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Kinetics of the Reduction of Neptunium(VI) by Dicarboxylic Acids

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The reduction of tracer concentrations of Np(VI) by dicarboxylic acids has been shown to proceed via formation of the 1:1 metal–ligand complex and to form Np(V) but not Np(IV). The rate constants were in the sequence oxalate < malonate > alkylmalonate ≃ succinate ≃ phthalate ≥ fumarate > glutarate. The results are consistent with a mechanism in which the rate-determining step involves loss of a methylene proton from the reductant.

Introduction

The redox reactions between metal cations and organic compounds have a number of interesting aspects involving the nature of the transition state, the mode of electron transfer, and the subsequent molecular rearrangement (or dissociation) of the organic species. There is also a practical aspect to such studies, as such reactions are involved in the biological and environmental behavior of many metals. The redox chemistry of the actinides, particularly neptunium and plutonium, is particularly interesting since oxidation states from III to VII can exist in aqueous solutions. Not only can three or four different oxidation states coexist simultaneously in some solutions but disproportionation reactions of the V and IV states can also occur along with actinide–ligand redox reactions.

Np(VI) reduction by oxalic acid was studied between pH 0.3 and 0.9, and the rate was shown to be directly dependent on the total Np(VI) and total oxalic acid concentrations and inversely on the hydrogen ion concentration.[2] These authors proposed formation of $NpO_2(OH)(H_2C_2O_4)^+$ as the rate-limiting step. The reduction of Pu(VI) by oxalic acid between pH 1 and 3 followed a similar rate expression.[3] The Pu(V) formed disproportionated to Pu(VI) and Pu(IV) rapidly. A careful investigation of the interaction of Np(V) and oxalic acid between pH 0.3 and 1.1 found direct reduction to Np(IV) and disproportionation to Np(VI) and Np(IV) both occurring in significant amounts with the ratio of disproportionation to direct reduction increasing with pH.[4]

These earlier studies used macro concentrations of actinide ions. However, in most situations of biological or environmental contamination, trace concentrations are more likely. Our investigations have used tracer concentrations of Np(VI) and extended the kinetic measurements to several dicarboxylate ligands. We have also studied the redox behavior of macro concentrations with an actinyl(VI) specific-ion electrode[5] in order to compare the kinetics at micro- and macro-level concentrations of Np(VI).

Experimental Section

Reagents and Equipment. All the chemicals employed were of reagent grade or better.

In order to guarantee against the reduction of Np(VI) by materials other than the dicarboxylic acids under investigation, special precautions were taken. All aqueous solutions were prepared from water redistilled from a basic permanganate solution while all the glassware used in the reduction and extraction procedure was pretreated with hot $HNO_3 + NaBrO_3$ solutions and rinsed carefully with redistilled water prior to use.

Stock solutions of 0.01–0.05 M in the dicarboxylic acids were prepared by dissolving the reagent grade acid in redistilled water. Working solutions were obtained by dilution with appropriate amounts of aqueous NaCl solution to maintain an ionic strength of 0.10 M. The adjustments of pH were performed with reagent grade NaOH and $HClO_4$ solutions by using a Corning 130 pH meter.

Thenoyltrifluoroacetone, HTTA (Aldrich Chemical Co.), was purified by sublimation at about 60 °C. The extraction solution of 0.50 M HTTA in toluene was shaken with a solution of 0.01 M $NaBrO_3$ + 0.10 M HNO_3 for about $^1/_2$ h to destroy any possible reducing impurities and then washed with 0.01 M HNO_3 to remove any bromate that may remain in the organic phase.

