P. B. *Am. J. Sci.* 1977, *277*, 697. [e] Lesht, D., M.A. Thesis, University of Missouri—Columbia, 1977. [f] Bauman, J. E., Jr.; Siebert, R. M.; Almon, W. R.; Hostetler, P. B. *Chem. Phys. Aqueous Gas Solutions* [*Proc. Symp.*] 1975, 77. [g] Sillen, L. G.; Martell, A. E. "Stability Constants of Metal Ion Complexes", 2nd ed.; Chemical Society: London, 1967; Spec. Publ. 17, p 754. [h] Almon, W. R., M.A. Thesis, University of Missouri—Columbia, 1973. [i] Plummer, L. N.; Sundquist, E. T. *Geochim. Cosmochim. Acta* 1982, *46*, 247. [j] Benes, P.; Selecká, H. *Radiochim. Radioanal. Lett.* 1973, *13*, 339. [k] Zirino, A.; Yamamoto, S. *Limnol. Oceanogr.* 1972, *17*, 661. [l] Pyartman, A. K.; Kolobov, N. P.; Merkul'eva, L. E.; Mironov, V. E. *Zh. Neorg. Khim.* 1974, *19*, 2217. [m] Mironov, V. E.; Pyartman, A. K.; Kolobov, N. P. *Zh. Fiz. Khim.* 1976, *50*, 1967. [n] Mironov, V. E.; Kolobov, N. P.; Komarova, A. V.; Mavrin, I. F. *Ibid.* 1974, *48*, 1645. [o] Pyartman, A. K.; Kolobov, N. P.; Merkul'eva, L. E.; Solov'ev, Yu. B.; Mironov, V. E. *Zh. Neorg. Khim.* 1975, *20*, 141. [p] Rages, D., M.A. Thesis, University of Missouri—Columbia, 1978. [q] Ryan, M. P.; Bauman, J. E., Jr. *Inorg. Chem.* 1978, *17*, 3329. [r] Schindler, P.; Reinert, M.; Gamsjaeger, H. *Helv. Chim. Acta.* 1969, *52*, 2327. [s] Zirino, A.; Yamamoto, S. *Limnol. Oceanogr.* 1972, *17*, 661. [t] Balko, B.; Bowen, P.; Berger, R. L.; Anderson, K. *J. Biochem. Biophys. Methods* 1981, *4*, 1. [u] Dervin, J.; Faucherre, J. *Bull Soc. Chim. Fr.* 1973, 2926. [v] Dervin, J.; Faucherre, J. *Ibid.* 1973, 2930. [w] Babinets, A. E.; Zhorov, V. A.; Mitropol'skii, A. Yu; Bezborodov, A. A. *Geol. Zh.* 1977, *37*, 109. [x] Doughty, D. T.; Stewart, R. P., Jr.; Gordon G. *J. Am. Chem. Soc.* 1981, *103*, 3388. [y] Woods, M.; Mitchell, M. L.; Sullivan, J. C. *Inorg. Nucl. Chem. Lett.* 1978, *14*, 465. [z] Cleveland, J. M. "The Chemistry of Plutonium"; Gordon and Breach: New York, 1970. [aa] Rhai, D.; Serne, R. J. *J. Environ. Qual.* 1977, *6*, 89.

long extrapolation of this line to the pK value of H_2O (15.7) predicts a satisfactory value for the magnitude of the rate constant for the CO_2/OH^- reaction, viz., log $k_7 = 3.6$ in comparison with log $k_{obsd} = 3.9$[313] at 25 °C.

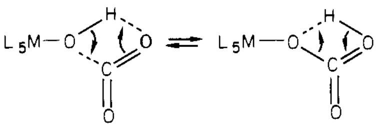
It is also known (see section B) that the decarboxylation reaction occurs with retention of the M–O bond, such that the principle of microscopic reversibility dictates that retention of this bond should also occur during CO_2 uptake. This is in line with the much higher rate of CO_2 uptake than normal substitution reactions involving M–O bond breakage. In addition, the kinetic data in Table XXXI and the tendency in Figure 4 illustrate that the rates of CO_2 uptake are only moderately sensitive to the nature of the central metal ion, the nonparticipating ligands, effects resulting from substitution in the trans position, and the overall charge on the metal hydroxo complex. These observations emphasize the secondary bond formation character of the CO_2 uptake process.

The activation parameters for k_7 are presented as an isokinetic plot in Figure 4. The significance of such a plot has been emphasized elsewhere.[315–318] The linear relationship stems from eq 73 where $\Delta G_0^\ddagger$ is the intrinsic free energy of activation and β_0 is the isokinetic temperature.

$$\Delta H^\ddagger = \Delta G_0^\ddagger + \beta_0 \Delta S^\ddagger \qquad (73)$$

From a linear least-squares fit of the data in Figure 4 it follows that $\Delta G_0^\ddagger = 59.8 \pm 0.5$ kJ mol^{-1} and $\beta_0 = 318 \pm 6$ K. Since no significant deviation from the line is observed for any of the data points, it was concluded[315] that a common mechanism is operative. Furthermore, the process does not involve the formation or breakage of any metal–ligand bonds since, if this were the case, different isokinetic plots of similar slope, but varying intercepts, would have been expected for different metal ions.[315,316] This is considered as further confirmation[315] of the assumption that all CO_2 uptake reactions proceed via secondary oxygen–carbon bond formation.

The pressure dependence of k_7 for CO_2 uptake by $M(NH_3)_5OH^{2+}$ (M = Co(III), Rh(III), Ir(III) was studied[103] under conditions where $K_3 \gg [H^+]$, such that eq 71 simplified to $k_{obsd} = k_7[CO_2(aq)]$. Kinetic data were obtained using a high pressure stopped-flow apparatus[319] and plots of ln k_7 vs. pressure were found to be linear within the experimental error limits concerned. The volumes of activation were reported[103] to be -10.1 ± 0.6 (M = Co(III)), -4.7 ± 0.8 (M = Rh(III)) and -4.0 ± 1.0 (M = Ir(III)) cm^3 mol^{-1} at 25 °C and an ionic strength of 0.5 M. These values are in agreement with a bond formation process in which the volume decrease is ascribed to intrinsic volume changes since no major contribution from changes in solvation is expected to occur during the CO_2 uptake process. These and other arguments[103,313] led to the suggestion that the intimate mechanism of a CO_2 uptake reaction may be visualized in terms of the transition state:



During CO_2 uptake the MO–H and C–O bonds are broken, whereas these are formed during the reverse aquation process (see section B). This involves nucleophilic attack by the OH ligand on CO_2, accompanied by a concerted transfer of the OH proton to one of the CO_2 oxygens.

A number of *cis*-aquo carbonato complexes can undergo ring closure to produce bidentate carbonato species as outlined in eq 68. These reactions are usually slow since they are controlled by the rate of metal–oxygen bond breakage for the aquo/hydroxo ligand cis to the monodentate carbonato ligand. A summary of the rate and activation parameters for this step is given in Table XXXII. In two cases[320,321] it was found that ring closure of a hydroxo–carbonato species is significantly slower than for the corresponding aquo–carbonato species. This can be ascribed to the greater strength of the metal–hydroxo bond.

At this stage it is appropriate to comment on the chosen notation[322] for some aquo–carbonato species in Table XXXII. Although the two possible forms, viz., $-(OH_2)OCO_2$ and $-(OH)OCO_2H$, are kinetically indistinguishable, the former notation is preferred due to the following arguments. On the basis of the considerable amount of kinetic data available on the decarboxylation of monodentate carbonato species (see section B), it is apparent that once a monodentate carbonato species is protonated, carbon dioxide is liberated at a rate which is virtually independent of the nature of the metal center and the surrounding ligands. Therefore, it seems unlikely that a $-(OH)OCO_2H$ species would not also be equally reactive and, therefore, cannot be considered as a stable intermediate. Furthermore, our formulation is also in good agreement with the observation that for a series of trans carbonato complexes the aquo ligand is indeed more basic than the carbonato ligand.[322]

(2) Via Anation by Bicarbonate/Carbonate Ion. According to the general reaction system outlined in eq

TABLE XXIX. Evidence for Carbonato Complex Formation

metal ion	identified complexes	method	ref
UO_2^{2+}	$UO_2(CO_3)_3(CDMBA)_4$	IR, TG	*a*, *b*
	$UO_2(CO_3)_2(CDMBA)_2$		
	$UO_2(CO_3)(OH)_2(CDMBA)_2$		
	$(UO_2)_2CO_3^+$, $(UO_2)_3(CO_3)_2^{2+}$, $(UO_2)_6(CO_3)_5^{2+}$	emf	*c*
	$(UO_2)_6(CO_3)_6$, $(UO_2)_6(CO_3)_7^{2-}$, $(UO_2)_6(CO_3)_6^{8-}$		
	$(UO_2)_6(CO_3)_5(OH)_2$-$n$$H_2O$(S), $(UO_2)_6(CO_3)_6$(S)	chem. anal.	*c*
	$Na_4(UO_2)(CO_3)_3$(S)		
	$UO_2(CO_3)_3^{4-}$	^{13}C NMR	356
	$(UO_2)_2(CO_3)(OH)_3^-$	Raman	*d*
	$(UO_2)_2(CO_3)(OH)_3^-$, $UO_2(CO_3)_2^{2-}$, $UO_2(CO_3)_3^{4-}$	Raman	*d*
	$(UO_2)_3(CO_3)_6^{6-}$, $(UO_2)_2(CO_3)(OH)_3^-$, $UO_2(CO_3)_3^{4-}$	polarog.	*e*
	$(UO_2)_3(OH)_3CO_3^+$, $\{(UO_2)_{11}(OH)_{24}(CO_2)_6^{2-}\}$	emf	275
Sc^{3+}	$Sc(CO_3)_2^-$, $Sc(CO_3)_3^{3-}$, $Sc(CO_3)_4^{5-}$, $Sc(CO_3)_6^{9-}$	pH	*f*
Y^{3+}	$Y_2(CO_3)_3 \cdot 5H_2O$, $(NH_4)Y(CO_3)_2 \cdot 3H_2O$	chem. anal., emf	*g*
Zr^{4+}	$Zr(CO_3)_3^{2-}$, $ZrO(CO_3)_2^{2-}$, $Na[Zr(OH)_3CO_3]$, $(NH_4)HZrO(CO_3)_3$	chem. anal.	*h*
La^{3+}	$La_2(CO_3)_3 \cdot 5H_2O$, $(NH_4)La(CO_3)_2 \cdot 2H_2O$	chem. anal.	*g*
Nd^{3+}	$(NH_4)_2CO_3 \cdot 8Nd_2(CO_3)_3 \cdot 32H_2O$, $(NH_4)Nd(CO_3)_2 \cdot H_2O$	chem. anal.	*g*
	$Nd_2(CO_3)_3 \cdot 3H_2O$	emf	311
Eu^{3+}	$Eu_2(CO_3)_3 \cdot 3H_2O$, $Eu(OH)CO_3 \cdot 0.25H_2O$	emf	311
	$Eu(OH)CO_3 \cdot 0.6H_2O$	emf	311
Gd^{3+}	$Gd_2(CO_3)_3 \cdot 3H_2O$, $(NH_4)Gd(CO_3)_2 \cdot 3H_2O$	emf	*g*
Dy^{3+}	$Dy_2(CO_3)_3 \cdot 4H_2O$, $2(NH_4)_2CO_3 \cdot 3Dy_2(CO_3)_3 \cdot 15H_2O$	emf	*g*
	$(NH_4)Dy(CO_3)_2 \cdot 3H_2O$	emf	*g*
Er^{3+}	$2(NH_4)_2CO_3 \cdot 3Er_2(CO_3)_3 \cdot 20H_2O$	emf	*g*
	$(NH_4)Er(CO_3)_2 \cdot 3H_2O$	emf	*g*
Yb^{3+}	$Yb(OH)CO_3 \cdot 0.7H_2O$, $Yb(OH)CO_3 \cdot H_2O$, $Yb_2(CO_3)_3 \cdot 2H_2O$	emf	311
Hf^{4+}	$Hf(CO_3)_4^{4-}$	sorption on $Fe(OH)_3$	*h*
Th^{4+}	$Th(CO_3)_4^{4-}$	sorption on $Fe(OH)_3$	*h*

[a] Vera, P. J.; Galiano, S. J. A.; Parellada, B. R.; Bellido, G. A. *Junta Energ. Nucl.*, 1975, *Rep. JEN (Spain) 305*, 1. [b] Vera, P.; Galiano, S. J. A.; Parellada, B. R.; Bellido, G. A. *Ibid.* 1975, *JEN 306*, 1. [c] Double, G.; Pongi, N. K.; Hurwic, J. *Bull. Soc. Chim. Fr.* 1980, 354. [d] Maya, L.; Begun, G. M. *J. Inorg. Nucl. Chem.* 1981, *43*, 2827. [e] Maya, L. *Inorg. Chim. Acta.* 1982, *65*, L13. [f] Komissarova, L. N.; Shatskii, V. M.; Zhorov, V. A. *Zh. Neorg. Khim.* 1971, *16*, 2347. [g] Tselik, I. N.; Deineka, G. F.; Fedorenko, V. D.; Shvartsman, V. Ya. *Ibid.* 1968, *14*, 2356. [h] Upor, E.; Nagy, G. *Acta. Chim.* (*Budapest*) 1973, *78*, 47.

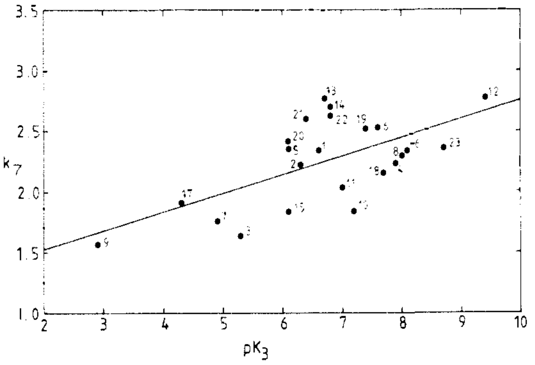


Figure 3. Plot of log k_7 vs. pK_3 for various CO_2 uptake reactions at 25 °C. (See Table XXXI for the data numbering system.)

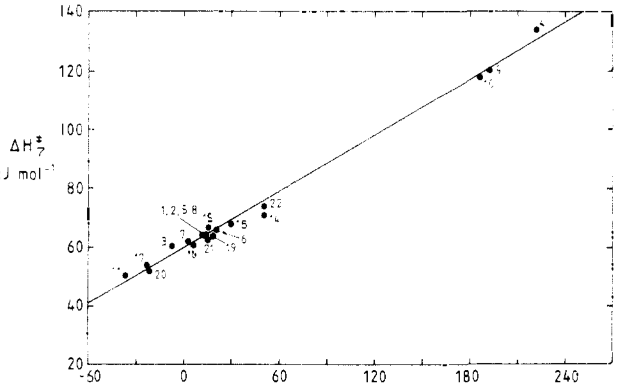


Figure 4. Plot of $\Delta H_7^\ddagger$ vs. $\Delta S_7^\ddagger$ for various CO_2 uptake reactions. (See Table XXXI for the data numbering system.)

64–66 it should be possible to form carbonato complexes via anation reactions of the metal aquo/hydroxo species with bicarbonate/carbonate ion. Such substitution reactions are expected to be significantly slower than CO_2 uptake since they involve, and are usually governed by, the breaking of the metal–oxygen bond. Typical water exchange rate constants for complexes of the type $M(NH_3)_5OH_2^{3+}$ (M = Co(III), Rh(III)), are of the order of 1×10^{-6} s^{-1} at 25 °C.[323,324] To our knowledge only one such system was investigated in detail,[325] viz., the formation of Co(tren)CO_3^+ via anation by HCO_3^- and CO_3^{2-}. The Co(tren)$(OH)_2^+$ species is stable in basic medium and does not undergo any cis to trans isomerization.[320,325–328] It is therefore an ideal system to study such an anation process. At pH >10.5 no interference of the competing reaction with CO_2(aq) was detected, and the kinetic data exhibit a linear dependence on [total carbonate]. A detailed analysis of the kinetic data produces the rate constants (4.0 ± 1.5) × 10^{-4} and (4.7 ± 0.1) × 10^{-2} M^{-1} s^{-1} for the anation by CO_3^{2-} and HCO_3^- at 50 °C, respectively. A surprising feature is that the anation by HCO_3^- is significantly faster than the anation by CO_3^{2-}. It was suggested[325] that partial proton transfer from bicarbonate to Co(tren)$(OH)_2^+$ could result in the formation of an aquo–hydroxo species such that the subsequent substitution reaction closely parallels the substitution of an aquo instead of hydroxo ligand, and so accounts for the difference in reactivity. At high pH, the major reaction path is anation by CO_3^{2-}, for which $\Delta H^\ddagger$ = 100 kJ mol^{-1} and $\Delta S^\ddagger$ = 8 J K^{-1} mol^{-1}. This reaction probably follows the normal I_d mode of substitution (i.e., a dissociative interchange process) for Co(III) complexes.[329,330] The

TABLE XXX. Thermodynamic Quantities for Metal Carbonato Species

metal ion	carbonate species	thermodynamic quantity	ref
Mg^{2+}	$MgCO_3$	ΔG_f°, S°, C_p°	290, *a*
Ca^{2+}	$CaCO_3$, $CaMg(CO_3)CO_2$, $CaMn(CO_3)_2$, $CaFe(CO_3)_2$,	ΔG_f°	*a*
	$CaCo(CO_3)_2$, $CaNi(CO_3)_2$, $CaCu(CO_3)_2$, $CaZn(CO_3)_2$	ΔG_f°	*a*
Mn^{2+}	$MnCO_3$	ΔG_f°	*a*
Fe^{2+}	$FeCO_3$	ΔG_f°	*a*, *b*
Co^{2+}	$CoCO_3$	ΔG_f°	*a*
Ni^{2+}	$NiCO_3$	ΔG_f°	*a*
Cu^{2+}	$CuCO_3$	ΔG_f°	*a*, *b*
	$Cu_2(CO_3)(OH)_2$	ΔH_f°	*c*
Zn^{2+}	$ZnCO_3$, $Zn_5(OH)_6(CO_3)_2$	ΔG_f°	*a*, *d*
Hg^{+}	Hg_2CO_3	ΔH_f°, S°	*e*
Hg^{2+}	$HgCO_3$, $HgHCO_3^+$, $Hg(OH)CO_3^-$, $HgCO_3\cdot 2HgO$	ΔH_f°, S°	*e*
Pb^{2+}	$PbCO_3$	ΔH_{sol}°, ΔS_{sol}°, $\Delta C_p^\circ{}_{sol}$, ΔH_f°, S°, C_p°	296
Cs^{2+}	$CsCO_3$	ΔH_f°, S°, C_p°	*f*
Cs^{+}	Cs_2CO_3, $CsHCO_3$, $Cs_2CO_3\cdot 0.5H_2O$, $\cdot\cdot 1.5H_2O$,	ΔH_{sol}°, ΔH_f°	*g*
	$-\cdot 3H_2O$, $\cdot\cdot 5H_2O$, $-\cdot 8H_2O$	ΔH_f°	*g*
Rb^{+}	Rb_2CO_3, $RbHCO_3$, $Rb_2CO_3\cdot 0.5H_2O$, $-\cdot 1.5H_2O$,	ΔH_{sol}°, ΔH_f°	*g*
	$-\cdot 3H_2O$, $-\cdot 8H_2O$, $-\cdot 9H_2O$	ΔH_f°	*g*
Y^{3+}	$Y_2(CO_3)_3$, $-\cdot 3H_2O$	ΔH_{sol}°, ΔH_f°, ΔG_f°, ΔS_f°	*h-j*
La^{3+}	$La_2(CO_3)_3\cdot 0.5H_2O$, $-\cdot 3H_2O$, $-\cdot 6H_2O$, $-\cdot 8H_2O$	ΔH_{sol}°, ΔH_f°, ΔG_f°, ΔS_f°	*h-j*
Ce^{3+}	$Ce_2(CO_3)_3$, $-\cdot 0.5H_2O$, $-\cdot 3H_2O$, $-\cdot 8H_2O$	ΔH_{sol}°, ΔH_f°, ΔG_f°, ΔS_f°	*h-k*
Pr^{3+}	$Pr_2(CO_3)_3$, $-\cdot 0.5H_2O$, $\cdot\cdot H_2O$, $-\cdot 3H_2O$, $-\cdot 8H_2O$	ΔH_{sol}°, ΔH_f°, ΔG_f°, ΔS_f°	*h-k*
Nd^{3+}	$Nd_2(CO_3)_3$, $-\cdot H_2O$, $-\cdot 3H_2O$, $-\cdot 4H_2O$	ΔH_{sol}°, ΔH_f°, ΔG_f°, ΔS_f°	*h-k*
Sm^{3+}	$Sm_2(CO_3)_3$, $-\cdot 3H_2O$	ΔH_{sol}°, ΔH_f°, ΔG_f°, ΔS_f°	*h-k*
Eu^{3+}	$Eu_2(CO_3)_3$, $-\cdot 3H_2O$	ΔH_{sol}°, ΔH_f°, ΔG_f°, ΔS_f°	*h*, *i*
Gd^{3+}	$Gd_2(CO_3)_3$, $-\cdot 3H_2O$	ΔH_{sol}°, ΔH_f°, ΔG_f°, ΔS_f°	*h-k*
Tb^{3+}	$Tb_2(CO_3)_3$, $-\cdot 1.3H_2O$, $-\cdot 2.3H_2O$, $-\cdot 3H_2O$	ΔH_{sol}°, ΔH_f°, ΔG_f°, ΔS_f°	*h*, *i*
Dy^{3+}	$Dy_2(CO_3)_3$, $-\cdot H_2O$, $-\cdot 3H_2O$	ΔH_{sol}°, ΔH_f°, ΔG_f°, ΔS_f°	*h*, *i*
Ho^{3+}	$Ho_2(CO_3)_3$, $-\cdot 2H_2O$, $-\cdot 3H_2O$	ΔH_{sol}°, ΔH_f°, ΔG_f°, ΔS_f°	*h*, *i*
Er^{3+}	$Er_2(CO_3)_3$, $-\cdot 3H_2O$	ΔH_{sol}°, ΔH_f°, ΔG_f°, ΔS_f°	*h-k*
Tm^{3+}	$Tm_2(CO_3)_3$, $-\cdot 3H_2O$	ΔH_{sol}°, ΔH_f°, ΔG_f°, ΔS_f°	*h*, *i*
Yb^{3+}	$Yb_2(CO_3)_3$, $-\cdot H_2O$, $-\cdot 2H_2O$, $-\cdot 3H_2O$, $\cdot\cdot 6H_2O$	ΔH_{sol}°, ΔH_f°, ΔG_f°, ΔS_f°	*h-k*
Lu^{3+}	$Lu_2(CO_3)_3$, $-\cdot H_2O$, $-\cdot 3H_2O$, $-\cdot 6H_2O$	ΔH_{sol}°, ΔH_f°, ΔG_f°, ΔS_f°	*h*, *i*

[a] Roosenberg, P. E.; Foit, F. F., Jr. *Geochim. Cosmochim. Acta* 1979, *43*, 951. [b] Reiterer, F.; Johannes, W.; Gamsjaeger, H. *Mikrochim. Acta* 1981, *1*, 63. [c] Richardson, D. W.; Brown, R. R. *Rep. Invest.—U.S., Bur. Mines*, 1974, *5*, RI-7851. [d] Schinder, P.; Reinert, M.; Gamsjaeger, H. *Helv. Chim. Acta* 1969, *52*, 2327. [e] Khodakovskii, I. L.; Shikima, N. D. *Geokhimiya* 1981, 671. [f] Paukov, I. E.; Rakhmenkulov, F. S.; Luk'yanova, I. G. *Zh. Fiz. Khim.* 1970, *44*, 256. [g] Raffelini; F.; My Le V. *C. R. Hebd. Seances Acad. Sci., Ser. C* 1971, *273*, 92. [h] Maier, A. I.; Bas'kova, N. A. *Izv. Akhad. Nauk SSSR, Neorg. Mater.* 1977, *13*, 1055. [i] Karapet'yants, M. Kh.; Maier, A. I.; Bas'kova, N. A. *Ibid.* 1977, *13*, 1279. [j] Bas'kova, N. A.; Maier, A. I.; Karapet'yants, M. Kh. *Tr. Mosk. Khim-Tekhnol. Inst.* 1974, *81*, 8. [k] Batkibekova, M.; Usubaliev, D.; *Zh. Fiz. Khim.* 1974, *48*, 1615.

