volume/formula weight (containing 1 mol of actinide) *vs.* atomic number for all series of tetravalent complex fluorides including $K_7M_6F_{31}$[17] and $Rb_7M_6F_{31}$.[17] This is shown in Figure 2. (If the volume/fluoride ratio is considered for all of these series, there is considerable crowding and overlap.) The similar shapes of all of the curves is obvious.

The convergence toward a limiting value for volumes in a series of isostructural compounds has been discussed by Bartlett.[18] The new lattice constants for the actinide tetrafluorides yield volumes which are decreasing quite slowly with atomic number. If other tetrafluorides, both simple and complexed, of the transberkelium actinides maintain their same coordination and symmetry, we predict little further decrease in over-all size.

Acknowledgment.—Joseph A. Leary and Arthur N. Morgan of the Los Alamos Scientific Laboratory supplied a sample of very pure PuF_4. Their assistance is gratefully acknowledged.

[17] T. K. Keenan, *Inorg. Nucl. Chem. Letters*, **3**, 391 (1967).

[18] N. Bartlett, *Angew. Chem. Intern. Ed. Engl.*, **7**, 433 (1968).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
ARIZONA STATE UNIVERSITY, TEMPE, ARIZONA 85281

On the Rare Earth Dioxymonocarbonates and Their Decomposition

BY RHEAL P. TURCOTTE, JAMES O. SAWYER, AND LEROY EYRING

Received August 16, 1968

The polymorphic forms of $Ln_2O_2CO_3$ have been prepared and further characterized by high-temperature X-ray diffraction, tensimetric, and infrared methods. The X-ray study reveals a regular variation with atomic number for cell parameters and decomposition temperatures. The intermediate $Ln_2O_3 \cdot yCO_2$ reported by others is shown to be a mixture of $Ln_2O_2CO_3$ (II) + Ln_2O_3. The crystal structures for the polymorphic forms (type I, tetragonal; type IA, monoclinic; type II, hexagonal) are further elucidated by thermal expansion measurements and by the infrared data. In particular, the orientation of carbonate groups in the three structures is correlated to the resulting vibrational modes in the region 600–1800 cm^{-1}.

Introduction

The lanthanide oxalates and carbonates and their decompositions have been the subject of many investigations. The proposed intermediates are many but are not well characterized. Discrepencies observed in this laboratory indicated a need for the systematic study of the most stable of the intermediate products formed during oxalate decompositions.

Several recent thermogravimetric analysis studies of the decomposition of rare earth oxalates and carbonates indicate the formation of a stable monocarbonate.[1-4] Ropp and Gritz[1] reported the formation of a monocarbonite for the heavier members while Head and Holley[2,3] suggested that the decomposition of the hydrated tricarbonate may be described as

$$Ln_2(CO_3)_3 \cdot xH_2O \longrightarrow Ln_2(CO_3)_3 \longrightarrow Ln_2O_2CO_3 \longrightarrow Ln_2O_3 \cdot yCO_2 \longrightarrow Ln_2O_3$$

where x varies from compound to compound and the composition $Ln_2O_3 \cdot yCO_2$ ($y < 1$) is not always observed. Sastry, *et al.*,[4] showed that three different types of rare earth carbonates can be prepared: $Ln_2(CO_3)_3 \cdot 8H_2O$, $Ln_2O_3 \cdot 2CO_2 \cdot 2H_2O$, and $Ln_2O_3 \cdot 2.5CO_2 \cdot 3.5H_2O$. In the case of neodymium carbonate decomposition, an additional intermediate compound corresponding to the stoichiometry $Nd_2O_3 \cdot 0.3CO_2$ was found just prior to the formation of the oxide. Glasner and Steinberg,[5] in studying the decomposition of the light rare earth oxalates, found the sequence of intermediates

$$Ln_2(C_2O_4)_3 \longrightarrow Ln_2(C_2O_4)(CO_3)_2 \longrightarrow Ln_2(CO_3)_3 \longrightarrow Ln_2O_{0.6} \cdot (CO_3)_{2.4} \longrightarrow Ln_2O(CO_3)_2$$

Work in this laboratory by Sawyer, *et al.*,[6] has revealed the existence of three polymorphic crystalline forms of $Ln_2O_2CO_3$. All are layer-type structures built up of slabs of $(Ln_2O_2{}^{2+})_n$ polymers and $CO_3{}^{2-}$ groups. Type I has the square $(Ln_2O_2{}^{2+})_n$ layers found in LnOCl and related compounds, while type II has the hexagonal $(Ln_2O_2{}^{2+})_n$ layers found in the A-form sesquioxides. Sawyer, *et al.*, found evidence for the existence of type I for La, Pr, Nd, Sm, Eu, and Gd. The pattern for $La_2O_2CO_3$ (I) is very similar to that of tetragonal $Bi_2O_2CO_3$ and can be indexed on the basis of this structure. After continued heating of $La_2O_2CO_3$ (I) in air at 420–500°, some reflections in the original pattern split, suggesting a monoclinic dis-

[1] R. C. Ropp and E. E. Gritz in "Rare Earth Research, III," L. Eyring, Ed., Gordon and Breach, New York, N. Y., 1965, p 719.

[2] E. L. Head and C. E. Holley, Jr., in "Rare Earth Research, II," K. S. Vorres, Ed., Gordon and Breach, New York, N. Y., 1964, p 51.

[3] E. L. Head and C. E. Holley, Jr., in "Rare Earth Research, III," L. Eyring, Ed., Gordon and Breach, New York, N. Y., 1965, p 707.

[4] R. L. N. Sastry, S. R. Yoganarisimhan, P. N. Mehrotra, and C. N. R. Rao, *J. Inorg. Nucl. Chem.*, **28**, 1165 (1966).

[5] A. Glasner and M. Steinberg, *ibid.*, **22**, 39 (1961).

[6] J. O. Sawyer, P. Caro, and L. Eyring, to be submitted for publication.

TABLE I

PREPARATION OF INFRARED SAMPLES FROM THE OXALATES

	Initial treatment			Final treatment		
Final product	Atm	Temp, °C	Time, hr	Atm	Temp, °C	Time, hr
$La_2O_2CO_3$ (I)	Pumping, X-ray furnace	To 200	2	730 mm of CO_2, X-ray furnace	To 560 (quench)	1
$La_2O_2CO_3$ (IA)	Air	1000	$^1/_{12}$	Flowing CO_2	450	2
$La_2O_2CO_3$ (II)	Air	1000	$^1/_{12}$	Flowing CO_2	780	3
$Pr_2O_2CO_3$ (I + carbon)	Pumping, X-ray furnace	To 200	2	730 mm of CO_2, X-ray furnace	505	1
$Pr_2O_2CO_3$ (IA + carbon)	Flow CO_2	550	2	Flow CO_2	450	8
$Pr_2O_2CO_3$ (II)	Flow CO_2	780	20			
$Nd_2O_2CO_3$ (II)	Air	420	14,400			
$Sm_2O_2CO_3$ (II)	Pumping, X-ray furnace	To 200	2	730 mm of CO_2, X-ray furnace	715	48

tortion of the original cell. This monoclinic form (type IA) has also been prepared for Pr and Nd. The type II polymorph, prepared for La, Pr, Nd, and Sm, and possibly for Gd, is satisfactorily indexed on a hexagonal unit cell.

