Lanthanide Ion Catalysis of the *trans–cis* Isomerization of *trans*-Bis(oxalato)-diaquochromate(III) and *trans*-Bis(malonato)diaquochromate(III) [1]

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The lanthanide ion catalyzed trans–cis *isomerizations of* trans-bis(oxalato)diaquochromate(III) *and* trans-bis(malonato)diaquochromate(III) *have been studied. A linear free energy relationship was found correlating the catalytic rate constants for the oxalate reaction with the corresponding formation constants of complexes formed between simple monocarboxylic acids and the light (La–Gd) members of the lanthanide series. This result indicates that for this portion of the series, the reaction mechanism is related to the formation of monocarboxylate complex intermediates. When the ionic radius of the lanthanide ion decreases below a particular value (as in the latter half of the series), the metal ion remains coordinated to both carboxylates of the oxalate ion rather than simply binding to only one carboxylate. In either situation, isomerization to the* cis *product eventually occurs, and the lanthanide ion is released.*

The reaction rates associated with the trans-bis(malonato)diaquochromate(III) *reaction were found to be significantly slower than those of the corresponding oxalate system. However, in the malonate system, no linear free energy relationship was found relating the catalytic rate constants with the corresponding formation constants of monocarboxylic acids. One does find a linear relationship between the catalytic rate constants for the malonate reaction and the log K_1 values for the corresponding lanthanide/malonate complexes. During the course of the* trans–cis *isomerization, the lanthanide ion chelates the dissociated malonate group of a pentavalent Cr(III) intermediate. In this mechanism, the lanthanide ion does not aid in ring opening, and neither does it singly bond to the intermediate.*

Introduction

The *trans–cis* isomerization of *trans*-Cr(chelate)$_2$-(H$_2$O)$_2^-$ has been investigated by many workers for the specific systems where chelate = C$_2$O$_4$ (oxalate)

or C$_3$H$_2$O$_4$ (malonate). One of the important questions regarding these reactions has been the effect of external catalysts on the mechanism of the reaction. Ashley and Hamm [3] reported on the utility of both transition metal ions and non-transition metals as catalysts for the isomerization of the oxalate complex, while Frank and Huchital [4, 5] extended these studies while examining the isomerization of the malonate complex. In each series of investigations, the favored mechanistic pathway for the catalyzed isomerization was thought to be that of metal assisted ring opening.

One interesting finding in the Ashley and Hamm study was that the most effective catalytic agents for the isomerization of the oxalate complex were the trivalent ions of lanthanum and cerium [3]. Catalytic rate constants for these two ions were found to be two to three times greater than those obtained for Cu(II), which was in turn found to be the most effective transition metal catalyst. It is well known that certain transition metal ions (Hg(II) being the most widely studied) can attack coordinated ligands, alter the rate of ligand replacement, participate in the removal of unidentate ligands, and promote dechelation [6]. These reactions are those commonly associated with transition metal ions. On the other hand, lanthanide ions are not normally considered to function as effective agents in metal-assisted dechelation reactions. The more common applications for lanthanide ions have been as shift reagents in NMR spectroscopy [7], luminescent phosphors for lamps and cathode ray tubes [8], substitutional probes for Ca(II) in proteins and enzymes [9], and as reagents in organic synthesis [10].

We report now the results of systematic studies on the catalytic effects of lanthanide ions on the isomerization of both *trans*-bis(oxalato)diaquochromate(III) and *trans*-bis(malonato)diaquochromate(III). Catalytic rate constants and activation parameters have been determined for all trivalent ions of the lanthanide series (excluding Ce and Pm) and for yttrium as well. Examination of the trends observed across the series enabled conclusions to be drawn regarding the proposed mechanisms for the isomerizations. Finally, attempts were made to correlate the

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rate constants obtained for the various members of the lanthanide series with general systematic theories, and the data serve as a means to test the validity of these various classification schemes.