TABLE XXXI. Rate and Activation Parameters for CO_2 Uptake Reactions[h]

complex ion	pK_3[a]	k_7, $M^{-1}\ s^{-1}$	$\Delta H_7^\ddagger$, kJ mol^{-1}	$\Delta S_7^\ddagger$, J K^{-1} mol^{-1}	ref
(1) $Co(NH_3)_5OH^{2+}$	6.6	220 ± 40	64 ± 4	15 ± 12	312
(2) ($\alpha\beta S$)-Co(tetren)OH^{2+}	6.3	166 ± 15	64 ± 5	14 ± 17	327
(3) *cis*-Co(tren)$(OH_2)OH^{2+}$	5.3	44 ± 2	61 ± 1	−8 ± 1	320
(4) *cis*-Co(tren)$(OH)_2^+$	7.9	170 ± 10	134 ± 25	222 ± 92	320
(5) *cis*-Co$(en)_2(OH_2)OH^{2+}$	6.1	225 ± 15	64 ± 4	14 ± 13	*b*
(6) *trans*-$Co(NH_3)_4(CN)OH^+$	7.6	338 ± 32	66 ± 6	21 ± 21	*c*
(7) *cis*-Co(cyclam)$(OH_2)OH^{2+}$	4.9	57 ± 4	62 ± 4	3 ± 15	314
(8) *cis*-Co(cyclam)$(OH)_2^+$	8.0	196 ± 24	64 ± 2	12 ± 8	314
(9) *trans*-Co(cyclam)$(OH_2)OH^{2+}$	2.9	37 ± 0.1	121 ± 1	193 ± 2	314
(10) *trans*-Co(cyclam)$(OH)_2^+$	7.2	70 ± 0.2	118 ± 3	186 ± 8	314
(11) *cis*-$Cr(C_2O_4)_2(OH_2)OH^{2-}$	7.0	170 ± 10	51 ± 1	−36 ± 5	350
(12) Cu$(gly)_2$OH	9.4	590 ± 30			314
(13) $Ir(NH_3)_5OH^{2+}$	6.7	590 ± 30			*d*
(14) $Rh(NH_3)_5OH^{2+}$	6.8	490 ± 120	71 ± 4	50 ± 13	*d*
(15) *cis*-Rh$(en)_2(OH_2)OH^{2+}$	6.1	69 ± 18	67 ± 2	16 ± 7	*e*
(16) *cis*-Rh$(en)_2(OH)_2^+$	8.1	215 ± 29	61 ± 1	5 ± 3	*e*
(17) *trans*-Rh$(en)_2(OH_2)OH^{2+}$	4.3	81 ± 3	54 ± 4	−23 ± 13	322
(18) *trans*-Rh$(en)_2(OH)_2^+$ [f]	7.7	140 ± 20	68 ± 4	30 ± 12	322
(19) *trans*-Rh$(en)_2(OCO_2)$OH	7.4	330 ± 80	64 ± 3	19 ± 10	322
(20) *trans*-Rh$(en)_2$(Cl)OH^+	6.1	260 ± 12	52 ± 5	−22 ± 18	315
(21) *trans*-Rh$(en)_2$(Br)OH^+	6.4	395 ± 33	63 ± 5	16 ± 16	315
(22) *trans*-Rh$(en)_2$(I)OH^+	6.8	422 ± 43	74 ± 3	50 ± 11	315
(23) Zn(CR)OH^+	8.7	225 ± 23			*g*

[a] Acid dissociation constant of corresponding aquo complex ion (see eq 66). [b] Wan, W. K., Ph. D. Thesis, SUNY, Buffalo, NY 1978. [c] Krishnamoorthy, C. R.; Palmer, D. A.; van Eldik, R.; Harris, G. M. *Inorg. Chim. Acta* 1979, *35*, L361. [d] Palmer, D. A.; Harris, G. M. *Inorg. Chem.* 1974, *13*, 965. [e] Palmer, D. A.; van Eldik, R.; Kelm, H.; Harris, G. M. *Ibid.* 1980, *19*, 1009. [f] The rate constant for CO_2 uptake for this species is third order. For comparison purposes it is represented here as *$k(CO)_2$, with $(CO_2) = 0.01$ M, a typical value in a large proportion of the data reported.* [g] Woolley, P. *Nature (London)* 1975, *258*, 677. [h] Temperature 25 °C; ionic strength 0.5 M.

TABLE XXXII. Rate and Activation Parameters for Ring-Closure Reactions of Monodentate Carbonato Complexes at 25 °C

complex ion	k_6, s^{-1}	$\Delta H_6^{\ddagger}$, kJ mol^{-1}	$\Delta S_6^{\ddagger}$, J K^{-1} mol^{-1}	ref
cis-$Co(tren)(OH_2)OCO_2^{+}$ [a]	5×10^{-2}	52 ± 2	−95 ± 7	320
cis-$Co(tren)(OH)OCO_2$	$\sim 1 \times 10^{-4}$ [b]			320
cis-$Co(cyclam)(OH_2)OCO_2^{+}$ [a]	2.3×10^{-2}	57 ± 7	−87 ± 24	314
cis-$Co(en)_2(OH_2)OCO_2^{+}$ [a]	1.1×10^{-1} [c]	58 ± 8	−67 ± 21	320, 321
cis-$Co(en)_2(OH)OCO_2$	6×10^{-5}	117 ± 13	71 ± 38	321
cis-$Cr(C_2O_4)_2(OH_2)OCO_2^{3-}$	$\sim 2.4 \times 10^{-2}$ [d]			350
cis-$Rh(en)_2(OH_2)OCO_2^{+}$	very slow[e]			[f]

[a] These species are reported in the literature as hydroxobicarbonato complexes, we however prefer the given notation (see discussion), data at 20 °C only available. [c] Extrapolated from quoted activation parameters. [d] Mean value of data reported in the acidity range 7.09 ⩽ pH ⩽ 9.18. [e] Reaction is complete when heated under reflux for 1 h at pH ~ 7. [f] Palmer, D. A.; van Eldik, R.; Kelm, H.; Harris, G. M. *Inorg. Chem.* 1980, *19*, 1009.

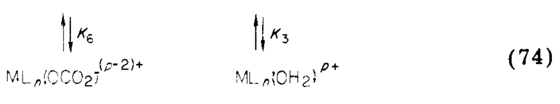
so-formed carbonato–hydroxo species can undergo slow ring closure as referred to before.[320,325]

B. Aquation Reactions

Various reaction routes exist for the aquation of carbonato complexes in aqueous solution since such processes can in general occur via acid- and base-catalyzed aquation. Furthermore, the nature of the carbonato complex, i.e., whether carbonate acts as a monodentate, bidentate, or bridged ligand, will determine the detailed mechanism of the aquation process. We have, therefore, further subdivided this subsection to treat the various aspects separately.

(1) Acid-Catalyzed Aquation of Monodentate Carbonato Complexes. On treating monodentate carbonato complexes of the type $ML_n(OCO_2)^{(p-2)+}$ with acid, $CO_2(aq)$ is released and the corresponding aquo complex is formed (see eq 67). These reactions are in general rapid (stopped-flow rate), which suggests that no M–O bond breakage occurs during aquation. Indeed, isotope labeling experiments[331,332] have proved conclusively that acid-catalyzed aquation takes place without metal–oxygen bond breakage. The rate-determining step is, therefore, not the substitution of a water molecule for the carbonate/bicarbonate ion, but rather a decarboxylation reaction involving O–C bond breakage in the carbonate group.

Acid-catalyzed decarboxylation of a series of monodentate carbonato complexes was found to proceed according to the general mechanism[333] shown in eq 74



$$\begin{tikzcd} ML_n(OCO_2H)^{(p-1)+} \arrow[r, "k_8"] \arrow[d, shift left] & ML_n(OH)^{(p-1)+} + CO_2(aq) \arrow[d, shift left] \\ ML_n(OCO_2)^{(p-2)+} \arrow[u, shift left, "K_6"'] & ML_n(OH_2)^{p+} \arrow[u, shift left, "K_3"'] \end{tikzcd} \qquad (74)$$

(reverse of eq 70). Protons have been omitted from this scheme and k_8 is the rate-determining decarboxylation rate constant, and K_3 and K_6 are acid-dissociation constants. According to this mechanism only the protonated bicarbonato species is capable of undergoing decarboxylation. For the above mechanism,

$$k_{obsd} = k_8[H^+]/\{K_6 + [H^+]\} \qquad (75)$$

such that k_{obsd} exhibits the expected sigmoid pH dependence (for an example see Figure 5) for all the systems quoted in Table XXXIII. Under conditions where $[H^+] >> K_6$ (usually at pH <5), eq 75 simplifies to $k_{obsd} = k_8$. Furthermore, the pH dependence of k_{obsd} enables one to estimate the value of K_6, which is in general of the same order of magnitude as the first dissociation constant of carbonic acid (K_1).

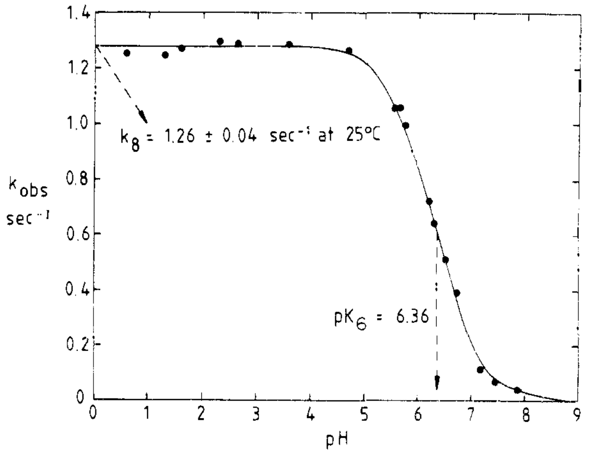


Figure 5. Plot of k_{obsd} vs. pH for the reaction *trans*-$Rh(en)_2(Cl)OCO_2 + H^+ \rightarrow$ *trans*-$Rh(en)_2(Cl)OH^+ + CO_2$ at 25 °C and an ionic strength of 0.5 M. Data taken from ref 315.

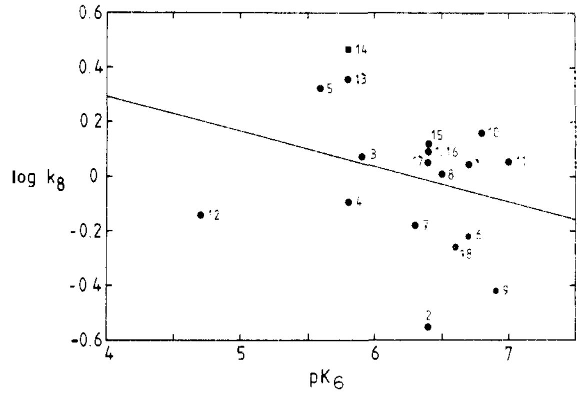


Figure 6. Plot of log k_8 vs. pK_6 for various decarboxylation reactions of monodentate carbonato complexes. (See Table XXXIII for the data numbering system.)

The results in Table XXXIII illustrate that the nature of the central metal ion and surrounding ligands has a minor influence on the magnitudes of K_6 and k_8. The acid dissociation constant (K_6) of the bicarbonato species should reflect the strength of the M–O bond and indirectly that of the O–C bond, which determines the magnitude of k_8. Figure 6 illustrates that k_8 decreases approximately with decreasing K_6 (increasing pK_6). The two species which are most markedly deviant are $Co(tetren)OCO_2H^{2+}$ and *cis*-$Rh(en)_2(OH_2)OCO_2H^{2+}$; however, reasonable explanations have been offered for their behavior.[315] Notwithstanding the scatter in Figure 6, the correlation between the acidity of the parent

TABLE XXXIII. Rate and Activation Parameters for Decarboxylation Reactions of Monodentate Carbonato Complexes[f]

complex ion	pK_6	k_8, s^{-1}	$\Delta H_8^{\ddagger}$, kJ mol^{-1}	$\Delta S_8^{\ddagger}$, J K^{-1} mol^{-1}	ref
(1) $Co(NH_3)_5OCO_2H^{2+}$	6.4	1.25 ± 0.06	71 ± 2	−2 ± 4	333
	6.7	1.10 ± 0.05	70 ± 1	−8 ± 4	*a*
(2) ($\alpha\beta S$)-Co(tetren)OCO_2H^{2+}	6.4	0.28 ± 0.03	65 ± 8	−36 ± 18	327
(3) *cis*-Co(tren)$(OH_2)OCO_2H^{2+}$	5.9	1.19 ± 0.06	60 ± 2	−43 ± 5	352
(4) *cis*-$Co(en)_2(OH_2)OCO_2H^{2+}$	5.8	0.81 ± 0.04	60 ± 3	−46 ± 12	*b*
(5) *trans*-$Co(en)_2(OH_2)OCO_2H^{2+}$	5.6	2.1 ± 0.1	58 ± 7	−42 ± 25	*b*
(6) *cis*-$Co(en)_2(NH_3)OCO_2H^{2+}$	6.7	0.60 ± 0.02	68 ± 2	−17 ± 7	*c*
(7) *trans*-$Co(en)_2(NH_3)OCO_2H^{2+}$	6.3	0.66 ± 0.02	70 ± 4	−13 ± 12	*c*
(8) *trans*-$Co(en)_2(Cl)OCO_2H^{+}$	6.5	1.02 ± 0.05	73 ± 5	0 ± 17	353
(9) *trans*-$Co(NH_3)_4(CN)OCO_2H^{+}$	6.9	0.38 ± 0.01	90 ± 4	46 ± 12	*d*
(10) $Ir(NH_3)_5OCO_2H^{2+}$	6.8	1.45 ± 0.07	79 ± 2	25 ± 4	*a*
(11) $Rh(NH_3)_5OCO_2H^{2+}$	7.0	1.13 ± 0.06	71 ± 2	−4 ± 4	*a*
(12) *cis*-$Rh(en)_2(OH_2)OCO_2H^{2+}$	4.7	0.72 ± 0.02	81 ± 1	24 ± 4	*e*
(13) *trans*-$Rh(en)_2(OH_2)OCO_2H^{2+}$	5.8	2.92 ± 0.08	46 ± 1	−82 ± 2	322
(14) *trans*-$Rh(en)_2(OCO_2H)_2^{+}$	5.8	2.26 ± 0.05	68 ± 1	−9 ± 3	322
(15) *trans*-$Rh(en)_2(OCO_2)OCO_2H$	6.4	1.3 ± 0.1			322
(16) *trans*-$Rh(en)_2(Cl)OCO_2H^{+}$	6.4	1.26 ± 0.04	73 ± 2	−1 ± 7	315
(17) *trans*-$Rh(en)_2(Br)OCO_2H^{+}$	6.4	1.12 ± 0.03	76 ± 1	11 ± 3	315
(18) *trans*-$Rh(en)_2(I)OCO_2H^{+}$	6.6	0.55 ± 0.04	72 ± 1	−10 ± 5	315

[a] Palmer, D. A.; Harris, G. M. *Inorg. Chem.* 1974, *13*, 965. [b] Wan, W. K. Ph.D. Thesis, State University of New York at Buffalo, New York, 1978. [c] Ficner, S. A. Ph.D. Thesis, State University of New York at Buffalo, New York, 1980. [d] Krishnamoorthy, C. R.; Palmer, D. A.; van Eldik, R.; Harris, G. M. *Inorg. Chim. Acta* 1979, *35*, L361. [e] Palmer, D. A.; van Eldik, R.; Kelm, H.; Harris, G. M. *Inorg. Chem.* 1980, *19*, 1009. [f] Temperature of 25 °C; ionic strength of 0.5 M.

species and its rate of decarboxylation is obvious. As for the various trans Rh(III) species, it is clear that the labilizing effect of the ligand trans to the bicarbonate group decreases in the order $H_2O > OCO_2H^- > OCO_2^{2-} > Cl^- > Br^- \sim NH_3 > I^-$, although the magnitude of this effect is diminished as it operates on the more remote C–O bond.[315] Certainly crystallographic studies are not sensitive enough to register a trans effect on the C–O bond lengths (see Table XVIII).

The activation parameters for k_8 exhibit a good isokinetic relationship (Figure 7), from which it follows that $\Delta G_0^{\ddagger} = 73.2 \pm 0.4$ kJ mol^{-1} and $\beta_0 = 318 \pm 13$ K. These are indeed very close to those reported for the reverse CO_2 uptake process in Figure 4. This illustrates that a common mechanism is operative, viz., the formation or breakage of secondary oxygen–carbon bonds. The pressure dependence of k_8 for the decarboxylation of $M(NH_3)_5OCO_2^+$ (M = Co(III), Rh(III), Ir(III)) was studied[103] at high $[H^+]$, i.e., where $[H^+] >> K_6$, such that $k_{obsd} = k_8$. The volumes of activation were reported[103] to be +6.8 ± 0.3 (M = Co(III)), +5.2 ± 0.3 (M = Rh(III)), and +2.5 ± 0.4 (M = Ir(III)) cm^3 mol^{-1} at 25 °C and an ionic strength of 0.5 M. Although the magnitude of $\Delta V^{\ddagger}$ is rather small, it can be assigned to intrinsic volume changes during the release of CO_2. A combination of the above values and those found[103] for the corresponding formation reactions, along with partial molar volume measurements, enabled the construction of reaction volume profiles.[103] These indicate that the transition state has a volume approximately halfway between that of the reactant and product species.

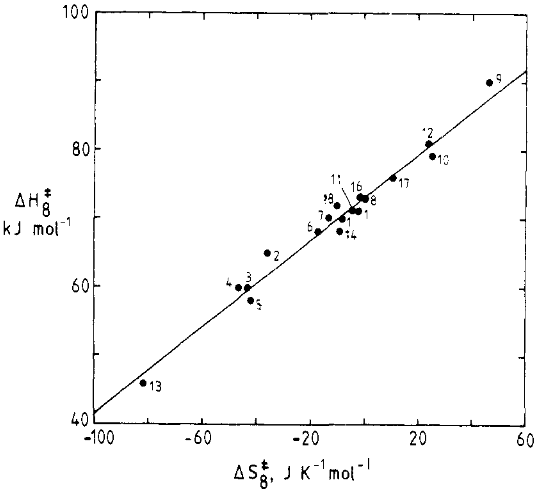
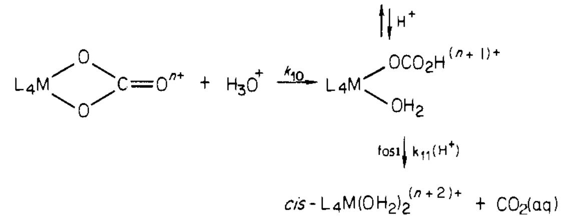


Figure 7. Plot of $\Delta H_8^{\ddagger}$ vs. $\Delta S_8^{\ddagger}$ for various decarboxylation reactions of monodentate carbonato complexes. (See Table XXXIII for the data numbering system.)

(2) Acid-Catalyzed Aquation of Bidentate Carbonato Complexes. The aquation of $Co(NH_3)_4CO_3^+$ is one of the earliest investigated bidentate systems.[334] With the aid of ^{18}O tracer experiments, Posey and Taube[335] demonstrated that the acidification proceeds via a rate-determining acid-catalyzed ring-opening step (the reverse of reaction 68), followed by a fast decarboxylation step of the monodentate bicarbonato species as discussed in the previous section. Similar findings were reported for a series of such complexes as summarized in Tables XXXIV and XXXV. The ring-opening process obeys the rate law

$$k_{obsd} = k_9 + k_{10}[H^+] \tag{76}$$

where k_9 and k_{10} represent the rate constants for the "water"- and acid-catalyzed ring-opening reactions as illustrated in reaction 77. Here k_{11} represents the



(77)

decarboxylation rate constant of the ring-opened monodentate carbonato intermediate, which is usually a fast

TABLE XXXIV. Rate and Activation Parameters for "Water-Catalyzed" Ring-Opening Reactions[i]

complex ion	I, M	k_9, s^{-1}	$\Delta H_9^\ddagger$, kJ mol^{-1}	$\Delta S_9^\ddagger$, J K^{-1} mol^{-1}	ref
(1) $Co(NH_3)_4CO_3^+$	0.5	$(1.3 \pm 0.2) \times 10^{-4}$	50 ± 21	−155 ± 79	334
(2) $Co(en)_2CO_3^+$		$(1.2 \pm 0.2) \times 10^{-4}$	75 ± 13	−63 ± 38	*a*
(3) $Co(pn)_2CO_3^+$		$(1.0 \pm 0.2) \times 10^{-4}$	75 ± 13	−63 ± 38	*a*
(4) $Co(tn)_2CO_3^+$		$(0.8 \pm 0.2) \times 10^{-4}$	67 ± 13	−88 ± 38	*a*
(5) $Co(tren)CO_3^+$	0.5	$(1.7 \pm 0.2) \times 10^{-4}$	63 ± 8	−105 ± 21	326
(6) *cis*-$Co(en)(NH_3)_2CO_3^+$	0.5	$(0.3 \pm 0.1) \times 10^{-4}$	71 ± 21	−100 ± 50	326
(7) *cis*-$Co(en)(H_2O)_2CO_3^+$ [b]	1.0	7.1×10^{-2}	169 ± 34	+300 ± 122	*c*
(8) *trans*-$Co(en)(NH_3)_2CO_3^+$	0.5	$(1.1 \pm 0.6) \times 10^{-4}$	79 ± 21	−59 ± 50	326
(9) α-$Co(trien)CO_3^+$	0.5	$(1.5 \pm 1.2) \times 10^{-4}$	84 ± 13	−29 ± 29	326
(10) β-$Co(trien)CO_3^+$	0.5	$(0.1 \pm 0.1) \times 10^{-4}$	71 ± 13	−96 ± 38	326
(11) α-$Co(Me_2trien)CO_3^+$	1.0	$\sim 3 \times 10^{-4}$	64 ± 13	−100 ± 42	339
(12) $Co(Me_2[14]dieneN_4)CO_3^+$	0.5	7.5×10^{-5}	115 ± 28	+65 ± 89	338
(13) $Co(py)_4CO_3^+$	1.0	$(1.3 \pm 0.1) \times 10^{-6}$	138 ± 4	+109 ± 8	342
(14) *cis*-$Co(py)_2(H_2O)_2CO_3^+$	1.0	$(7.5 \pm 1.6) \times 10^{-5}$	111 ± 1	+49 ± 4	*d*
(15) *cis*-$Co(py)_2(CO_3)_2^-$	0.5	$(5.2 \pm 0.5) \times 10^{-5}$	96 ± 4	−4 ± 17	*e*
(16) α-$Co(edda)CO_3^-$	2.0	$(2.9 \pm 0.2) \times 10^{-3}$	71 ± 8	−59 ± 29	341
	0.5	2.2×10^{-3}	88 ± 13	0 ± 50	*f*
(17) β-$Co(edda)CO_3^-$	2.0	$(9.8 \pm 4.3) \times 10^{-4}$	88 ± 25	−8 ± 84	341
	0.5	3.8×10^{-4}	88 ± 13	+8 ± 50	*f*
(18) $Co(nta)CO_3^{2-}$	2.0	$(3.0 \pm 0.8) \times 10^{-3}$	53 ± 11	−117 ± 38	*g*
(19) *cis*-$Rh(en)_2CO_3^+$	0.5	$(9.5 \pm 1.0) \times 10^{-6}$	95 ± 6	−21 ± 21	*h*
(20) $Cr_2([9]aneN_3)_2(OH)_2CO_3^{2+}$	1.0	$(1.7 \pm 0.1) \times 10^{-5}$	86 ± 10	−48 ± 34	345

[a] Sastri, V. S.; Harris, G. M. *J. Am. Chem. Soc.* 1970, *92*, 2943. [b] A clear distinction cannot be made between this species or $Co(en)(CO_3)_2^-$ as the reactant. [c] Coddington, P. M.; Hyde, K. E. *Inorg. Chem.* 1983, *22*, 2211. [d] Glenister, J. F.; Hyde, K. E.; Davies, G. *Ibid.* 1982, *21*, 2331. [e] Hyde, K. E.; Hyde, E. W.; Moryl, J.; Baltus, B.; Harris, G. M. *Ibid.* 1980, *19*, 1603. [f] Garnett, P. J.; Watts, D. W. *Inorg. Chim. Acta* 1974, *8*, 313. [g] Dasgupta, T. P.; Harris, G. M. *Inorg. Chem.* 1974, *13*, 1275. [h] Palmer, D. A.; van Eldik, R.; Kelm, H.; Harris, G. M. *Ibid.* 1980, *19*, 1009. [i] Temperature, 25 °C.