Experimental Part

The rare earth carbonates studied were obtained by decomposition of the corresponding oxalates. The oxalates of La, Pr, Nd, Sm, Gd, Dy, and Er were prepared by homogeneous precipitation at 60–75° by adding a dimethyl oxalate solution to the 99.9% pure oxide dissolved in 0.2 *N* HNO_3. In the X-ray and thermogravimetric experiments the hydrated, air-dried oxalates were heated to 200° with continuous pumping. The CO_2 pressure was then set at 730 mm and the taking of data was commenced.

The conditions for preparation of the samples for infrared measurements are summarized in Table I. In all cases the monocarbonates were obtained by decomposition of the corresponding hydrated oxalate under the conditions shown. The $Bi_2O_2CO_3$ was a reagent grade commercial product. All infrared samples were characterized by their Debye–Scherrer powder patterns. The low-angle lines for the case of Pr are shown in Figure 1.

The thermal expansion data and transformation temperatures were obtained with a modified Mauer–Bolz[7] high-temperature chamber mounted on a Norelco diffractometer. The pressure was set at 730 mm of CO_2 and the copper radiation ($\lambda(K_\alpha)$ 1.54178 Å) was nickel filtered. The oxalate samples were applied *via* a water slurry to 0.030-in. thick alumina slides before mounting in the platinum–20% rhodium wound furnace. Samples resting on the diameter of the cylindrical furnace tube are heated from both sides and from above. By means of optical pyrometric measurements, temperature gradients have been found to be of the order of 1%.[8] Temperatures were determined by a Pt–10% Rh thermocouple which was first calibrated by silver lattice expansion measurements. There was good agreement with the precise data of Simmons and Balluffi[9] over the entire temperature range. From previous studies[8] it was kown that for samples of high emissivity, the thermocouple temperature must be reduced by 3° per 100° in order to give close agreement with temperatures of phase changes which are accurately known. This correction was applied in the present study when samples were known to have a high carbon content. Transition temperatures were taken as that temperature at which first traces of a new phase were detectable. Lattice parameters were calculated on a Control Data Corp. 3400 computer using a B-106 program supplied by Mueller, Heaton, Miller, and Gvildys of Argonne National Laboratory and modified by Burnham.[10]

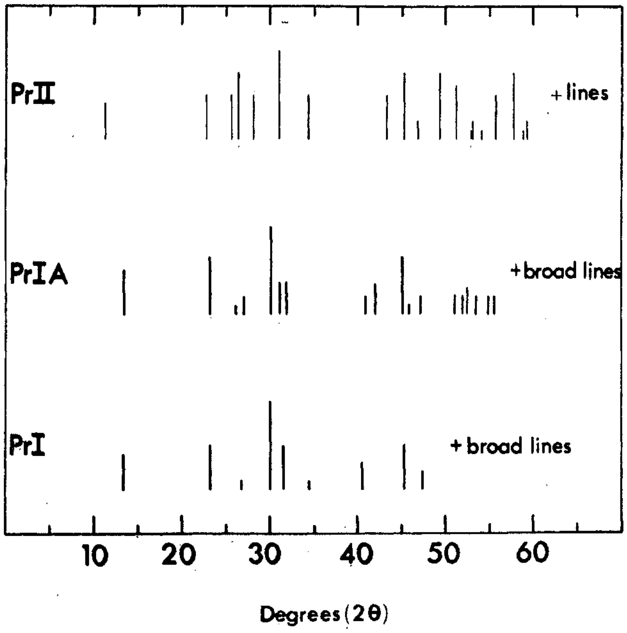

Figure 1.—X-Ray diffraction patterns of the polymorphic forms of $Pr_2O_2CO_3$.

The tensimetric experiments were made on an Ainsworth automatic recording thermobalance. The oxalate samples were continuously pumped while heating at 200° at which point the atmosphere was adjusted to 730 mm of CO_2 pressure.

The infrared spectra were taken in KBr pellets on a Beckman IR-12.

Results and Discussion of the High-Temperature X-Ray and Thermogravimetric Analysis

The Formation of $Ln_2O_2CO_3$ (I).—In the present investigation, all phases formed prior to the dioxycarbonate were amorphous in the annealing times allowed (several hours at a given temperature with temperature steps of 20–60°). In all cases the type I polymorph

---

(7) F. A. Mauer and L. H. Bolz, National Bureau of Standards Report 3148, U. S. Government Printing Office, Washington, D. C., 1953 (revised, Nov 1959).

(8) L. Eyring, M. Jenkins, J. O. Sawyer, V. Scherer, T. L. Felmlee, G. Stone, R. Turcotte, J. Warmkessel, and G. R. Weber, *Technical Progress Report*, COO-1109-25, AEC Contract No. AT(11-1)-1109, Arizona State University, Tempe, Ariz., 1967.

(9) R. O. Simmons and R. W. Balluffi, *Phys. Rev.*, **119**, 600 (1960).

(10) D. A. Burnham, Thesis, Arizona State University, Tempe, Ariz., 1967.

was first formed from $Ln_2(CO_3)_3$ as shown by thermogravimetric analysis experiments. Temperatures of formation (450–550°) were not carefully observed as it was apparent from earlier long annealing experiments that this phase could be prepared at much lower temperatures.

The X-ray patterns consisted only of broad, low-angle lines and were progressively poorer with increasing atomic number so that for $Er_2O_2CO_3$ (I) the pattern was of such poor quality that it cannot be certain that it was indeed of tetragonal symmetry.

Using two low-angle reflections (101, 103) easily read for all members at 600 ± 10°, lattice parameters and cell volumes were obtained as based on the tetragonal indexing. There is a regular variation of these with decreasing cation radius as shown in Table II.