To our knowledge, the present work represents the first attempt to systematically evaluate the catalytic behavior of all members of the lanthanide series in homogeneous, solution phase media.

Experimental

Materials

Potassium *trans*-bis(oxalato)diaquochromate(III) was prepared following the procedure of Kaufman and Faoro [11]. The purity of the complex was checked by a quantitative comparison (determination of molar absorptivities) of the spectra of the initial *trans* complex and the *cis* isomerization product with the reported literature data [12]. In all cases, the synthesized *trans* complex was determined to be free of any *cis* contamination.

Potassium *trans*-bis(malonato)diaquochromate(III) was prepared in the manner described by Frank and Huchital [4]. The same method of spectral characterization as just described indicated that the *trans* complex was prepared virtually free from any *cis* contamination.

The lanthanide nitrates used in the present study were of at least 99.9% purity, and were obtained from either Alfa Products, Aldrich Chemical Company, Research Chemicals, or American Potash and Chemical Corporation. Lanthanide chlorides were used as received from either Alfa Products, American Potash and Chemical Corporation, or Allied Chemical Corporation. Stock solutions of all lanthanide salts were prepared by weight, and were subsequently standardized through titration with standard EDTA [13]. All other reagents and chemicals were ACS grade or its equivalent.

Kinetic Measurements

All kinetic measurements were carried out on a Cary Model 219 spectrophotometer. Constant temperature in the cell compartment was maintained using a bath fitted with a Thermistep Temperature Controller (Model 71, Yellow Springs Instrument Co.), and a bath cooler (Model PBC–4, Neslab Instruments).

Stock solution of sodium nitrate (2.00 M) and the lanthanide salt (*ca.* 0.30–0.40 M) were prepared. These solutions (and any glass distilled water used in the kinetic runs) were adjusted to pH 3.0 with HNO_3 or HCl. All pH measurements were made with either a Fisher Accumet model 520 or an Orion model 701A pH meter. Both meters were equipped with micro combination electrodes (suitable for direct insertion into the absorption cuvettes), and

these were calibrated daily with pthalate and phosphate buffer solutions.

Kinetic runs were performed by premixing appropriate volumes of stock solutions and distilled water in 1 cm spectrophotometer cells, and then these reagents were equilibrated to the desired temperature in the water bath. These initial procedures were then followed by the addition of accurately weighed amounts of solid *trans*-Cr(chelate)$_2$(H$_2$O)$_2^-$ complexes, so that the final concentrations of the oxalate and malonate complexes were 14 and 35 mM respectively. The higher concentrations used for the malonate system were required by the need to use the initial rate method of data analysis with this system.

Treatment of Data

The isomerization of the oxalate complex was followed by the increase in absorption at 416 nm, corresponding to the absorption maximum of the *cis* product. Pseudo first-order rate constants were obtained after linear regression analysis was used to obtain the slope associated with plots of $\ln(A_\infty - A)$ *vs.* time. Where necessary, values for A_∞ were estimated using the Mangelsdorf method [14]. Catalytic rate constants for each lanthanide ion were calculated from the slopes of plots relating k_{obs} with the concentration of the lanthanide ions.

The *trans–cis* isomerization of the malonate complex was observed to be considerably slower than that of the oxalate complex, and as a result the pseudo first-order rate constants were obtained from initial rate data over the first 2–3% of the reaction. In this system the data were obtained by following the increase in absorbance at 566 nm, the absorption maximum of the *cis* product. From absorbance *vs.* time plots, initial reaction rates (Abs. units sec^{-1}) were obtained. These initial gradients were converted into concentration units (M sec^{-1}) using the known molar absorptivity of the *cis* product. Pseudo first-order rate constants were then calculated by dividing the concentration rates by the known concentration of the *trans* complex. Catalytic rate constants for each lanthanide ion were then calculated as just described.

The calculations of initial rates, pseudo first-order rate constants, catalytic rate constant, and the Mangelsdorf method analyses were all carried out using programs written for a Commodore PET computer [15]. Mangelsdorf method analyses also required a curve fitting program written for an Apple II+ computer [16].