TABLE XXXV. Rate and Activation Parameters for "Acid-Catalyzed" Ring-Opening Reactions[l]

complex ion	I, M	k_{10},[a] M^{-1} s^{-1}	$\Delta H_{10}^\ddagger$, kJ mol^{-1}	$\Delta S_{10}^\ddagger$, J K^{-1} mol^{-1}	ref
(1) $Co(NH_3)_4CO_3^+$	0.5	(1.5 ± 0.1)	64 ± 4	−26 ± 16	334
(2) $Co(en)_2CO_3^+$		(0.6 ± 0.05)	59 ± 13	−54 ± 38	*b*
(3) $Co(pn)_2CO_3^+$		(0.5 ± 0.05)	59 ± 13	−54 ± 38	*b*
(4) $Co(tn)_2CO_3^+$		(0.8 ± 0.05)	50 ± 13	−79 ± 38	*b*
(5) $Co(bpy)_2CO_3^+$	1.0	2.2×10^{-4}	93 ± 7	−6 ± 20	340
(6) $Co(phen)_2CO_3^+$	1.0	1.5×10^{-4}	85 ± 8	−36 ± 21	340
(7) $Co(tren)CO_3^+$	0.5	(2.0 ± 0.05)	46 ± 4	−84 ± 17	326
(8) $Co(cyclam)CO_3^+$	0.5	1.3×10^{-3}	86 ± 2	−11 ± 5	344
(9) $Co(cyclen)CO_3^+$	0.5	7.0×10^{-3}	100 ± 3	+51 ± 10	337
(10) *cis*-$Co(en)(NH_3)_2CO_3^+$	0.5	(0.9 ± 0.05)	67 ± 4	−17 ± 13	326
(11) *cis*-$Co(en)(H_2O)_2CO_3^+$ [c]	1.0	2.2×10^{-1}	51 ± 9	−87 ± 32	*d*
(12) *trans*-$Co(en)(NH_3)_2CO_3^+$	0.5	(8.9 ± 0.3)	42 ± 4	−84 ± 13	326
(13) α-$Co(trien)CO_3^+$	0.5	(5.2 ± 0.1)	63 ± 4	−21 ± 13	326
(14) β-$Co(trien)CO_3^+$	0.5	(0.2 ± 0.02)	71 ± 4	−21 ± 13	326
(15) α-$Co(Me_2trien)CO_3^+$	1.0	2×10^{-2}	92 ± 5	+32 ± 17	339
(16) β-$Co(Me_2trien)CO_3^+$	1.0	5.5×10^{-4}	87 ± 2	−16 ± 6	339
(17) $Co(Me_2(14)dieneN_4)CO_3^+$	0.5	1.5×10^{-2}	81 ± 1	−6 ± 2	338
(18) $Co(Me_6(14)dieneN_4)CO_3^+$	0.25	8.0×10^{-3}	70 ± 21	−42 ± 71	*e*
(19) α-$Co(dmtr)CO_3^+$	1.0	1.8×10^{-2}			343
(20) β-$Co(dmtr)CO_3^+$	1.0	5.6×10^{-4}			343
(21) $Co(py)_4CO_3^+$	5.0	$(8.0 \pm 0.5) \times 10^{-6}$	97 ± 4	−17 ± 13	342
(22) *cis*-$Co(py)_2(H_2O)_2CO_3^+$	1.0	$(3.4 \pm 0.2) \times 10^{-4}$	82 ± 5	−36 ± 18	*f*
(23) $Co(py)_3(H_2O)CO_3^+$	1.0	4×10^{-4}			*f, g*
(24) *cis*-$Co(py)_2(CO_3)_2^-$	0.5	(5.9 ± 0.6)	71 ± 4	+8 ± 17	*h*
(25) $Co(gly)_2CO_3^-$	2.0	8	92	+84	350
(26) α-$Co(edda)CO_3^-$	2.0	(118 ± 1)	50 ± 4	−33 ± 33	341
	0.5	83	67 ± 4	+21 ± 13	*i*
(27) β-$Co(edda)CO_3^-$	2.0	(2.4 ± 0.1)	45 ± 1	−84 ± 4	341
	0.5	3.0	71 ± 4	+8 ± 13	*i*
(28) $Co(nta)CO_3^{2-}$	2.0	(41.9 ± 0.8)	66 ± 2	−6 ± 6	*j*
(29) *cis*-$Rh(en)_2CO_3^+$	0.5	$(7.8 \pm 1.0) \times 10^{-6}$	104 ± 15	+8 ± 46	*k*
(30) $Rh_2((9)aneN_3)_2(OH)_2CO_3^{2+}$	1.0	$(1.7 \pm 0.1) \times 10^{-4}$	63 ± 1	−106 ± 2	345
(31) $Cr_2((9)aneN_3)_2(OH)_2CO_3^{2+}$	1.0	$(3.8 \pm 0.3) \times 10^{-5}$	66 ± 2	−106 ± 8	345
(32) $Cr(C_2O_4)_2CO_3^{3-}$	2.0	(2.0 ± 0.2)	61 ± 2	−33 ± 8	350

[a] $k_{10} = k_{12}K_7$ (see discussion). [b] Sastri, V. S.; Harris, G. M. *J. Am. Chem. Soc.* 1970, *92*, 2943. [c] A clear distinction could not be made between this species and $Co(en)(CO_3)_2^-$ as the reactant. [d] Coddington, P. M.; Hyde, K. E. *Inorg. Chem.* 1983, *22*, 2211. [e] Kernohan, J. A.; Endicott, J. F. *J. Am. Chem. Soc.* 1969, *91*, 6977. [f] Glenister, J. F.; Hyde, K. E.; Davies, G. *Inorg. Chem.* 1982, *21*, 2331. [g] Laier, T.; Schaffer, C. E.; Springborg, J. *Acta Chem. Scand., Ser. A* 1980, *A34*, 343. [h] Hyde, K. E.; Hyde, E. W.; Moryl, J.; Baltus, R.; Harris, G. M. *Inorg. Chem.* 1980, *19*, 1603. [i] Garnett, P. J.; Watts, D. W. *Inorg. Chim. Acta* 1974, *8*, 313. [j] Dasgupta, T. P.; Harris, G. M. *Inorg. Chem.* 1974, *13*, 1275. [k] Palmer, D. A.; van Eldik, R.; Kelm, H.; Harris, G. M. *Ibid.* 1980, *19*, 1009. [l] Temperature, 25 °C.

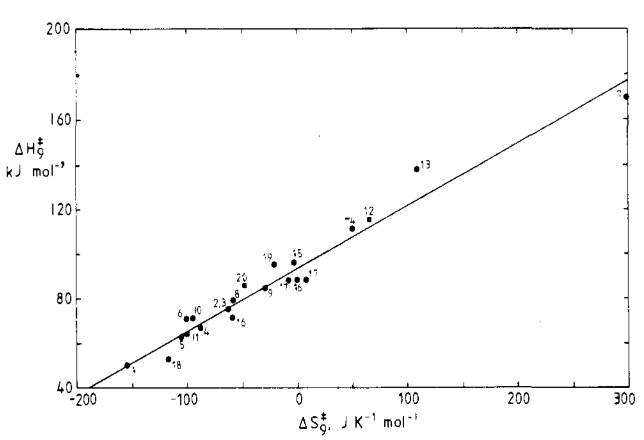
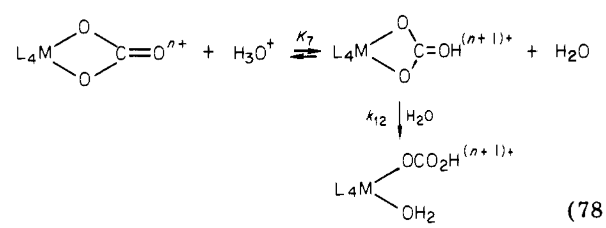


Figure 8. Plot of $\Delta H_9^{\ddagger}$ vs. $\Delta S_9^{\ddagger}$ for various "water-catalyzed" ring-opening reactions of bidentate carbonato complexes. (See Table XXXIV for the data numbering system.)

step (see subsection B1 and further discussion), such that this step is not rate determining.

Solvent isotope effects[336-339] led to the suggestion that the acid-catalyzed ring-opening step (k_{10}) actually consists of a rapid preprotonation equilibrium followed by a rate-determining ring-opening reaction.



(78)

As a result, eq 76 modifies to

$$k_{\mathrm{obsd}} = \frac{k_9 + k_{12}K_7[\mathrm{H}^+]}{1 + K_7[\mathrm{H}^+]} \tag{79}$$

which can be further simplified to

$$k_{\mathrm{obsd}} = k_9 + k_{12}K_7[\mathrm{H}^+] \tag{80}$$

since it is known that K_7 for the protonation of a carbonyl group is very small.[336] If this were not the case, the simplification that $1 + K_7[\mathrm{H}^+] \sim 1$ would have been invalid, and k_{obsd} vs. $[\mathrm{H}^+]$ should have been nonlinear. It follows that k_{10} is replaced by the product $k_{12}K_7$. The values of k_9 and k_{10} (i.e., $k_{12}K_7$), and their corresponding activation parameters, are summarized in Tables XXXIV and XXXV, respectively.

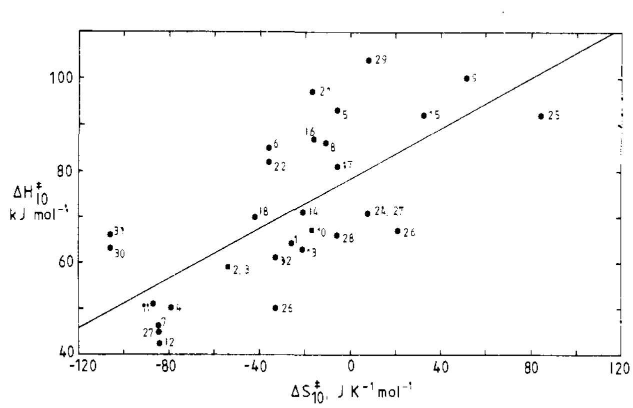


Figure 9. Plot of $\Delta H_{10}^{\ddagger}$ vs. $\Delta S_{10}^{\ddagger}$ for various acid-catalyzed ring-opening reactions of bidentate carbonato complexes. (See Table XXXV for the data numbering system.)

TABLE XXXVI. Rate and Activation Parameters for the Decarboxylation of Some Ring-Opened Carbonato Complexes[a]

complex[b]	k_{11}, s⁻¹	$\Delta H_{11}^{\ddagger}$, kJ mol⁻¹	$\Delta S_{11}^{\ddagger}$, J K⁻¹ mol⁻¹	ref
$\mathrm{Co(nta)CO_3}^{2-}$	57.1 ± 2.5	64 ± 4	−3 ± 13	*c*
α-$\mathrm{Co(edda)CO_3}^-$	55.0 ± 4.6	46 ± 3	−54 ± 8	341
β-$\mathrm{Co(edda)CO_3}^-$	2.3 ± 0.1	68 ± 6	−8 ± 21	341
$\mathrm{Co(en)_2CO_3}^+$	0.37			336
$\mathrm{Co(tren)CO_3}^+$	1.5			326

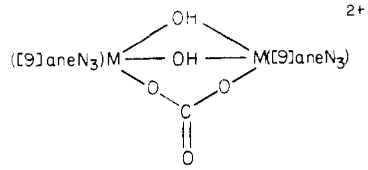
[a] Ionic strength of 2.0M and a temperature of 25 °C. [b] Complex prior to acidification. [c] Dasgupta, T. P.; Harris, G. M. *Inorg. Chem.* 1974, *13*, 1275.

The values of k_9 in Table XXXIV vary within 4 orders of magnitude. Furthermore, the nature of the central metal atom, the surrounding nonparticipating ligands and the overall charge on the complex influence the magnitude of k_9 and its corresponding activation parameters, as expected for a metal–oxygen bond breakage process. The activation parameters exhibit a good isokinetic relationship (Figure 8), which demonstrates the common nature of the processes involved. The values of k_{10} in Table XXXV vary within 6 orders of magnitude, which once again emphasizes the influence of the nonparticipating ligands and the charge of the complex on the strength of the metal–oxygen bond. The factors that govern the relative magnitudes of k_{10} obviously include a stereochemical component. The influence of the electronic structure of the ligand, however, is not clearly delineated for this type of reaction. Francis and Jordan[340] proposed a correlation between the value of k_{10} and pK_a of the amine ligands for a series of $\mathrm{CoN_4CO_3}^+$ complexes.[341-344] Obviously the more acidic the ligands are, then the stronger will be the Co–O bond. However, this correlation is only valid for a limited number of systems, and steric arguments must also be taken into account.[341] A further complication in the interpretation of k_{10} arises from the fact that k_{10} is actually a combination of two constants, viz., k_{12} and K_7. These constants may in fact behave very differently towards stereochemical and other effects. The overall activation parameters $\Delta H_{10}^{\ddagger}$ and $\Delta S_{10}^{\ddagger}$ result in a poor isokinetic plot (Figure 9). This demonstrates the significant role played by the nature of the central metal atom and the nonparticipating ligands during the acid-catalyzed ring-opening process. Furthermore, the complex nature of k_{10} could partially account for the large scatter in Figure 9 since the overall activation parameters are indeed composite quantities, viz., $\Delta H_{10}^{\ddagger} = \Delta H_7^{\circ} + \Delta H_{12}^{\ddagger}$ and $\Delta S_{10}^{\ddagger} = \Delta S_7^{\circ} + \Delta S_{12}^{\ddagger}$.

In a few cases (see Table XXXVI), plots of k_{obsd} vs. $[\mathrm{H}^+]$ tend to reach a limiting value at high $[\mathrm{H}^+]$. Under such conditions the rate of the ring-opening reaction ($k_{10}[\mathrm{H}^+]$ or $k_{12}K_7[\mathrm{H}^+]$) is enhanced to such an extent that the decarboxylation step (k_{11}, which is independent of $[\mathrm{H}^+]$) becomes rate determining (see eq 77). The values of k_{11} are within the expected range and in good agreement with corresponding data in Table XXXIII. The activation parameters for β-$\mathrm{Co(edda)CO_3}^-$ fall on the isokinetic plot in Figure 7, but those for Co(nta)-$\mathrm{CO_3}^{2-}$ and α-$\mathrm{Co(edda)CO_3}^-$ do not fit this relationship. In the latter cases, k_{11} is very large indeed, which indicates that some form of specific interaction, probably involving the amido group cis to the bicarbonato ligand, which hinders the decarboxylation process in the majority of cases but does not occur in these systems.[341]

(3) **Acid-Catalyzed Aquation of Bridged Carbonato Complexes.** The examples in the previous two subsections clearly illustrate that mono- and bidentate carbonato complexes exhibit completely different acid-catalyzed aquation kinetics (compare eq 74 and 75). The question remains, how do bridged carbonato complexes behave under such conditions?

Wieghardt and co-workers[345,346] recently reported the syntheses and X-ray analyses of two carbonato-bridged complexes, viz. (see Table XXI)



M = Cr(III), Rh(III)

The acid-catalyzed aquation of these complexes was studied[345] to clarify their structural habit in aqueous solution. The data underline the typical bidentate character of the carbonate ligand and the results are included in Tables XXXIV and XXXV. The Cr(III) complex exhibits a strong contribution from the "water-catalyzed" reaction path.

Dasgupta and co-workers[347] recently reported the isolation and structure of two binuclear Co(III) complexes containing carbonate as a bridging group. The acid-catalyzed aquation of $(NH_3)_5Co(\mu\text{-}CO_3)Co(NH_3)_5{}^{4+}$ produces kinetic data[348] identical to that for $Co(NH_3)_5OCO_2{}^+$.[348] These results are in disagreement with those reported above for the Rh(III) and Cr(III) bridged species,[345] so that it is doubtful whether the Co(III) bridged species really exists in this form in aqueous solution. Preliminary measurements[349] on the acid-catalyzed aquation of $(NH_3)_3Co(\mu\text{-}OH)_2(\mu\text{-}CO_3)Co(NH_3)_3{}^{2+}$ gave kinetic data similar to that reported for the Rh(III) and Cr(III) bridged species,[350] thus emphasizing the bidentate character of the carbonato ligand.

(4) **Base-Catalyzed Aquation of Carbonato Complexes.** In contrast to acid-catalyzed aquation studies, relatively little has been reported on the base-catalyzed aquation reactions of carbonato complexes. In one of the first studies Francis and Jordan[321] suggested that $Co(en)_2CO_3{}^+$ undergoes hydrolysis according to a two-step process in which first the intermediate $Co(en)_2(OH)OCO_2$ is produced, followed by loss of carbonate to form $Co(en)_2(OH)_2{}^+$. Their kinetic data suggested a mechanism as outlined in eq 81 for which $k_{obsd} = k_{-14}$

$$Co(en)_2CO_3{}^+ + H_2O \underset{k_{-13}}{\overset{k_{13}}{\rightleftharpoons}} Co(en)_2(OH)OCO_2 + H^+$$

$$Co(en)_2CO_3{}^+ + OH^- \underset{k_{-14}}{\overset{k_{14}}{\rightleftharpoons}} Co(en)_2(OH)OCO_2 \qquad (81)$$

$+ k_{-13}[H^+] + k_{13}[H_2O] + k_{14}[OH^-]$. The magnitude of the various rate constants in (81) and their activation parameters could be estimated[321] from the pH dependence of k_{obsd}. Typical values for k_{14} and k_{-14} are 3.2 $\times 10^{-3}$ M^{-1} s^{-1} and 6.5 $\times 10^{-5}$ s^{-1} at 26 °C, respectively.[321] An ^{18}O tracer study showed that the k_{14} path proceeds with Co–O bond cleavage. Endicott and co-workers[351] reported a similar finding for the base-catalyzed aquation of $Co(Me_6[14]dieneN_4)CO_3{}^+$ and three different isomeric $Co(Me_6[14]aneN_4)CO_3{}^+$ species. Both the ring-opening and subsequent decarboxylation reactions were studied in detail[351] and exhibit an $[OH^-]$ dependence of the general form:

$$k_{obsd} = k_{15}' + k_{15}''[OH^-] + k_{15}'''[OH^-]^2 \qquad (82)$$

The authors offer a thorough discussion of various possible reaction routes, including the role of ligand stereochemistry in determining the net reactivity in terms of nucleophilic scavenging of the five-coordinate ring-opened intermediate.

Base-catalyzed aquation of $Co(tren)CO_3{}^+$ was reported[352] to include two ring-opening (Co–O bond breakage) reactions, similar to those outlined in (81), followed by

$$Co(tren)(OH)OCO_2 + OH^- \xrightarrow{k_{16}} Co(tren)(OH)_2{}^+ + CO_3{}^{2-} \qquad (83)$$

The reported values of k_{13} for this complex are in very good agreement with those measured during the acid-catalyzed aquation reaction.[326] The rate and activation parameters for the base-catalyzed reactions were reported[352] to be $k_{14} = 3.6 \times 10^{-3}$ M^{-1} s^{-1} at 25 °C ($\Delta H^{\ddagger} = 72 \pm 8$ kJ mol^{-1}, $\Delta S^{\ddagger} = -50 \pm 25$ J K^{-1} mol^{-1}) and $k_{16} = 6 \times 10^{-5}$ M^{-1} s^{-1} at 40 °C ($\Delta H^{\ddagger} = 103 \pm 5$ kJ mol^{-1}, $\Delta S^{\ddagger} = -4 \pm 17$ J K^{-1} mol^{-1}). The authors conclude that reaction 83 includes the complete substitution of $CO_3{}^{2-}$ by OH^-, i.e., Co–O bond breakage. In a subsequent study,[325] the $[OH^-]$ dependence of k_{16} was investigated in more detail, and a "water-path" was detected kinetically for the substitution of carbonate in the $Co(tren)(OH)OCO_2$ species ($k = 1 \times 10^{-4}$ s^{-1} at 50 °C). Finally, no substitution of carbonate or loss of CO_2 was found in the base hydrolysis of *trans*-$Co(en)_2(Cl)OCO_2$.[353] The reaction product was *trans*-$Co(en)_2(OH)OCO_2$ under all conditions, and the kinetic data correlate well with those usually observed[354] for the hydrolysis of complexes of the type *trans*-$Co(en)_2(Cl)L^{n+}$. Finally, it should be noted that all the mentioned base-catalyzed aquation reactions are thought to proceed via a conjugate base mechanism.

C. Exchange, Substitution, and Isomerization Reactions

The previous review on the chemistry of metal carbonato complexes[1] included a detailed discussion on ligand and isotope exchange reactions in which deuterium, ^{14}C, and ^{18}O labeling was employed. Following a series of earlier studies, Harris et al.[355] reported a revised general mechanism for carbonate exchange reactions of complexes of the type $CoN_4CO_3{}^+$. In this they modified their earlier suggestion of a dual mechanism, partly dissociative and partly associative, to a dual dissociative path consisting of decarboxylation of the ring-opened monodentate carbonato species (reaction 84) and a dual associative path consisting of CO_2 uptake by the monodentates (reaction 85). In reference

$$CoN_4(OH_2)OCO_2H^{2+} \rightleftharpoons CoN_4(OH_2)OH^{2+} + CO_2$$

$$CoN_4(OH)OCO_2H^+ \rightleftharpoons CoN_4(OH)_2{}^+ + CO_2 \qquad (84)$$

$$CoN_4(OH)OCO_2H^+ + CO_2 \rightleftharpoons CoN_4(OCO_2H)_2{}^+$$

$$CoN_4(OH)OCO_2 + CO_2 \rightleftharpoons CoN_4(OCO_2H)OCO_2 \qquad (85)$$

to our earlier remarks[322] concerning the stability of protonated carbonato species, it is obvious that the bicarbonato products in (85) can only exist in the de-

TABLE XXXVII. Rate and Activation Parameters for Ring Closure in (Carbonato)diaminecobalt(III) Systems[a]

ligand	10^5C, s^{-1}	10^5D, $M^{-1}\ s^{-1}$	$\Delta H_C^{\ddagger}$, kJ mol^{-1}	$\Delta S_C^{\ddagger}$, J K^{-1} mol^{-1}	$\Delta H_D^{\ddagger}$, kJ mol^{-1}	$\Delta S_D^{\ddagger}$, J K^{-1} mol^{-1}
en	92 ± 3	208 ± 8	138 ± 8	159 ± 33	89 ± 3	0 ± 8
pn	30 ± 13	300 ± 30	196 ± 33	351 ± 125	49 ± 8	−130 ± 25
tn	19 ± 0.5	71 ± 3				

[a] At 25 °C taken from ref 365.

