

Table V. Summary of Crystal Data and Intensity Collection

Crystal Parameters	
cryst syst, space group	triclinic, $P\bar{1}$
$a$ , Å	12.279 (4)
$b$ , Å	12.815 (2)
$c$ , Å	4.894 (2)
$\alpha$ , deg	93.63 (2)
$\beta$ , deg	91.81 (3)
$\gamma$ , deg	89.51 (2)
$V$ , Å <sup>3</sup>	768.1 (7)
$Z$	2
calcd density, g/cm <sup>3</sup>	2.250
temp, °C	23
abs coeff, cm <sup>-1</sup>	13.6
formula	C <sub>10</sub> H <sub>2</sub> F <sub>12</sub> O <sub>4</sub> Pd <sub>1</sub>
fw	520.5
Measurement of Intensity Data	
diffractometer	CAD4
radiation	Mo K $\alpha$ ( $\lambda = 0.71069$ Å), graphite monochromatized
scan range, $2\theta$ , deg	0-50
unique reflectns measd	333.4 ( $+h, \pm k, \pm l$ )
no. of obsd reflectns <sup>a</sup>	2073 [ $F_o^2 \geq 2.0(F_o^2)$ ]
refinement	full-matrix least squares
no. of parameters	248
$R^b$	0.063
$R_w^b$	0.084
GOF	3.3
$p^b$	0.03

<sup>a</sup> The intensity data were processed as described in "CAD4 and SDP User's Manual", Enraf-Nonius, Delft, Holland, 1978. The net intensity  $I$  is given as  $I = [K/(NPI)](C - 2B)$ , where  $K = 20.166 \times$  attenuator reactor,  $NPI =$  ratio of fastest possible scan rate to scan rate for measurement,  $C =$  total count, and  $B =$  total background count. The standard deviation in the net intensity is given by  $[\sigma(I)]^2 = (K/NPI)^2[C + 4B + (pI)^2]$ , where  $p$  is a factor used to downweight intense reflections. The observed structure factor amplitude  $F_o$  is given by  $F_o = (I/Lp)^{1/2}$ ; where  $Lp =$  Lorentz and polarization factors. The  $\sigma(I)$ 's were converted to the estimated errors in the relative structure factors  $\sigma(F_o)$  by  $\sigma(F_o) = 1/2(\sigma(I)/I)F_o$ . <sup>b</sup> The function minimized was  $\sum w(|F_c| - |F_o|)^2$ , where  $w = 1/[\sigma(F_o)]^2$ . The unweighted and weighted residuals are defined as  $R = (\sum ||F_o| - |F_c||) / \sum |F_o|$  and  $R_w = [(\sum w(|F_o| - |F_c|))^2 / (\sum w|F_o|)^2]^{1/2}$ . The error in an observation of unit weight (GOF) is  $[\sum w|F_o| - |F_c|^2 / (NO - NV)]^{1/2}$ , where  $NO$  and  $NV$  are the number of observations and variables, respectively.

**Solution and Refinement of the Structure.** The structure was solved by conventional heavy-atom techniques. Pd atoms were placed on the special positions 0, 0, 0 and  $1/2, 1/2, 1/2$  so that each molecule is centric. Difference-Fourier calculations were used to locate all remaining non-hydrogen atoms. The atomic scattering factors were

taken from the usual tabulation,<sup>23</sup> and the effects of anomalous dispersion were included in  $F_c$  by using Cromer and Ibers<sup>24</sup> values of  $\Delta f'$  and  $\Delta f''$ . A table of observed and calculated structure factor amplitudes is available.<sup>25</sup> The two hydrogen atom positions were calculated and included in the structure factor calculations but were not refined. All non-hydrogen atoms were refined by using anisotropic thermal parameters. The final difference-Fourier map did not reveal any chemically significant features. The largest peaks in this map were 0.5 e/Å and were located near the fluorine atoms. Some disorder was evident in the fluorine positions; however, the residual electron density in the final difference-Fourier map did not suggest an obvious disorder model. Therefore, this point was not pursued. The final positional and thermal parameters of the atoms appear in Table I. The labeling scheme is shown in Figure 1.