The stock solution of ^{237}Np tracer was prepared from high-purity $^{237}NpO_2$ (Oak Ridge National Laboratory) by dissolution in fuming HNO_3, evaporation to dryness, and redissolution in HCl. ^{233}Pa, the β-emitting daughter of ^{237}Np, was separated from the stock solution every few days by ion exchange. The radiochemical purity was checked on a Canberra Series 80 multichannel analyzer with a Ge–Li detector (Canberra Industries) to monitor the absence of the γ-ray (0.31-MeV) peak of ^{233}Pa. The solutions of Np(VI) were prepared by fuming an aliquot of the stock with concentrated $HClO_4$ for several hours, dissolving the wet residue with redistilled water, and neutralizing the excess amount of $HClO_4$ with NaOH until the pH of the solution was about 3–4. At this pH, the addition of 10 μL of this Np(VI) solution to the reaction mixture in the kinetics experiments did not change the pH of the latter. The completeness of oxidation to Np(VI) was verified with the TTA-extraction procedure.[6]

Handifluor (Mallinckrodt) was used as the scintillation solution for counting the α activity of ^{237}Np on a Packard Model 3320 liquid scintillation counter. The quenching effect of TTA was eliminated by use of high instrument gain (>20%).

Linear regression analyses of the experimental data were performed on either a Z-80 microcomputer system or a Tl-59 calculator.

Procedures. For the study of the reduction of Np(VI) using the solvent extraction technique, an aliquot of $^{237}Np(VI)$ tracer was mixed with the solution of the dicarboxylic acid under investigation and 0.50 mL of the reaction mixture was removed at regular intervals. This sample was placed in an extraction vial containing 1.00 mL of 0.50 M TTA in toluene and 0.50 mL of 0.25 M sodium acetate (pH 4) in water. The buffer ability of the acetate solution was sufficient to guarantee the complete extraction of Np(VI) while Np(V) remained completely in the aqueous phase. The extraction vial was shaken vigorously for 5 min and then centrifuged. A 0.50-mL aliquot was removed from each phase and mixed with 5.0 mL of scintillation solution for α counting.

In order to check the extent of reduction of Np(VI) to Np(IV), 0.50 mL of the reaction mixture was placed in an extraction vial containing 1.0 mL of 0.50 M TTA in toluene and 0.5 mL of 0.5 M HNO_3 solution. The pH of the resulting aqueous phase was about 0.6. Under these conditions, only Np(IV) would be extracted into the organic phase.

Unless otherwise noted, all the results were obtained at the ionic strength of 0.10 M (NaCl) and total ^{237}Np concentration, $[Np]_T$, of 3×10^{-5} M in the reaction mixture.

The experimental system used to follow the reduction by potentiometry using the actinyl(VI)-coated wire electrode (CWE) duplicated that described previously.[5] A calibration curve of voltage vs. [Np(VI)] was determined for the NpO_2^{2+} CWE prior to the kinetics experiments. The potential change was followed as a function of the time after injection of an aliquot of the dicarboxylic acid stock into the Np(VI)

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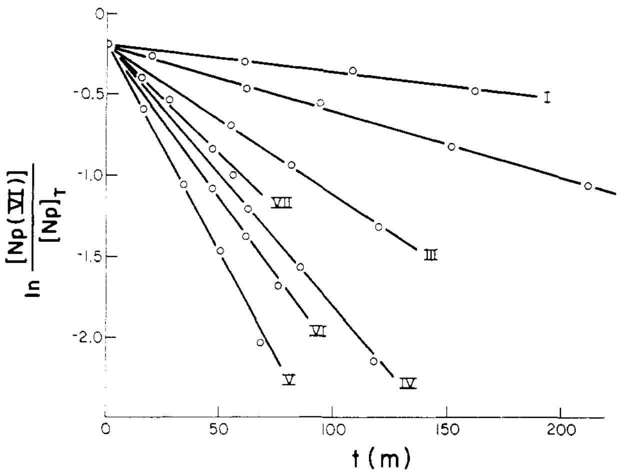

Figure 1. Reduction of Np(VI) by malonic acid at different pH values ($T \simeq 23$ °C, $I = 0.10$ M (NaCl), $[\text{malonic acid}]_T = 5 \times 10^{-3}$ M): (I) 1.39; (II) 1.75; (III) 1.99; (IV) 2.20; (V) 2.82; (VI) 3.13; (VII) 3.38.

working solution. The rate constants were calculated from the EMF vs. time relation and the calibration curve.