TABLE II

LATTICE PARAMETERS OF $Ln_2O_2CO_3$(I) AT 600 ± 10°

Ln	Cation radius, Å	*a* and *b*, Å	*c*, Å	*V*, $Å^3$
La	1.15	4.16	14.05	243
Pr	1.09	4.09	13.50	224
Nd	1.08	4.04	13.45	219
Sm	1.04	3.99	13.07	209
Gd	1.02	3.94	13.00	203
Dy	0.99	3.93	12.90	198
Er	0.96	3.92	12.75	193

Since only low-angle reflections were available, limits of error were high and are estimated as follows: *a*, ±0.03 Å; *c*, ±0.09 Å; *V*, ±5 $Å^3$. It is probable that the leveling off of these parameters for the heavy members is due to increasing oxygen–oxygen repulsion of neighboring carbonate groups as the cation becomes smaller.

The Transformation of $Ln_2O_2CO_3$ (I) to $Ln_2O_2CO_3$ (II).—It has been found that the transformation of type I to type II $Ln_2O_2CO_3$ is observed for the light lanthanides at any temperature greater than 400°. At 400°, however, the transformation requires several months for completion so that temperatures obtained in the present X-ray study can only be comparative and are not equilibrium data. With similar rates of heating, first traces of the type II polymorph were detected at temperatures as follows: La, 552°; Pr, 635°; Nd, 710°; and Sm, 690°. There is no definite indication of type II formation for the heavier members. Earlier long annealing experiments[6] were in agreement with this, with no evidence of type II found for members beyond Gd. It is interesting that the rare earth sesquioxides show similar behavior with increasing temperatures required for the C form (cubic) to A form (hexagonal) transition for the lighter members, with only C form found for the heavy members. Since the type II carbonate can in fact be considered as layers of A form oxide separated by C–O layers, the temperature trends found for the I (tetragonal) → II (hexagonal) transformation and the probable nonexistence of the type II polymorph for heavier members seem to be directly related to the well-known trends for polymorphic ranges of existence of the rare earth sesquioxides.

In analogy to the irreversibility of the rare earth oxide C to A form conversion, the type I to type II transformation gave no indication of reversibility and was in all cases slow, extending over a large temperature range at the rates of heating previously mentioned. Furthermore, the rate of transformation seemed to be greatly affected by the presence of carbon and/or the particle size. In one experiment, the $La_2O_2CO_3$ (I) formed by oxalate decomposition underwent slow conversion to $La_2O_2CO_3$ (II) at 550–650°. At 670° the transformation was rapid to the point of about 70% conversion; however, a temperature of 800° was necessary for its completion. In contrast, the $La_2O_2CO_3$ (I) formed upon cooling the La_2O_3 (in CO_2) converted so slowly at 770° that even after 5 hr the transformation was only 40% complete. A decrease in carbon content in the former case due to the reaction $C + CO_2 \rightarrow CO$ and the complete lack of carbon in the latter case seem to be the most probable reasons for the observed variations in rate of conversion.

Although early experiments (below 500°) indicated a transformation of type I (tetragonal) → type IA (monoclinic) → type II (hexagonal) for the case of lanthanum and the Pr IA compound has been prepared in bulk, no evidence for this monoclinic phase was found in the high-temperature X-ray study. There is at present no satisfactory explanation of this discrepency, although factors such as carbon content, sample thickness, and heating and cooling rates may be involved.

The poorly resolved infrared spectra for the Yb and Y dioxymonocarbonates given by Glasner, *et al.*,[11,12] definitely indicate a type I compound for the former and probably a type I for the latter. Since Lu, which is the last of the lanthanide elements, has an ionic size nearly the same as that of yttrium, it undoubtedly also forms as the type I compound. It is probable then that the type I compound of all the rare earths could be prepared, but, as indicated by the tensimetric curves of Head and Holley,[3] those of the heavier members decompose at temperatures only slightly higher than that at which they are formed from the tricarbonate.

The Decomposition of $Ln_2O_2CO_3$.—At the typical rates of heating the decomposition to oxide proceeds over about a 50° temperature span. For the samarium compound, it was clearly observed that when types I and II coexisted, as the temperature was increased, the type I polymorph decomposed first. For this case, where the product of both decompositions was C form oxide, the temperature difference was 50–75°. For La, where the mixture of type I and type II was attainable, both decomposed at the same temperature to give A form sesquioxide with a slight indication that type I decomposed at a faster rate than type II. For Pr and Nd, the type

---

(11) A. Glasner, E. Levy, and M. Steinberg, *J. Inorg. Nucl. Chem.*, **25**, 1119 (1963).

(12) A. Glasner, E. Levy, and M. Steinberg, *ibid.*, **26**, 1143 (1964).

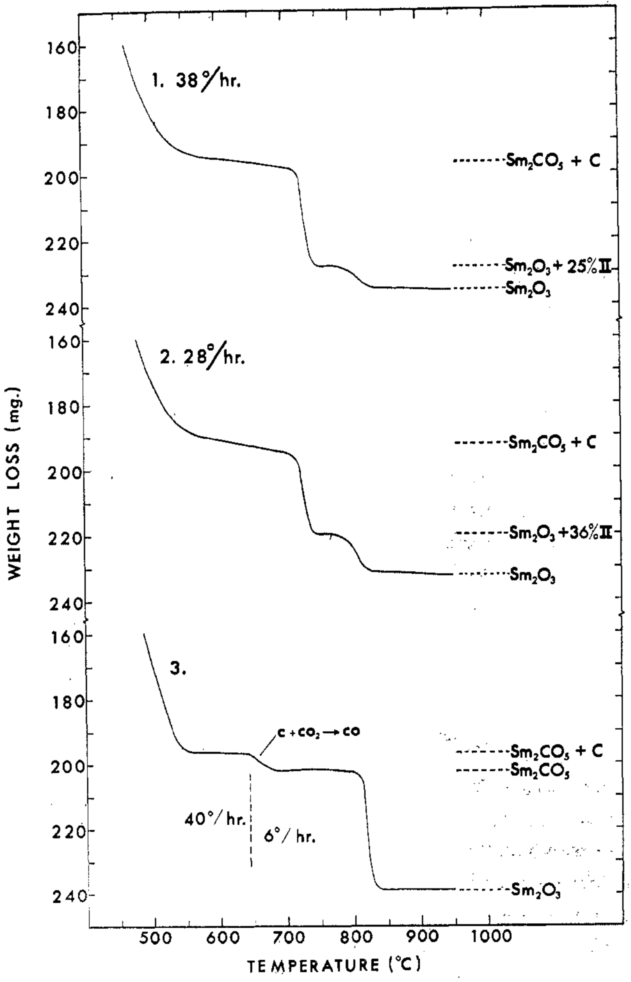

Figure 2.—Thermograms showing the decomposition of samarium dioxymonocarbonate as a function of heating rate.

I → type II conversion was complete before decomposition to the oxide occurred. (This is also usually true for La.)