Results and Discussion

Isomerization of trans-Cr(C$_2$O$_4$)$_2$(H$_2$O)$_2^-$

The lanthanide ion catalyses of the isomerization of the oxalate complex were carried out at

TABLE I. Catalytic Rate Constants and Activation Parameters for the *trans-cis* Isomerization of *trans*-Bis(oxalato)diaquochromate(III).

| Lanthanide Ion	$10^2 k_{Ln^{3+}}$ (M^{-1} s^{-1})			$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (cal/mol-deg)
	15 °C	25 °C	30 °C		
La^{3+}	3.04	8.00	11.4	15.1	−13.0
Pr^{3+}	4.56	9.75	16.0	13.7	−17.1
Nd^{3+}	4.35	11.4	16.2	14.9	−12.8
Sm^{3+}	4.44	11.4	16.2	14.7	−13.7
Eu^{3+}	4.77	11.3	17.3	14.4	−14.6
Gd^{3+}	4.12	9.94	14.8	14.3	−15.2
Tb^{3+}	3.85	9.73	14.6	14.9	−13.1
Dy^{3+}	2.79	9.27	14.3	18.6	−1.02
Ho^{3+}	2.31	9.91	14.4	21.3	7.87
Er^{3+}	3.68	9.80	14.7	15.7	−10.6
Tm^{3+}	3.08	9.64	15.0	17.9	−3.09
Yb^{3+}	4.52	11.4	15.9	14.2	−15.2
Lu^{3+}	3.24	10.8	16.4	18.5	−1.06
Y^{3+}	2.11	7.78	12.2	20.1	3.54
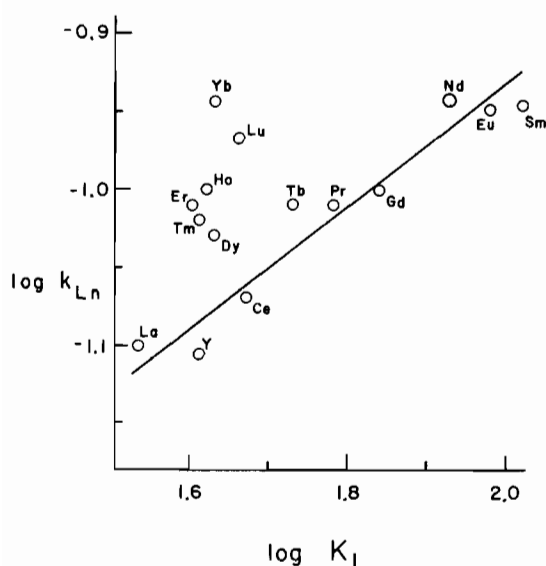
Fig. 1. Log—Log plot of the catalytic rate constants for the lanthanide ion catalyzed *trans—cis* isomerization of *trans*-bis(oxalato)diaquochromate(III) (25 °C, I = 1.5 M adjusted with $NaNO_3$) *vs.* the formation constants for the lanthanide/propionate complexes (25 °C, I = 2.0 M).

pH 3 and 1.5 M total ionic strength using $NaNO_3$ or NaCl as the supporting electrolyte. The catalytic rate constants obtained for the entire lanthanide series at 15, 25, and 30 °C are reported in Table I, along with the associated activation parameters.

For the light members of the lanthanide series (La through Gd), a linear free energy relationship was found when plotting the catalytic rate constants for the oxalate complex isomerization and the corresponding formation constants [17] of simple monocarboxylic acids. For instance, three carboxylic acids (acetic, propionic, and 2-methylpropanoic acids) all gave nearly identical plots of log k_{Ln} *vs.* log K_1. A representative example of this trend is shown in Fig. 1. However, with the heavy lanthanide ions (Tb through Lu), the linear relationship between log k_{Ln} and log K_1 is lost. Even though the formation constant of the lanthanide/carboxylate complexes continues to increase as one passes from Tb to Lu [17], one finds that the rate constant for the oxalate complex isomerization does not increase in a similar fashion.