Results

Identification of the Valency State of Np after Reduction. The reduction by oxalic ($[H_2Ox]_T = 2.5 \times 10^{-4}$, pH 1.1) and malonic ($[H_2Mal]_T = 5.0 \times 10^{-3}$ M, pH 2.2) acids was measured at both ambient (ca. 22 °C) and elevated temperature (ca. 50 °C). The initial activity was found to be divided between the VI and V oxidation states when the samples were sampled regularly over 100 min. These data confirmed that Np(VI) was reduced to Np(V) but no further reduction to Np(IV) was observed under these conditions.

Effect of Light on the Reaction. It was reported that the reduction of Pu(VI) could be slowed or even eliminated by protecting the solution from light[7] and that Np(VI) was reduced to Np(V) in nitric acid solution when exposed to ultraviolet light.[8] Experiments were conducted to test the sensitivity to light of the redox reactions between Np(VI) and oxalic, malonic, and succinic acids. At pH 1.4 and total organic acid concentrations of $(1-5) \times 10^{-3}$ M, no effect of room light on the reduction rate was measured. Subsequently, all experiments were performed without taking special precautions to avoid light exposure.

Reaction Order with Respect to [Np(VI)]. By maintaining a constant $[H^+]$ and a relatively large excess of the dicarboxylic acid, the reaction order with respect to [Np(VI)] was derived from the variation of ln ($[Np(VI)]/[Np]_{total}$) with time. Figure 1 shows the results for the reduction by malonate using the solvent extraction technique. For all the dicarboxylic acids investigated, a straight-line relation was obtained, indicating that the reaction was pseudo first order in [Np(VI)]. From the slope, k_{obsd}, the pseudo-first-order rate constant was calculated.

In the potentiometric experiments, the potential change with time was followed for malonic, succinic, and phthalic acid systems. The calibration curve of EMF vs. log $[NpO_2^{2+}]$ had a slope designated as $S°$. The same electrode immersed in the Np(VI)–dicarboxylate system showed a slope S for the change in potential with time. The relationship

$$-\ln \frac{[NpO_2^{2+}]}{[Np]_T} = \frac{2.303St}{S^\circ} + \text{constant} \qquad (1)$$

was derived for the rate, where the pseudo-first-order rate constant, k_{obsd}, is equal to

$$k_{obsd} = \frac{2.303S}{S^\circ} \qquad (2)$$

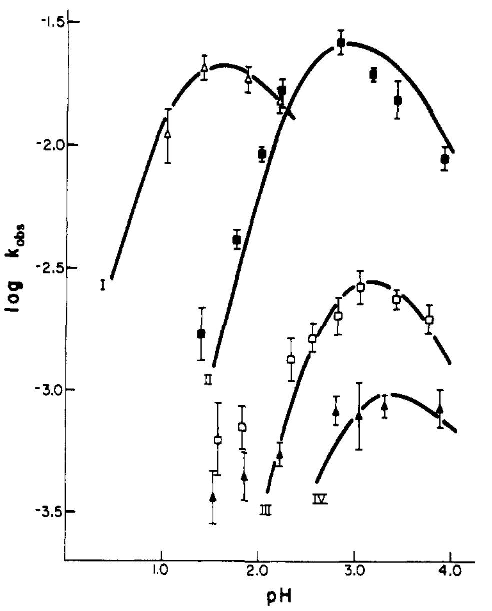

Figure 2. Variation of log k_{obsd} with pH at 23 °C and $I = 0.10$ M (NaCl): (I) 1.0×10^{-3} M oxalic acid; (II) malonic acid; (III) methylmalonic acid; (IV) dimethylmalonic acid. II–IV are 5.0×10^{-3} M. The solid lines are the scaled values of log ($[NpO_2L]/[Np]_T$) from eq 3.

From EMF data, k_{obsd} was calculated to be 1.1×10^{-2} m^{-1} when $[\text{malonic acid}]_T = 4.7 \times 10^{-3}$ M and $[H^+] = 10^{-3}$ M. This value can be compared to the k_{obsd} value of 1.8×10^{-2} m^{-1} for the same conditions by the solvent extraction method. The potential changes in the phthalate and succinate systems were too small to provide reliable values of k_{obsd}.