**Acknowledgment.** The authors are grateful to members of the 3M Analytical and Properties Research Laboratory for the physical measurements on Pd(F<sub>6</sub>acac)<sub>2</sub> and its derivatives and to Professors J. P. Fackler, Jr., and Shinichi Kawaguchi for preprints of their work. The National Science Foundation is acknowledged for partial support of the X-ray diffraction and structure-solving equipment at the University of Minnesota (Grant CHE77-28505). L.H.P. also acknowledges support by the National Science Foundation (Grant CHE-8108490) of his contribution to this paper.

**Registry No.** Pd(F<sub>6</sub>acac)<sub>2</sub>, 64916-48-9; Pd(F<sub>6</sub>acac-*O*,-*O'*)(F<sub>6</sub>acac-*C*)py, 85976-96-1; Pd(F<sub>6</sub>acac-*O*,*O'*)(F<sub>6</sub>acac-*O*)py, 85976-97-2; [Pd(F<sub>6</sub>acac-*O*,*O'*)(py)<sub>2</sub>](F<sub>6</sub>acac), 85976-99-4; [Pd-(py)<sub>4</sub>](F<sub>6</sub>acac)<sub>2</sub>, 65353-63-1; Pd(F<sub>6</sub>acac-*O*,*O'*)(F<sub>6</sub>acac-*C*)Ph<sub>3</sub>As, 85977-00-0; Pd(F<sub>6</sub>acac-*O*,*O'*)(F<sub>6</sub>acac-*O*)Ph<sub>3</sub>As, 85977-01-1; [Pd-(F<sub>6</sub>acac-*O*,*O'*)(Ph<sub>3</sub>As)<sub>2</sub>](F<sub>6</sub>acac), 78128-23-1; Pd(F<sub>6</sub>acac-*O*,-*O'*)(F<sub>6</sub>acac-*C*)(*i*-PrNH<sub>2</sub>), 85977-02-2; Pd(F<sub>6</sub>acac-*O*,*O'*)(F<sub>6</sub>acac-*O*)(*i*-PrNH<sub>2</sub>), 85977-03-3; [Pd(F<sub>6</sub>acac-*O*,*O'*)(*i*-PrNH<sub>2</sub>)<sub>2</sub>](F<sub>6</sub>acac), 85977-05-5; [Pd(*i*-PrNH<sub>2</sub>)<sub>4</sub>](F<sub>6</sub>acac)<sub>2</sub>, 85977-07-7; Pd(F<sub>6</sub>acac-*O*,-*O'*)(F<sub>6</sub>acac-*C*)( $\eta^1$ -C<sub>4</sub>H<sub>9</sub>S<sub>2</sub>), 85977-08-8; Pd(F<sub>6</sub>acac-*O*,*O'*)(F<sub>6</sub>acac-*O*)( $\eta^1$ -C<sub>4</sub>H<sub>9</sub>S<sub>2</sub>), 85977-09-9; Pd(F<sub>6</sub>acac-*O*,*O'*)(F<sub>6</sub>acac-*C*)(*t*-C<sub>4</sub>H<sub>9</sub>NC), 85977-10-2; Pd(F<sub>6</sub>acac-*O*,*O'*)(F<sub>6</sub>acac-*O*)(*t*-C<sub>4</sub>H<sub>9</sub>NC), 85995-10-4.

**Supplementary Material Available:** Tables S-1-S-3 showing observed and calculated structure factor amplitudes for Pd(F<sub>6</sub>acac)<sub>2</sub>, weighted least-squares planes, and anisotropic thermal parameters and their standard deviations (11 pages). Ordering information is given on any current masthead page.

