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Spectra and Thermal Decompositions of Metal Formates

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Infrared spectra of a few transition metal and rare earth formates have been studied. The separation between the ν_{asym} and ν_{sym} frequencies of the carboxylate ion is not very diagnostic in understanding the nature of metal-anion bonding in the formates. The metal-oxygen stretching frequencies, however, provide some evidence for metal-formate coordination. Electronic spectra show that there is strong coordination between the formate ion and transition metal ions. Thermal decompositions of transition metal and rare earth formates have been studied employing t.g.a. and d.t.a. Rare earth formates just as the acetates first decompose to oxycarbonates and then to the sesquioxides; the heavier rare earth formates decompose at lower temperatures. All the evidence seems to indicate greater covalency of the metal-anion bonds in the heavier rare earth formates.

Introduction

In this laboratory we have examined the infrared spectra and thermal decompositions of rare earth carbonates,[1] nitrates,[2] nitrites,[2] acetates[3] and dicarboxylates.[3] Such studies have been useful in understanding the thermal decomposition behaviour with the nature of metal-anion bonding in these compounds. In rare earth carbonates[1,4] and nitrates[2,5] clear evidence has been found for the coordination of the metal by the anions on the basis of the splitting of some of the anion bands arising out of the lower symmetry of the coordinated anions; in addition, bands are seen (below 300 cm^{-1}) due to metal-oxygen stretching vibrations, particularly in the heavier rare earth derivatives. It appears that there is greater covalency in the metal-anion bonds of the heavier rare earth compounds.

In metal acetates, the separation, $\Delta\nu_{(COO^-)}$, between the ν_{asym} and ν_{sym} frequencies of the carboxylate ion[6] is rather insensitive to the coordination of the acetate ion to the metal.[3,7] Edwards and Hayward[4] have recently shown how $\Delta\nu_{(COO^-)}$ fails to be diagnostic in establishing the mode of coordination of acetate ions to transition metals, while electronic spectra clearly established strong coordination in these acetates; these workers have placed the acetate ion close to water in the spectrochemical and nephelauxetic series. In the literature, there are some reports on the thermal decomposition of the formates of transition metals[8] as well as of rare earths.[9-14] However, there have been no spectroscopic studies of the metal-formate bonding; thermal decomposition data are particularly lacking on the heavier rare earth formates where one would expect greater metal-anion covalency. As part of our programme in the study of the spectra and thermal decomposition of rare earth compounds, we have presently examined the infrared spectra and decomposition of a few typical rare earth formates. For purposes of comparison we have studied the infrared and electronic spectra and thermal decomposition of cobalt(II), nickel(II), and copper(II) formates.

Experimental Section

All the rare earth formates were prepared by the reaction of rare earth nitrates with formic acid.[14,15] The resulting formates were recrystallized from formic acid. Cobalt(II), nickel(II) and copper(II) formates were prepared by the reaction of the corresponding carbonates with formic acid.[16]

The infrared spectra of the formates were recorded on a Perkin-Elmer Model-521 double grating spectrometer. Samples were prepared as KBr pellets or mulls in Nujol. The electronic spectra were obtained using the Beckman DU spectrophotometer (Model 2400) with the reflectance attachment; magnesium carbonate was used as the reference for

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(1) R. L. N. Sastry, S. R. Yoganarasimhan, P. N. Mehrotra, and C. N. R. Rao, *J. Inorg. Nucl. Chem.*, *28*, 1165 (1966).

(2) K. C. Patil, R. K. Gosavi, and C. N. R. Rao, *Inorg. Chim. Acta*, *1*, 155 (1967).

(3) K. C. Patil, G. V. Chandrashekhar, M. V. George, and C. N. R. Rao, *Canadian J. Chem.*, *46*, 257 (1968).

(4) J. R. Ferraro, A. Quattrochi, K. C. Patil, and C. N. R. Rao, *J. Inorg. Nucl. Chem.*, *31*, 3667 (1969).

(5) J. R. Ferraro and A. Walker, *J. Chem. Phys.*, *42*, 1237 (1965); *ibid.*, *43*, 2689 (1965).

(6) C. N. R. Rao, « Chemical Applications of Infrared Spectroscopy », Academic Press, New York, 1963.

(7) D. A. Edwards and R. N. Hayward, *Canadian J. Chem.*, *46*, 3443, (1968).