[H$^+$] Dependency. When the total acid concentration was kept constant, the pseudo-first-order rate constant, k_{obsd}, varied as a function of $[H^+]$ as shown in Figure 2 for oxalic, malonic, methylmalonic, and dimethylmalonic acids. The observation of a maximum in k_{obsd} agrees with the data from the reduction of Np(VI) by oxalate.[9] The sequence of the pH values for the maximum k_{obsd} in each system follows that of the pK_a values of the acids and reflects the formation of the 1:1 complex as the acid anion forms. This suggests that the reduction proceeds by means of the intermediate complex NpO_2L (L^{2-} = dicarboxylate ligand). Moreover, it would seem that the $NpO_2L_2^{2-}$ complex is much less reactive to redox.

This correlation was further checked by measurements of the reduction rate for the Np(VI)–malonic acid system in which the pH was constant at 2.82 and the total malonic acid concentration varied from 5.0×10^{-4} to 5.0×10^{-2} M. k_{obsd} increased as the acid concentration increased to 5.0×10^{-3}–1.0×10^{-2} M and then decreased with further increases in acid concentration.

If the assumption that NpO_2L is the species reducing is true, k_{obsd} should be proportional to $[NpO_2L]$ or, at constant total Np concentration, to $[NpO_2L]/[Np]_T$. This latter fraction can be shown to be equal to

$$[NpO_2L]/[Np]_T = \beta_1 C_T Y/(Y^2 + \beta_1 C_T Y + \beta_2 C_T^2) \qquad (3)$$

where

$$Y = 1 + K_{1a}^{-1}[H^+] + (K_{1a}K_{2a})^{-1}[H^+]^2$$

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Table I. Calculated Values of the Stability Constants for the NpO_2L Species[a]

ligand	Z^-_{eff}	log β_1(calcd)	log β_2(est)	log β_{UO_2L}[13]
oxalate	−1.56	6.17	10.21	6.36 ($\mu = 0.1$ M)
malonate	−1.44	5.57	9.59	5.66 ($\mu = 1.0$ M)
succinate	−1.20	4.41	...	3.87 ($\mu = 0.5$ M)
maleate	−1.27	4.79	...	4.46 ($\mu = 1.0$ M)
fumarate	−1.03	3.53	...	
phthalate	−1.24	4.60	...	4.81 ($\mu = 0.1$ M)
CHDCA[b]	−1.41	5.48	...	...
methylmalonate	−1.41	5.48	9.39	5.56 ($\mu = 0.5$ M)
dimethylmalonate	−1.40	5.46	9.37	5.55 ($\mu = 0.5$ M)

[a] Z^+_{eff} of $NpO_2^{2+} = +3.3$. [b] CHDCA = 1,4-cyclohexanedicarboxylate.

C_T is the total acid concentration and equals $[H_2L] + [HL^-] + [L^{2-}]$. β_1 and β_2 are the stability constants for the formation of NpO_2L and NpO_2L^{2-}, respectively (Table I), while K_{1a} and K_{2a} are the stepwise acid dissociation constants of H_2L.

In Figure 2, the experimental values of log k_{obsd} and the calculated curves for $\log([NpO_2L]/[Np]_T)$ are shown as a function of pH. The calculated curves have been scaled to match approximately the maximum values of k_{obsd}. The coincidence of the curves is good for oxalic and malonic acids. The poor agreement for methylmalonic and dimethylmalonic acids in the region of higher $[H^+]$ is possibly due to the formation of the MHL species. For all four acids, the maximum values of k_{obsd} on the experimental curves do occur at the same $[H^+]$ as for the calculation, which supports the model that the NpO_2L complex is, indeed, the intermediate in the redox mechanism and $NpO_2L_2^{2-}$ inhibits the reaction. Taube[10] explained a similar observation that $MnC_2O_4^+$ undergoes decomposition more readily than does $Mn(C_2O_4)_2^-$ as being due to a higher activation energy for the decomposition of the 1:2 complex.