TABLE XXXVIII. Characteristic IR Absorption Bands for Metal-Carbon Dioxide Complexes

compound	ν_{CO_2}, cm^{-1}	ref
$[Ti(\eta^5\text{-}C_5H_5)_2]_2CO_2$	1440, 1360	407
$Mo(PMe_2Ph)_4(CO_2)_2$	1760, 1510, 1335	445
$Fe(PMe_3)_3(H)(PMe_2CH_2CO_2)$	1610, 1592, 1328	415
Co(pr-salen)(CO_2)(K)(THF)[a]	1650 s, 1280 ms, 1215 s, 745 s	431
Co(pr-salen)(CO_2)(Na)	1680, 1278, 1213	470
Co(pr-salen)(py)(CO_2)(Na)	1700, 1273, 1208	470
$Rh_2(PPh_3)_5(Cl)_2CO_2$	1630	408
$Rh(CO)(OH)(PPh_3)_2CO_2$	1966 vs, 1620 s, 1351 s, 821 s	452
	1602, 1351, 821	453
$Rh_2(PPh_3)_3(H)_2(Cl)_3(CHCl_2)CO_2 \cdot CHCl_3$	1480, 1430, 1380, 1270, 1175, 1090, 1000, 975 857, 765, 745, 725, 705, 695	409
$Rh_2(PPh_3)_3(Me)(H)(Cl)_5CO_2$	1480, 1430, 1380, 850, 760, 740, 690	409
Rh(diphos)(Cl)CO_2[b]	1712	*c*, *d*
Rh(Cl)(PNP)CO_2[e]	1660 vs, 1628 s	428, 455
$Rh(Cl)(PBu\text{-}n_3)_2CO_2$	1668, 1630, 1165, 1120	447
$Rh(Cl)(PEt_2Ph)_3CO_2$	1670 vs, 1635 sh, 1255 m, 963 m, 780 m	447
$Rh(Cl)(PEt_2Ph)_2CO_2$	1658 vs, 1620 vs, 1238 m, 827 m	447
$Rh(Cl)(PMe_2Ph)_3CO_2$	1657 vs, 1627 vs, 1217 m, 996 m, 823 m	447
$Rh(Cl)(PMePh_2)_2CO_2$	1673 vs, 1635 sh, 1290 m, 1000 m, 822 m, 760 m	447
$Rh_2(PPh_3)_3(CO)_2(CO_2)_2 \cdot C_6H_6$	1600, 1355, 825	456
$Rh_2(PPh_3)_3(CO)_2CO_2 \cdot C_6H_6$	1498, 1368, 813	429
$Rh_2(H)_2(PPh_3)_6CO_2 \cdot C_6H_5CH_3$	1460, 1300	443, 457
$Ir(CO)(OH)(PPh_3)_2CO_2$	1636 m, 1310 s, 815 m	452, 453
$Ir(dmpe)_2(Cl)CO_2$[f]	1550, 1230	405
$Ni_2[P(C_6H_{11})_3]_4CO_2$	1735	467
$Ni[P(C_6H_{11})_3]_2CO_2 \cdot 0.75\ C_6H_5CH_3$	1740 vs, 1698 vw, 1150 s, 1094 ms, 845 s	430
$Ni(PEt_3)_2CO_2$	1660 vs, 1635 vs, 1203 vs, 1009 s, 828 s	426
$Ni(PBu\text{-}n_3)_2CO_2$	1660 vs, 1632 vs, 1200 vs, 1008 s, 825 s	426
$Pt(PPh_3)_2CO_2$	1640 s, 1370 s, 1320 s	408
$Pd(CH_3)(PEt_2)CO_2$	2610 w, 1610 s, 1350 s, 825 m	*g*
$Pd(CH_3)(PMePh_2)CO_2 \cdot (CH_3)_2CO$	2605 w, 1605 s, 1405 s, 1350 s, 835 m	*g*
$Pd(C_2H_4)(PEt_3)_2CO_2$	2600 w, 1630 s, 1350 s, 830 m	*g*
$Pd(C_2H_4)(PMePh_2)_2CO_2$	2600 w, 1605 s, 1400 s, 1360 s, 832 m	*g*
$Cu(CH_3COO)[P(C_6H_{11})_3]CO_2$	2600 m, 1610 s, 1420 m, 1380 s, 830 m, 650 m	424
$Cu(CH_3COO)(PPh_3)_2CO_2$	2620 w, 1600 vs, 1320 s, 821 m, 648 w	489
$Cu_2(PPh_3)_4CO_2$	1475 s, 1330 m, 835 w	406
Cu(eph)CO_2[h]	2350 m, 2380 s	461
Cu(eph)CO_2[h]	1549, 1344, 800	463
$[(C_6H_5)Ag(CO_2)Ag]_n$	1496 s, 1326 s, 828 s	471

[a] pr-salen = *N*,*N*′-ethylenebis(salicylideneiminato). [b] diphos = $(Ph)_2PCH_2CH_2P(Ph)_2$. [c] Albano, P.; Aresta, M.; Manassero, M. *Inorg. Chem.* 1980, *19*, 1069. [d] Albano, P.; Aresta, M.; Manassero, M. *Cong. Naz. Chem. Inorg.* 1979, 83. [e] PNP = 2,6-bis((diphenylphosphino)methyl)pyridine. [f] dmpe = $(CH_3)_2PCH_2CH_2P(CH_3)_2$. [g] Ito, T.; Tsuchiya, H.; Yamamoto, A. *Chem. Lett.* 1976, 851. [h] eph = $C_6H_5CH(OH)CH(NHCH_3)CH_3$.

protonated form. Analysis of the available kinetic data illustrated[355] that the above mechanism is valid for N_4 = $(NH_3)_4$, $(en)_2$, $(pn)_2$, $(tn)_2$, *cis*-$(NH_3)_2$en, *trans*-$(NH_3)_2$en, and *trans*-$(NH_3)_2$tn. Furthermore, this mechanism is also in line with the general mechanistic feature of metal carbonato complexes as discussed in parts A and B of this section.

In a later study, Francis and Jordan[340] compared the oxygen exchange kinetics of HCO_3^- and $Co(NH_3)_5OCO_2^+$. Their findings underline the earlier suggestion of Dasgupta and Harris[333] that the rates of oxygen exchange are controlled by the hydration of CO_2. Recently,[356] ^{13}C NMR techniques were employed to determine activation parameters for the carbonate exchange on the uranyl tris(carbonato) complex.

Relatively few studies have been reported on substitution reactions of metal carbonato complexes that involve replacement of the carbonato ligand itself. In some cases evidence for the occurrence of such reactions has been observed in the form of intermediate steps in substitution reactions of other complexes. For example, Sastri and Ramam[357] found that the rate of substitution of $Cr(C_2O_4)_3^{3-}$ by edta depended on the bicarbonate ion concentration. They suggested the formation of $Cr(C_2O_4)_3HCO_3^{4-}$ and $Cr(C_2O_4)_2HCO_3^{2-}$ intermediates, which can react with edta to give the observed reaction product. The remaining studies concerning the substitution amenability of $Co(CO_3)_3^{3-}$, a species whose complex chemical nature has been discussed before.[1,2,358] The stability of this species depends markedly on the temperature and bicarbonate concentration[359,360] and the occurrence of dimeric species has been suggested.[361] In the reaction of $Co(CO_3)_3^{3-}$ with ammonia, a blue *cis*-$Co(NH_3)_2(CO_3)_2^-$ species is produced, which was then believed to isomerize to the trans species.[359] However, a later study[362] confirmed that the trans solution is a mixture of the cis species and $Co(NH_3)_4(CO_3)^+$. In a similar way, the complexes $Co(DH)_2CO_3^-$

and $Co(DH)_2C_2O_4^-$ were prepared by substitution of $Co(CO_3)_3^{3-}$ with dimethylglyoxime (DH_2), producing the first complex, followed by reaction with oxalate to produce the second species.[363]

Davies and Hung[364,365] reported kinetic data for a series of substitution reactions of $Co(CO_3)_3^{3-}$ with py, en, pn, and tn. They found that solutions of $Na_3[Co(CO_3)_3]\cdot 3H_2O$ in 0.1–1.0 M sodium bicarbonate are stable under ordinary laboratory conditions, and used the latter for their mechanistic studies. This solution reacts with py[364] to produce *cis*-$Co(py)_2(CO_3)_2^-$ and no evidence for the formation of the trans isomer[366] could be found. The suggested mechanism includes two rapid equilibrations in which HCO_3^- stabilizes the $Co(CO_3)_3^{3-}$ species[358]

$$Co(CO_3)_3^{3-} + H_3O^+ \xrightleftharpoons{\text{fast}} Co(CO_3)_2(OCO_2H)(H_2O)^{2-} \quad K_h$$

$$Co(CO_3)_2(OCO_2H)(H_2O)^{2-} + H_2O \xrightleftharpoons{\text{fast}} Co(CO_3)_2(H_2O)_2^- + HCO_3^- \quad K_{H_2O}$$

$$Co(CO_3)_3^{3-} + py \xrightarrow{k_{17}} Copy(CO_3)_2(OCO_2)^{3-}$$

$$Co(CO_3)_2(OCO_2H)(H_2O)^{2-} + py \xrightarrow{k_{18}} Copy(CO_3)_2(OCO_2H)^{2-} + H_2O$$

$$Co(CO_3)_2(H_2O)_2^- + py \xrightarrow{k_{19}} Copy(CO_3)_2(H_2O)^- + H_2O$$

$$Copy + py \xrightarrow{\text{fast}} Co(py)_2(CO_3)_2^- \qquad (86)$$

where Copy represents all the monosubstituted pyridine species. This mechanism is in line with the empirical rate law

$$k_{\text{obsd}} = \left[\frac{A[H^+] + B[H^+]/[HCO_3^-]}{1 + C[H^+]}\right][py] \qquad (87)$$

from which it follows that $k_{17} \leq 7 \times 10^{-3}$, $k_{18} = A/C = (2.2 \pm 0.3) \times 10^{-2}$, $k_{19} \geq 0.17\ M^{-1}\ s^{-1}$, $K_h = (1.3 \pm 0.1) \times 10^9\ M^{-1}$, and $K_{H_2O} \leq 6 \times 10^{-2}$ M at 25 °C and an ionic strength of 1.0 M. The ratio $[Co(CO_3)_2(HCO_3)(H_2O)^{2-}]/[Co(CO_3)_3^{3-}]$ varied from 0.2 to 12.4 over the range of experimental conditions. The indication that $k_{19} >> k_{18}$ suggests that the aquo ligands are more readily replaced by pyridine than is coordinated carbonate.

In their subsequent study,[366] the formation of chelated $Co(diamine)(CO_3)_2^-$ complexes was found to proceed via unusually stable, half-bonded diamine species. The formation of these intermediates was suggested to occur via an associative interchange mechanism for en or pn as the diamine ligand.

$$Co(CO_3)_3^{3-} + H_3O^+ \xrightleftharpoons{\text{fast}} Co(CO_3)_2(HCO_3)(H_2O)^{2-}$$

$$Co(CO_3)_3^{3-} + L\text{-}L \xrightleftharpoons{\text{fast}} \{Co(CO_3)_3^{3-}\cdot L\text{-}L\}$$

$$Co(CO_3)_2(HCO_3)(H_2O)^{2-} + L\text{-}L \xrightleftharpoons{\text{fast}} \{Co(CO_3)_2(HCO_3)(H_2O)^{2-}\cdot L\text{-}L\}$$

$$\{Co(CO_3)_3^{3-}\cdot L\text{-}L\} \xrightarrow[H^+]{k_{20}} Co(L\text{-}L)(CO_3)_2(HCO_3)^{2-}$$

$$\{Co(CO_3)_2(HCO_3)(H_2O)^{2-}\cdot L\text{-}L\} \xrightarrow{k_{21}} Co(L\text{-}L)(CO_3)_2(HCO_3)^{2-} + H_2O \qquad (88)$$

The kinetic data fit the empirical rate law

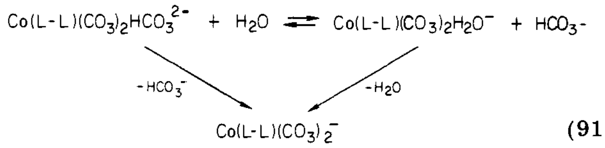
$$k_{\text{obsd}} = A[H^+]/(1 + B[H^+]) \qquad (89)$$

from which it follows that the precursor complex formation constants are of the order of $2 \times 10^3\ M^{-1}$, $k_{20} \leq 0.1$, and $k_{21} = 6\ s^{-1}$ at 25 °C and an ionic strength of 1.0 M. Alternatively, the [L-L] independence of k_{obsd} could point to a dissociative mechanism in which a five-coordinate intermediate $Co(CO_3)_2(HCO_3)^{2-}$ reacts with the diamine.

The subsequent ring-closure reactions follow the rate law

$$k_{\text{obsd}} = C + D[HCO_3^-] \qquad (90)$$

for which the rate and activation parameters are summarized in Table XXXVII. The suggested mechanism consists of the reactions:



(91)

In the case of L-L = en or pn, evidence for higher order ammine complex formation was presented.[366]

More recently[367] it was reported that sulfite reacts with $Co(CO_3)_3^{3-}$ to produce two products, viz., either $Co(CO_3)_2(OH_2)SO_3^{3-}$ or $Co(CO_3)_2(HCO_3)SO_3^{4-}$, and subsequently a bis(sulfito) species. The rate of the first step ($k = (1.6 \pm 0.2) \times 10^{-2}\ M^{-1}\ s^{-1}$ at 25 °C, pH = 9.52 and an ionic strength of 1.75 M) is in good agreement with the value of k_{18} (reactions 86) reported for the substitution by py,[364] such that a similar type of mechanism is probably operative. The rate of the second step is independent of $[SO_3^{2-}]$, and therefore requires either ring opening trans to the first sulfite group or loss of H_2O or HCO_3^- cis to it to be rate determining.

A number of studies have reported kinetic data on isomerization reactions of carbonato complexes that involve the geometrical rearrangement of a chelated ligand present in such systems. Dasgupta and Harris[368] reported data for the α to β isomerization of $Co(trien)CO_3^+$. The pH dependence of the process suggests that the α complex produces the ring-opened species α-*cis*-$Co(trien)(OH_2)OCO_2^+$ that can either isomerize directly or via its hydroxo form to the ring-opened β analogue, followed by ring closure. The observed rate constants vary between 1×10^{-4} and 3×10^{-4} s^{-1} at 55 °C depending on the pH (7 and 10, respectively) of the solution. A similar α to β isomerization process was found to occur for the $Co(edda)CO_3^-$ species,[341,369] with rate constants of the order of 3×10^{-4} s^{-1} at 30 °C. This reaction presumably also includes the formation of a ring-opened carbonate species prior to the isomerization step.

D. Miscellaneous Reactions

In this section we cover photochemical, radiochemical, redox, and catalytic reactions of metal carbonato complexes.

Hoffman and co-workers[370-378] have reported a series of papers on the continuous and flash photolysis of some carbonato–ammine Co(III) complexes. Continuous irradiation[373] at 254 nm of solutions of $Co(NH_3)_5OCO_2^+$, $Co(NH_3)_4CO_3^+$, and $Co(en)_2CO_3^+$ resulted in partial photoaquation and photoredox reactions. For irradiation of the $Co(NH_3)_4CO_3^+$ complex, $Co(NH_3)_4(H_2O)_2^{3+}$ was identified as the aquation product, and $\Phi_{aq} = 0.11 \pm 0.03$ and $\Phi_{Co^{2+}} = 0.07$ at pH 6.4 and 25 °C. This observation added ring opening, followed by aquation, to the list of processes that can result from charge-transfer excitation of Co(III) complexes. It was further reported[373] that the presence of O_2 had no effect on the values of $\Phi_{Co^{2+}}$, but that 1 M 2-propanol in the absence of O_2 caused the quantum yield to double. This was considered as evidence that the CO_3^- radical is scavenged to generate the $(CH_3)_2\dot{C}OH$ radical, since the latter is known to be a good reducing agent[379] capable of converting Co(III) complexes to Co^{2+}(aq) with rate constants in the order of 10^7–10^9 M^{-1} s^{-1}.[19,380] In this way the oxidizing CO_3^- radical is converted into a reducing radical and $\Phi_{Co^{2+}}$ is doubled.

The flash photolysis[373] of the above-mentioned complexes generated the CO_3^- radical, and a long-lived transient species in the case of $Co(NH_3)_4CO_3^+$ and $Co(en)_2CO_3^+$. This was shown to be an aquo–carbonato species produced during ring opening of the carbonate ligand. $Co(NH_3)_5OCO_2^+$ did not yield this intermediate and there was no evidence to indicate that photoaquation occurs. In general the authors[373] reported a good correlation with the ground-state aquation reactions of metal carbonato complexes (subsection B). They propose that excitation of the complexes produces a charge-transfer singlet state, which generates, via radiationless transition, the charge-transfer triplet state and a ligand excited state. The charge-transfer triplet state is the precursor to the redox reaction, whereas protonation of the carbonato ligand in the ligand excited state is viewed as causing ring opening and aquation.

One study[381] has come to our attention in which $Pt(PPh_3)_2CO_3$ reacts either thermally or photochemically in alcoholic solvents to produce $Pt(PPh_3)_2$ in situ and the release of an equimolar amount of CO_2, whereas another study[382] reports the reaction between $Pt(PPhMe_2)_2CO_3$ and triorganotin hydrides.

It has, in general, been shown that Co(II) is produced during γ irradiation of Co(III) complexes. An ESR study[383] demonstrated that this is also true for the γ irradiation of $Co(NH_3)_4CO_3^+$. In a pulse radiolysis study,[384] aquated electrons (e^-_{aq}) were allowed to react with $NpO_2(CO_3)_3^{4-}$, $NpO_2(CO_3)_2^{3-}$, $Np(CO_3)_5^{6-}$, and $PuO_2(CO_3)_3^{4-}$, and rate constants between 2×10^9 and 2×10^{10} M^{-1} s^{-1} were reported. Calculations indicated that the reaction of e^-_{aq} with the $MO_2(CO_3)_3^{4-}$ species (M = Np(VI), Pu(VI)) is diffusion controlled. Similarly, the rate constant for the reaction of e^-_{aq} with $UO_2(CO_3)_3^{4-}$[385] was reported[386] to be $(1.32 \pm 0.01) \times 10^{10}$ M^{-1} s^{-1}.

Redox reactions of metal carbonato species were induced either electrochemically or photochemically. Cyclic chronopotentiometry[387] was used to elucidate the complex reaction sequence of uranium(V) in bicarbonate–carbonate solutions. The following reaction scheme was suggested for the reduction of $UO_2(CO_3)_3^{4-}$:

$$UO_2(CO_3)_3^{4-} + e^- \rightarrow UO_2(CO_3)_3^{5-}$$

$$UO_2(CO_3)_3^{5-} + HCO_3^- \rightleftarrows UO_2(HCO_3)(CO_3)^{2-} + 2CO_3^{2-}$$

$$UO_2(CO_3)_3^{5-} + UO_2(HCO_3)(CO_3)^{2-} \rightarrow UO_2(CO_3)_3^{4-} + UO_2(HCO_3)(CO_3)^{3-}$$

$$UO_2(HCO_3)(CO_3)^{3-} \rightarrow \text{to stable U(IV) species} \qquad (92)$$

With the aid of ac polarography, Matusinovic and Smith[388] obtained rate constants for the homogeneous reduction of pentaamminecobalt(III) complexes by Eu(III), and reported a value of 4.5 M^{-1} s^{-1} at 25 °C for the reduction of $Co(NH_3)_5OCO_2^+$. Keenan and coworkers[389,390] have studied a series of $M/MO/CO_3^{2-}/CO_2$ electrodes at 350 °C in fused KNO_3. Two types of reactions were found:

$$M + CO_3^{2-} \rightarrow MO + CO_2 + 2e^-$$

$$M = \text{Co, Ni, Pd, Pt}$$

$$MO + CO_3^{2-} \rightarrow M + CO_2 + O_2 + 2e^- \qquad (93)$$

$$M = \text{Fe, Zn, Ag, Ta, Cu}$$

The authors[390] find a direct correlation between the crystal field stabilization energies of the metal carbonato complexes and the above classification (93) of the metals into the two distinct types of reactions. This supports their hypothesis that metal carbonato complexes are the critical species in these electrode reactions. Photoinduced electron transfer was found[391] to occur between $Os(bpy)_3^{2+}$ and $Co(NH_3)_5OCO_2^+$ at a rate of 1×10^8 M^{-1} s^{-1}, which was estimated using the lifetime of the osmium species as 19.2 ns.

A few studies have been reported in which metal carbonato species exhibit catalytic effects. It was found[392] that $Mn(HCO_3)^+$ and $Co(HCO_3)^+$ catalyze the decomposition of hydrogen peroxide. The catalytic activity of such complexes can be arranged in the sequence Mn(II) > Co(II) > Ni(II) > Cu(II). Das and De[393] reported that complexes of the type $Co(N_4)CO_3^+$ catalyze the reduction of nitrobenzene by $NaBH_4$, and this activity was ascribed to the different oxidation state in which cobalt is capable of existing.

Many systems have been reported in which CO_2 or CO_3^{2-} exhibit catalytic properties in a variety of reactions. For instance, CO_2 was found to catalyze the exchange of oxygen with $Cr(NH_3)_5OH^{2+}$ in aqueous solutions,[394] and the rate law was of the form

$$\text{exchange rate} = k_{22}[Cr(NH_3)_5OH^{2+}] + (k_{23} + k_{24}[CO_2])[Cr(NH_3)_5OH^{2+}] \qquad (94)$$

At 25 °C and an ionic strength of 0.1 M, $k_{22} = 6.3 \times 10^{-5}$ s^{-1}, $k_{23} = 17 \times 10^{-5}$ s^{-1}, and $k_{24} = 7$ M^{-1} s^{-1}. A mechanism involving the formation of a carbonato–Cr(III) complex followed by quite rapid scrambling of the oxygen atoms was suggested to account for the obtained data. Similarly, substitution of $Cr(ox)_3^{3-}$ by edta was found[395] to be catalyzed by HCO_3^-, and the formation of intermediate carbonato complexes was suggested (see subsection C).