- (23) D. T. Cromer and J. T. Waber, "International Tables for X-ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974, Table 2.2.4; D. T. Cromer, *ibid.*, Table 2.3.1.  
 (24) D. T. Cromer and J. A. Ibers in ref 23.  
 (25) See paragraph at end of paper regarding supplementary material.

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## Kinetics and Mechanism of the Cerium(IV) Oxidation of Methylmalonic Acid and of Ethylmalonic Acid in Acid Media

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The kinetics and mechanism of the oxidation of methylmalonic acid and of ethylmalonic acid by cerium(IV) in acid media was studied with use of the stopped-flow technique. The observed rate law was found to be of the form  $-d[\text{Ce(IV)}]/dt = k_H[\text{Ce(IV)}][\text{RCH}(\text{CO}_2\text{H})_2]$ . The second-order rate constant,  $k_H$ , was found to be hydrogen ion dependent and of the form  $k_H = (k[\text{H}^+]^2 + k'[\text{H}^+] + k'')/([\text{H}^+] + K)$ . A mechanism consistent with these results is proposed.

### Introduction

The role played by the hydrogen ion in the oxidation of organic and inorganic substrates by metal ions sheds considerable light on the mechanism of these reactions and the possibility of intermediate complex formation. Some reactions

are acid catalyzed such as in the Ce(IV) oxidation of various alcohols<sup>1-3</sup> and carboxylic acids<sup>4,5</sup> while others such as the

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Table I. CO<sub>2</sub>:Ce(IV) Mole Ratio

expt no.	amt × 10 <sup>4</sup> , mol		mole ratio <sup>c</sup> CO <sub>2</sub> :Ce(IV)
	Ce(IV)	RCH-(COOH) <sub>2</sub>	
1	25	50 <sup>a</sup>	1:3.85
2	20	50 <sup>a</sup>	1:4.10
3	10	50 <sup>a</sup>	1:4.25
4	20	50 <sup>b</sup>	1:4.16
5	10	50 <sup>b</sup>	1:4.15

<sup>a</sup> Methylmalonic acid. <sup>b</sup> Ethylmalonic acid. <sup>c</sup> All runs were performed at 25 °C. [HClO<sub>4</sub>] = 3 M in all solutions.

Ce(IV) oxidation of hydrazine<sup>6</sup> and α-hydroxy carboxylic acids<sup>7-9</sup> are acid inhibited. In the soon to be reported Ag(II) oxidation of malonic acid, methylmalonic acid, and ethylmalonic acid, both catalysis and inhibition are observed. Replacement of the methylene hydrogen with an alkyl group causes the reaction to switch from being acid catalyzed to being acid inhibited. All three reactions however can be interpreted by a single scheme in which the relative importance of the rate-determining steps changes with a change in the substrate.

The results obtained in this paper on the Ce(IV) oxidation of methyl- and ethylmalonic acids along with the results of McAuley's study<sup>5,7</sup> on the Ce(IV) oxidation of malonic acid indicate that these reactions can also be interpreted by a single scheme. Acid inhibition, however, is not observed for any of these substrates.

### Experimental Section

**Reagents.** Triply distilled water was used in the preparation of all solutions. All chemicals used either were reagent grade or were of certified purity.

Cerium(IV) ammonium nitrate (Fisher) solutions were prepared immediately before use in Baker reagent grade perchloric and/or nitric acid.

The substrate solutions were also prepared just prior to use. The acidity of these solutions was the same as for the Ce(IV) solutions, to prevent acidity changes from occurring upon mixing.

The ionic strength was held constant at 5.0 M by the use of appropriate amounts of sodium perchlorate. Several runs were made to determine the Ce(III) dependency. The reaction was found to be independent of Ce(III).