(8) C. Duval, « Inorganic Thermogravimetric Analysis », 2nd Ed., Elsevier Publ. Co., Amsterdam, 1963.

(9) M. N. Ambrozhii and Y. A. Osipova, *Zh. Neorg. Khim.*, 3, 2716 (1958).

(10) V. E. Plyushchev, L. P. Shklover, and T. A. Trushina, *Zh. Neorg. Khim.*, 9, 210 (1964).

(11) V. E. Plyushchev, L. P. Shklover, L. M. Shkolnikova, G. P. Kuznetsova and G. V. Nadezerdina, *Dokl. Akad, Nauk. S.S.S.R.*, *160*, 366 (1965).

(12) V. E. Plyushchev, L. P. Shklover, L. M. Shkolnikova, G. P. Kuznetsova, and T. A. Trushina, *Zh. Obshch. Khim.*, 35, 1783 (1965).

(13) L. P. Shklover, V. E. Plyushchev, G. P. Kuznetsova, and T. A. Trushina, *Zh. Neorg. Khim.*, *10*, 1121 (1965).

(14) I. Mayer, M. Steinberg, F. Feignblott, and A. Glasner, *J. Phys. Chem.*, *66*, 1737 (1962).

(15) B. Sahoo, S. Panda, D. Patnaik, *J. Indian Chem. Soc.*, 37, 594 (1960).

(16) L. L. Bircumshaw and J. Edwards, *J. Chem. Soc.*, 1800 (1950).

Table I. Infrared frequencies and band assignments of rare earth and transition metal formates (cm^{-1})[a]

Formate	$\nu(COO^-)_{asym}$	$\nu(COO^-)_{sym}$	$\Delta\nu(COO^-)$	$\rho(COO^-)$	$\pi(COO^-)$ or $\pi(C—H)$[b]	$\nu(OCO)$	ν_{M-O}[c]
Na	1567	1366	201	1377	1073	772	—
Y	1578	1370	208	1430	1097	780	290
La	1575	1356	219	1388	1137	773	290
Sm	1575	1360	215	1410	1095	777	295
Ho	1575	1370	205	1430	1095	781	280, 300
Yb	1570	1336	234	1386	1065	750	300, 365
Lu	1580	1336	244	1388	1065	778	300, 370
Co^{II}	1563	1352	211	1454	1030	737	337
Ni^{II}	1569	1361	208	1406	1030	776	347
Cu^{II}	1596	1385	231	1401	1028	720	345

[a] Nomenclature of the bands is similar to that of Nakamoto.[19] [b] Very weak bands. [c] Tentatively assigned to metal-oxygen stretching by analogy to nitrates and carbonates.[4,5]

reflectance measurements. Thermogravimetric analysis (t.g.a.) and differential thermal analysis (d.t.a.) were carried out in dry air (at atmospheric pressure) employing recording instruments described in earlier papers from this laboratory.[2,3,17] The heating rates in the t.g.a. and d.t.a. studies were 10° min^{-1} and 16° min^{-1} respectively. The enthalpies of reactions were estimated from d.t.a. peak areas by employing external standards.[17]

Results and Discussion

Infrared spectra of rare earth and transition metal formates. The infrared frequencies and assignments of the formate ion (C_{2v} symmetry) have been reported by Itoh and Bernstein.[18] The important characteristic frequencies of the formate ion in rare earth and transition metal formates presently studied are shown in Table I. Typical infrared spectra are shown in Figure 1. It can be seen that the $\Delta\nu_{(COO^-)}$ in rare earth formates varies between 200 and 245 cm^{-1}, showing a slightly larger separation in the ytterbium and lutetium formates. The $\Delta\nu_{(COO^-)}$ in the lighter rare earth formates is comparable to that in sodium formate. Based on these $\Delta\nu_{(COO^-)}$ values in the rare earth formates one is tempted to conclude that metal-anion bonds are nearly of the same strength in rare earth formates with the exception of the ytterbium and lutetium compounds. However, such a comparison may not be warranted since the $\Delta\nu_{(COO^-)}$ values in Co^{II}, Ni^{II} and Cu^{II} formates are comparable to those in the lighter rare earth formates, even though the metal-anion bonds are likely to be appreciably covalent in these transition metal formates. Further, transition metal formates seem to show relatively high metal-oxygen stretching vibration frequencies (345 cm^{-1}). Ytterbium and lutetium formates also show bands in the region 300-370 cm^{-1}, possibly due to the metal-oxygen stretching; the lighter rare earth formates, however, show these bands at lower frequencies (Table I, Figure 1). We, therefore, feel that there is likely to be greater metal-oxygen covalency in the heavier rare earth formates.