The ability of HCO_3^- to donate or accept protons has been considered to be responsible for its catalytic effects in a number of reactions. For instance, the reaction between Cr(III) and edta is suggested[396] to involve proton acceptance by HCO_3^-; the catalytic effect of HCO_3^- during the complexation of Cr(III) with some aminopolycarboxylic acids was ascribed[397] to the enhancement of the deprotonation rate of the ion-pair intermediate, since HCO_3^- is a more effective Lewis base; the transfer of a proton from HCO_3^- to Ni(H_{-2}DGEN) is considered to account for the catalytic effect during the substitution reaction of the Ni(II) complex with edta (DGEN = *N*,*N*′-diglycylethylenediamine).[398] Ion-pair formation, in addition to the proton donation/acceptance phenomenon, was suggested to account for the catalytic effects of HCO_3^- and CO_3^{2-} in the intramolecular hydrolysis of glycinamide and glycine dipeptides coordinated to Co(III).[399] In one study, such ion-pair formation was found to retard the base hydrolysis of $Co(NH_3)_5C_2O_4H^{2+}$.[400]

It is apparent from the overall discussion and data presented in this section that the kinetic systems discussed are well understood and there is little need to pursue such investigations much further. Unresolved questions do remain in the application of similar processes in the geochemical and biochemical fields (see sections XII and XIII).

The Chemistry of Metal–Carbon Dioxide Complexes

In the previous sections we have dealt with the chemistry of metal carbonato complexes. These were mainly produced via CO_2 uptake by metal hydroxo species, during which the metal–oxygen bond remained intact. In this section we summarize the chemistry of metal–carbon dioxide complexes in which CO_2 interacts directly with the metal center during either a fixation or insertion process.

It is generally accepted that little is known about the reactions of CO_2 with transition-metal compounds, and their role in the reduction of CO_2.[401-404] The interest in the potential chemistry of CO_2 has been stimulated by the search for alternative petrochemical feedstocks,[405-407] and the investigation of the water-gas shift reaction.[404] In this respect CO_2 is the largest carbon source in the world:[401,408] ca. 330 ppm, i.e., 2.3×10^{12} tons in the atmosphere,[409] which is expected to increase during the coming years.[6,8,410-412] CO_2 has some important functional properties[401] (carbon is a Lewis acid and oxygen a Lewis base) that influence its coordination to metal centers.[408,413-415] In general, coordination activates ligands and creates favorable steric conditions for ligand interactions and numerous catalytic processes (ref 401, 404, 405, 408, 415–418). Questions that arise[401] are: does CO_2 coordination agree with real activation; what bonding modes are possible; what reaction routes do the different bonding modes prefer; are these influenced by the nature of the metal complex?

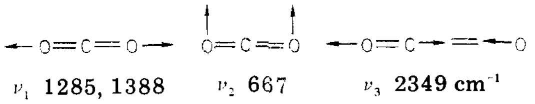
Some excellent reviews (ref 3, 401, 406, 408, 413, 414, 419, 420) have appeared in the literature, describing the reactions of transition-metal–CO_2 complexes. We, therefore, do not intend to give a complete survey of this topic, but rather to summarize those aspects of this field that bear on the chemistry of metal carbonato complexes. In the coming sections we will differentiate between fixation and insertion processes, although it is not always possible to distinguish between them completely since many insertion reactions proceed via a "fixation" intermediate. Furthermore, many systems are described as fixation processes, but really involve insertion reactions.[416,421-423] It follows that this differentiation is somewhat artificial, and we therefore classify all processes in which CO_2 is bound directly to the metal center as fixation, and those in which CO_2 is bound via the breakage of a metal–ligand or internal ligand bond, as insertion. In this sense CO_2 uptake by metal hydroxo complexes, as described in the previous section, can also be classified as an insertion reaction. However, for such uptake processes it was illustrated that the metal–oxygen bond remains intact, in contrast to the reactions reported in the forthcoming subsection on insertion processes.

IX. Preparation and Characterization

When reviewing the literature on metal–CO_2 complexes, one immediately realizes that fairly simple synthetic procedures are usually employed. These vary from bubbling CO_2 into a solution of the metal compound[403,413,424] to heating the complex in an autoclave under a CO_2 pressure of 10–15 atm.[405,425] Usually a CO_2 atmosphere[402,415,426] or a solvent saturated with CO_2[405,427,428] satisfies the required conditions for effective synthetic work. In some cases[413,429] metal–CO_2 complexes are prepared via the oxidation of a carbonyl ligand by oxygen. Alternatively, CO can sometimes be used to synthesize CO_2 complexes.

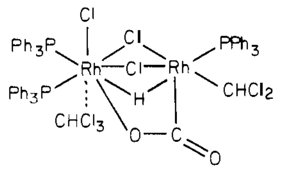
Characterization of metal–CO_2 complexes and CO_2 insertion products is usually done with IR and NMR spectroscopy. For some crystalline species, X-ray structure analyses were performed. To our knowledge the structures of two metal–CO_2 complexes have been resolved, viz. $[Ni(CO_2)\{P(C_6H_{11})_3\}_2]\cdot 0.75MePh$[430] and $[Co(pr\text{-}salen)(CO_2)K(THF)]_n$[431] (pr-salen = *N*,*N*′-ethylenebis(salicylidenaminato)). In the former, CO_2 is coordinated to the metal center in a η^2 mode, whereas in the latter species CO_2 is coordinated via the carbon atom to the Co(I) center. Numerous structures of CO_2 insertion products have been determined,[402,403,432-440] and these will be referred to in more detail in the section on CO_2 insertion reactions.

IR data have contributed significantly towards the characterization of metal–CO_2 complexes, and a summary of typical CO_2 vibrations in such complexes is given in Table XXXVIII. These can generally[3] be ascribed to 1500–1700 cm^{-1} for $\nu_{OCO}{}^{as}$; 1200–1400 cm^{-1} for $\nu_{OCO}{}^{s}$; around 1750 cm^{-1} for $\nu_{C=O}$; around 1150 cm^{-1} for $\nu_{C-O}{}^{as}$; 1750–1900 cm^{-1} for M–$\pi(CO_2)$; and around 820 cm^{-1} for $\nu_{C-O}{}^{s}$. In comparison, it should be kept in mind that gaseous CO_2 is a linear $D_{\infty h}$ triatomic molecule with three fundamental modes of vibration[441]



These are referred to as symmetric (ν_1) and asymmetric (ν_3) CO stretching modes, and ν_2 as the degenerate CO deformational mode (see section IIA).

In some cases NMR spectroscopy could be applied with success to elucidate the structure of metal–CO_2 complexes. Karsch[415] reported the application of ^1H and ^{31}P NMR to determine the structure of $Fe(PMe_3)_4CO_2$ and $Fe(PMe_3)_3(PMe_2CH_2CO_2)$. In another study, Yamaguchi[409] reported the ^1H NMR signals for the complex.

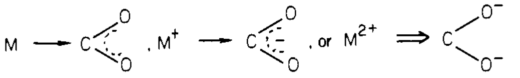


NMR spectroscopy has been used for the characterization of numerous CO_2 insertion products, and these will be referred to in more detail in the appropriate subsection.

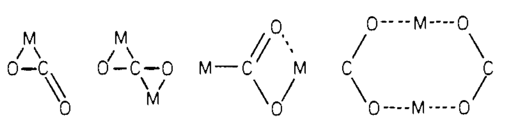
X. Carbon Dioxide Fixation Reactions

In general there is a paucity of information concerning CO_2 fixation reactions and other metal-promoted transformations,[402,442] although simple CO_2 addition is assumed to be the first step in a number of reactions.[408,413,414,427,443-446] Metal basicity is an important prerequisite to M–CO_2 formation.[431] Highly basic Ir(I),[405,427] Rh(I),[447] and Ni(0)[426,430] complexes have been found to cause CO_2 activation. In several cases, CO_2 seems to require a bifunctional system, i.e., acid–base, for its fixation and activation.[402,448] Therefore, in addition to the basic metal center, the assistance of an acidic partner is required.[431] A new class of CO_2 reversible carriers, which contain CO_2 intact and closely approach the requirements of a bifunctional system was recently discovered.[402,431] In addition to the above-quoted examples, reactions of CO_2 with transition-metal complexes have resulted[403] in the formation of metal CO_2 species,[406,414,449,450] which will be discussed in more detail in this section.

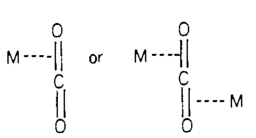
Various bonding modes of CO_2 to the metal M must be considered:[3,406,409,413,419] M–C bonding through electron donation from the metal,



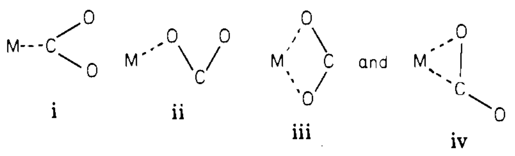
M–O bonding through transfer of the oxygen p electrons to the metal, M ← :O=C=O, M ←:O=C=O:→ M,



or complex formation.



In a theoretical study,[451] four models for M–CO_2 bonding modes were considered.



MO LCAO calculations in the CNDO/2 approximation illustrate that model ii is least favorable and that model iv is most favorable. This prediction is in good agreement with the recent structural observations on two metal–CO_2 complexes.[430,431]

We now turn to a detailed discussion of CO_2 fixation reactions, and will subdivide the following subsections according to the central metal atoms. By far the most CO_2 fixation studies were performed on Rh and Ir complexes, with fewer on Cu and Ni, and very few on the remaining metals.

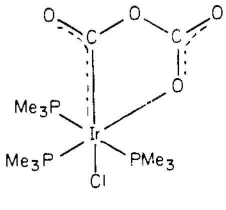
A. Rh–CO_2 Complexes

In the solid phase *trans*-$Rh(PPh_3)_2(OH)(CO)$ reacts with CO_2 gas to form $Rh(PPh_3)_2(OH)(CO)CO_2$, which loses CO_2 at reduced pressures.[452,453] Although the exact mode of coordination of CO_2 was not known at that stage, the investigators[452] found that on dissolution in methanol or acetone a bicarbonato species is produced, viz., $Rh(PPh_3)_2(CO)OCO_2H$. Later investigators[454] believed that the suggested change in coordination number (from 4 to 5) during the CO_2 fixation process is unreal and argue in favor of the direct formation of a bicarbonato complex, which would then be a typical insertion product. However, very recent studies report the formation of five-coordinate Rh–CO_2 complexes of the type $Rh(Cl)L_3CO_2$ and $Rh(X)L_4CO_2$ (L = phosphine or arsine, X = Cl or Br),[401] and $Rh(Cl)(PNP)CO_2$ (PNP = 2,6-bis((diphenylphosphino)methyl)pyridine).[428,455]

Evidence for the formation of bridged CO_2 complexes has also been reported. Iwashita and Hayata[429] found that $Rh_2(CO)_4(PPh_3)_4$ is easily oxidized by molecular oxygen to form $Rh_2(CO)_2(CO_2)(PPh_3)_3\cdot L_n$ (L = benzene, toluene, *o*-, *m*-, and *p*-xylene or mesitylene). Similar products were found by Vol'pin and co-workers,[456] where $[(PPh_3)Rh(CO)_2]_2\cdot C_6H_6$ was found to react with CO_2 in the presence of PPh_3 in benzene to produce $(PPh_3)_3Rh_2(CO)_2(CO_2)_2\cdot C_6H_6$. When air was passed through a benzene solution of this complex, CO_2 was released and $(PPh_3)_3Rh_2(CO)_2(CO_2)\cdot C_6H_6$ was produced, in agreement with the above species proposed by Vol'pin et al.[429] In another study,[457] it was found that CO_2 reacted with $Rh(H)(PPh_3)_4$ in toluene to produce $Rh_2(H)_2(PPh_3)_6(CO_2)\cdot$toluene, which released CO_2 when heated to 200 °C. Finally, Yamaguchi[409] showed that $(PPh_3)_3RhCl$ reacted with CO_2 in $CHCl_3$ to produce $(PPh_3)_3Rh_2(Cl)(\mu\text{-}Cl)_2(\mu\text{-}H)(\mu\text{-}CO_2)\cdot CHCl_3$, which could easily be converted to $(PPh_3)_3Rh_2(Me)(Cl)_3(\mu\text{-}Cl)_2(\mu\text{-}H)(\mu\text{-}CO_2)$.

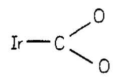
B. Ir–CO_2 Complexes

A series of Ir–CO_2 complexes have been reported in the literature that were prepared and characterized in a similar way as the corresponding rhodium complexes. These include $Ir(PPh_3)_2(OH)(CO)CO_2$[452,453] or $Ir(PPh_3)_2(CO)OCO_2H$,[454] and a series of complexes of the type $Ir(Cl)L_3CO_2$ and $Ir(X)L_4CO_2$[401] (see Rh–CO_2 section for abbreviations). A very interesting CO_2 fixation reaction was reported[427] for the species $Ir(Cl)(PMe_3)_3(C_8H_{14})$, which produces a novel CO_2 adduct with the structure:



It was suggested that stepwise uptake of CO_2 occurred and that $Ir(Cl)(PMe_3)_3CO_2$ is the reaction intermediate. Thermal decomposition of $Ir(Cl)(PMe_3)_3(C_2O_4)$ resulted in the formation of a carbonyl complex and a 1:1 Ir:CO_2 adduct. It was further suggested[427] that the formation of $Mo_2(PMe_2Ph)_6(CO)_2(CO_3)_2$ from *cis*-$Mo(N_2)_2(PMe_2Ph)_4$ and CO_2[445] may involve a similar mechanism as outlined above.

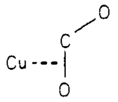
The importance of the basicity of the metal center was stressed by Bianco et al.,[458] who investigated the reaction of a series of Ir(I) and Ir(III) complexes with CO_2. They found that neither five- nor six-coordinated complexes reacted with CO_2, but that the more basic four-coordinated Ir(I) species produced CO_2 adducts from the species $Ir(OH)(CO)(PPh_3)_2$,[427] $Ir(L\text{-}L)_2Cl$ (L-L = $Me_2PCH_2CH_2PMe_2$, $Et_2PCH_2CH_2PEt_2$)[405] and $Ir(Cl)(PMe_3)_3(C_8H_{14})$.[427,459] Herskovitz[405] also reported a series of CO_2 adducts with Ir(I) complexes of the type $Ir(dmpe)_2Cl{\cdot}CO_2$ (dmpe = $Me_2PCH_2CH_2PMe_2$) and $Ir(diars)_2Cl{\cdot}CO_2$ (diars = *o*-phenylenebis(dimethylarsine)). The dmpe complex was found to dissolve in acetonitrile, acetone, and methylene chloride with liberation of CO_2. IR data are such that they favor an



bonding mode. Recently, the possible formation of complexes with CO_2 by the action of Lewis acids on $Ir(PPh_3)_2(CO)_2COOCH_3$ was reported.[460]

C. Cu–CO_2 Complexes

Quite some interest has been shown for the reversible CO_2 fixation by amino complexes of Cu(II). In earlier publications,[461,462] the formation of $Cu(Eph)_2{\cdot}CO_2$ (Eph = ephedrine) was reported. Later work[463] demonstrated that CO_2 formed an adduct with ephedrine, viz. $(Eph)CO_2$. IR and X-ray photoelectronic spectra[463] suggested that CO_2 entered into the coordination sphere of copper, that it was present in the bent form, probably



and that it formed an intramolecular hydrogen bond with the protons on Eph. A later ESR study[464] indicated that unstable carbamato structures are formed with reversible binding of CO_2. It attaches to Eph^- via the N–H bond to form a carbamate structure,[465] in contrast to the earlier claim[461,466] that CO_2 binds to the copper center.

For the reaction of $CH_3Cu^{I}P(C_6H_{11})_3$ with CO_2,[424] the formation of an insertion product $CH_3COOCuP(C_6H_{11})_3$ and an adduct $CH_3COOCu(CO_2)P(C_6H_{11})_3$ was reported. The latter species released CO_2 when heated to 150 °C. In another study,[450] $RCu(PPh_3)_2$ (R = Me, Et, *n*-Pr, *i*-Bu) was observed to react with CO_2 to produce an insertion/adduct product $(RCOO)Cu(CO_2)(PPh_3)_2$. Evidence for the formation of $Cu_2(CO_2)(PPh_3)_4$, where CO_2 is the bridging ligand, was also reported.[450]

D. Ni–CO_2 Complexes

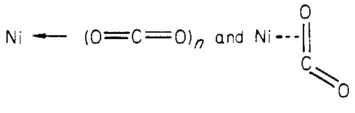
It is generally known that Ni(0) forms stable CO_2 complexes.[434,467] The first structure ever to be reported for a metal–CO_2 complex was for $Ni(PCy_3)_2(\eta^2\text{-}CO_2)$.[430] Later work[426] established that a common reaction could account for their formation, viz.

$$NiL_4 + CO_2 \rightarrow NiL_2(CO_2) \qquad (95)$$

for L = PEt_3, $PBu\text{-}n_3$ and $P(C_6H_{11})_3$.[430] The suggested mechanism[426] is

$$\begin{gathered} NiL_4 \xrightleftharpoons{\text{toluene}} NiL_3 + L \\ NiL_3 + CO_2 \rightleftharpoons NiL_3(CO_2) \\ NiL_3(CO_2) \rightleftharpoons NiL_2(CO_2) + L \qquad (96) \end{gathered}$$

Some matrix isolation experiments[416] demonstrated that two types of Ni–CO_2 complexes could be detected, viz.



Other studies indicated the possibility that CO_2 could act as a bridging ligand in Ni complexes.[450,467]

E. Other Metal–CO_2 Complexes

We will now present some information on the interaction of CO_2 with a wide range of metal clusters. Complexes of the type $M(CH_2Ph)_4$ (M = Ti, Zr) were found[425] to absorb 2 mol of CO_2 per mole of complex. Such fixation of CO_2 can proceed via an insertion process as found for

$$Ti_4(OEt)_{13}H + CO_2 \rightarrow Ti_4(OEt)_{13}(OOCH) \rightleftharpoons Ti_4(OEt)_{13}(CO_2)H \qquad (97)$$

The latter equilibrium has also been suggested for the formation of $Ru(H)(CO_2H)(PPh_3)_3$[408,443,468] and $Re(H)(CO_2)(Ph_2PCH_2CH_2PPh_2)_2$.[469]

The $Na(C_5H_5)Fe(CO)_2$ complex was found to undergo rapid CO_2 uptake in THF, followed by conversion (oxidation) to produce $[(C_5H_5)Fe(CO)_2]_2$, with the possibility that an adduct of the type $(C_5H_5)Fe(CO)_2CO_2^-$ is produced as an intermediate. A solution of Co(pr-salen)Na (see Table XXXVIII) was found[470] to react with CO_2 in THF to produce Co(pr-salen)(CO_2)Na, which loses CO_2 in vacuo. In the presence of pyridine a substance (py)Co(pr-salen)(CO_2)Na is produced. The X-ray structure of a very similar Co species was reported[431] (see earlier discussion). In these reactions it is possible that Na^+ acts as a Lewis acid in a concerted acid–base attack on CO_2 with Co(I) as the other partner.

One example exists in the literature[471] where a Ag complex, viz., $C_6H_5Ag{\cdot}nAgNO_3$, reacts with CO_2 in EtOH to produce $C_6H_5Ag(CO_2)Ag$. In another study[472] silver atoms were found to react with CO_2 at 10–25 K to produce $Ag(CO_2)$. Infrared, Raman, UV-visible spectroscopy and various molecular orbital calculations are in favor of an asymmetrically side-on bonded CO_2 complex, similar in nature to that reported[430] for the $Ni(CO_2)\{P(C_6H_{11})_3\}_2$ complex.

The $Pt(N_2O_2)(CO_2)(PPh_3)_2$ complex was suggested[473] to be the intermediate in the reaction

$$Pt(N_2O_2)(PPh_3)_2 + CO_2 \xrightarrow{\text{PhMe}} Pt(CO_3)(PPh_3)_2{\cdot}C_6H_5CH_3 + N_2O \qquad (98)$$

Theoretical predictions by Sakaki et al.[474] employing a CNDO-type semiempirical SCF-MO method lead to the conclusion that for Pt(0) complexes of the type $Pt(PPh_3)_2L$ (L = C_2H_2, C_2H_4, CS_2, CO_2) the s orbital of L contributes substantially to the Pt–L interaction, which suggests a large three-membered-ring type of interaction between Pt and L.

XI. Carbon Dioxide Insertion Reactions

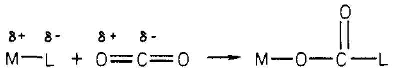
In contrast to N_2, CO_2 is rather reactive and can undergo insertion into a series of metal–ligand bonds.[413,414,442] The most common insertion reaction is found in the preparation of organic acids via the Grignard reagent (eq 99).[475] In this reaction the metal–carbon bond (Mg–R) is broken and CO_2 is inserted. Similar results have been observed with SO_2. Such insertion reactions play an important role in various catalytic processes. By analogy, the catalysis of CO_2 hydration[401] by the enzyme carbonic anhydrase, which is postulated to involve eq 100 (see section XIII) may be considered as a CO_2 insertion reaction, at least superficially.

$$RMgX + CO_2 \rightarrow RCO_2MgX \xrightarrow{H^+} RCO_2H \quad (99)$$

$$X = \text{halide}$$

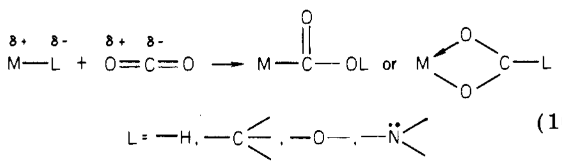
$$EnZnOH + CO_2 \rightleftarrows EnZnOCO_2H \quad (100)$$

In general, two possible insertion reactions can occur, depending on the nature of the metal–ligand bond[3,406,419]



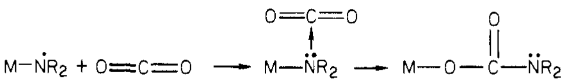
$$\overset{\delta+}{M}-\overset{\delta-}{L} + \overset{\delta+}{O}=\overset{\delta-}{C}=O \rightarrow M-O-\overset{\overset{O}{\|}}{C}-L$$

(101)



(102)

In many systems insertion is preceded by a fixation step, e.g.



$$M-\dot{N}R_2 + O=C=O \rightarrow M-\overset{\overset{O=C=O}{\uparrow}}{\ddot{N}R_2} \rightarrow M-O-\overset{\overset{O}{\|}}{C}-\ddot{N}R_2$$

(103)

The following presentation is subdivided according to the type of metal–ligand bond involved in the insertion reaction.

A. Insertion into M–H Bonds

A large number of papers has been published in recent years (ref 271, 403, 415, 419, 435, 442, 444, 476, 477) that stress the significance of CO_2 insertion reactions into M–H bonds. This aspect has also been covered by a number of review articles.[406,408,413,414,449] A summary of the different insertion reactions for various metal centers is given in Table XXXIX. The formation of cobalt-formato complexes has been suggested[421] to involve a CO_2 fixation step for different ligands L.[434,478,479]

$$\begin{array}{c} HCoL_4 + CO_2 \rightarrow HCoL_3(CO_2) + L \\ \downarrow \\ HCOOCoL_3 \end{array} \quad (104)$$

The species $HM(CO)_5^-$ (M = Cr, Mo, W) are the most prominent intermediates in the water-gas shift reaction. These react with CO_2 to produce formate species,[404] and therefore compete with bicarbonate complex formation.