The preceding observations are closely related to some thermogravimetric analysis experiments mentioned in the Introduction, where the high-temperature intermediate $Ln_2O_3 \cdot yCO_2$ was reported by Head and Holley[2,3] and $Nd_2O_3 \cdot 0.3CO_2$ by Sastry, *et al.*[4] It was apparent, as the X-ray studies proceeded, that this intermediate step corresponded to a mixture of $Ln_2O_2CO_3$ (II) and Ln_2O_3. To confirm this, three thermogravimetric experiments were made on a Ainsworth automatic recording balance. Starting samples were of nearly equal weight (within 0.5 mg) so the results are directly comparable. The plots in Figure 2 show conclusively that, as rates of heating are decreased, the proportion of the type II polymorph increases until at a 6°/hr heating rate only type II persists at higher temperatures and the type I → oxide decomposition temperature is passed without any weight loss. The absence of any weight change as type I transforms to type II demonstrates the polymorphic nature of the transformation. The weight loss with complete decomposition for the slow run was within 0.2% of the theoretical loss for $Sm_2O_3CO_3 \rightarrow Sm_2O_3$.

More complete information concerning these decompositions can be obtained from the work of Head and Holley.[2,3] Data obtained from their work as well as the present study are given in Table III. It is apparent that factors such as rate of heating, sample preparation, carbon content, particle size, etc., have a greater effect on decomposition temperatures than does the 230-mm CO_2 pressure difference which should cause decompositions to occur at higher temperatures in the present work rather than lower temperatures as observed. Although decomposition temperatures are definitely higher for those obtained by the thermogravimetric analysis method, the works are in qualitative agreement if one considers the nearly equal slopes of the curves obtained by plotting decomposition temperature *vs.* atomic number.

TABLE III

DECOMPOSITION TEMPERATURES OF $Ln_2O_2CO_3$

Compound decomposed	Decomposition temp, °C This work	 Head and Holley[2,3]	Product (Ln_2O_3)
$La_2O_2CO_3$ (II)	915	960	A form (hex.)
$Pr_2O_2CO_3$ (II)	845	825	A
$Nd_2O_2CO_3$ (II)	845	870	A
$Sm_2O_2CO_3$ (II)		810	C form (cubic)
$Eu_2O_2CO_3$ (II)		800	C
$Gd_2O_2CO_3$ (II)		770	C
$Nd_2O_2CO_3$ (I)		790	A (?)
$Sm_2O_2CO_3$ (I)	690	760	C
$Eu_2O_2CO_3$ (I)		710	C
$Gd_2O_2CO_3$ (I)	650	710	C
$Tb_2O_2CO_3$ (I)		670	C
$Dy_2O_2CO_3$ (I)	605	650	C
$Ho_2O_2CO_3$ (I)		630	C
$Er_2O_2CO_3$ (I)	600	620	C
$Tm_2O_2CO_3$ (I)		595 (?)	C
$Yb_2O_2CO_3$ (I)		620 (?)	C

It must be emphasized here that all temperatures of phase changes or decompositions reported are undoubtedly somewhat higher than those of the true equilibrium values.

The Carbonatation of Ln_2O_3.—Of the rare earth carbonates investigated, only the dioxymonocarbonates of La and Pr demonstrated reversibility of the decomposition reaction within times allowed. Head and Holley[2,3] previously gave proof of reversibility for the case of La and indicated that slow carbonatation took place for Nd_2O_3. No X-ray evidence for the carbonatation of Nd_2O_3 was observed in this investigation. It was found that upon cooling the La_2O_3 decomposition product some 100° below the decomposition temperature in the same CO_2 atmosphere, $La_2O_2CO_3$ (I) formed within a few minutes. However, when the Pr_2O_3 product was cooled, $Pr_2O_2CO_3$ (II) was obtained in a slow reaction (the ratio of A form Pr_2O_3 to $Pr_2O_2CO_3$ (II) was 60:40 at 773° after 24 hr). It is not clear why the carbonatation products are different in these two cases. Since no carbonatation was detected for other members of the series, it is likely that, if in fact there is a very slow reaction, the product will be $Ln_2O_2CO_3$ (II) for the lanthanides up to and including Gd since a type I product would be expected to form rapidly as in the case of La. For members beyond Gd, only the type I form is known, but it is doubtful that the heavy carbonates could be obtained by carbonatation (at 1 atm of CO_2 pressure) of the oxide since they are inherently thermally unstable.

The Thermal Expansion of $La_2O_2CO_3$ (I) and $La_2O_2CO_3$ (II).—Complete X-ray data as a function of temperature were taken of types I and II for $La_2O_2CO_3$, since the patterns were generally of highest quality as compared to the other rare earths investigated. Patterns were taken while increasing the temperature on a well-annealed $La_2O_2CO_3$ (II) sample until decomposition to the oxide occurred. The $La_2O_2CO_3$ (I) formed upon cooling was allowed to undergo a 40% conversion to the type II polymorph. Thus data for both forms were taken on the cooling cycle of this run and relative differences in cell parameters were more accurate than absolute errors would indicate. Errors at the 95% confidence level were ±0.007 Å for *a* and *b* and ± 0.02 Å for *c*. Expansion in the *a* and *b* directions was definitely nonlinear for the type I polymorph. In both cases *c*-axis expansion was linear within the limits of error.

The linear thermal expansion coefficients defined as $[(a_t - a_0)/a_0]/t$ (where a_0 is the lattice parameter at 0° and a_t is the parameter at $t°$) are recorded in Table IV for $La_2O_2CO_3$ (I), $La_2O_2CO_3$ (II), and La_2O_3. For the carbonate coefficients the estimated error is ±5%. It is to be noted that the expansion coefficient of type II in the *a* and *b* directions is comparable to but larger than that of the oxide, while, for both types, the *c*-axis coefficient is less than half that of the oxide. This is in good agreement with the proposed layer-type structures, since bonding for the carbonates differs from the oxide mainly in the *c* direction. The lower coefficients of expansion for the type II polymorph are correlated to the lack of reversibility of the type I to type II transformation. In this same vein it might be observed that the sesquioxide has a larger expansion coefficient than either carbonate in the *c* direction.

Results and Discussion of the Infrared Studies

Carbonate Spectra.—The spectrum of the carbonate group has been of great interest over the years for reasons of its inherent simplicity and the abundance of its compounds. The free carbonate molecule is planar and has D_{3h} symmetry. Theoretically there can be six $(3N - 6)$ vibrational normal modes, but owing to the symmetry of the group, two of these modes are degenerate giving four normal modes for the free ion. If, however, the internal symmetry of the group is altered, the degenerate modes may become nondegenerate and all six modes will then appear in the spectrum.