The break in the linear free energy relationship observed as one passes across the lanthanide series is significant since a number of thermodynamic properties are known to exhibit discontinuities in the vicinity of Gd [18]. This phenomenon is often referred to as the 'gadolinium break' and a variety of explanations have been presented as to its origin. These rationalizations are part of attempts to systematize the differences in observed chemistry caused by the changing basicity of the lanthanide ions. In our system, the break may be taken as to indicate a change in the mechanism for the lanthanide ion catalyzed isomerization as one moves from the light lanthanide ions to the heavy members of the series.

The proposed mechanism for the *trans—cis* isomerization of $Cr(C_2O_4)_2(H_2O)_2^-$ as catalyzed by lanthanide ions is shown in Fig. 2. For the light lanthanides (La through Gd), the predominant path-
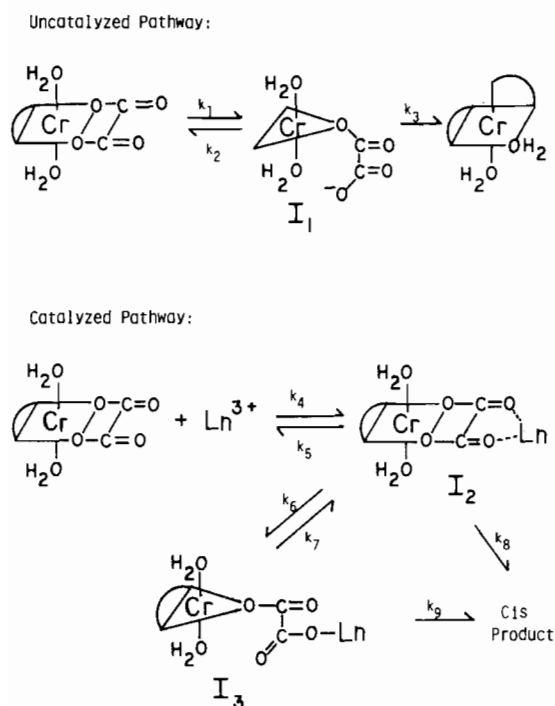
Uncatalyzed Pathway:

Catalyzed Pathway:

Fig. 2. Mechanism for the uncatalyzed and lanthanide ion catalyzed *trans–cis* isomerization of *trans*-bis(oxalato)-diaquochromate(III).

Fig. 3. Plot of log $\Delta H^{\ddagger}$ for each lanthanide ion catalyzed isomerization of *trans*-bis(oxalato)diaquochromate(III) *vs.* the ionic radii of the corresponding lanthanide ions [20].

way is *via* I_3. These ions are relatively large and apparently prefer to move from an unfavorable chelated position to a singly bonded mode with a carboxylate group. The data presented in Fig. 1 are consistent with such an explanation, since one observes that the catalytic rate constants correlate well with the strength (as evidenced by the K_1 values for the formation constants) of the metal/carboxylate complex. A lanthanide ion bound to a single carboxylate of the oxalate group would indeed correspond to binding of that ion by a monocarboxylic acid. This correlation is lost for the heavy lanthanide ions (Tb through Lu), indicating that some other type of intermediate forms during the isomerization. A chelated lanthanide/oxalate species (where the lanthanide ion is now bound in a bidentate manner) could account for the absence of any correlation with monocarboxylate species [19].