Insertion of CO_2 into the Fe–H bond was suggested[271] to occur via a fixation step:

$$Fe(H_2)(N_2)L_3 + S \rightarrow Fe(H_2)(N_2)L_2S + L \xrightarrow{+CO_2}$$
$$Fe(H_2)(CO_2)L_2S + N_2 \rightarrow HCOOFe(H)L_2S \xrightarrow[+CO_2]{-S}$$
$$HCOOFe(H)(CO_2)L_2 \rightarrow FeL_2(HCOO)_2 \quad (105)$$

$$L = PEtPh_2, PBuPh_2; S = \text{solvent}$$

It was reported[480] that a rhodium-carbonyl complex is formed via CO_2 insertion into a Rh–H bond. The overall reaction is

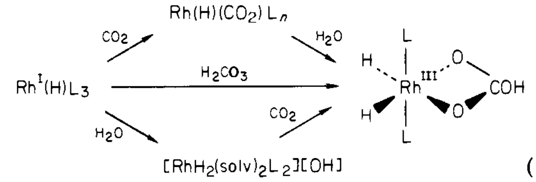
$$Rh(Cl)(PPh_3)_3 \xrightarrow[\text{HMPA, 100 °C}]{H_2\text{ (20 atm), }CO_2\text{ (20 atm)}} Rh(Cl)(CO)(PPh_3)_2 \quad (106)$$

and the suggested generalized mechanism can be formulated as

$$RhClL_3 \underset{L}{\overset{S}{\rightleftarrows}} RhClL_2(S) \xrightarrow{H_2} H_2RhClL_2(S) \xrightarrow{CO_2}$$
$$HRh(OOCH)ClL_2(S) \xrightarrow{H_2O}$$
$$S + HCOOH + HRh(OH)ClL_2$$
$$HCOOH \rightleftarrows H_2O + CO$$
$$RhClL_2(S) + CO \rightarrow RhCl(CO)L_2 + S \quad (107)$$

$$L = PPh_3; S = HMPA = \text{hexamethylphosphoramide}$$

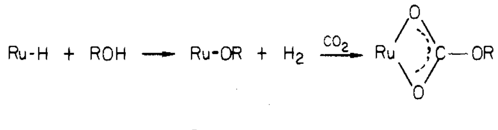
Ibers et al.[403] could not detect any formato product (insertion of CO_2) during the reaction of $Rh(H)L_3$ (L = $P(i\text{-}Pr)_3$, $PPh(t\text{-}Bu)_2$, $P(C_6H_{11})_3$) with CO_2. A bicarbonato product was isolated, viz., $(H)_2RhL_2(O_2COH)$, and the structure was determined for L = $P(i\text{-}Pr)_3$. Three possible reaction routes were suggested.



(108)

Which route dominates will depend on the experimental conditions. It was found[403] that the product is stable towards reductive elimination, and instead reduces CO_2 to give $Rh^I(CO)(O_2COH)L_2$. This step probably proceeds by CO_2 insertion leading to either $Rh(H)(CO_2H)(O_2COH)L_2$ or $Rh(H)(O_2CH)(O_2COH)L_2$, after which elimination of H_2O completes the reaction. The authors[403] stress the fact that no reaction between Rh(I)-hydride complexes and CO_2 occurs when H_2O is excluded.

Ashworth and Singleton[481] reported the formation of a bidentate carbonato complex $[Ru(O_2COR)(PMe_2Ph)_4]PF_6$ in the reaction of $[Ru(H)(PMe_2Ph)_5]PF_6$ with CO_2 in MeOH or EtOH. They suggest the following mechanism based on NMR and IR data.



(109)

B. Insertion into M–C Bonds

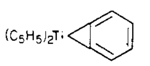
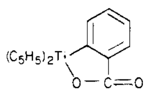
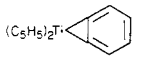
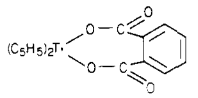
Various review papers (ref 406, 408, 413, 414, 419, 449) have treated typical CO_2 insertion reactions into

TABLE XXXIX. Insertion of CO_2 into M-H Bonds

metal center	reactant	product (P)	comments	ref
Co	$H(N_2)Co(PPh_3)_3$	$HCOOCo(PPh_3)_3$	$P \xrightarrow{CH_3I} HCOOCH_3$	408, 413, 414, 421, 478, 479
	$H(N_2)Co(PPh_3)_3$	$HOOCCo(PPh_3)_3$	$P \xrightarrow{CH_3I} CH_3COOH + CH_3COOCH_3$	408, 413, 414
	$H_3Co(PPh_3)_3$	$HCOOCo(PPh_3)_3$	$P \xrightarrow{CH_3I} HCOOCH_3$	408, 421, 479
	$H(N_2)Co(PPhEt_2)_3$	$HCOOCo(PPhEt_2)_3$	IR absorptions at 1610 and 1370 cm^{-1} for coordinated formate	421
	$H(N_2)Co(PPh_2Et)_3$	$HCOOCo(PPh_2Et)_3$		421
	$H_3Co(PPhEt_2)_3$	$HCOOCo(PPhEt_2)_3$		421
	$H_3Co(PPh_2Et)_3$	$HCOOCo(PPh_2Et)_3$		421
Cr	$HCr(CO)_5^-$	$HCOOCr(CO)_5^-$	IR and NMR evidence for formate species	404
Cu	$(HCuPPh_3)_6$	$HCOOCu(PPh_3)_2$	same product from Cu/formic acid reaction	*a*
Fe	$Fe(H_2)L'L_3$, $L' = H_2, N_2$, $L = PEtPh_2$	$(HCOO)_2FeL_2$	reaction occurs in solid state or in solution, IR indicates formate group	*b*
	$Fe(H_2)(N_2)L_3$, $L = PEtPh_2, PBuPh_2$	$(HCOO)_2FeL_2$	$Fe(H_2)L_4$ and $Fe(H_2)(L\text{-}L)_2$ do not react with CO_2	*c*
Rh	$Rh(H)(PPh_3)_n$, $n = 3, 4$	$Rh_2(O_2CO)(PPh_3)_5$	H_2O participates in the reaction	500
Ru	$Ru(H_2)(PPh_3)_4$ or $Ru(N_2)(H_2)(PPh_3)_3$ or $Ru(H_4)(PPh_3)_3$	$Ru(CO_2H)(H)(PPh_3)_3$	IR evidence for formato species	433
	$RuH_2(PPh_3)_4$	$(HCOO)Ru(H)(PPh_3)_3 \cdot C_6H_5CH_3$	reaction in toluene	443, 457, *d*
	$[Ru(H)(PMe_2Ph)_5]PF_6$	$[Ru(O_2COR)(PMe_2Ph)_4]PF_6$, $R = Me, Et$	reaction in MeOH or EtOH	481
Si	$HSiMeEt_2$	$HCOOSiMeEt_2$	in the presence of $RuCl_2(PPh_3)_3$, $RuH_2(PPh_3)_4$, or $Pd(PPh_3)_4$ as catalyst	*e*

[a] Beguin, B.; Denise, B.; Sneeden, R. P. A. *J. Organomet. Chem.* 1981, *208*, C18. [b] Bianco, V. D.; Doronzo, S.; Rossi, M. *J. Inorganomet. Chem.* 1972, *35*, 337. [c] Bianco, V. D.; Doronzo, S.; Gallo, N. *Inorg. Nucl. Chem. Lett.* 1980, *16*, 97. [d] Komiya, S.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* 1976, *49*, 784. [e] Koinuma, H.; Kawakami, F.; Kato, H.; Hirai, H. *J. Chem. Soc., Chem. Commun.* 1981, 213.

TABLE XL. Insertion of CO_2 into M-C Bonds

metal center	reactant	product (P)	comments	ref
Al	$AlEt_3$	Et_2AlO_2CEt	$P \xrightarrow{AlEt_3} Et_2AlOAlEt_2 + Et_3COAlEt_2$	475
Co	$(PPh_3)_2Co(CO)\cdot C_2H_5$	$(Ph_3P)Co(CO_3)_n(COOC_2H_5)$ $(Ph_3P)_2Co(OCOC_2H_5)_2$	CO_2 is released upon acidification	488
	$(PPh_3)_3Co(N_2)H +$ $H_2C = CHCHO$	$(Ph_3P)Co(CO_3)_n(COOC_2H_5)$, $(Ph_3P)_2Co(OCOC_2H_5)_2$	IR spectra characteristic for formulated products	487
Cu	$CH_3Cu(PPh_3)_2\cdot 0.5Et_2O$	$(CH_3COO)Cu(PPh_3)_2$	IR typical of acetate complex	489
	$CH_3CuP(C_6H_{11})_3$	$(CH_3COO)CuP(C_6H_{11})_3$	P obtained along with CO_2 adduct	424
	$PhC{\equiv}CCu\cdot(PBu\text{-}n_3)_2$	$PhC{\equiv}CCO_2Cu\cdot(PBu\text{-}n_3)_2$	process is reversible	422
	$RCuL_n$ $L_n = (PPh_3)_3; (PPh_3)_2\cdot 0.5Et_2O; R = Me$ $L_n = (PPh_3)_3; R = Et$ $L_n = (PPh_3)_2; R = n\text{-Pr}, i\text{-Bu}$	$(RCOO)Cu(PPh_3)_2$	all species identified as Cu(I) carboxylates from IR and NMR data	450
	$NCCH_2Cu\cdot(PBu\text{-}n_3)_x$	$NCCH_2CO_2Cu\cdot(PBu\text{-}n_3)_x$	process is reversible	490
Fe	$HFeCH_2CN(dmpe)_2$, $dmpe = Me_2PCH_2CH_2PMe_2$	$HFe(OOCCH_2CN)(dmpe)_2$	reaction performed in CH_3CN $P \xrightarrow[BF_3]{CH_3OH} NCCH_2COOMe$	485
Ir	$[Ir(PMe_3)_4]Cl$	$[Ir(H)(O_2CCH_2CN)(PMe_3)_4]Cl$	reaction performed in CH_3CN	*a*
Mn	Ph_2MnPCy_3	$(PhCOO)_2MnPCy_3$	same product from reaction with PhCOOH	*b*
Ni	$Ni(C_2H_5)_2bpy$	$(bpy)Ni(C_2H_5)(O_2CC_2H_5)$	$P \xrightarrow{CO_2} Ni(bpy)CO_3$	482
	$(bpy)Ni(C_2H_5)(O_2CC_2H_5)$	$Ni(bpy)(O_2CC_2H_5)_2$		482
	$Ni(\eta^3\text{-}2\text{-}CH_3C_3H_4)_2$	$\eta^3\text{-}2\text{-}CH_3C_3H_4Ni(OCOC_4H_7)PR_3$	reaction performed in the presence of PR_3, R = Me, Et	434, *c*
	$Ni(\eta^3\text{-}C_8H_{12})P(C_6H_{11})_3$	dimer and tetramer of $(C_6H_{11})_3PNiC_8H_{12}CO_2$	X-ray structure determined for both products	434
Pd	$(\eta^1,\eta^3\text{-}C_3H_5)_2Pd(PR_3)$, $R = CH_3, C_6H_{11}$	$(\eta^3\text{-}C_3H_5)Pd(O_2CC_3H_5)(PR_3)$		*c*
Rh	$(Ph_3P)_3RhPh$	$(Ph_3P)_3RhOOCPh$	crystals of $(Ph_3P)_3RhOOCPh\cdot 0.5C_6H_6$ were isolated	439
	$(C_6H_5)Rh(L\text{-}L)$, $L\text{-}L = Ph_2PCH_2CH_2PPh_2$	$(L\text{-}L)Rh(O_2C\text{-}C_6H_5)$	IR data suggest that the benzoate group is bidentate	*d, e*
Ti			structure confirmed by x-ray analysis[437]	413, 437
			formed in excess CO_2	408, 413
	$Ti(CH_2Ph)_4$	$(CH_2Ph)_3Ti(O_2CCH_2Ph)$	$P \xrightarrow{H^+} PhCH_2COOH$	408, 425
	$(C_5H_5)_2Ti(CH_3)_2$	$(C_5H_5)_2(CH_3)Ti(O_2CCH_3)$	$P \xrightarrow{CH_3OH} CH_3COOCH_3$	408, 425
	$(\eta^5\text{-}C_5H_5)_2Ti(\eta^3\text{-}C_4H_7)$	$(\eta^5\text{-}C_5H_5)_2Ti(O_2C\text{-}2\text{-}C_4H_7)$	$P \xrightarrow{HCl}$ 2-methyl-3-butenoic acid	*f*
Zn	$CH_3OZnOCH_3$	$CH_3OZnOCO_2CH_3$		491

[a] English, A. D.; Herskovitz, T. *J. Am. Chem. Soc.* 1977, *99*, 1648. [b] Maruyama, K.; Ito, T.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* 1979, *52*, 849. [c] Hung, T.; Jolly, P. W.; Wilke, G. *J. Organomet. Chem.* 1980, *190*, C5. [d] Albano, P.; Aresta, M.; Manassero, M. *Inorg. Chem.* 1980, *19*, 1069. [e] Albano, P.; Aresta, M.; Manessero, M. *Cong. Naz. Chem. Inorg.* 1979, 83. [f] Sato, F.; Iigima, S.; Sato, M. *J. Chem. Soc., Chem. Commun.* 1981, 180.

M-C bonds. Other authors (ref 403, 415, 419, 435, 442, 476, 477, 482) have especially stressed the significance of such reactions, which sometimes only occur as intermediate steps.[425,483] In a number of cases the reactions involve preliminary coordination of CO_2, followed by insertion[450,471,484,485] to produce a variety of products.[486] We summarize examples of these reactions in Table XL and make some comments concerning the chemistry involved.

Insertion of CO_2 into Co–C bonds follows two modes in which carboxylate and M–COOR fragments are formed.[487,488] By far the most M–C insertion reactions have been reported for copper complexes (see Table XL). The formation of acetate complexes via CO_2 insertion could be indicated by the isolation of similar products in the reaction with acetic acid.[489] In two cases, reversible insertion reactions occur with Cu complexes.[422,490] Similar reactions to those reported for $Ni(C_2H_5)_2bpy$[482] were found for the corresponding dimethyl complex. During the copolymerization of CO_2, the reaction of the Zn catalyst with CO_2 occurred in the following manner.[491]

$$Zn(C_2H_5)_2 + H_2O \rightarrow C_2H_5ZnOH + C_2H_6 \rightarrow C_2H_5(ZnO)_nH \xrightarrow{CO_2} \text{insertion products} \quad (110)$$

C. Insertion into M-N Bonds

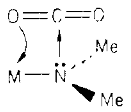
Relatively few systems have been presented where CO_2 insertion into M-N bonds occurs.[403,406,414,435,442,449] Representative examples are summarized in Table XLI. The most significant contribution in this area comes from Chisholm and Extine.[423,438,440,492-494] They isolated a series of carbamato complexes and determined the structure of some with X-ray diffraction data.[438,440,493] An interesting aspect reported by these authors is that

TABLE XLI. Insertion of CO_2 into M-N Bonds[a]

metal center	reactant	product (P)	comments	ref
Ti, V, Zr	$M(NMe_2)_4$	$M(O_2CNMe_2)_4$		423, 492, *a*
Ti	$Ti(NMe_2)_4$	$Ti(NMe_2)_n(O_2CNMe_2)_{4-n}$	X-ray structure of P for $n = 2$	493
Nb, Ta	$M(NMe_2)_5$	$M(O_2CNMe_2)_5$	X-ray structure of $Nb(O_2CNMe_2)_5$	423, 440, 492
W	$W(NMe_2)_6$	$W(NMe_2)_3(O_2CNMe_2)_3$	X-ray structure of P	438
	$W_2(NMe_2)_6$	$W_2(O_2CNMe_2)_6$		494
	$W_2(NMeEt)_6$	$W_2(O_2CNMeEt)_6$		494
Mo	$Mo_2(NMe_2)_6$	$Mo_2(NMe_2)_2(O_2CNMe_2)_4$	based on NMR evidence	*b*
	$Mo_2(NMe_2)_2(CH_2SiMe_3)_4$	$(Me_2N)(Me_2NCO_2)Mo_2(CH_2SiMe_3)_4$	based on NMR evidence	*c*
Hf	$Me_2Hf[N(SiMe_3)_2]_2$	$Me_2Hf[O_2CN(SiMe_3)_2]$	based on IR and NMR evidence	*d*
Mg	$(THF)Cl_2Mg_2MN$, $M = Ti, V$	$(THF)_3Cl_2Mg_2OM(NCO)$	reaction in THF	495, *e*
Pd	$PdMe_2L_2$, $L = PEt_3$, $PMePh_2$, PPh_3	$PdMe(O_2CNRR^1)L_2$, $R = H, Et$; $R^1 = Ph, Et, n\text{-}Bu, CH_2Ph$	$Pd_2Me_2(\mu\text{-}CO_3)(PPh_3)_3$ was isolated on heating corresponding P in toluene	*f*
P	$P(NMe_2)_nX_{3-n}$, $X = Cl, F$	$P(O_2CNMe_2)_nX_{3-n}$	characterized by IR and NMR	496
U	$(C_5H_5)_2U^{IV}(NEt_2)_2$	$(C_5H_5)_2U(O_2CNEt_2)_2$	characterized by IR and NMR	497

[a] See footnotes in Table XLII.

all the observed species are labile towards CO_2 exchange.[423,494] The complexes ML_n* ($n = 4, 5$—see Table XLI), W_2L_6*, and $W(NMe_2)_3L_3$* ($L = O_2{}^{12}CNMe_2$, $L^* = O_2{}^{13}CNMe_2$) react with $^{12}CO_2$ to give ML_n, W_2L_6, and $W(NMe_2)_3L_3$. It was found that mixtures of ML_n and ML_n* scramble CO_2 in the presence of a CO_2 atmosphere.[423,492] A plausible mechanism was suggested to be[423,440] $M(O_2CNMe_2)_n \rightleftarrows M(O_2CNMe_2)_{n-1}(NMe_2) + CO_2$ for which NMR evidence was presented for M = Nb.[440] Further evidence comes from mechanistic studies[493] in which the stepwise formation of such carbamato complexes could be observed and various models for CO_2 exchange were suggested. These insertion reactions differ from the other types discussed so far in that they are catalyzed by the presence of HNR_2. Insertion can therefore follow the normal mode[438]



or proceed according to[493]

$$CO_2 + HNR_2 \rightleftarrows HO_2CNR_2$$

$$M\text{-}NR_2 + HO_2CNR_2 \rightarrow MO_2CNR_2 + HNR_2 \qquad (111)$$

It should be mentioned that similar reactions were also observed for the insertion of COS and CS_2.[492,494]

Evidence has been presented[495] for the attack of CO_2 on N during insertion of CO_2 into the Mg-N bond, probably involving the intermediate

$$\text{—M—N—C(=O)—OMgCl}, \quad M = Ti, V$$

The insertion of CO_2 into P-N bonds of a series of species containing NMe_2 and $CH_3NCH_2CH_2NCH_3$ as ligands was also found to occur for COS and CS_2.[496] A similar result was obtained for the insertion into the U-N bond.[497]

D. Insertion into M-O Bonds

Insertion of CO_2 into M-O bonds results in the formation of carbonato or similar type complexes (ref 426, 427, 430, 445, 498–500). In section VIIIA the formation of carbonato complexes via CO_2 uptake by hydroxo ligands was discussed in detail. The latter reactions all proceed with retention of the M-O bond and therefore differ in principle from insertion type processes, although very similar reaction products may be formed.[501,502] Various papers have stressed the significance of CO_2 insertion reactions into M-O bonds (ref 403, 406, 408, 413–415, 435, 442, 449). A summary of such reactions is given in Table XLII.

Cupric methoxide exhibits reversible CO_2 fixation through insertion into the Cu-O bond.[503,504] Stability of the carbonato complexes can be controlled by the number of other ligands coordinated to the metal center. Insertion of CO_2 into Ir-O and Rh-O bonds[416] produces monodentate bicarbonato complexes, but it is uncertain whether this process involves M-O or O-H bond rupture, and whether CO_2 initially attacks the metal or the OH ligand. Such bicarbonato complexes have been shown to be unstable in an aqueous medium (see section VIIIB). A series of Mo complexes[435,505] exhibit completely reversible CO_2 insertion; the mechanism in the solid state proceeds via a direct attack on either M or OR, while the mechanism in solution is suggested to be

$$X\text{-}H + CO_2 \rightarrow XCOOH$$

$$X\text{-}H = \text{organic molecule}$$

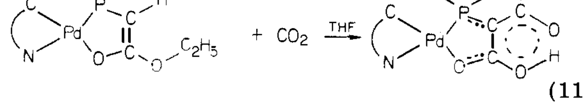
$$M\text{-}X + XCOOH \rightarrow M\text{-}O_2CX + X\text{-}H \qquad (112)$$

Identification of Rh-bicarbonato complexes[403,416] suggests that the previously supposed[452] CO_2 complex, viz., $Rh(PPH_3)_2(OH)(CO)(CO_2)$, is more in line with a bicarbonato complex (see Table XLII). The formation of the $Ti\text{-}CO_3$ species[402] is suggested to follow a route that corresponds to CO_2 disproportionation.[445,498,499]

$$2CO_2 + 2e^- \rightarrow CO_3{}^{2-} + CO \qquad (113)$$

E. Other Insertion Reactions

It was recently reported[436] that reversible CO_2 insertion into a Pd(II) complex occurred via carbon–carbon bond formation. This is the first example where reversible CO_2 fixation has been fully characterized by X-ray diffraction for C–N = 8-methylquinoline.



(114)

TABLE XLII. Insertion of CO_2 into M–O Bonds

metal center	reactant	product (P)	comments	ref
Fe, Ti, Nb, Zr, $n = 3, 4, 5, 4$, resp.	$M(OR)_n$	$M(OR)_{n-1}(O_2COR)$	analysis of P by IR	*g*
Cu	$Cu(OCH_3)_2$	$Cu(O_2COCH_3)_2$	in pyridine as solvent, reversible process	503
	(t-BuO)Cu(CN-t-Bu)	(t-$BuOCO_2$)Cu(CN-t-$Bu)_3$	in C_6H_6 as solvent, and in the presence of t-BuNC, reversible process	504
	$C_6H_5OCu(PPh_3)_2$	$[HOCO_2Cu(PPh_3)_2]_n$	reaction performed in moist THF	*h*
Ir	$(Ph_3P)_2(CO)Ir(OH)$	$(Ph_3P)_2(CO)Ir(OCO_2H)$	in C_2H_5OH as solvent	418
Mo	$Mo_2(OCH_2CHMe_3)_6$	$Mo_2(OCH_2CMe_3)_4(O_2COCH_2CMe_3)_2$	in hydrocarbon solvents, reaction is completely reversible	505
	$Mo_2(OR)_6$, R = Me_3Si, Me_3C, Me_2CH, Me_3CCH_2	$Mo_2(OR)_4(O_2COR)_2$	reaction occurs in solid state or in solution, IR and NMR characterization, X-ray structure for R = Me_3C	435
Rh	$Rh(CO)(OH)L_3$, L = $P(C_6H_{11})_3$, PPh_3	$L_3Rh(OCO_2H)(CO)$	IR characterization	403, 418, 501
Ti	$(C_5H_5)_2Ti(CO)_2$	$[((C_5H_5)_2Ti)_2CO_3]_2$		402
W	W_2(O-t-$Bu)_6$	W_2(O-t-$Bu)_4(O_2CO$-t-$Bu)_2$	process is reversible, toluene as solvent	494

[a] Muetterties, E. L. *Inorg. Chem.* 1974, *12*, 1963. [b] Chisholm, M. H.; Reichert, W. W. *Ibid.* 1978, *17*, 767. [c] Chisholm, M. H.; Rothwell, I. P. *J. Chem. Soc., Chem. Commun.* 1980, 985. [d] Andersen, R. A. *Inorg. Chem.* 1979, *18*, 2928. [e] Sabota, P.; Trzebiatowska, B. J.; Janas, Z, *J. Organomet. Chem.* 1976, *118*, 253. [f] Ozawa, F.; Ito, T.; Yamamato, A. *Chem. Lett.* 1979, 735. [g] Hidai, M.; Hikita, T.; Uchida, Y. *Chem. Lett.* 1972, 521. [h] Yamamoto, T.; Kubota, M.; Yamamoto, A. *Bull Chem. Soc. Jpn.* 1980, *53*, 680.