**Stoichiometric Measurements.** A gas buret was used to determine the stoichiometry of the reactions studied. Known amounts of the two reactants were mixed, and the volume of CO<sub>2</sub> evolved at a known pressure and temperature was measured. From the volume of CO<sub>2</sub> liberated, the number of moles was calculated and the mole ratio of CO<sub>2</sub>:Ce(IV) determined.

**Kinetic Measurements.** The Aminco-Morrow stopped-flow apparatus<sup>10</sup> was used for all kinetic runs. The detector used was an R-136 photomultiplier tube (PMT) powered by a Hewlett-Packard 6515A dc power supply. The PMT output was fed into an Aminco linear-log photometer, and the logarithmic signal (absorbance) was displayed with use of a Tektronix 5103N storage oscilloscope. The reaction was followed by measuring the change in absorbance of Ce(IV) at 290 nm. The temperature was maintained constant at 25.0 ± 0.1 °C.

### Results

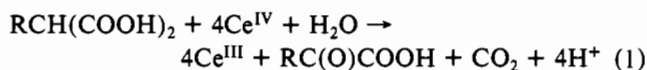
**Stoichiometry.** The CO<sub>2</sub>:Ce(IV) mole ratio was determined under conditions similar to those established for the kinetic

Table II. Dependency of *k*<sub>obsd</sub> upon the Methylmalonic Acid Concentration

10 <sup>4</sup> × [Ce(IV)], M	[C <sub>4</sub> H <sub>6</sub> O <sub>4</sub> ], M	<i>k</i> <sub>obsd</sub> , <sup>a</sup> s <sup>-1</sup>
2.0	0.10	0.204
2.0	0.050	0.099
2.0	0.025	0.0495
2.0	0.0125	0.0240
2.0	0.0062	0.0130

<sup>a</sup> [HClO<sub>4</sub>] = 3 M for all experiments.

measurements. These results were consistent with the overall reaction

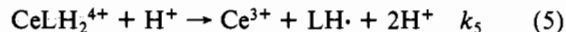
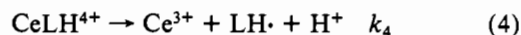
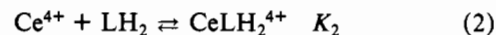


where R = CH<sub>3</sub> or C<sub>2</sub>H<sub>5</sub>. Table I contains the experimental results for both substrates. It can be seen that these results are in good agreement with the predicted value of 1:4.0 from reaction 1.

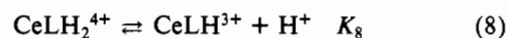
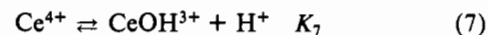
It is obvious from the total reaction presented above that a series of intermediates must be formed and consumed before the final products are reached. In order to achieve the observed stoichiometry, it is a kinetic necessity that the first redox step(s) be rate determining with all subsequent steps being rapid.

### Kinetics and Mechanism

The mechanism most consistent with our result is



where LH<sub>2</sub> represents either organic substrate. Equations 4–6 are the rate-determining steps. Also necessary in the consideration of the mechanism are the equilibria



Appropriate combination of the above steps yields the rate law  $-d[\text{Ce}(\text{IV})]/dt =$

$$\frac{4(K_2k_5[\text{H}^+]^2 + K_2k_4[\text{H}^+] + k_6K_2K_8)[\text{LH}_2] \times [\text{Ce}(\text{IV})]}{([\text{H}^+] + K_7 + K_2[\text{H}^+][\text{LH}_2] + K_2K_8[\text{LH}_2])} \quad (I)$$

Under the experimental conditions with cerium(IV) present in limiting quantity the rate expression becomes

$$\frac{d[\text{Ce}(\text{IV})]}{dt} = k_{\text{obsd}}[\text{Ce}(\text{IV})] \quad (I)$$