Table IV

Linear Thermal Expansion Coefficients

Compound	*a*, *b* × 10^5 (100°)	*a*, *b* × 10^5 (800°)	*c* × 10^5 (20 → 800°)
$La_2O_2CO_3$ (I)	1.35	1.87	0.63
$La_2O_2CO_3$ (II)	1.17	1.17	0.58
La_2O_3[a]	0.81	1.03	1.26, 1.70

[a] S. Stecura and W. J. Campbell, U. S. Department of the Interior, Bureau of Mines, Report of Investigations, No. 5847, Mines Bureau, Pittsburgh, Pa., 1957.

The nomenclature of Herzberg[13] is used here and a graphical representation of the normal modes may be found in his text. Herzberg gives the frequencies for the four modes of the free ion as: ν_1, 1063 cm^{-1}; ν_2, 879 cm^{-1}; ν_3, 1415 cm^{-1}; and ν_4, 680 cm^{-1}, with the ν_3 and ν_4 modes being degenerate. The ν_1 symmetrical stretching mode is infrared inactive for the free ion but may become active in the crystalline stage. Its presence and the splitting of degenerate modes indicate the presence of a dipole within the carbonate group. The D_{3h} symmetry of the free ion is thus lowered either to C_{2v} or C_s symmetry.

Halford[14] has shown that the difference in spectra for the two mineral forms of $CaCO_3$ is due to the differences in the symmetries of sites occupied by the carbonate group. In aragonite, the ν_3 and ν_4 modes indicate splitting of the degenerate vibrations and the ν_1 mode is activated. This indicates a lowering of molecular symmetry from D_{3h} in calcite to either C_{2v} or C_s in aragonite. Halford argues that the centers of mass of symmetric molecules are usually situated on sites and that in order for this to be so, the site group must be a subgroup of the molecular group. In calcite there are two types of sites, those belonging to groups D_3 and C_{3i}. Since only the D_3 group is a subgroup of the D_{3h} group (which the spectrum indicates as the CO_3^{2-} symmetry) the carbonate ion is assigned to this site, the cation occupying the C_{3i} site. Likewise, in the aragonite structure there are equal numbers of C_i and C_s sites and again, since the C_i group is not a subgroup of C_s (which the spectrum indicates as the CO_3^{2-} symmetry), the carbonate ion is assigned to the C_s site, the cation occupying C_i sites. It should be mentioned that use of Halford's symmetry tables and indeed the basis of this type of analysis requires crystallographic knowledge of the space group to which the crystal belongs. Such crystallographic data are frequently unknown or not known with certainty. The presence of superstructure reflections due to scattering by light atoms such as carbon or oxygen is often not detected. Furthermore, the *a priori* assumption by Halford that a symmetric molecule is situated in a crystal such that its center of mass is on a site does not seem justifiable. It seems rather that the highly directional bonding capabilities of these symmetric molecules would frequently necessitate occupation of off-site positions in order to attain the condition of minimum free energy. Nevertheless, as will be demonstrated, a consideration of symmetry elements generated by the CO_3^{2-} group and its nearest neighbors is useful in relating spectra and crystal structures.

---

(13) G. Herzberg, "Molecular Spectra and Molecular Structure, II. Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1945, p 179.

(14) R. S. Halford, *J. Chem. Phys.*, **14**, 8 (1946).

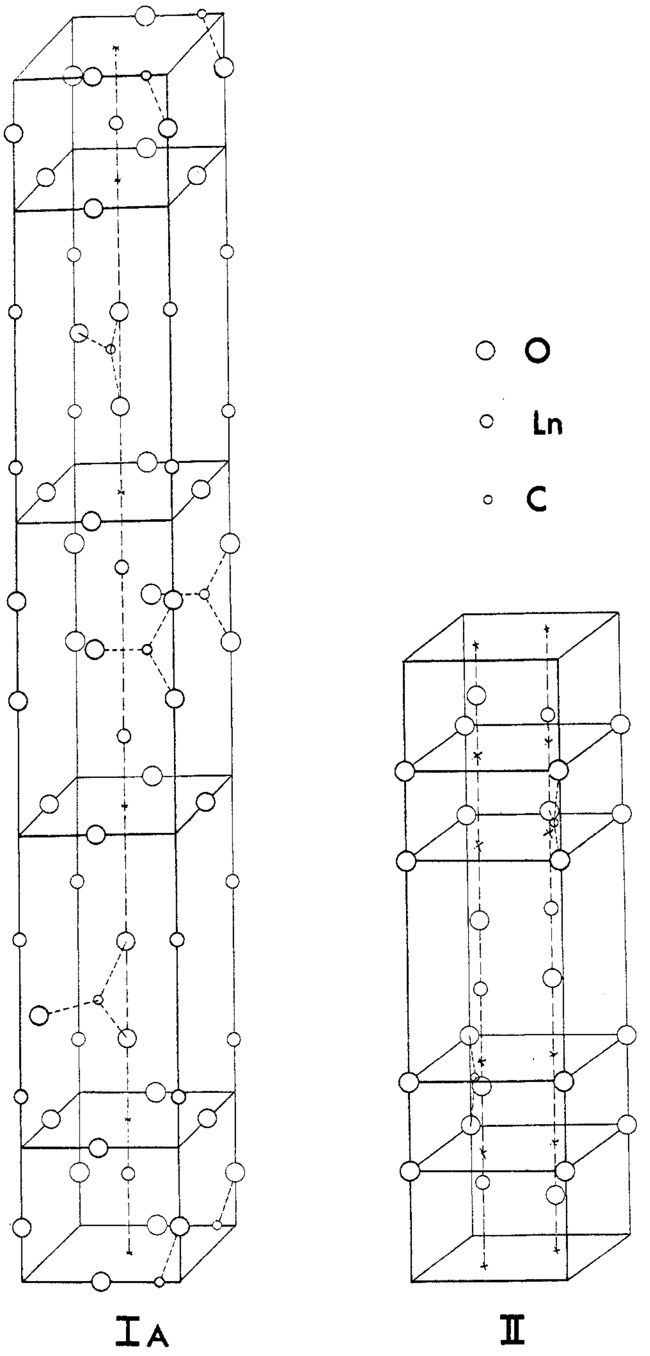

Figure 3.—Representation of proposed crystal structure of the types IA and II dioxymonocarbonates.

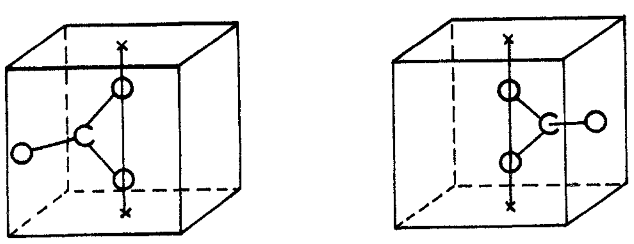

Figure 4.—Reasonable orientations of the CO_3^{2-} group in the type I structure.