Insertion into C–H bonds has also been reported for some Pd complexes, and a series of carboxylic acids could be prepared in this fashion.[506] Indirect insertion into Si–Si bonds seems to occur in eq 115.[507] A similar

$$Me_3SiHgSiMe_3 + CO_2 \xrightarrow{-Hg} O{=}C(SiMe_3)OSiMe_3 \qquad (115)$$

reaction was reported for the insertion of CS_2.

Finally, it should be mentioned that a series of processes has been discussed in the literature that at some stage may involve CO_2 insertion reactions of the types discussed so far. These include CO_2 attack on an inorganic ligand,[508,509] insertion into M–Si bonds,[510] insertion into an organic molecule in the presence of a metal,[482,511,512] the formation of an intermediate CO_2 complex.[513] The role played by CO_2 insertion reactions in general during the water-gas shift has been emphasized in detail elsewhere.[514]

As a final comment in the section on the chemistry of metal CO_2 complexes, we would like to draw attention to the wide range of reactions involved in typical fixation and insertion processes. The similarity in the reactions with CO_2, COS, and CS_2 is striking, and could be of significant interest in future developments. Many questions remain unanswered and future studies should include[401] synthetic and spectroscopic investigations of metal CO_2 and related complexes, mechanistic investigations of fixation and insertion reactions, the study of CO_2 coupling reactions with itself and other organic substrates, probably catalyzed by metal centers, and the role of such processes in pollution related areas.

Applied Metal Carbonate Chemistry

XII. Geochemistry and Oceanography

As mentioned in the Introduction, this section is meant to provide the chemist with an insight into the role of carbon dioxide and carbonates in natural systems. Emphasis is given to those systems which involve interaction with metals or metal-containing species. We do not attempt to provide a complete review of these two topics as would satisfy either the geochemist or oceanographer. Moreover, some information relevant to this section has been included in prior sections, such as the effect of salinity, or chlorinity, on carbonate equilibria (section III), or the structures of naturally occurring minerals (section V). In some instances, isolated examples have been chosen to represent applied aspects of carbonate chemistry and are therefore not meant to indicate that they are unique in this sense.

A. Mineralization and Transport

The equilibria treated in section III are fundamental to modeling the chemistry of most complex natural water systems,[515] be they groundwaters, hydrothermal solutions, rivers, lakes, or oceans. Helgeson[516] stressed the importance of aqueous phase chemistry in applying constraints on phase relationships in geological systems and allowing for mass transfer among mineral assemblages. The aqueous phase is directly involved in many geological processes such as weathering, sedimentation, diagenesis, metamorphism, hydrothermal metasomatism, ore deposition, volcanism and igneous intrusions. Although Helgeson refers mainly to chloride salts as being the dominant constituent of the aqueous phases in these processes, carbonates and sulfates also play important roles, e.g., pH control, precipitation, complexation, Eh control, mineral replacement, etc.

The economic impact at a local level is exemplified by the case where the activity of $CO_2(aq)$ was modeled for a particular flowing geothermal well in which other salts (e.g., NaCl, $CaCl_2$, etc.) are present. These calculations led to quantitative predictions for scaling and gas evolution.[517]

Calcite, $CaCO_3$, is the most common form of carbonate and much is known about its crystallization behavior. The rapid rate of crystallization was discussed briefly in section IV. The solubility of calcite decreases with temperature at any given CO_2 pressure.[518] For conditions generally associated with natural solutions, calcite can be precipitated by release of CO_2, but not by cooling. The solubility of $CaCO_3$ as calcite, aragonite, and vaterite has recently been measured and modeled over the temperature range 0–90 °C.[149] At constant p_{CO_2}, the ratio of calcite solubilities in NaCl solutions and pure water increases with increasing salt concentration, particularly at higher temperatures. However, addition of $CaCl_2$ or $NaHCO_3$ gives rise to two competing effects, viz., the same ionic strength effect as in the NaCl case and the counteracting common ion effect. The complexing of carbonate by other cations at higher temperatures has an unknown effect on $CaCO_3$ solubility. Nonetheless, as a general rule, boiling of natural waters containing Ca^{2+} and HCO_3^- ions (i.e., the applied pressure falls below the vapor pressure) can cause deposition of $CaCO_3$. The composition of adjacent fluid inclusions in hydrothermal minerals provides strong evidence that boiling has taken place in at least some hydrothermal systems, although it may not be the most common event in the formation of such deposits.[518] As a direct consequence of this finding, the chemistry of flashing of geothermal waters could be explained in terms of eq 116. Thus the release of CO_2

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3(\downarrow) + CO_2(\uparrow) + H_2O \quad (116)$$

is responsible for the observed deposition of calcite. A further consequence of reaction 116 is to raise the concentration of carbonate that results in further hydrolysis to produce more HCO_3^- and OH^-, particularly prior to calcite precipitation. This accounts for the initial sharp increase in pH to 9.2 at this particular well,[519] compared to 6.5 as would be expected if the original groundwater were just allowed to cool slowly from the reservoir temperature of ca. 165 ± 8 °C to ambient temperature.

Note that the formation of insoluble carbonate scales, mainly of calcium, is economically important not only because it tends to reduce the porosity of the host rock in oil wells, but also because it reduces the efficiency of heat exchangers in power generating plants. Some of the commercially available scale inhibitors function by reducing the rate of the second-order reaction shown in eq 116; however, the main effect is to reduce the rate of nucleation of $CaCO_3$, which occurs as a second stage to reaction 116, by passivating the surface crystallization sites.[520]

Replacement reactions, such as the substitution of wall rock calcite by sulfide minerals, are also important mineralization processes.[518] One such example involves the localization of Zn as sphalerite from its transporting complex by means of eq 117. The reaction is assumed

$$CaCO_3(s) + Zn(HS)_3^- \rightleftarrows ZnS(s) + Ca^{2+} + HCO_3^- + 2HS^- \quad (117)$$

to be favored by decreasing temperature that would provide a mechanism for replacing limestone with sphalerite.[518]

It may also be suggested that anhydrite, $CaSO_4$, is formed in a similar reaction

$$CaCO_3(s) + H_2S + 3H_2O \rightleftarrows CaSO_4(s) + CO_2 + 4H_2 \quad (118)$$

in an oxidizing region adjacent to a rising column of thermal fluid which comes into contact with aerated, nonthermal ground water. However, thermodynamic calculations show that the concentration of H_2S is far too low with respect to $[H_2]$ to allow anhydrite to coexist as a stable phase.[521]

Dolomite, $CaMg(CO_3)_2$, is the next most important mineral and in solutions saturated with respect to both calcite and dolomite, the following replacement equilibrium can be considered

$$2CaCO_3(s) + Mg^{2+} \rightleftarrows CaMg(CO_3)_2(s) + Ca^{2+} \quad (119)$$

with the ratio of $a_{Ca^{2+}}/a_{Mg^{2+}} \sim 1$ at room temperature. Thus, for normal seawater, for which this ratio is ca. 0.19, calcite should be converted to dolomite, but if the $m(Ca)/m(Mg)$ ratio is increased to ca. 0.5, dolomitization will cease. Existing solubility measurements at low temperatures can be unreliable because the rates of reaction are very slow below 200 °C; although the stability of dolomite relative to calcite apparently decreases with increasing temperature.[518] Therefore, whether calcite, dolomite, or magnesite is precipitated depends on the $a_{Ca^{2+}}/a_{Mg^{2+}}$ at a given temperature so that, for example, a hydrothermal solution rich in magnesium will react with (dolomitize) calcite until this ratio reaches the equilibrium value. Again it should be stressed that this reaction is very sluggish at lower temperatures. Furthermore, unless the CO_2 content is sufficiently high the phase precipitated may well be brucite, $Mg(OH)_2$, or a silicate mineral. In fact, Holland[518] suggests that the formation of tremolite, eq 120,

$$5CaMg(CO_3)_2(s) + 8SiO_2(s) + H_2O \rightleftarrows Ca_2Mg_5Si_8O_{22}(OH)_2(s) + 3CaCO_3(s) + 7CO_2(g) \quad (120)$$

may have considerable influence on the CO_2 content of rising hydrothermal solutions.

Although strontianite, $SrCO_3$, is only one-tenth as soluble as calcite at 25 °C, it becomes increasingly more soluble than calcite above 200 °C so that coupled with the relative low activity of Sr^{2+} in most ground waters, $a_{Sr^{2+}}/a_{Ca^{2+}} < 0.01$, it is not surprising that calcite is more commonly precipitated than strontianite in hydrothermal systems. Most strontianite is apparently precipitated at or below 100 °C for the above reasons.

Witherite, $BaCO_3$, follows a similar pattern to strontianite, although its solubility is close to that of calcite at 25 °C. In the absence of CO_2 the solubility of witherite increases with added salt concentration (LiCl > NaCl > KCl), but this effect is a composite of the individual contributions from ionic strength; complexing of Ba^{2+} with Cl^-; Li^+, Na^+, and K^+ interactions with HCO_3^- and CO_3^{2-}; plus interaction of these cations with OH^-.[518] Witherite is less abundant than barite, $BaSO_4$. Ratios of $a_{Ba^{2+}}/a_{Ca^{2+}}$ needed for the preferential precipitation of $BaCO_3$ over $CaCO_3$ are ca. 0.4 at 25 °C and 15.3 at 225 °C, whereas general natural solutions exhibit ratios $\ll 0.4$.

Many other, more complex, phase rearrangements occur in nature resulting in multicomponent systems such as, for example, the $CaO–Al_2O_3–SiO_2–H_2O–CO_2$ system. Under certain conditions of temperature, pressure, and CO_2 concentration the following equilibrium can be studied.[522]

$$\underset{\text{calcite}}{2CaCO_3(s)} + \underset{\text{anorthite}}{CaAl_2Si_2O_8(s)} + \underset{\text{quartz}}{SiO_2(s)} \rightarrow \underset{\text{grossularite}}{Ca_3Al_2(SiO_4)_3(s)} + CO_2 \quad (121)$$

To quote more examples of this type would add little to the concept of this section, which is more aimed at creating an awareness of general behavior.

Complexation of metal ions by carbonate to form more soluble species which may then be transported by ground waters is an important aspect both in waste disposal[523] and in the formation of mineral deposits. However, complexation resulting in the formation of insoluble carbonates is an equally important consideration and the more probable of the two processes. Vuceta and Morgan[524] modeled the complexing of the transition-metal ions Cu, Pb, Cd, Co, Ni, Zn, Hg, Mn, and Fe by a variety of anions CO_3^{2-}, SO_4^{2-}, Cl^-, F^-, Br^-, PO_4^{3-}, OH^-, and neutral ligands such as NH_3, edta, citric acid, etc. in the presence of potential solid adsorbates, SiO_2, $Fe(OH)_3$, and MnO_2 over the pH range 6.2–8 in oxic fresh water. These results show that both $CuCO_3$ and $CdCO_3$ precipitate at the higher pH end of the scale and that, depending on the choice of the stability constant for $Cu(OH)_2$, solid malachite ($Cu_2(OH)_2CO_3$) is either formed as the dominant species at high pH or it is totally absent from the speciation diagram. Copper is also readily removed from solution by adsorption on SiO_2. The speciation of the Zn and Pb systems is strongly pH dependent with $Zn^{2+}/ZnCO_3$, and $PbCO_3/Pb^{2+}$ being the most abundant species at high pH. For the mercury system, the hydroxide and halide (Cl, Br) forms are significantly more stable than the carbonate complex.

Complexation of Ge, W, Ga, and Mo was judged[525] to be strongest by HCO_3^-, CO_3^{2-}, and SO_4^{2-} compared to Cl^-, F^-, S^{2-}, and organic anions. Elenbogena[526] gauged the general ability of anions to form complexes to be in the order $CO_3^{2-} \gg SO_4^{2-} > HCO_3^- \gg Cl^-$, but obviously specific interactions alluded to earlier[524] modify and even reverse such general trends in certain cases. Pittwell[527] tabulates a vast range of metal ions in terms of their interactions with aqueous anionic species. Based on absorption spectra, ability to dissolve the metal oxide, carbonate, or sulfide, and on stability constant data, this formulation indicates that carbonate has the most widely applicable coordinating powers. However, factors such as temperature, ionic strength, redox control, valence state, etc. are not discussed.

The solubility of CO_2 in molten rocks is of interest. For example, in granitic and basaltic melts, CO_2 is substantially less soluble than water, amounting to 0.2–0.3% by weight at 101 MPa total pressure and 0.4–0.5% at 304 MPa (where $p_{CO_2} \sim 0.6 \times$ total pressure).[528]

Another facet of this topic involves the utilization of the unit cell parameters of a mineral to provide geological information as to the history of a given deposit. In the case of the mineral francolite, $Ca_{10-x-y}Na_xMg_y(PO_4)_{6-z}(CO_3)_3F_{0.43}F_2$, the a parameter shows variations of ca. 9.32–9.37 Å when taken from deposits throughout the world.[529] Francolite is generally metastable with respect to fluorapatite and effects of weathering, metamorphism, and geological time cause systematic changes in the composition of francolite (N.B., a = 9.36 Å for fluorapatite).

B. Isotopic Exchange Reactions

An estimation of the natural abundances of the carbon isotope ^{12}C and ^{13}C in petroleum, gas, and other organic deposits is central to an understanding of the origins and subsequent history of such deposits. The origin may be either biogenic in low temperature zones (i.e., near surface regions), or abiogenic where higher temperatures were encountered (>80 °C). Carbon dioxide and methane are often found together as a result of bacterial decomposition of organic matter. The observed fractionation factors between these two gases are relatively large and favor a higher ^{13}C content in CO_2 as compared to CH_4. The magnitude of this discrepancy decreases with temperature and therefore reflects the temperature to which the system was subjected.

Bottinga,[530] for one, has calculated the ^{13}C:^{12}C distribution ratio between CH_4 and CO_2, as well as the ratios for CO_2:graphite and graphite:methane, using spectroscopic data over the temperature range, 0–700 °C. One path for carbon exchange is provided by the equation

$$CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2 \qquad (122)$$

which involves the water-gas shift reaction, and is also known as the steam-reformation reaction of methane. In the absence of concrete experimental data, confirmation of these calculations is not available. In addition, other authors[531] have predicted different fractionation factors, particularly at higher temperatures, based on similar calculations. Bottinga[530] also stated that isotopic ratios calculated by these methods indicate that tropospheric CO_2 and CH_4 cannot be in isotopic equilibrium because the current ratio corresponds to an estimated temperature at 200 °C.

To our knowledge, only one positive set of experimental results exist on the kinetics of this isotopic exchange reaction via eq 122,[532] although a study published 1 year earlier did indicate that no exchange occurred after heating the gaseous mixture to 500 °C for 10.5 days.[533] This is in keeping with the second study's findings[532] that equilibrium would only be achieved at 400 °C after 8 × 10^4 years. These results would therefore suggest that under normal geothermal conditions with temperatures of ca. 200 °C, isotopic exchange does not reach equilibrium. In other words, for natural gas deposits which do not experience higher interim temperatures, the isotopic ratio reflects that of the source.[534,535] On the other hand, at much higher temperatures that may result from, say, a magmatic intrusion, isotopic equilibrium may be approached, and the value of the ratio at that higher temperature would then be "frozen in" after subsequent cooling.

A further complication is the effect of surface catalysis.[536–541] Even the walls of the glass ampules used in the above-mentioned experiments may provide catalytic input. Certain metal oxides, including those likely to be found in nature, are very effective catalysts. Nonetheless, Giggenbach[542] has processed these kinetic data[532] in terms of the known isotopic ratios found in different natural gas wells throughout the world. He also points out that in view of the slow rate of chemical and isotopic equilibration, isotopic ratios only serve as an accurate geothermometer for very deep wells and that the results may otherwise be biased by secondary reactions or by a net flux of methane or carbon dioxide with incongruent isotopic compositions. An example of such a secondary reaction is the dilution of the ^{13}C content of CO_2 by the decomposition of more ^{12}C-rich carbonates within a sample of montmorillonite during an experiment to determine the catalytic effect of this clay on the CH_4:CO_2 exchange reaction at 400 °C.[532]

The $\delta^{13}C$ value for dissolved HCO_3^- associated with oil and natural gas wells can also be valuable as an indicator of the history of the deposit. Carothers and Kharaka[543] have discussed their experimental findings for some 15 oil and gas fields in the light of the conclusions of previous workers concerning the possible mechanisms for producing various $\delta^{13}C$ values. Perhaps the simplest of these mechanisms pertains to shallow ground waters where equilibration with atmospheric CO_2, with its present value of −7‰, should lead to a similar isotopic value for the dissolved carbonates. Bacteria known as methanogens can operate at 50 °C to produce methane by the reverse reaction of eq 122, thereby depleting the ^{13}C in the CH_4 by ca. 60‰ while enriching the remaining CO_2. Other bacteria aid in the reduction of SO_4^{2-} present in the ground water by degradation of organic matter to form HCO_3^- and HS^-. By this process organic matter with $\delta^{13}C$ values of ca. −25‰ produce typical $\delta^{13}C$ values in HCO_3^- of ca. −20‰. The concentration of SO_4^{2-} determines the final $\delta^{13}C$ value.

For deeper deposits, thermal decomposition of organic matter is probably an important source of aqueous HCO_3^-, which may precipitate to form secondary carbonate cements often associated with such fields. The constraints of CH_4/CO_2 carbon exchange discussed above then control further changes in the $\delta^{13}C$ content of the HCO_3^-.

Another important exchange reaction is that between CO_2 and CO, especially at high temperatures where CO becomes relatively more stable. Brander and Urey[544] showed very early that this process is catalyzed on the surfaces of quartz, gold, and silver. They reported an activation energy of ca. 472 kJ mol^{-1} and noted that hydrogen and water increase the rate of exchange in keeping with the reaction

$$^{13}CO_2 + H_2 \rightleftarrows {}^{12}CO + H_2O \qquad (123)$$

which is known to be operative at 800 °C. As water and hydrogen are known to be strongly adsorbed by quartz at these temperatures, the equivalent surface reaction (eq 124) was proposed. This mechanism was more

$$^{13}CO_2 + H(ads) \rightleftarrows {}^{12}CO + OH(ads) \qquad (124)$$

difficult to visualize as taking place on a gold or silver surface and is obviously different in the absence of water vapor and hydrogen. Subsequent work[545] in quartz tubes ($^{14}CO_2$, ^{12}CO) established that although the same activation energy is obtained at high temperatures, 900–870 °C, it decreases dramatically to ca. 46 kJ mol^{-1} at 550–650 °C. It was reasoned that at the higher temperature region the reaction is more homogeneous, whereas at lower temperatures exchange occurs exclusively on a limited number of active sites on the vessel walls. However, even above 900 °C the reaction appears complex due to the fact that it is first order with respect to CO_2 and only a half with respect to CO.

Over various carbon surfaces the kinetics of CO_2/CO exchange, referred to in this case as an oxygen transfer reaction, can be described by a general rate expression, which is also valid for metal and metal oxide surfaces.[546] However, under most conditions (in this study temperatures were varied from 500 to 1000 °C), reaction 125 can be considered as a "preequilibrium step" which

$$CO_2 \rightleftarrows CO + O(ads) \qquad (125)$$

establishes the oxygen activity. The rate of the second step (eq 126) is then determined by the simple ex-

$$C + O(ads) \rightarrow CO \qquad (126)$$

pression, $k_2p_{CO_2}/p_{CO}$. Strong oxygen adsorption was observed, although not of the Langmuir type, with rapid surface diffusion establishing equilibrium between adsorbed oxygen at different sites. Contrary to some previous claims, these authors[546] found that reactions 125 and 126 can occur at different sites.

Carbon dioxide and monoxide are believed to exchange carbon via eq 123 over an iron catalyst with a different mechanism for much faster oxygen exchange involving only water and CO at 170 °C.[547] Sakata et al.[548] rationalized the oxygen exchange mechanism over γ-Fe_2O_3 in terms of the migration of Fe^{3+} to bound CO sites, followed by oxidation/reduction to CO_2 and Fe^{2+}. Lattice oxygen diffusion rate is too slow to contribute to this step, although it can participate in the subsequent rapid and irreversible reoxidation of Fe^{2+} to Fe^{3+}. Adsorbed molecular oxygen serves to increase the rate of exchange by participating in both steps of the redox process.

In the case of ZnO, CO_2 and CO are both adsorbed over the temperature range 25–300 °C and exchange oxygen atoms with the metal oxide.[549] Carbon exchange is again far slower and is postulated to occur when a uniquely bound CO molecule is oxidized by the surface to then be released as CO_2.

Another surface mechanism is proposed for the steam reforming of ethane over a Ni–Al_2O_3 catalyst at 217 °C.[550] Here methane is formed by hydrogenation of surface carbon formed as an intermediate in the steam re-forming reaction (i.e., reverse Fisher–Tropsch reaction)

$$C_nH_{2n+2} + nH_2O \rightleftarrows nCO + (2n+1)H_2 \qquad (127)$$

rather than by the reaction

$$CO + 3H_2 \rightleftarrows CH_4 + H_2O \qquad (128)$$

The proof for this hypothesis was obtained from experiments in which ^{13}CO was added to the reaction mixture and yet no appreciable $^{13}CH_4$ was detected. Although this reaction scheme does not involve CO_2, it seems worthy of mention as adsorbed carbon may well play an important role in exchange reactions of the type discussed above.

A brief mention should also be made of the use of $\delta^{13}C$ and $\delta^{18}O$ values in determining the probable origin, or sequence of formation, of carbonate containing minerals. For example, a carbonate–fluorapatite (francolite) with the approximate composition, $(CaNaMgSr)_{10}(PO_4CO_3SO_4)_6F_{2-3}$, may be of diagenetic origin (i.e., formed by replacement of carbonate within existing sediments), or authigenic (i.e., formed by precipitation, in this case, within anoxic sediments).[551] In the former case, the carbon isotopic composition would reflect that of the precursor and the water as well as being sensitive to temperature. Authigenic francolite may contain either light or heavy carbon depending on the environment during the organic degradation process which was responsible for the formation of the carbonate originally.

Finally, as a general comment on isotopic fractionation, it becomes apparent that a knowledge of such values provides a powerful tool in determining the origin of mineral and oil/gas formations, but only when combined with other pertinent information. Moreover, as stressed above, the use of $\delta^{13}C/\delta^{12}C$ ratios for methane and carbon dioxide as a geothermometer should apparently be restricted to very high temperature regions due to the kinetic restrictions of the equilibration reaction, although catalysis still may account for the near equilibrium ratios found in lower temperature regions.

C. Oceanography

Estimates of the total current release of CO_2 to the atmosphere indicate that approximately one-half (1.5 ppm) is being continuously removed.[552,553] The most obvious carbon sinks are the oceans and the biosphere. As it has been proposed[554,555] that the land biota reservoir is decreasing at a rate comparable to fossil fuel combustion, the role of CO_2 uptake by the waters of the world has probably been underestimated in earlier studies. In other words, if no yet unknown sink for carbon exists, the oceans must be the major scavenger for atmospheric CO_2.[552,553,556]

The pH of most bodies of exposed water, typically 7.6–8.3 for ocean waters, is governed mainly by the carbonate buffering system, which involves the hydrolysis equilibria (section III) as a function of temperature, depth, and salinity (or chlorinity).[119,134,141,557] Other contributions to this system are found in the solubility equilibria of principally $CaCO_3$ and $Mg(OH)_2$, and the exchange of CO_2 between the atmosphere and the water surface. The first dissociation constant for boric acid should also be included in any rigorous model for the pH of seawater.