A plot of log $\Delta H^{\ddagger}$ for each lanthanide ion catalyzed isomerization *vs.* the ionic radius [20] of the corresponding lanthanide ion is shown in Fig. 3. Linearity is observed for the first half of the lanthanide series, but not for the second half. This correlation supports our conclusion that the mechanism for the isomerization changes approximately halfway through the series, and indicates that the size of the lanthanide ion is an important factor in determining the pathway of the reaction. Of course, the size of the ion determines the basicity of the cation, and the lanthanide ions function as better Lewis
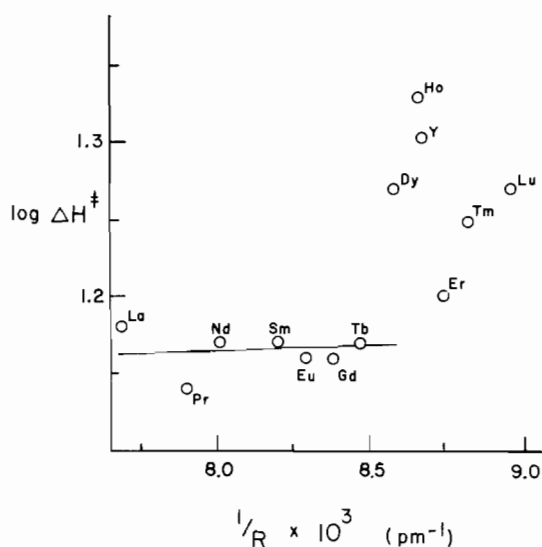
acids as one crosses the series. For the light lanthanides, an increase in basicity leads to an increase in reaction rate, but apparently this requirement reaches a limiting factor at Gd and plays a less important role with the heavy lanthanide ions.

A very important question when considering the systematics of lanthanide ions concerns the position of yttrium with respect to the members of the lanthanide series. While not being an actual member of the series, the chemical properties of Y(III) are extremely similar to those of La(III), and the ionic size of Y(III) is the same as that of Ho(III). Thus, Y(III) normally behaves as one of the heavy lanthanide ions, and makes up a significant portion of the natural sources of heavy lanthanide elements [18]. For the oxalate isomerization reaction, the catalytic rate constant obtained with Y(III) was approximately 20% smaller than that of Ho(III), and essentially the same as that of La(III). This difference might indicate some participation of the f-orbitals in the intermediate complex.

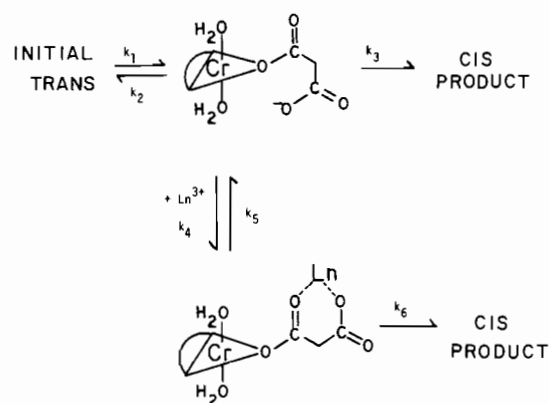*Isomerization of* trans-$Cr(C_3H_2O_4)_2(H_2O)_2^-$

The lanthanide ion catalyses of the isomerization of the malonate complex were carried out under the same conditions of pH and ionic strength as for the oxalate complex. However, the malonate complex isomerizations were observed to proceed at considerably slower rates relative to the oxalate complex reactions, and consequently the initial rate method of determining reaction rates (and hence, rate constants) were necessitated. Catalytic rate constants at 25, 30, and 35 °C are reported in Table II, and the associated activation parameters are provided as well.

TABLE II. Catalytic Rate Constants and Activation Parameters for the *trans–cis* Isomerization of *trans*-Bis(malonato)diaquochromate(III)