Nakomoto, *et al.*,[15] in a study of coordination compounds, showed that the splitting of the ν_3 mode and the intensity of the ν_1 mode becomes greater as one proceeds from unidentate to bidentate compounds. If one assumes a planar carbonate ion, a consideration of bond lengthening or shortening of individual C–O bonds reveals that the molecule may have D_{3h}, C_{2v}, or C_s symmetry, and the spectrum will distinguish between D_{3h} symmetry, on the one hand, and C_{2v} or C_s symmetry on the other.

It should be noted, as did Adler and Kerr[16,17] in their carbonate mineral studies, that the absence of a band cannot always be considered meaningful since there are known cases of apparent accidental degeneracy. However, splitting of bands which are nondegenerate is generally an indication of nonequivalent carbonate groups in a given structure.

It is important to recognize that the splitting of degenerate modes for carbonate minerals is only slight as compared to the coordination compounds of Nakamoto, *et al.*[15] This is not surprising, since in the latter cases a given carbonate group does in fact "see" only one or two metal ions for unidentate and bidentate compounds, respectively. In simple carbonate compounds, however, a given CO_3^{2-} group "sees" many cations in the crystal field and one can no longer speak of unidentate or bidentate character but must be concerned with the nature of the crystal field with respect to each oxygen of the carbonate group. By such an analysis, the inequalities or equality of the three C–O bonds can be deduced and the spectrum can then be interpreted in terms of the crystal structure or *vice versa*.

The Crystal Structures.—The proposed structures[6] for types I and II are illustrated in Figure 3. For the type I structure, which is isostructural to that reported by Lagercrantz and Sillén[18] for $Bi_2O_2CO_3$, the orientation of the CO_3^{2-} groups was not known. As a result of the infrared study, the orientations as depicted have been assigned after first determining that the most reasonable metal atom coordination is obtained by placement of the carbonate group with two oxygens on cell corners.

The type I unit cell is half that shown and since the proposed carbonate ordering destroys the fourfold symmetry, the cell must be considered as pseudotetragonal. In this structure, all carbonate groups have two oxygens on one of the fourfold axes of the tetragonal array of metal atoms. There are then two possible positions for the third oxygen as shown in Figure 4—either at a face or at a diagonal.

If one considers a monoclinic distortion of the simple cell, it is apparent that there are three possible ways to orient the carbonate group since there are two diagonal positions and one facial position available to the third oxygen as shown by a top view of the distorted structure in Figure 5. The double cell shown in Figure 3 is the simplest unit cell possible containing

---

(15) K. Nakamoto, J. Fujita, S. Tanaka, and M. Kobayashi, *J. Am. Chem. Soc.*, **79**, 4904 (1957).

(16) H. H. Adler and P. F. Kerr, *Am. Mineralogist*, **48**, 124 (1963).

(17) H. H. Adler and P. F. Kerr, *ibid.*, 839 (1963).

(18) A. Lagercrantz and L. Sillén, *Arkiv Kemi, Mineral. Geol.*, **A25** (20), 1 (1948).

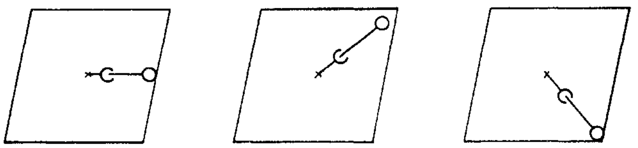

Figure 5.—Reasonable orientations of the CO_3^{2-} group in the type IA structure.

the three carbonate types which we believe exist in the pseudomonoclinic type IA structure (*c* axis unique with $\gamma \approx 91°$).

In the type II structure, there are six metal atom nearest neighbors, each set of three describing an equilateral triangle normal to (with one set above and the other below) the plane of the CO_3^{2-} group. There is only one reasonable orientation for the carbonate group in this case since there would be great oxygen–oxygen repulsion for an orientation not at the diagonal.

The Infrared Spectra.—The spectra of all three forms of the dioxymonocarbonate for La and Pr, as well as that for $Nd_2O_2CO_3$ (II) and $Sm_2O_2CO_3$ (II), are shown in Figures 6 and 7. The spectrum for $Bi_2O_2CO_3$ is also shown since it is closely related to the type I structure. The frequencies of the free carbonate ion as given by Herzberg[13] are also indicated schematically by lines at the bottom of Figure 6. These spectra can be interpreted in terms of the proposed structures, and, in fact, the orientations of the carbonate groups in types I and IA were suggested by the infrared analysis.

The type II spectrum is least complicated and most easily related to its structure. It is generally similar to spectra of a number of carbonate minerals. The splitting of the degenerate ν_3 mode and the appearance of the ν_1 mode indicate a dipole moment for the carbonate group and of the two possible symmetries an inspection of the metal nearest neighbors as shown in Figure 8 reveals that the symmetry is C_{2v}. The degeneracy of the ν_4 modes must be removed but splitting of this band is not detected. There are other examples of this accidental degeneracy in the literature (see Adler and Kerr[16]). The weak side bands apparent in these spectra are expected and are due to harmonic effects, lattice modes, and combinations of the lattice and fundamental modes.

The types I and IA spectra are far more complicated. Since the ν_1 and ν_2 modes are nondegenerate, the splitting observed for these can only be interpreted in terms of nonequivalent carbonate groups. The splitting of the ν_3 mode is also far more pronounced than is common to carbonate minerals and is therefore also ascribed to nonequivalent CO_3^{2-} groups. As shown previously, for the tetragonal type I, there are two possible orientations, and for the monoclinic type IA there are three possible orientations of the carbonate group. That all of these possibilities are realized is evident in the spectra.

The type I spectrum shows twofold splitting of the ν_2, ν_3, and ν_4 modes (most easily seen for $La_2O_2CO_3$ (I)).