Starting with eq I the factor of 4 has been absorbed into all of the succeeding rate constants, where

$$k_{\text{obsd}} = \frac{(K_2k_5[\text{H}^+]^2 + K_2k_4[\text{H}^+] + k_6K_2K_8)[\text{LH}_2]}{[\text{H}^+] + K_7 + K_2[\text{H}^+][\text{LH}_2] + K_2K_8[\text{LH}_2]} \quad (II)$$

Since the reaction is always first order with respect to LH<sub>2</sub>, it is reasonable to assume that  $[\text{H}^+] + K_7 \gg K_2[\text{H}^+][\text{LH}_2] + K_2K_8[\text{LH}_2]$ . Equation II therefore simplifies to

$$k_{\text{obsd}} = \frac{(K_2k_5[\text{H}^+]^2 + K_2k_4[\text{H}^+] + k_6K_2K_8)[\text{LH}_2]}{[\text{H}^+] + K_7} \quad (III)$$

Tables II and III contain the first order rate constant, *k*<sub>obsd</sub>, defined by eq I. The dependency of *k*<sub>obsd</sub> upon the substrate

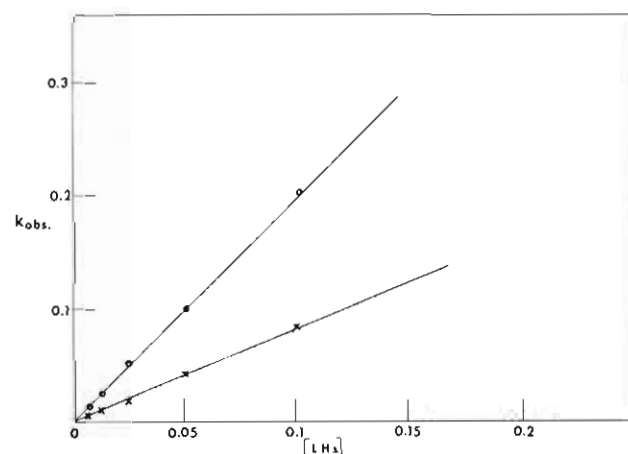
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**Table III.** Dependency of  $k_{\text{obsd}}$  upon the Ethylmalonic Acid Concentration

$10^4 \times$ [Ce(IV)], M	[C <sub>5</sub> H <sub>8</sub> O <sub>4</sub> ], M	$k_{\text{obsd}}^a$ , s <sup>-1</sup>
2.0	0.100	0.084
2.0	0.050	0.0426
2.0	0.025	0.0159
2.0	0.0125	0.0104
2.0	0.00626	0.0059

<sup>a</sup> [HClO<sub>4</sub>] = 3 M for all experiments.**Table IV.** Variation of  $k_{\text{H}}$  with Acidity (Methylmalonic Acid)

[H <sup>+</sup> ], M	$k_{\text{obsd}}^a$ , s <sup>-1</sup>	$k_{\text{H}}$ , M <sup>-1</sup> s <sup>-1</sup>	$(k_{\text{H}}([H^+] + 0.18) - 0.17)/[H^+]$
5.0	0.301	4.01	4.12
4.0	0.256	3.41	3.52
3.0	0.183	2.44	2.65
2.0	0.133	1.77	1.84
1.0	0.86	1.15	1.19
0.5	0.064	0.853	0.82
0.25	0.063	0.84	0.76

<sup>a</sup> The concentration of methylmalonic acid was 0.075 M and of Ce(IV) was  $2.0 \times 10^{-4}$  M for all runs.**Figure 1.** Plot of  $k_{\text{obsd}}$  vs. [LH<sub>2</sub>]: (O) methylmalonic acid; (X) ethylmalonic acid.

concentration is shown in Figure 1.