Lanthanide Ion	$10^5 \ k_{Ln^{3+}} \ (M^{-1} \ s^{-1})$			ΔH^* kcal/mol	ΔS^* cal/mol K
	25 °C	30 °C	35 °C		
La^{3+}	1.19	2.67	6.30	29.9	19.2
Pr^{3+}	1.36	2.77	4.52	21.2	−9.76
Nd^{3+}	1.64	3.10	4.96	19.7	−14.3
Sm^{3+}	1.57	2.53	3.82	15.7	−27.9
Eu^{3+}	1.61	2.78	5.29	21.0	−10.2
Gd^{3+}	1.87	2.74	4.12	13.7	−34.3
Tb^{3+}	1.44	2.29	3.18	13.9	−34.2
Dy^{3+}	2.00	2.52	2.84	5.84	−60.4
Ho^{3+}	1.57	2.16	3.94	16.2	−2.63
Er^{3+}	1.84	2.14	2.98	8.19	−52.8
Tm^{3+}	1.89	2.36	2.93	7.29	55.7
Yb^{3+}	2.26	2.62	3.27	6.20	−59.1
Lu^{3+}	1.63	2.27	3.29	12.2	−39.5
Y^{3+}	1.47	2.33	2.89	11.9	−40.8
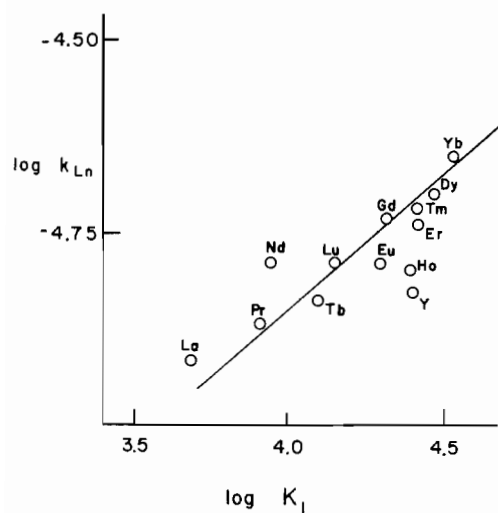
Fig. 4. Log–Log plot of the catalytic rate constants for the lanthanide ion catalyzed *trans–cis* isomerization of *trans*-bis(malonato)diaquochromate(III) (25 °C, I = 1.5 *M* adjusted with NaNO₃) *vs.* the formation constants for the lanthanide/malonate complexes (25 °C, I = 0.1 *M*).

Fig. 5. Mechanism for the lanthanide ion catalyzed *trans–cis* isomerization of *trans*-bis(malonato)diaquochromate(III).

Unlike the oxalate system, no linear free energy relationship was found relating the catalytic rate constants for the malonate isomerization reaction with the formation constants of corresponding lanthanide/monocarboxylate complexes. This lack of correlations similar to those obtained with the oxalate system (and the extreme slowness of the reactions) argues that the *trans–cis* isomerization of the malonate complex proceeds by a different mechanism. This proposal finds further support

in the observation that a plot of log k_{Ln} for the malonate reaction *vs.* log K_1 for the lanthanide/malonate complexes (with the ligand binding the metal ion in a bidentate manner between two ionized carboxylate groups) is linear. This plot is shown in Fig. 4.

The proposed mechanism for the lanthanide ion catalyzed *trans–cis* isomerization of $Cr(C_3H_2O_4)_2(H_2O)_2^-$ is shown in Fig. 5. This mechanism is very similar to that proposed by Frank [5] for isomerization of the malonate complex as catalyzed by alkaline earth and transition metal ions. In this mechanism, the lanthanide ion is not involved in monodentate bonding of any type, and always binds to the malonate group in a bidentate manner. This proposal is supported by the observations that no
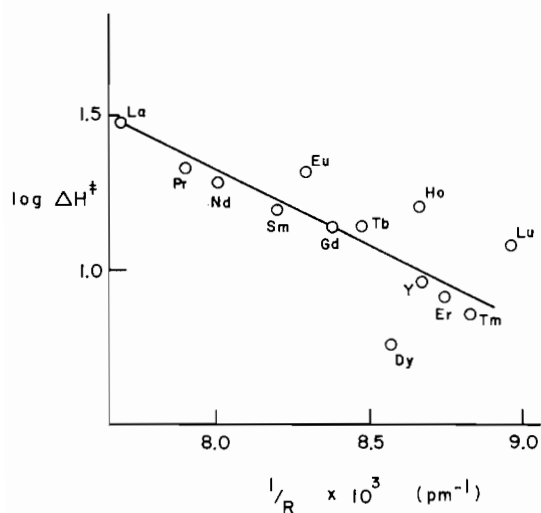
Fig. 6. Plot of $\Delta H^{\ddagger}$ for each lanthanide ion catalyzed isomerization of *trans*-bis(malonato)diaquochromate(III) *vs.* the ionic radii of the corresponding lanthanide ions [20].