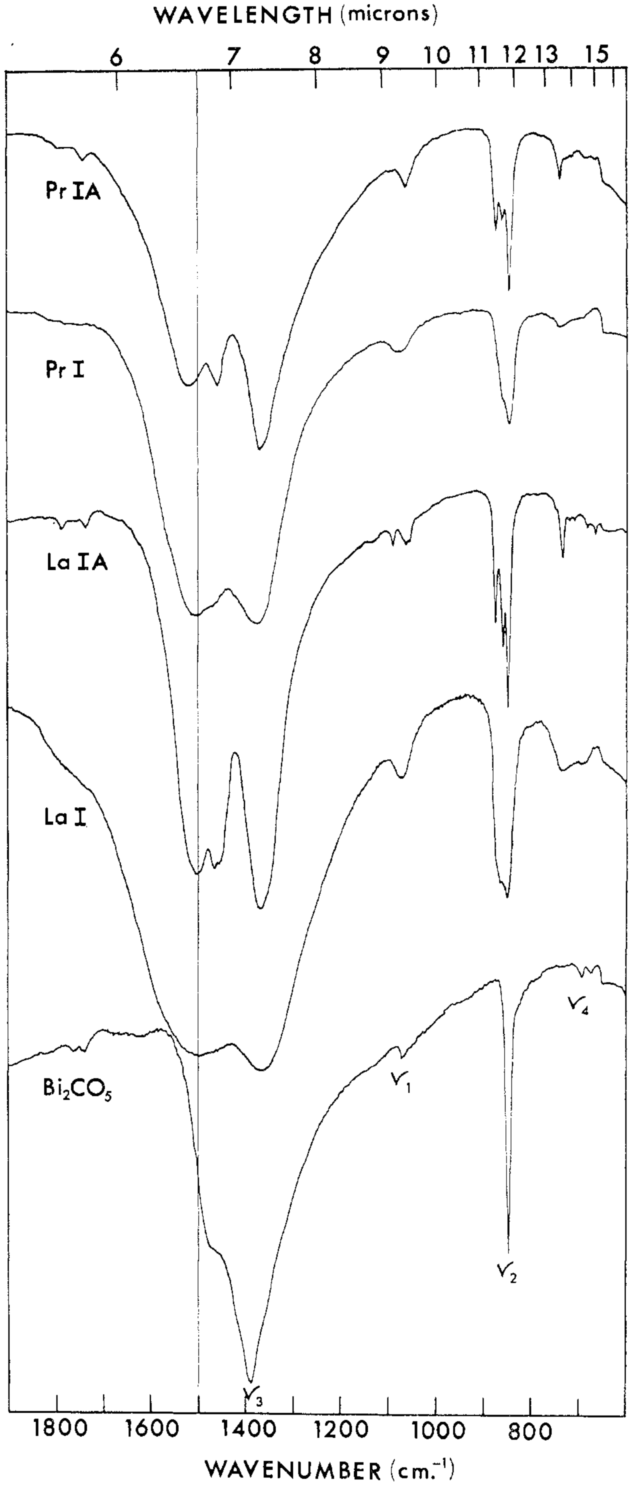

Figure 6.—Infrared spectra of the I and IA forms of the dioxymonocarbonates.

The type IA spectrum shows threefold splitting of the ν_2 and ν_3 modes and multiple splitting of the ν_4 mode (six bands are theoretically possible due to degeneracy of this mode). The ν_1 mode for the case of lanthanum is also split and a more careful scan of this mode showed definite threefold splitting for La, but for Pr the splitting remained unresolved.

There are a number of examples of splitting of *individual modes* in carbonate spectra for reasons which

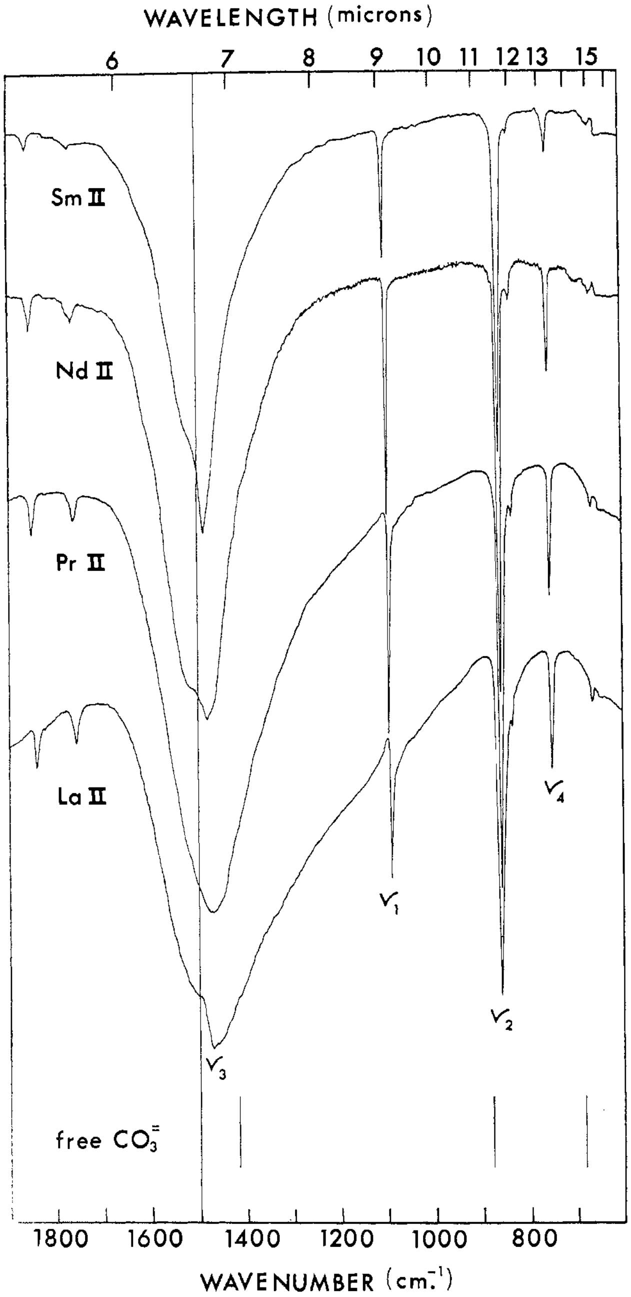

Figure 7.—Infrared spectra of the type II dioxymonocarbonates.

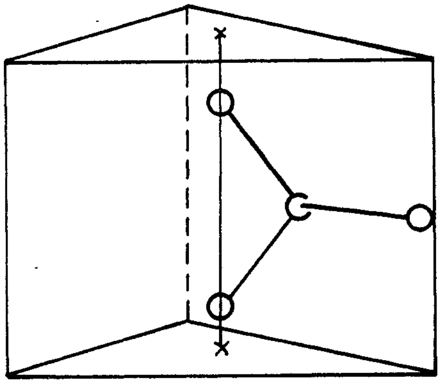

Figure 8.—Reasonable orientation of the CO_3^{2-} group in the type II structure.

are usually but not always clear. It appears that multiple splitting of *all modes* as we have found for the types I and IA compounds can only be interpreted as due to more than one CO_3^{2-} type. The minerals shortite, huntite, and parisite which contain two nonequivalent CO_3^{2-} groups show similar splitting of *all modes* in their spectra.[17] It is interesting that the ν_3 mode of the simple carbonate compounds containing only one CO_3^{2-} type falls at 1460 ± 10 cm^{-1} but compounds having more than one type of group have bands which are considerably shifted from this frequency.