The second-order rate constant,  $k_{\text{H}}$ , is defined by eq IV.

$$k_{\text{H}} = k_{\text{obsd}}/[LH_2] \quad (\text{IV})$$

This rate constant,  $k_{\text{H}}$ , was found to be hydrogen ion dependent. Tables IV and V give the effect of acidity upon the  $k_{\text{H}}$  values for methyl- and ethylmalonic acids, respectively. A combination of eq III and IV gives the acid dependency of  $k_{\text{H}}$ :

$$k_{\text{H}} = \frac{K_2 k_5 [H^+]^2 + K_2 k_4 [H^+] + k_6 K_2 K_8}{[H^+] + K_7} \quad (\text{V})$$

The linear form of eq V is

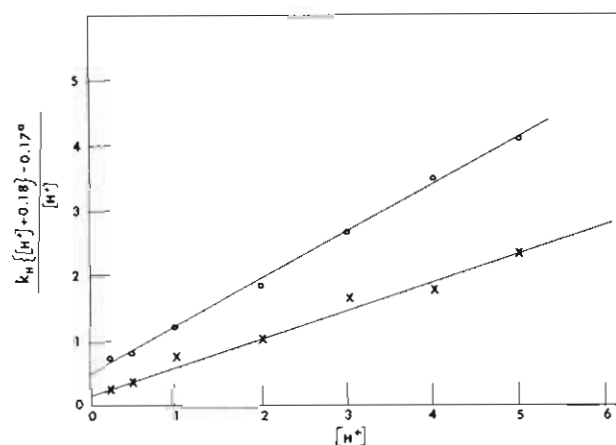
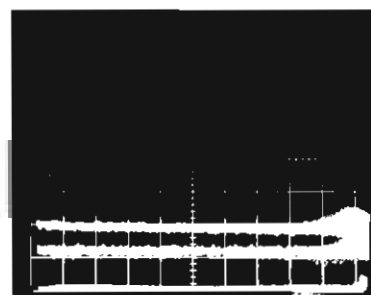
$$\frac{k_{\text{H}}([H^+] + K_7) - k_6 K_2 K_8}{[H^+]} = K_2 k_5 [H^+] + K_2 k_4 \quad (\text{VI})$$

These results are shown plotted in Figure 2, with  $K_7$  set at 0.18 M. For the product of  $k_6 K_2 K_8$  values of 0.17 and 0.03 s<sup>-1</sup> were used for methylmalonic acid and ethylmalonic acid, respectively.

In this mechanism the two intermediate complexes, CeLH<sub>2</sub><sup>4+</sup> and CeLH<sup>3+</sup>, are formed via kinetically indistinguishable pathways. This is so since  $K_2 K_8 = K_3 K_7$ . The rate-determining step is the electron transfer within these complexes leading to the formation of a free radical.

**Table V.** Variation of  $k_{\text{H}}$  with Acidity (Ethylmalonic Acid)

[H <sup>+</sup> ], M	$k_{\text{obsd}}^a$ , s <sup>-1</sup>	$k_{\text{H}}$ , M <sup>-1</sup> s <sup>-1</sup>	$(k_{\text{H}}([H^+] + 0.18) - 0.03)/[H^+]$
5.0	0.167	2.22	2.30
4.0	0.121	1.61	1.68
3.0	0.114	1.52	1.60
2.0	0.0676	0.901	0.97
1.0	0.0367	0.489	0.55
0.50	0.0238	0.317	0.37
0.25	0.0156	0.208	0.24

<sup>a</sup> The concentration of the ethylmalonic acid was 0.075 M and of Ce(IV) was  $2.0 \times 10^{-4}$  M for all runs.**Figure 2.** Plot of  $(k_{\text{H}}([H^+] + 0.18) - 0.17)/[H^+]$  vs. [H<sup>+</sup>]: (O) methylmalonic acid; (X) ethylmalonic acid. For methylmalonic acid the value of 0.17 was used for the product  $k_6 K_2 K_8$ . For ethylmalonic acid the value of 0.03 was used.**Figure 3.** Stopped-flow trace showing complex formation between Ce(IV) and diethylmalonic acid.