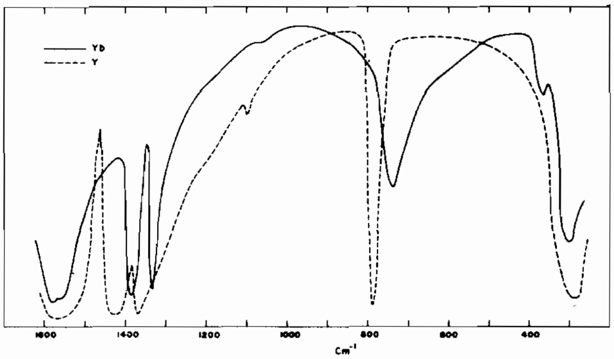

Figure 1. Infrared spectra yttrium and ytterbium formates in the 1600-250 cm^{-1} region.

The infrared data on formates do not give any clear indication regarding the nature of coordination. In the rare earth formates, the $\Delta\nu_{(COO^-)}$ values may be taken to indicate that the formate ion is present as a bidentate ligand. However, the high formal positive charges of the metal as well as the tendency to favour high coordination numbers by lanthanide elements suggest that it is likely that bridged formate groups are present in these systems. Similar observations have been made with regard to rare earth acetates.[7] In order to ascertain the nature of coordination, we have examined the electronic spectra of three transition metal formates which may be somewhat akin to the heavier rare earth formates with regard to metal-anion bonding.

Electronic spectra of transition metal formates. The data on the electronic spectra of cobalt(II), nickel(II) and copper(II) formates are shown in Table II; the spectra are closely comparable to those of the corresponding acetates.[7] The spectra of the cobalt(II) and nickel(II) formates are typical of octahedral coordination.[20] In the case of the cobalt(II) formate, the 19400 cm^{-1} band shows splitting similar to that found in many other octahedral complexes. We have assigned the shoulder at 20,730 cm^{-1} to the $^4T_{1g} \rightarrow {}^2T_{1g}(H)$, which probably borrows the intensity by mixing with the spin-allowed transition. Employing the method of Underhill and Billing,[21] we have calculated the values of Dq and the Raccah parameter, B, to be 925 cm^{-1} and 833 cm^{-1} respectively. Using the value of B for the free ga-

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(17) K. J. Rao and C. N. R. Rao, *J. Materials Sci.*, *1*, 238 (1966).
(18) K. Itoh and H. J. Bernstein, *Canadian, J. Chem.*, *34*, 170 (1956).
(19) K. Nakamoto, « Infrared Spectra of Inorganic and Coordination Compounds », John Wiley, New York, 1963.
(20) C. J. Ballhausen, « Introduction to Ligand Field Theory », McGraw Hill Book Co., New York, 1962.
(21) A. E. Underhill and D. E. Billing, *Nature*, *210*, 834 (1966).

seous ion (972 cm^{-1}), the nephelauxetic ratio, β_{35}, was found to be 0.86. In the case of Ni^{II} formate, Dq, B and β_{35} were found to be 921 cm^{-1}, 848 cm^{-1} and 0.82 respectively; the free ion value for B was taken as 1030 cm^{-1}. These results from the electronic spectra show that the formate ion is close to water or acetate ion in the spectrochemical and nephelauxetic series.

Table II. Electronic spectra of cobalt(II), nickel(II) and copper(II) formates

Formate	ν_{max}, cm^{-1}	Assignment
Cobalt(II)	17,390	$^4T_{1g}(F) \rightarrow {}^4A_{2g}$
	19,420	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
	20,730	$^4T_{1g}(F) \rightarrow {}^2T_{1g}(H)$
Nickel(II)	9,000	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$
	13,790	$^3A_{2g}(F) \rightarrow {}^1E_g(D)$
	15,040	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$
	25,320	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$
Copper(II)	14,980	$^2E_g \rightarrow {}^2T_{2g}$
	26,320	Charge-transfer

Cupric formate shows a band around 14,980 cm^{-1} which may be assigned as due to the $^2E_g \rightarrow {}^2T_{2g}$ transition;[20,22] the shoulder around 2600 cm^{-1} is probably the charge-transfer band.[22,23] The spectrum of Cu^{II} formate is quite similar to that of Cu^{II} acetate which is a distorted octahedral complex; the bonding (and structure) in these two compounds are also similar, both containing Cu—Cu bonds.[24]