Considering the type I spectrum, the twofold splitting is interpreted as due to equal numbers of the face and diagonal CO_3^{2-} types as depicted in Figure 4. As shown in Figure 5, there are two diagonal positions in the IA structure which give rise to twofold splitting of the bands due to the diagonally oriented group in the type I structure. Thus the type IA spectrum, with threefold splitting of modes with an intensity ratio of 1:1:2, indicates equal numbers of the diagonal types with twice as many face type groups as there are either one of the diagonal types.

The appearance of the ν_1 mode in these spectra indicates a molecular symmetry of either C_{2v} or C_s. An examination of the structures reveals that both types of CO_3^{2-} in the tetragonal form have C_{2v} symmetry while in the monoclinic form the face type group has C_{2v} symmetry and both diagonal types have C_s symmetry.

From these considerations it is proposed that the carbonate groups are oriented in type I to give a unit cell which is half that shown in Figure 3, having one carbonate group of each type. The alternative explanation of random orientation of the carbonate groups is also a possible explanation of the data, but since the different types do differ in energy (using this model) one would be hard pressed to explain the equal numbers of face and diagonal types. For this reason, the ordered unit cell is proposed as the more likely state of this structure. The distortion and further carbonate ordering of the simple cell gives the monoclinic IA type with one CO_3^{2-} group each in the two possible diagonal positions and two CO_3^{2-} groups in the face position (per unit cell).

An obvious difference exists between the spectra of the type I compounds and that of $Bi_2O_2CO_3$ which are believed to be isostructural. For this compound the small *a* and *b* cell length of 3.87 Å is sufficient reason for there to be only diagonally oriented carbonate groups because of increased oxygen–oxygen repulsion for the face type. The $Bi_2O_2CO_3$ spectrum in fact gives no indication of nonequivalent carbonate groups and the splitting of the ν_3 and ν_4 modes is typical of other carbonate spectra exhibiting dipole character. The unexpected shift in frequencies (most noticeably for the ν_3 mode) is not easily predicted since one must consider the much greater mass and different electronic characteristics of the bismuth cation. Since, in fact, the bismuth compound has a smaller *a*-axis length than does the lanthanum compound even though the cation size is greater, it is apparent that the electronic and mass effects are significant and the spectral differences are therefore to be expected. A more detailed discussion of the crystallography of these compounds is to be found in the paper by Sawyer, *et al.*[6]

It may be noted that the usual effects of the lanthanide contraction are carried over to the spectra of these compounds. For the type II compound the increase in frequency of a mode with increasing atomic number (decreasing cation radius) does occur regularly for all four modes.

Acknowledgment.—We are grateful to Miss K. Reimer for taking the infrared spectra and to the United States Atomic Energy Commission for financial support.

Contribution from the Department of Chemistry,
University College, Dublin, Ireland

Infrared Spectra of Bicarbonate Ions Formed in Solid Alkali Halides by Oxyanion Oxidation

By P. M. Maguire and H. E. Rubalcava[1]

Received July 8, 1968

When heated, pressed disks of several alkali halides react with substances such as potassium permanganate in the presence of water and carbon dioxide to yield bicarbonate ions occupying anion sites in the host alkali halides. This method has been used to disperse the bicarbonate ion in nine alkali halides for use in studies of the effect of environment on vibrational spectra. In favorable cases, infrared spectra have been obtained virtually free of interfering absorption due to such substances as potassium carbonate, and as a consequence erroneous vibrational assignments made by earlier investigators have been corrected. The ease of formation of carbonaceous species has been related to properties of the host alkali halides, and it is shown that the carbon and hydrogen in the carbonaceous species come mostly from atmospheric water and carbon dioxide.

Introduction

We have discovered in a study of the infrared spectra of the chlorate ion dispersed in various alkali halides[2] that this ion, and other oxidizing oxyanions, in the presence of traces of water and carbon dioxide, will react in solid alkali halide disks to yield monomer bicarbonate ion when the disks are heated. The presence of the bicarbonate ion was deduced from the excellent agreement of our results for the wave number of the strong bands of HCO_3^- in KCl, KBr, and KI with those obtained for the same systems by Bernitt, *et al.*[3] (hereafter referred to as BHH). We have obtained HCO_3^- spectra virtually free of absorption bands due to species closely related to monomer bicarbonate such as K_2CO_3, and dispersed CO_3^{2-}, whereas BHH, who used bicarbonate salts as a source of monomer bicarbonate, obtained spectra obscured by strong absorption due to such unwanted species. This has enabled us to correct some misassignments made by BHH, and, with our technique of *in situ* generation of monomer HCO_3^-, we have increased the number of host environments from the three reported by BHH to the nine indicated in Table I.

Table I

Yields and Products Formed by Heating an Oxidizing Agent in Alkali Halide Disks[a]

	Alkali halide								
	KCl	KBr	KI	RbCl	RbBr	RbI	CsCl	CsBr	CsI
$KMnO_4$	As	Am	Al	As	Am	As	As	As	Al
	Bl	Bm	Bm	Bl	Bm	Bl	Bl	Bl	Bm
	Cm	Cm	Cm	Cm	Cm	Cm	Cm	Cm	Cm
		Dm			Dm			Dl	
	El	Em	Em	El	Em	El	El	El	Em
$KClO_3$			Al					As	Al
	0	0	Cs	0	0	0	0		
			Dl						Dl
$KHCO_3$	As	As	As						
	Bl	Bl	Bl	...	...	...	...	...	...
	Fm	Fm	Fm						

[a] Notation: Capital letters denote product species: A = HCO_3^-, B = M_2CO_3 (M = K, Rb, or Cs), C = CO_3^{2-}, D = XO_3^- or MXO_3 (X = Br or I), E = MnO_2, F = HCO_2^-. Small letters denote relative yield: s = small; m = medium; l = large. 0 denotes that no reaction was detected. ... denotes that the system was not investigated.

Experimental Section

Chemicals.—Merck "Suprapur" and reagent grade alkali halides were used. These Analar grade chemicals were used without further purification: $KClO_3$, $KHCO_3$, KIO_3, $KMnO_4$, $K_2Cr_2O_7$, MnO_2, HCO_2K, and BaO_2.

Sample Preparation.—Mixtures of the oxidizing salt (or potassium bicarbonate) and the alkali halide were mixed with an agate pestle and mortar or by flash evaporation. Usually the mixtures were ground for 10 min while exposed to the lab-

---

[1] To whom correspondence regarding this paper should be addressed.

[2] P. M. Maguire and H. E. Rubalcava, unpublished investigations.

[3] D. L. Bernitt, K. O. Hartman, and I. C. Hisatsune, *J. Chem. Phys.*, **42**, 3553 (1965).