Amjad and McAuley<sup>5</sup> obtained the same mechanism for the oxidation of malonic acid by Ce(IV). They showed, using ESR, that the odd electron was located on the methylene carbon atom and therefore the rate-determining step involved the loss of the methylene proton. The importance of the methylene proton is clearly demonstrated in our work. In the monosubstituted malonic acid substrates, one methylene proton is still present, and the same mechanism can be used to explain all of the results. When dimethyl- and diethylmalonic acids were used, the results were completely different. Carbon dioxide was not evolved. Rather, there was a deepening of the yellow color of cerium(IV), indicating the formation of a complex between the two reactants. Figure 3 shows replicate stopped-flow results indicating complexation between diethylmalonic acid and Ce(IV). The base line (lowest line) is acidified solvent run against itself to establish a zero absorbance value. The middle line is the acidified solvent run against an acidified cerium(IV) solution with [Ce(IV)] equal to  $2 \times 10^{-4}$  M. The third line is Ce(IV) at the above concentration run against 0.0064 M diethylmalonic acid. Each trace has been run at 0.05, 0.1, and 1 s/division, and the

sensitivity is 0.02 absorbance unit/division. This figure clearly shows the deepening of color mentioned above.

That complexation as an initial step is likely has already been proposed by Kemp and Waters,<sup>11</sup> who oxidized malonic acid with Mn(III), and by Amjad and McAuley,<sup>5</sup> who oxidized malonic acid with Ce(IV). The initial complex formed was moderately stable, taking several days to be lost via a redox step. We feel it is reasonable to assume that the monosubstituted acids also complex with Ce(IV) prior to the redox step, and so complexation steps (reactions 2 and 3) were included in the mechanism.

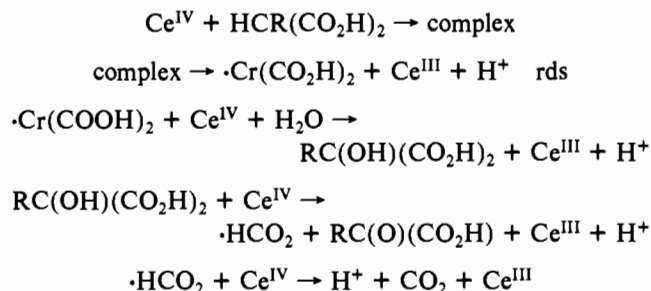
Equation VI indicates that the relative value of  $k_5/k_4$  can be obtained by taking the ratio of the slope to the intercept from Figure 2. These values are 2.5 and 1.5 for methyl- and ethylmalonic acids, respectively, indicating that for both acids, steps 4 and 5 of the mechanism are of comparable importance. For malonic acid McAuley obtained a value of 0.22 for this ratio, showing that there is a considerably smaller acid dependency for the unsubstituted acid compared to that for the substituted acids. A comparison of the slopes ( $K_2k_5$  for methylmalonic acid to  $K_2k_5$  for ethylmalonic acid) and of the intercepts ( $K_2k_4$  for methylmalonic to  $K_2k_4$  for ethylmalonic acid) yields values of 1.8 and 3.0, respectively. The latter value contains an appreciable error since it is obtained from the extrapolated values of the intercepts. Since the methyl group is a more effective electron-donating group than the ethyl group, methylmalonic acid would be a somewhat stronger Lewis base than ethylmalonic acid, resulting in its having a larger value of  $K_2$ . This is consistent with the dissociation constants of the two acids; for methylmalonic acid  $K_{a1} = 0.87 \times 10^{-3}$  whereas for ethylmalonic acid  $K_{a1} = 1.3 \times 10^{-3}$ . If this interpretation is correct, then the two acids would have similar

$k_4$  and  $k_5$  values. McAuley's results for malonic acid, however, are different from those for the substituted acids. This is not surprising, however, since malonic acid contains two methylene H atoms rather than one.