Thermal decomposition of cobalt(II), nickel(II) and copper(II) formates. The Co^{II} and Ni^{II} formates show two stages of decomposition corresponding to the formation of anhydrous formate in the t.g.a. and d.t.a. curves (Figures 2 and 3). The t.g.a. results show that anhydrous Co^{II} formate first decomposes to a mixture of Co and CoO which is then oxidized to Co_3O_4. In the case of Ni^{II} formate, the final product is a mixture of Ni and NiO. Copper(II) formate does not show any stage corresponding to the dehydration in the t.g.a. curve (Figure 3) and decomposes directly to CuO around 225°C; the d.t.a. curve also shows only one endothermic peak. The reactions corresponding to the initial decompositions of these transition metal formates are:

$$2Co(HCO_2)_2 \rightarrow Co + CoO + 2CO + 2CO_2 + H_2O + H_2 \quad (1)$$

$$2Ni(HCO_2)_2 \rightarrow Ni + NiO + 2CO + 2CO_2 + H_2O + H_2 \quad (2)$$

$$2Cu(HCO_2)_2 \rightarrow 2CuO + 3CO + CO_2 + H_2O + H_2 \quad (3)$$

Reaction (2) for nickel(II) formate differs from that proposed by Bircumshaw and others[8,16] who did not find any evidence of NiO in the products of decomposition. Reactions (1) and (3) are in general agreement with the literature.[8] It may be noted that the decomposition temperatures of all the three transition metal formates are quite low and well below 350°C. This is what we would expect on the basis of the fairly covalent metal-anion bonding in these compounds.

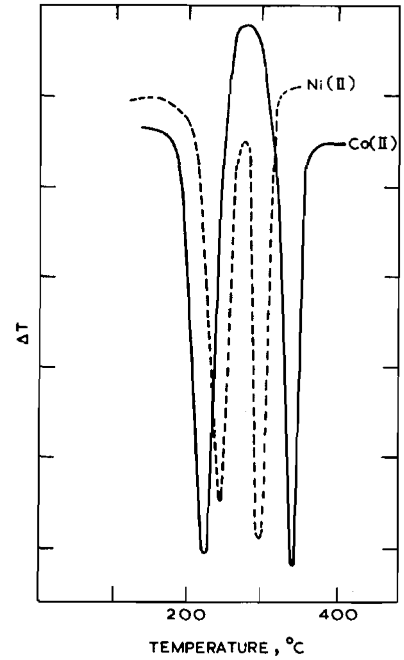

Figure 2. d.t.a. curves for the decomposition of cobalt(II) and nickel(II) formates. Copper(II) formate shows only one peak at 225°C.

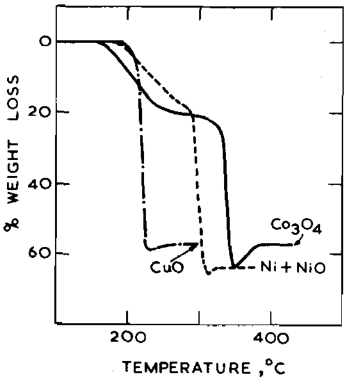

Figure 3. t.g.a. curves for the decomposition of hydrated cobalt (II), nickel (II) and copper (II) formates.

Thermal decomposition of rare earth formates. We could prepare lanthanum, samarium, holmium and yttrium formates in the anhydrous state. The ytterbium and lutetium formates could only be obtained in the hydrated form and they could be readily dehydrated by heating to ~200°C. The d.t.a. curve of lutetium and ytterbium formates showed two stages of dehydration just as the corresponding acetates.[3] Typical t.g.a. and d.t.a. curves for the decomposition of anhydrous rare earth formates are given in Figures 4 and 5. The t.g.a. curves show that all the rare earth formates, $Ln(HCO_2)_3$, decompose first to the oxycarbonates, $Ln_2O_3 \cdot CO_2$ and then to the

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(24) M. Bukowoska-Strzyzewska, *Acta Cryst.*, *19*, 357 (1965).
(22) L. L. Funck and T. R. Ortolano, *Inorg. Chem.*, *7*, 567 (1968).
(23) A. Chakravorty and T. S. Kannan, *J. Inorg. Nucl. Chem.*, *29*, 1691 (1967) and the references cited therein.

sesquioxides, Ln_2O_3. The formation of the oxycarbonate could be confirmed by infrared spectroscopy.[1,3,4] There is no evidence for the formation of the normal carbonate, $Ln_2(CO_3)_3$, in the t.g.a. curves. The important t.g.a. results on the decomposition of anhydrous rare earth formates are shown in Table III. We may note that the formation of oxycarbonates has been found to be the first stage in the decomposition of rare earth carbonates as well as acetates.