Comparison of Rate Constants. On the basis of the assumption that the species NpO_2L is involved in the rate-determining redox step, we can define k_1, the rate constant for the reaction

$$NpO_2L \xrightarrow{k_1} NpO_2^+ + L^{-\cdot} \qquad (4)$$

where

$$k_1 = k_{obsd}(Y^2 + \beta_1 C_T Y + \beta_2 C_T)/\beta_1 C_T Y \qquad (5)$$

The values of β_1 and β_2 are not available in the literature since the reduction of Np(VI) by the acids precludes their measurement. A modified Born equation[11] was utilized to calculate the stability constants of NpO_2L complexes from the effective charges on the NpO_2^{2+} cation (Z^+_{eff}) and on the dicarboxylate anion (Z^-_{eff}). These effective charges, Z^+_{eff} and Z^-_{eff}, were estimated by the same equation from the stability constants of NpO_2F^+ [12] and Sm^{3+} dicarboxylates,[13] respectively. These values of β_1 were used also in the calculations of k_{obsd} for Figure 2 and are listed in Table I. The estimated values of β_2 (for NpO_2L_2) are also listed. The UO_2L values[13] are given to indicate the similarity of our calculated values for NpO_2L.

The rate constants, k_1, for the different carboxylic acids are listed in Table II. The sequence of increasing reaction rate constants, within error limits, is consistent with the order of increasing complexation stability. The error limits are calculated from the uncertainties of k_{obsd} at the pH quoted. For malonic acid, the measurements with varying pH and H_2L concentrations provided 15 values of k_1. For values of $[NpO_2L]/[Np]_T$ between 0.2 and 0.8, an average k_1 of $3.2\ (\pm 0.6) \times 10^{-2}$ is obtained. Accordingly, an uncertainty of 20% in the k_1 values is a reasonable estimate.

Activation Parameters. Since the deprotonation of the organic acids and the formation of the NpO_2L complex are involved in redox equation 4, it is necessary to use the ΔH values for the complexation and acid dissociation in order to calculate the rate constant k_1 from k_{obsd} at different temperatures. As an approximation, we can assume that the ΔH values for the complexation and acid dissociations are small so the ratio of k_1/k_{obsd} remains constant within the temperature range. The enthalpy and entropy of activation were calculated from the temperature dependency of rate constant k_1 by the Eyring formulation of absolute reaction rates[14]

$$k_1 = \chi \frac{\kappa T}{h} \exp\left(\frac{\Delta H^{\ddagger}}{RT}\right) \exp\left(\frac{\Delta S^{\ddagger}}{R}\right) \qquad (6)$$

where χ is the transmission coefficient, assumed to have a value of 1. κ is Boltzmann's constant and h is Planck's constant. The $\Delta G^{\ddagger}$ values were obtained from the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values. The experimental activation parameters listed in Table III suggest that the large negative entropy change is responsible for the slow reduction of Np(VI) by some of the acids investigated.

The assumption of $\Delta H \approx 0$ was tested by calculation of the rate constants at different temperatures utilizing the available ΔH values for acid association and complexation of malonic acid with UO_2^{2+}.[13] The resulting values of the activation parameters were essentially the same as those calculated with the assumption of $\Delta H \approx 0$.

Discussion

These experiments are consistent with the formation of the 1:1 complex as the intermediate. Previous studies at lower values of pH[2,3] had proposed protonated species such as NpHL as the intermediate. However, the agreement between the experimental and calculated curves in Figure 2 provides direct evidence that the major intermediate complex in our systems is NpO_2L in all cases.

These experiments did not allow measurement of the oxidation products of the dicarboxylic acids. However, studies of Ce^{4+} reduction by malonic[15] and alkylmalonic[16] acids may provide insight into the probable products. The proposed mechanism in these systems is given by eq 7 and 8. The

$$Ce^{4+} + HCR(CO_2H)_2 \rightarrow \cdot Cr(CO_2H)_2 + Ce^{3+} + H^+ \qquad (7)$$

$$Ce^{4+} + \cdot CR(CO_2H)_2 + H_2O \rightarrow RC(OH)(CO_2H)_2 + Ce^{3+} + H^+ \qquad (8)$$

hydroxy acid can react further with the Ce^{4+} to form formic acid and/or CO_2. Since our tracer systems have an excess of dicarboxylic acid, the net oxidation reaction would seem to be unlikely to involve stoichiometries of 4:1 metal to dicarboxylic acid ratios. It would seem more likely that the reduction of NpO_2^{2+} would proceed only to the stage equivalent to eq 7.