In section IV it was stressed that the rates of CO_2 hydrolysis in "pure" water at pH values normally encountered in sea water are such that equilibrium is obtained within several minutes. The recent kinetic data of Johnson[558] show that the same time periods apply to sea water. Given effective agitation, which one may expect for surface waters extending to an average of 70 m in oceans, the rate of transfer of CO_2 from the atmosphere to the surface water is far more rapid than either the rate of CO_2 hydrolysis, which occurs within minutes, or the rate of mixing, which may take hours.[181] Thus, the surface waters in nature should be very near equilibrium with the adjacent atmosphere with respect to CO_2.

Takahashi and co-workers[552] have reviewed the "Carbonate Chemistry of the Surface Waters of the World Oceans". The main parameters used in their discussion are: the Revelle factor $\{(dp_{CO_2}/p_{CO_2})/(dTC/TC)\}_{TA,T,S}$, where p_{CO2} is the partial pressure of CO_2 and TC is the total "carbonate" = $\{CO_2'(aq) + HCO_3^- + CO_3^{2-}\}$; and the titration alkalinity, TA, which is defined as the equivalent amount of acid required to bring the pH of a liter of sea water to the bicarbonate/carbonic acid end point and can be approximated as follows:

$$\mathrm{TA} = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [HPO_4^{2-}] + [OH^-] - [H^+] \qquad (129)$$

The mean value for the Revelle factor for the world's ocean surfaces was estimated at 10.0 ± 0.5,[552] while the alkalinity, temperature, and salinity generally fall in the ranges 2.2–2.4 mequiv/kg, −1 to 27 °C, and 33–37‰, respectively. At the time of their review, 1980,[552] the partial pressure of CO_2 was ca. 33.4 mPa. In very general terms, the alkalinity values were considered to follow two major trends: the warm water and Antarctic trends, which mainly owe their differences to the differences in calcium ion concentration.

Baes[556] pointed out that precipitation of $CaCO_3$, as well as photosynthesis and decay are biogenically controlled in the ocean. Photosynthesis accounts for a lowering of the total carbon budget of surface waters leading to a supersaturation of $CaCO_3$ where this process is particularly active. Thus, these biological processes must be included in models of CO_2 absorption by surface waters.[556]

It should be noted that mixing of waters in the ocean is sluggish beyond the surface region. Circulation is commonly expressed in terms of two processes, namely, advection along layers of similar density (isopycnals) and turbulent mixing which occurs vertically across these density gradients.[556]

From the above discussion it is obvious that the solubility of $CaCO_3$ is important to sea-water chemistry. Edmond and Gieskes[119] have critically reviewed these data for sea water and have derived eq 130 and 131 for

$$K_{sp}' \text{ (calcite)} = (0.1614 + 0.02892\mathrm{Cl} - 0.0063t)10^{-6} \qquad (130)$$

$$K_{sp}' \text{ (aragonite)} = (0.5115 + 0.02892\mathrm{Cl} - 0.0063t)10^{-6} \qquad (131)$$

the apparent solubility products for $CaCO_3$ in its calcite and aragonite forms to within an estimated uncertainty of ±5%. Jacobson and Langmuir[559] determined a value for pK_{sp}(calcite) of 8.42 at 25 °C which compares closely with 8.41 obtained from eq 130 at 25 °C and Cl = 0, i.e., at infinite dilution. However, when these authors took ion pairing of $Ca(HCO_3^-)^+$ and $CaCO_3^\circ$ into account they arrived at a value for K_{sp} of 8.47, which emphasizes that until a better model for 2:1 and 2:2 electrolytes is found, these ion pairs can be neglected.

In order to assess the effect of pressure on the apparent solubility constants, the temperature dependence of the apparent volume changes were estimated[560] to within ±1 $cm^3\ mol^{-1}$ (eq 132 and 133). Bradshaw[560]

$$\Delta V' \text{ (calcite)} = -(35.4 - 0.23t) \qquad (132)$$

$$\Delta V' \text{ (aragonite)} = -(32.8 - 0.23t) \qquad (133)$$

determined the apparent molar volume of carbon dioxide in sea water (Sl = 35‰ and 23 °C) to be 33.4 $cm^3\ mol^{-1}$ which is well within the range of partial molar volumes quoted for $CO_2(aq)$ in water (see sections II and III). Under the same conditions, he derived a value for the difference between the apparent molar volumes of HCO_3^- and CO_3^{2-} in artificial sea water (i.e., it contained no boric acid) of 22.5 $cm^3\ mol^{-1}$. This compares favorably with 20.37 $cm^3\ mol^{-1}$ obtained[109] at 25 °C in 0.725 m NaCl for the sodium salts. Note that $\phi_v(HCO_3^-) - \phi_v(CO_3^{2-})$ in pure water at 25 °C is 23.9 $cm^3\ mol^{-1}$,[109] assuming $\phi(Na^+) = -5.7\ cm^3\ mol^{-1}$.

As in the case of natural ground waters, trace metals can be complexed in sea water by such anions as chloride, hydroxide, bicarbonate, carbonate, sulfate, etc.

Identification of such species is difficult due to the low concentrations involved against the high background of salt concentrations. To quote but one example, examination of deposits accumulated in the Black Sea led to the identification of many of the trace metals present, so that by using known stability constant data estimates could be made in this indirect manner of their original concentrations in the sea.[561] Bicarbonato and carbonato complexes were postulated to exist in the relative amounts depending on the pH of such metals as Cu, Zn, Ni, Co, Be, and Sr in their +2 oxidation states. The uranium species, $UO_2CO_3^0$, $UO_2(CO_3)_2^{2-}$, and $UO_2(CO_3)_3^{4-}$ apparently exist in relatively high abundances, with the latter species becoming the dominant uranium form at high pH.[561] In regards to uranium, this behavior parallels that observed in natural ground waters,[562,563] where the mobility of uranium is enhanced by the presence of aqueous carbonate. Extraction of uranium from sea water onto $TiO_2{\cdot}nH_2O$ columns[564] and the formation of "hydrothermal ematite" in certain uranium deposits[563] both appear to rely on the adsorption of the negatively charged uranium carbonates, particularly $UO_2(CO_3)_3^{4-}$, on grains or colloidal particles, in the latter case, of metal oxides.

XIII. Biochemistry

In this section we discuss the interaction of $CO_2/HCO_3^-/CO_3^{2-}$ with metalloenzymes and other bioinorganic species. Since the earlier review on metal carbonato complexes by Kristhnamurthy et al.,[1] much work has been done in this area and a more complete coverage can now be presented. The enzyme within this field that has attracted the most attention over the past 10 years is certainly carbonic anhydrase. A recent extensive review[565] dealt with its structure and activity, and some aspects related to metal carbonato chemistry will be treated in subsection A. All other bioinorganic species that show significant interaction with CO_2/HCO_3^- will be treated in subsection B.

A. Carbonic Anhydrase

Quite some time ago it was realized that the dehydration of HCO_3^- to form CO_2 in the human lung, and the hydration of CO_2 as it passes into the bloodstream, must proceed with the aid of a catalyst. In the early sixties, biochemists succeeded in isolating various forms of carbonic anhydrase which were shown to be responsible for the catalytic action in the CO_2–HCO_3^- system.[566] Carbonic anhydrase is one of the most efficient biocatalysts known and is of obvious physiological importance in rapidly maintaining the CO_2–HCO_3^- equilibrium,[567] particularly in view of the fact that hydration of CO_2 and dehydration of HCO_3^- are indeed relatively slow processes under normal conditions (see section IV). Carbonic anhydrase is a zinc metalloenzyme made up of one polypeptide chain with a molecular weight of about 29 000 and occurs in various forms: one of high specific activity designated carbonic anhydrase C and two of low activity designated A and B.[568] Most mammals have forms B and C.[569] A main question focuses on the mode of binding of CO_2 at the active site of the enzyme, since this knowledge would be of much value in understanding the catalysis mechanism. It is quite certain that CO_2 does not coordinate directly to the Zn metal.[568] Numerous studies have been undertaken in efforts to elucidate the fundamental mechanism involved. It is generally accepted that Zn^{2+} must be coordinated to three imidazoles of histidines and a water molecule in order to achieve its catalytic activity.[570]

TABLE XLIII. Activation Parameters

enzyme	substrate	$\Delta H^\ddagger$, kJ mol^{-1}	$\Delta S^\ddagger$, J K^{-1} mol^{-1}
none	CO_2[a]	72.3	30.9 ± 0.4
	HCO_3^-[b]	62.7	81.1 ± 0.8
HCAC[c]	CO_2[a]	31.6 ± 0.6	25.4 ± 0.7
	HCO_3^-[b]	30.5 ± 0.7	39.5 ± 1.1
HCAB[d]	CO_2[a]	15.8 ± 0.9	101 ± 0.6
	HCO_3^-[b]	18.7 ± 1.5	105 ± 0.9

[a] Hydration at pH 7.5. [b] Dehydration at pH 7.2. [c] Human carbonic anhydrase C. [d] Human carbonic anhydrase B.

The pH dependence of the catalytic activity is characterized by a pK_a near 7.[569,570] Human carbonic anhydrase C has a maximum turnover number of 1 × 10^6 s^{-1} at 25 °C, compared to a value of 2 × 10^5 s^{-1} for carbonic anhydrase B.[569,571] The corresponding activation parameters are shown in Table XLIII.[571] In the case of bovine carbonic anhydrase, it was found[567,570] that the Michael's constant (K_m) for CO_2 hydration is essentially constant at pH 5.9–10.2; pK_a values of 6.85 and 7.35 in H_2O and D_2O, respectively; $k_{cat} = 8.3 \times 10^5$ s^{-1} at 25 °C in the basic form during CO_2 hydration; $k_{cat} = 3.8 \times 10^5$ s^{-1} at 25 °C in the acidic form during dehydration of HCO_3^-; $K_M^{H_2O}/K_M^{D_2O} = 3.3$; $K_M^{HCO_3^-}/K_M^{DCO_3^-} = 2.6$; $k_{cat}^{H_2O}/k_{cat}^{D_2O} = 3.3$ for hydration; $k_{cat}^{H_2O}/k_{cat}^{D_2O} = 4.3$ for dehydration. From these tendencies, the authors[567] conclude that only mechanisms which utilize proton transfer as part of the rate-determining step can be correct. Very similar results were reported for spinach carbonic anhydrase.[572] It follows that the basic form of the enzyme is active towards CO_2 hydration, whereas the acidic form is active towards HCO_3^- dehydration.[570] Two models have been proposed[569,570] concerning the chemical nature of the catalytic group that has a pK_a around 7. This group might be a histidine side chain linked to the metal ion indirectly via one or more water molecules, or it may involve ionization of a metal-coordinated water molecule to produce a Zn–OH species. In the case of the latter possibility, the activity of the enzyme cannot be ascribed to the nucleophilicity of the hydroxo ligand only, since a rate constant for CO_2 uptake (see Figure 3—section VIIIA) of ca. 300 M^{-1} s^{-1} at 25 °C would then be expected, which is much slower than the observed value. Other factors must therefore play a significant role in such a process.

X-ray studies[573] have demonstrated that human carbonic anhydrase C has an ellipsoidal molecular shape and that the Zn atom is positioned in the center of the molecule at the bottom of a crevice, constituting the active site. Infrared studies by Wang[574] have illustrated that the binding site of carbonic anhydrase is a hydrophobic surface or cavity which loosely binds CO_2. A detailed mechanism was presented[70,568,570] in which the Zn-bound water molecule provides both donor and acceptor functions, and it was suggested[70] that rapid proton transfer occurs between the water molecules in the cavity. The participation of a basic imidazole group in the proton transfer process has also been stressed.[405,575] Attention was drawn[70,569] to a serious dilemma, originating when rates exceeding diffusion-controlled processes are obtained. However, this probably could be solved[576] when proton transfer between enzyme and buffer species (eq 134) is taken into

$$E + BH \rightleftarrows EH^+ + B^- \qquad (134)$$

account. It follows[569] that CO_2 and HCO_3^- can combine with the enzyme at diffusion-controlled rates, and that proton exchange can occur very rapidly through buffer mediation.

Silverman and co-workers[577] developed an ^{18}O exchange technique to study exchange between H_2O and HCO_3^- catalyzed by human carbonic anhydrase C. They presented results that supported the hypothesis that there is a proton-transfer step in the mechanism involving the enzyme and buffers in solution.[578] They found[579] that as the buffer concentration is increased a change in rate-determining step occurs. In the absence of buffers, the rate is determined by alternating hydration–dehydration steps at equilibrium which do not require proton transfer to the enzyme. At low buffer concentrations, proton transfer is rate limiting and the catalytic exchange rate increases with buffer concentration. Further studies by this group illustrate similar results for the exchange of ^{18}O between CO_2 and H_2O catalyzed by bovine carbonic anhydrase,[580] human carbonic anhydrase,[581] brush-border carbonic anhydrase from dog kidney,[582] and red cell suspensions.[583]

^{13}C NMR techniques have also been used to study the CO_2/HCO_3^- system in the presence of various carbonic anhydrases.[584–586] The results are in accord with mechanisms that suggest metal-bonded OH adds directly to the carbon of enzyme-bound CO_2 so that dehydration proceeds via HCO_3^- coordinated directly to the metal.[585] The CO_2 could be bound close to the metal through an interaction with the protein part of the enzyme active site. However, HCO_3^- binds directly to the metal. Very recently[587] a model was suggested in which the enzyme has a water molecule on the metal ion at the active site and this results in a rate of water exchange independent of pH.

A number of theoretical studies have computed the nature of the CO_2 hydration process.[588–590] In one study only the schemes with a direct reaction between buffer and enzyme gave consistent data.[591] Monte Carlo calculations demonstrate[592] that the field of Zn^{2+} dominates the carbonic anhydrase reaction, and four steps could be identified: CO_2 approaches $Zn–OH_2$ and forms a precursor complex in which both reactants maintain original geometry; a complex is formed between CO_2 and H_2O; removal of the complex by sandwiching a molecule of water between Zn^{2+} and the complex; deprotonation at one side of the complex and protonation of an oxygen atom at a different side.

Finally, it is significant that carbonic anhydrase will affect the absorption characteristics of carbon dioxide.[593] Tsao[594] proposed a two-zone model to describe the phenomena at the gas–liquid interface during CO_2 absorption in the presence of carbonic anhydrase. In a later study by Alper et al.,[595] the absorption data were found to be compatible with classical mass transfer models and suggest that the carbonic anhydrase distribution in the liquid is probably uniform. These findings contradict the earlier observations made by Tsao,[594] but the discrepancies were rationalized.[595] Deckwer and co-workers published a series of papers[596–598] on various aspects of the absorption of CO_2 under the influence of carbonic anhydrase. At high pH (9.6–11.1), the reaction is first order in CO_2 and the rate constant is proportional to the enzyme concentration with an activation energy of 38 kJ mol^{-1}.[596,597] At low pH (~6.5), the catalytic power of the enzyme is considerably reduced and the results do not fit a simple first-order process.[597]

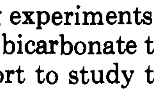
B. Other Enzymes

Another series of enzymes that has received considerable attention over the past 10 years are the carboxylases. Various studies[599,600] were launched to identify the active species of "CO_2", i.e., CO_2 or HCO_3^-, utilized in the ribulose bisphosphate carboxylase reaction

$$\text{D-ribulose 1,5-bisphosphate} + \text{“}CO_2\text{”} + H_2O \xrightarrow{Mg^{2+}} 2\ \text{D-3-phosphoglycerate} + 2H^+ \qquad (135)$$

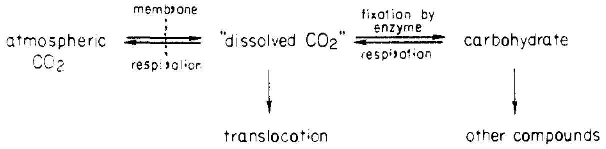
Earlier suggestions include the formation of a Mg^{2+}–CO_2 complex prior to the carboxylation of ribulose bisphosphate. ^{14}C labeling experiments[599,600] demonstrated that the obtained data could all be explained in terms of CO_2 being the active species. In another study,[601] it was concluded that it is rather the HCO_3^- species that is utilized in the reactions of pyruvate and phosphoenolypyruvate carboxylases. Certainly the role of bound metal ions in CO_2 fixation by carboxylases is very important[602] and should exhibit a close correlation with the carbonic anhydrase system. In this respect, several lines of evidence were reported[602] to indicate that Mn^{2+} is a constitutive component of pyruvate carboxylase, and is involved in the carboxylation process.[603] The role of adenosine triphosphate (ATP) in such reactions has been considered in terms of the coupling of ATP hydrolysis and CO_2 fixation.[604] Kinetic evidence indicates that the first step involves the fixation of CO_2 with concurrent hydrolysis of ATP, for which various possible reaction mechanisms were considered.[604] In general,[605] the enzyme must first be activated by preincubation with a divalent cation (Mg^{2+}, Mn^{2+}, Ni^{2+}, or Co^{2+}) and CO_2, for maximum catalytic activity.[606–608]

Various aspects of the binding of metal ions and anions like HCO_3^- to the enzyme transferrin have been investigated. Apotransferrin was found[609] to bind simultaneously to Fe^{3+} and HCO_3^- to produce a complex $(HCO_3)_2$–Fe_2–transferrin with the suggested structure.



Competitive binding experiments showed that oxalate displaced the bound bicarbonate to produce an oxalato complex. In an effort to study the role of bound bicarbonate in the metal-complexing function of transferrin, NMR experiments were performed on copper transferrin and copper transferrin–HCO_3^-.[610] It turns out that at least one rapidly exchanging water molecule is located so close to the metal in copper transferrin that it can be considered as one of its ligands. Binding of HCO_3^- alters the exchange rate and may be due to direct steric hindrance by HCO_3^- bound near the metal ion or conformational changes induced in transferrin by the binding of HCO_3^-.[610] Other interesting reactions reported in the literature include the formation of an intermediate nta–Fe(III)–tf species during the reaction of Fe^{III}nta with transferrin, which subsequently decomposes to nta and Fe(III)–transferrin.[611,612] In the presence of HCO_3^-, the complex transferrin $[Fe^{III}HCO_3^-]_2$ is formed in the above reaction.[612] Later studies have found that carbonate must be bound to Fe(III) prior to the binding of the metal to transferrin.[613,614] Kojima and Bates[615] reported the formation of Fe^{2+}–transferrin–CO_3^{2-} which was subsequently oxidized by O_2 to yield Fe^{3+}–transferrin–CO_3^{2-} at a rate of 4×10^{-3} M^{-1} s^{-1}. In an earlier study, they[616] reported the reductive release of iron from Fe^{3+}–transferrin–CO_3^{2-}, and the kinetic data suggested a mechanism that includes the protonation of two groups during the release of iron.

Similar studies have been performed on the reaction of CO_2/HCO_3^- with other biologically important species such as chloroplasts[617,618] and phytoplankton.[619] These interactions, and those referred to above, stress the biochemical significance of the distribution of carbon isotopes.[620] Along these lines a model could be suggested to explain the isotopic fractionation associated with photosynthesis.[620]



(136)

Finally, we would like to draw attention to a series of studies that involves the the reaction of CO_2/HCO_3^- with hemoglobin,[621,622] red cells, and plasma,[623,624] and the role played by the CO_2–HCO_3^- equilibrium during the process of breathing.[625–628]

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List of Abbreviations

	Ligands
acac	acetylacetone
adao	8-amino-3,6-diazaoctanoate
L-ala	L-alaninate
$[9]aneN_3$	1,4,7-triazacyclononane
$[12]aneN_4$ = cyclen	1,4,7,10-tetraazacyclododecane
$[13]aneN_4$	1,4,8,11-tetraazacyclotridecane
$[14]aneN_4$ = cyclam	1,4,8,11-tetraazacyclotetradecane
C(5,14)-*meso*-Me_6-$[14]aneN_4$ = tetd	C(5,14)-*meso*-5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane
C(5,12)-*rac*-Me_6-$[14]aneN_4$ = tetb	C(5,12)-*rac*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane
$[15]aneN_4$	1,5,9,12-tetraazacyclopentadecane
$[16]aneN_4$	1,5,9,13-tetraazacyclohexadecane
bpy	bipyridine
CDMBA	cetyldimethylbenzylammonium radical
cupferron	*N*-nitroso-*N*-phenylhydroxylamine
cy	cyclopentadiene
DH	dimethylglyoxime
diars	*o*-phenylenebis(dimethylarsine)
$Me_2[14]dieneN_4$	5,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene
$Me_4[14]dieneN_4$	5,6,12,13-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene
trans-$Me_6[14]dieneN_4$	5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene
diphos	1,2-bis(diphenylphosphino)ethane
dmpe	1,2-bis(dimethylphosphino)ethane
dmtr	4,7-dimethyltriethylenetetramine
dpt	dipropyltriamine = 4-azaheptane-1,7-diamine
i-dtma	*N*,*N*-bis(2-aminoethyl)glycine
dtnd	3,7-dithianonane-1,9-diamine
edda	ethylenediaminediacetate
en	ethylenediamine
$Me_4[12]eneN_3$ = dla	2,4,4,9-tetramethyl-1,5,9-triazacyclododec-1-ene
fars	*o*-phenylenebis[[γ-(dimethylarsino)propyl]methylarsine]
gly	glycinate
HDPA	2,2′-bipyridylamine
mal	malinate
mda	(methylimino)diacetate
mdpt	4-methyl-4-azaheptane-1,7-diamine
nta	nitrilotriacetate
ox	oxalate
phen	*o*-phenanthroline
S,*S*-pyhn	1,6-bis[2(*S*)-pyrrolidyl]-2,5-diazahexane
picol	2-pyridinecarboxylate
pip	2-[[[2-(2-pyridyl)ethyl]imino]ethyl]pyridine
pn	propylenediamine
S-praH	(*S*)-2-amino-1-propanol
pren	(2*S*,2′*S*)-1,1′-ethylenedi-2-pyrrolidinecarboxylate
py	pyridine
qars	*o*-phenylenebis[[*o*-(dimethylarsino)phenyl]methylarsine]
teed	*N*,*N*,*N*′,*N*′-tetraethylethylenediamine
terpy	2,2′:6′,2″-terpyridine
3,2,3-tet	4,7-diaza-1,10-decanediamine
5,7-Me_2-2,3,2-tet	4,6-dimethyl-3,7-diaza-1,9-nonanediamine
1,5,7,11-Me_4-2,3,2-tet	6,8-dimethyl-2,5,9,12-tetraazatridecane
tetars	ethylenebis[[γ-(dimethylarsino)propyl]phenylarsine]

tetren	($\alpha\beta$S)tetraethylenepentamine ($\alpha S,\beta S$)
tmtd = tmpd	*N,N,N′,N′*-tetramethyl-1,3-propanediamine
tn	trimethylenediamine
tpam	tris(2-pyridyl)amine
tren	*N,N′,N″*-triaminotriethylamine
trien	triethylenetetramine
3,8-Me_2trien	3(*S*),8(*S*)-dimethyltriethylenetetramine
L-val	L-valinate
	Spectral
br	broad
m	medium
sh	shoulder
s	strong
vs	very strong
vw	very weak
w	weak

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