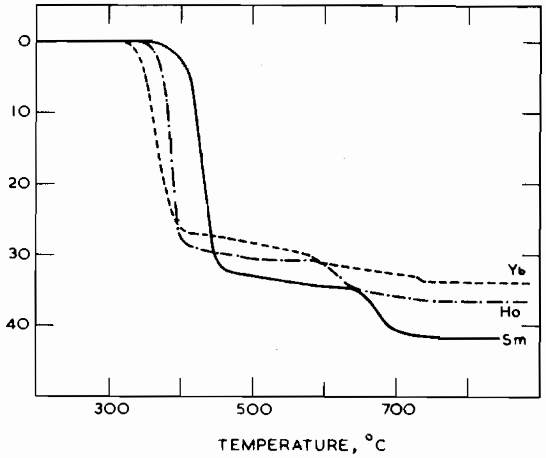

Figure 4. t.g.a. curves for the decomposition of samarium, holmium and ytterbium formates.

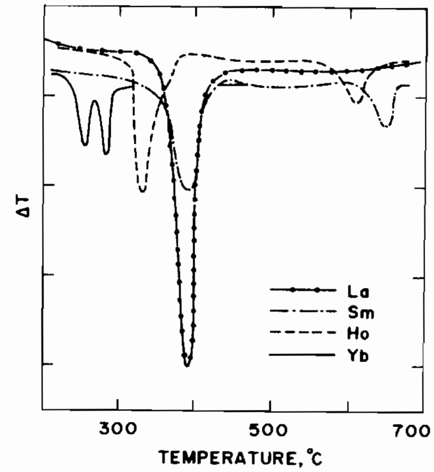

Figure 5. d.t.a. curves for the decomposition of lanthanum, samarium, holmium and ytterbium formates. The peak corresponding to lanthanum formate appears above 850°C.

Table III. Important t.g.a. and d.t.a. results on the thermal decomposition of rare earth formates, $Ln(HCO_2)_3$

Ln	Oxycarbonate formation temperature $Ln_2O_3 . CO_2$ (°C)	ΔH [a] kcal/mole	Minimum oxide formation temperature Ln_2O_3 (°C)
La	375	127	825
Sm	350	63	755
Ho	335	43	745
Yb	315	32	740
Lu	255	—	706
Y	304	—	715

[a] From the areas of peaks corresponding to the formate oxycarbonate decomposition.

The d.t.a. curves of the anhydrous lanthanum, samarium, holmium and yttrium formates showed two peaks corresponding to the formation of oxycarbonates and the oxides (Figure 5). Ytterbium formate, however, showed two peaks between 230° and 290°C, which may be ascribed to the formation of the normal carbonate and the oxycarbonate. Lutetium formate similarly showed three peaks between 250° and 320°C possibly corresponding to the different stages of decomposition of the formate to the oxycarbonate. Such stages in the decomposition of the formate to the oxycarbonate were not found in the t.g.a. curves; a similar observation has been made in the decomposition of rare earth acetates.[3] Both lutetium and ytterbium formates did not show distinct d.t.a. peaks for the decomposition of the oxycarbonates to the oxides. In all the rare earth formates studied, the d.t.a. decomposition temperatures agree well with the temperatures indicated by the t.g.a. curves. Our t.g.a. and d.t.a. results on lanthanum, samarium and yttrium formates, however, differ slightly from the literature reports.[9-13]

Estimates of the enthalpy changes, ΔH, associated with the decomposition of anhydrous formates to the oxycarbonates were made comparing the areas of the curves of d.t.a. by employing appropriate standards.[3,17] The results (Table III) show that ΔH varies in the order, La > Sm > Ho > Yb. The formation temperature of the oxycarbonate (from the formate) also decreases progressively from lanthanum to lutetium; a similar trend is seen in the decompositions of the oxycarbonates to the oxides. These trends may result from the greater covalency of the anion-metal bonds in the heavier rare earth salts, an observation which finds some support from our infrared studies.