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Table II. Reduction of Np(VI) by a Series of Dicarboxylic Acids ($T \simeq 23$ °C, $I = 0.10$ M (NaCl))

acid	$[H_2L]_T$, M	pH	k_{obsd}, m^{-1}	k_1,[a] m^{-1}
oxalic	2.5×10^{-4}	1.4	$(1.5 \pm 0.2) \times 10^{-2}$	$(2.9 \pm 0.3) \times 10^{-2}$
malonic	5.0×10^{-3}	2.2	$(1.7 \pm 0.2) \times 10^{-2}$	$(5.9 \pm 0.7) \times 10^{-2}$
methylmalonic	5.0×10^{-3}	2.4	$(1.7 \pm 0.2) \times 10^{-3}$	$(6.7 \pm 0.8) \times 10^{-3}$
dimethylmalonic	5.0×10^{-3}	2.6	$(8.4 \pm 1.0) \times 10^{-4}$	$(2.0 \pm 0.2) \times 10^{-3}$
succinic	5.0×10^{-3}	4.0	$(1.7 \pm 0.3) \times 10^{-3}$	$(2.9 \pm 0.6) \times 10^{-3}$
maleic	5.0×10^{-3}	3.0	$(7.0 \pm 1.1) \times 10^{-4}$	$(2.4 \pm 0.4) \times 10^{-3}$
phthalic	5.0×10^{-3}	2.6	$(7.0 \pm 1.0) \times 10^{-4}$	$(2.6 \pm 0.4) \times 10^{-3}$
fumaric	5.0×10^{-3}	2.8	$(5.1 \pm 0.9) \times 10^{-4}$	$(1.9 \pm 0.4) \times 10^{-3}$
glutaric	5.0×10^{-3}	4.0	$<1.0 \times 10^{-4}$	$<2 \times 10^{-4}$
CHDCA[b]	5.0×10^{-3}	3.4	$<1.0 \times 10^{-4}$	$<4 \times 10^{-4}$
control	0.10 M NaCl	3.1	6.0×10^{-5}	

[a] Calculated from k_{obsd} by eq 5. [b] CHDCA = 1,4-cyclohexanedicarboxylic acid.

Table III. Activation Values

acid	T, K	k_1, s^{-1}	$\Delta H^\ddagger$, kJ/mol	$\Delta S^\ddagger$, J/(mol K)	$\Delta G^\ddagger$, kJ/mol
oxalic (2.5×10^{-4} M, pH 1.1)	294.7	3.4×10^{-4}	90 ± 7	−7 ± 21	92 ± 13
	306.7	1.3×10^{-3}			
	312.2	8.7×10^{-3}			
	317.4	4.8×10^{-3}			
	321.7	7.9×10^{-2}			
malonic (5.0×10^{-3} M, pH 2.2)	295.2	7.4×10^{-4}	70 ± 10	−64 ± 25	89 ± 17
	307.2	2.7×10^{-3}			
	312.0	4.1×10^{-3}			
	316.9	6.1×10^{-3}			
	322.2	8.6×10^{-2}			
methylmalonic (5.0×10^{-3} M, pH 2.4)	307.7	1.0×10^{-4}	88 ± 9	−16 ± 29	93 ± 17
	313.7	2.2×10^{-3}			
	318.2	3.5×10^{-3}			
	323.2	5.8×10^{-3}			
dimethylmalonic (5.0×10^{-3} M, pH 3.0)	296.2	2.0×10^{-5}	43 ± 13	−183 ± 33	98 ± 22
	308.2	3.1×10^{-5}			
	318.2	5.7×10^{-5}			
	338.2	1.3×10^{-4}			
succinic (5.0×10^{-3} M, pH 4.0)	295.2	4.9×10^{-5}	66 ± 9	−103 ± 42	97 ± 22
	307.0	1.5×10^{-4}			
	313.4	1.9×10^{-4}			
	318.2	3.0×10^{-4}			
	338.1	1.8×10^{-4}			
maleic (5.0×10^{-3} M, pH 3.0)	308.9	1.0×10^{-4}	87 ± 12	−43 ± 42	100 ± 25
	316.9	2.2×10^{-4}			
	324.7	5.0×10^{-4}			
	331.9	1.1×10^{-3}			
phthalic (5.0×10^{-2} M, pH 3.0)	296.2	3.5×10^{-5}	38 ± 8	−20 ± 25	100 ± 16
	307.1	5.2×10^{-5}			
	318.2	9.2×10^{-5}			
	333.0	2.2×10^{-4}			
	338.2	2.5×10^{-4}			
fumaric (5.0×10^{-2} M, pH 3.0)	296.2	1.8×10^{-5}	37 ± 23	−209 ± 84	99 ± 41
	318.2	4.8×10^{-5}			
	338.2	1.3×10^{-4}			