TABLE III. Catalytic Rate Constants for the Lanthanide Ion Catalyzed Isomerization of Both the Oxalate and Malonate Complexes at 25 °C (pH = 3, I = 1.5 *M* adjusted with NaCl). The Numbers in Parentheses Represent the Corresponding Values in Sodium Nitrate Medium.

Lanthanide Ion	Oxalate Complex $10^2 k_{Ln^{3+}}(M^{-1} s^{-1})$		Malonate Complex $10^5 k_{Ln^{3+}}(M^{-1} s^{-1})$	
La^{3+}	10.5	(8.00)	2.40	(1.19)
Pr^{3+}	13.2	(9.75)	2.53	(1.36)
Nd^{3+}	14.1	(11.4)	2.70	(1.64)
Sm^{3+}	13.5	(11.4)	2.73	(1.57)
Er^{3+}	7.88	(9.80)	2.68	(1.84)
Ho^{3+}	8.32	(9.91)		

correlation exists between k_{Ln} and K_1 (monocarboxylate acids), while such a correlation is demonstrable between k_{Ln} and K_1 (malonate ligand binding in a bidentate fashion).

Application of the steady state approximation to the mechanism of isomerization as presented in Fig. 5 leads to the following rate law:

$$\frac{-d\,[trans]}{dt} = k_{obs}\,[trans]$$

where:

$$k_{obs} = k_1 \left[\frac{k_3(k_5 + k_6) + k_4 k_6\,[Ln^{3+}]}{k_5(k_2 + k_3) + k_6(k_2 + k_3) + k_4 k_6\,[Ln^{3+}]}\right]$$

The form for k_{obs} reveals a first-order dependence on the lanthanide ion concentration. The last term in the denominator indicates that at high lanthanide ion concentration, the rate of the reaction should level off. Such a saturation in rate with respect to concentration has been observed by Frank [5] when studying the isomerization as catalyzed by transition metal ions. In the present study, the same saturation effect was noted when the supporting electrolyte was NaCl, but not when $NaNO_3$ was used. We will comment on this difference in due course, but the experimental results are seen to be entirely consistent with the mechanism proposed in Fig. 5.

As in the oxalate system, a plot of log $\Delta H^{\ddagger}$ for each lanthanide ion isomerization *vs.* the ionic radius of the corresponding ion was constructed. As may be seen in Fig. 6, linearity is observed across essentially the entire lanthanide series. This observation is also consistent with the proposed

mechanism. As the ionic radii of the lanthanide ions decreases, the acidity of the ions increases and thus their affinity for a malonate ligand increases. At the same time, one finds that the catalytic rate constant increases with the increasing acidity of the lanthanide ion, as one would predict from examination of the mechanism in Fig. 5. If metal ion acidity is the deciding factor in determining the reaction rate, then Y(III) ought to exhibit a rate much closer to that of Ho(III), since these two ions should have essentially identical acidity properties. This prediction is borne out by the data of Figs. 4 and 6.

Isomerization Reactions in NaCl Medium

The lanthanide ion catalyzed isomerizations reported above were performed at pH 3 and 1.5 *M* ionic strength, using $NaNO_3$ as the supporting electrolyte. Frank [5] reported that the nature of the supporting electrolyte could affect the rate of isomerization. In order to learn if this observation could be extended to the catalytic reactions of lanthanide ions, a series of experiments were performed in which NaCl was used as the supporting electrolyte.