It is not possible to obtain a reasonable estimate of  $k_6$ . Only the product,  $k_6K_2K_8$ , could be obtained. The values 0.17 and 0.03 s<sup>-1</sup> for methyl- and ethylmalonic acids, respectively, were the values that linearized the results shown in Figure 2. Their contributions are important only at the lowest acidities used. At acidities of 1 M and above, this product,  $k_6K_2K_8$ , had a negligible effect on the linearity of the plot.

More important is that the best fit value of  $K_7 = 0.18$  M for the hydrolysis of Ce<sup>4+</sup> is in excellent agreement with that found by McAuley. This is supportive of the correctness of the proposed mechanism.

The overall mechanism including the rate-determining step (rds) and subsequent steps is



where R = CH<sub>3</sub> or C<sub>2</sub>H<sub>5</sub>. This results in a CO<sub>2</sub>:Ce(IV) mole ratio of 1:4.0, which was observed. Where R = H, the RC(O)(CO<sub>2</sub>H) molecule is further oxidized to formic acid, resulting in a CO<sub>2</sub>:Ce(IV) mole ratio of 1:3.0.

**Registry No.** Cerium, 7440-45-1; methylmalonic acid, 516-05-2; ethylmalonic acid, 601-75-2.

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## Mixed-Ligand Chelate Extraction of Lanthanides with 1-Phenyl-3-methyl-4-acyl-5-pyrazolones

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A study of the equilibrium extraction behavior of series of representative trivalent lanthanide ions (La, Pr, Eu, and Yb) was carried out with either chloroform solutions of selected 1-phenyl-3-methyl-4-acyl-5-pyrazolones (acyl = decanoyl, phenacetyl, 3-phenylpropionyl, and *p*-*tert*-butylbenzoyl) (HP) alone or these solutions in combination with 1,10-phenanthroline (phen), trioctylphosphine oxide (TOPO), or methyltrioctylammonium chloride (R<sub>3</sub>R'NCl). The results demonstrate that these lanthanides are extracted as LnP<sub>3</sub> or, in the presence of phen or TOPO, as LnP<sub>3</sub>·phen or LnP<sub>3</sub>·TOPO, or, in the presence of R<sub>3</sub>R'N<sup>+</sup>Cl<sup>-</sup>, as R<sub>3</sub>RN<sup>+</sup>LnP<sub>4</sub><sup>-</sup>. The extraction constants ( $K_{\text{ex}}$ ),  $K_{\text{ex}}(\text{phen})$ ,  $K_{\text{ex}}(\text{TOPO})$ , and  $K_{\text{ex}}$ , are discussed in terms of structure-behavior interrelations.

### Introduction

As a part of a systematic evaluation of the use of chelating extractants in the separation of trivalent lanthanide ions, the equilibrium extraction behavior of a series of representative lanthanide ions with either chloroform containing 8-quinolinol (HQ), 5,7-dibromo-8-quinolinol (HQ'), and 1-phenyl-3-methyl-4-octanoyl-5-pyrazolone (HP) alone or these solutions in combination with 1,10-phenanthroline (phen) or methyltrioctylammonium chloride (R<sub>3</sub>R'NCl) was studied in detail.<sup>1-4</sup>

The extracted species were found to be the complexes LnQ<sub>3</sub>·*n*HQ (*n* = 2,3) for 8-quinolinol, LnQ<sub>3</sub>·HQ for 5,7-dibromo-8-quinolinol, and LnP<sub>3</sub> for 1-phenyl-3-methyl-4-octanoyl-5-pyrazolone (HPMOP). In the presence of phen or R<sub>3</sub>R'NCl, the formation of mixed-adduct and self-adduct ion pairs, LnQ<sub>3</sub>·2HQ·phen and R<sub>3</sub>R'N<sup>+</sup>·LnQ<sub>4</sub><sup>-</sup>·HQ, was observed for HQ whereas for HQ' the formation of simple adducts and

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