The studies of Ce^{4+} reduction indicated that the unpaired electron in $\cdot CR(CO_2H)_2$ was located on the methylene carbon and the rate-determining step involved loss of a methylene proton.[15] This model was supported by the studies in ref 16, which found that the rate decreased as a methyl and, then, an ethyl group replaced one of the methylene protons of malonic acid. Moreover, dimethylmalonic acid, with no methylene proton, complexed with Ce^{4+} but no redox was observed.[16] Our data (Table II) showed a sequence in reaction rates of malonate > methylmalonate ≈ succinate > dimethylmalonate, which would support the model proposed in ref 15 and 16.

Table IV. Comparison of $\Delta G^\ddagger$ for the Reduction of Different Oxidants by Oxalic Acid with the Oxidation Potentials

oxidant	std potential, V[19]	ionic strength, M	$\Delta H^\ddagger$, kJ/mol	$\Delta S^\ddagger$, J/(mol K)	$\Delta G^\ddagger$, kJ/mol
Ce(IV)-Ce(III)	1.70	1.0	66.1	7.1	64.0[a]
Mn(III)-Mn(II)	1.51	2.0	74.1	−13	77.8[b]
Np(VI)-Np(V)	1.14	0.1	90	−7	92[c]
VO_2^+-VO^{2+}	1.00	4.0	100.0	2.5	99.6[d]

[a] Calculated from the data in ref 17. [b] Calculated from the data in ref 18. [c] This work. [d] Calculated from the data in ref 19.

Our data suggest that not only is the presence of methylene protons a factor but so also is the stability of the 1:1 complex. The observed rate sequence

oxalate < malonate > succinate > glutarate

reflects a decrease in rate constant with log β_1 except for oxalate, which has no methylenic protons.

A comparison of the free energies of activation for the interaction of oxalic acid with different oxidants is shown in Table IV, together with their standard oxidation potentials. The similarity in $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values for different oxidants implies that they oxidize oxalic acid by the same mechanism. According to Marcus theory,[20] in the redox reaction of a series of oxidants with a given reagent such that ΔG° is essentially the only parameter varied, a plot of $\Delta G^\ddagger$ vs. ΔG° should be linear. ΔG° is the standard free energy of the elementary electron-transfer step and is equal to $-nFE^\circ$ + constant for a series of related redox reactions. Although the values of ΔG° are not available for those reactions, it is obvious that the free energy of activation increases when the oxidation potential of the oxidants decreases (ΔG° becomes less negative), which suggests that linear free energy relationships are probably applicable in the reduction of Np(VI) by oxalic acid and, presumably, by the other dicarboxylic acids.

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Registry No. Np, 7439-99-8; oxalic acid, 144-62-7; malonic acid, 141-82-2; methylmalonic acid, 516-05-2; dimethylmalonic acid, 595-46-0; succinic acid, 110-15-6; maleic acid, 110-16-7; phthalic acid, 88-99-3; fumaric acid, 110-17-8; glutaric acid, 110-94-1; 1,4-cyclohexanedicarboxylic acid, 1076-97-7.

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