The representative lanthanide ions chosen for this study were La(III), Pr(III), Nd(III), Sm(III), Er(III), and Ho(III) (oxalate system only). The catalytic rate constants obtained with NaCl are collected in Table III along with the corresponding values obtained when $NaNO_3$ was used as the supporting electrolyte. Generally, it was observed that the catalytic rate constants were larger in the NaCl medium compared to those obtained in the $NaNO_3$ medium. This trend can be explained when one considers that lanthanide ions are known to form both inner-sphere and outer-sphere complexes with simple anions. A well known inner-sphere complex can be formed between lanthanide ions and the nitrate anion [21], while chloride ions apparently only form outer-sphere complexes with lanthanide ions [22–26].

Thus, when $NaNO_3$ was employed as the supporting electrolyte, the effective (*i.e.*, free) concentrations of the lanthanide ions would be expected to be decreased relative to those in NaCl media. These lower effective lanthanide ion concentrations would then in turn yield lower rates for the catalytic reactions. The observation that saturation of the observed rates was only observed in NaCl media implies that the lanthanide ion concentration may indeed become high enough as to observe the predicted behavior. In $NaNO_3$ media, increasing the amount of lanthanide ion only results in the generation of ion pairs, and hence the concentration of free lanthanide ion cannot be made sufficiently high as to observe the saturation effect. Similar effects corresponding to the presence of ion pair depression of rate constants have been observed in the Mg(II) catalyzed isomerization of the oxalate complex [27].

In spite of these differences, the mechanistic details proposed for the $NaNO_3$ studies still are valid for reactions carried out in NaCl media. The same linear free energy plots were observed in the NaCl media as had been obtained in the $NaNO_3$ media, and the trends observed across the lanthanide series were duplicated in the two media systems. One difference was noted: for the oxalate system, the rate constants obtained for lanthanides heavier than Gd were found to be slightly lower in NaCl media relative to $NaNO_3$ media. At the moment, the origin of this difference is not clear and further studies are planned to investigate the effect of the supporting electrolyte.

Systematic Trends in the Catalytic Data

While the use of lanthanide ions as catalytic reagents is receiving increasing amounts of attention [28], essentially all of these studies have been carried out under heterogeneous conditions and relatively few have attempted to survey the catalytic reactivity of the entire lanthanide series [29]. The work detailed in our investigation represents the first systematic investigation of homogeneous catalysis by lanthanide ions, and as such it is worth commenting on the overall trends apparent in the results.

It has been observed that the formation constants associated with a particular ligand often exhibit a discontinuity at Gd, and often a second dividing point can be noted approximately halfway through the La—Gd and Gd—Lu sequences [30]. Much has been made of these 'tetrad' or 'double-double' effects, and Sinha has tried to explain the trends through his 'inclined-W' hypothesis (where the properties of the complexes are related to the orbital angular momentum of the metal ion) [31]. We have attempted to carry out such correlations, and one finds that no recognizable 'W' plots can be constructed with either rate constants or activation parameters when considering the oxalate data. Of course, the mechanism change which was determined to take place halfway across the series must of necessity complicate any correlation, as Sinha has noted [31]. Better 'W'-type plots were obtained with the malonate system, but we have already shown that the rate constants obtained for the malonate isomerizations correspond to the strength of the lanthanide/malonate complex and any correlation with angular momentum must be viewed as being strictly fortuitous.

A rationale for the change in mechanism observed with the oxalate isomerizations may lie with the observation that the hydration numbers of the lanthanide ions are not constant across the series. The number of coordinated water molecules seems to undergo a change somewhere at the Sm-Eu-Gd portion of the series [33], and most workers favor a decrease from nine to eight coordinated waters in this region. Such a decrease would be very effective in reducing the radii of the hydrated ions, and it is very likely that the driving force for the change in mechanism associated with the oxalate reaction originates in this change in hydration number. No such change was noted with the malonate reaction, as the larger malonate chelate ring apparently is sufficiently flexible as to accommodate the lanthanide ion regardless of its size.

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