Table III. Summary of Rate and Activation Parameters for the Solvolysis of $Pd(Me_5dien)py^{2+}$ as a Function of Solvent at 25 °C and 0.1 M ptsa

solvent	10^5k_1, M^{-1} s^{-1}	ΔH^*, kJ mol^{-1}	ΔS^*, J K^{-1} mol^{-1}	ΔV^*, cm^3 mol^{-1}
EtOH	7.4 ± 0.1	86 ± 3	−38 ± 11	−4.1 ± 0.1
MeOH	4.1 ± 0.1	87 ± 4	−39 ± 14	−6 ± 1
H_2O	1.87 ± 0.04[a]	69 ± 4	−105 ± 14	−3.1 ± 0.1
Me_2SO	52.8 ± 0.6	69 ± 2	−78 ± 8	≈0
DMF	90.1 ± 1.5	63 ± 2	−91 ± 7	−3.4 ± 0.3[b]
MeCN	1310 ± 42	60 ± 5	−77 ± 17	−2.4 ± 0.6[b]

[a] k_1 value for solvolysis during the reaction with OH^-. [b] Temperature = 30 °C.

convert the solvento species completely into the aqua form. Thus it follows that the water introduced with the addition of 0.1 M ptsa will have no significant effect on the solvolysis reactions under investigation.

The temperature and pressure dependencies of k_1 as a function of solvent (Table I) were used to calculate the activation parameters (ΔH^*, ΔS^*, and ΔV^*) in the usual way,[11] and the results are summarized in Table III. For these calculations, k_1 was converted to a second-order rate constant in order to take the different solvent concentrations into consideration. The reactivity sequence $H_2O < MeOH < EtOH < Me_2SO < DMF < MeCN$ is in good agreement with that reported for solvolysis reactions of sterically unhindered Pt(II) and Pd(II) complexes, viz. k_1 is usually larger for dipolar aprotic than for protic solvents.[18-20] On the contrary, a reverse reactivity order ($H_2O > MeOH > Me_2SO$) was reported for solvolysis of the sterically hindered $Pd(Et_4dien)X^+$ complexes.[21-23] The chemical shifts of the methyl protons indicated that smaller solvent molecules can interact better with the crowded Pd(II) center than the larger ones. It was suggested on the basis of the ΔS^* values that solvolysis is associative for water as solvent but dissociative for Me_2SO and DMF as solvents.[23] However, in later work[21] the error limits of the ΔS^* data were taken into account and the results (including ΔV^* data) were interpreted in terms of an I_a mechanism. The present data, however, exhibit a good agreement with data for nonhindered systems, and there is no reason to believe that a change in mechanism is at hand.

The values of ΔV^* in Table III are all small and slightly negative and do not exhibit a specific trend with the nature of the solvent. The solvation of the $Pd(Me_5dien)py^{2+}$ complex in the ground and transition states is expected to be very similar, since the entering and leaving groups are neutral and no substantial change in dipole moment is expected. This is in agreement with similar findings for solvolysis of Pt(II) complexes,[24] where the solvent–substrate interaction is not of much kinetic significance because the nucleophilic discrimination factors change to approximately the same extent when the solvent is changed for various complexes. Our ΔV^* data, therefore, mainly reveal intrinsic effects in which the volume decrease associated with the binding of the entering solvent molecule is partially compensated for by the volume increase associated with the square-pyramidal to trigonal-bipyramidal transition as mentioned before. The partial molar volumes of the solvent molecules, as estimated from their densities at 20 °C, are 58.4 (EtOH), 40.4 (MeOH), 18.0 (H_2O), 70.9 (Me_2SO), 77.0 (DMF), and 52.2 cm^3 mol^{-1} (MeCN), from which it follows that there is no apparent correlation with the corresponding values of ΔV^*. Our earlier work has demonstrated that the extent of volume collapse during bond formation depends on the size of the entering solvent molecule, up to a point where this collapse is hindered by steric effects for large entering molecules.[12,25] It follows that this volume collapse could be very small in the case of a large molecule such as Me_2SO. The overall value of ΔV^* is therefore mainly controlled by steric and intrinsic effects. Finally, it should be mentioned that ΔV^* data of similar magnitude were reported for solvent exchange on $Pd(H_2O)_4^{2+}$ (-2.2 ± 0.2 cm^3 mol^{-1})[7] and for solvolysis of $Pd(H_2O)_3Me_2SO^{2+}$ (-1.7 ± 0.6 cm^3 mol^{-1}),[26] which are both believed to occur according to an associative mechanism.

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Registry No. $Pd(Me_5dien)py^{2+}$, 117226-34-3; MeOH, 67-56-1; EtOH, 64-17-5; Me_2SO, 67-68-5; DMF, 68-12-2; MeCN, 75-05-8.

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ESR Studies of Intramolecular Electron Transfer in Malonic Acid Radical Chelates of Cerium(IV)

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The reduction of Ce(IV) complexed to dicarboxymethyl (malonic acid radical; $^{\bullet}CH(COOH)_2$) has been directly investigated by kinetic electron spin resonance spectrometry in aqueous perchloric acid media at 298 K. The corresponding first-order rate constant has a value of $k_{11} = (1.5 \pm 0.3) \times 10^3$ s^{-1}. Free (M_1) and Ce(IV)-chelated (M_2) dicarboxymethyl radicals have slightly different magnetic parameters [$g(M_1) = 2.0039$, $a(H_\alpha)(M_1) = 20.3$ G, $g(M_2) = 2.0035$, $a(H_\alpha)(M_2) = 19.6$ G] and coexist in equilibrium, the ratio $r = [M_2]/[M_1]$ being a function of both [Ce(IV)] and [H^+]. The stability constant of the radical chelate, $K_8 = 242 \pm 31$ M^{-1}, is considerably larger than that of malonic acid itself, $K_5 = 1.14$ M^{-1}. The product K_8k_{11}, which represents the overall rate constant for dicarboxymethyl radical oxidation by Ce(IV), has a value within the range of those measured for the direct oxidations of substituted secondary alkyl radicals by Ce(IV), Co(III), and Ti(IV).

Introduction

Electron-transfer reactions between transition metal cations and alkyl radicals is an area of current interest.[1-5] They are relatively fast processes with rate constants in the range 10^5–10^6 M^{-1} s^{-1} and can proceed in principle either by a direct mechanism or by

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one involving prior metal–carbon bond formation.[2]

In this paper we explore a third possibility, i.e., intramolecular electron transfer in a radical–metal transient intermediate where the redox sites are kept farther apart. This is realized here as the dicarboxymethyl (malonic acid radical); $^{\bullet}CH(COOH)_2$) chelate of Ce(IV), which has been directly investigated by electron spin resonance spectrometry.[6,7] The information obtained illustrates some of the unique features of these systems and includes (1) magnetic parameters of free (M_1) and complexed (M_2) radicals, (2) the stability constant for the equilibrium

$$M_1 + Ce(IV) \xrightarrow{8} M_2$$

which results in a value 200-fold larger than the one corresponding to malonic acid itself,[8] and (3) kinetic data for the redox reaction

$$M_2 \xrightarrow{11} Ce(III) + \text{products}$$

Very interestingly the overall rate constant for malonyl radical oxidation by Ce(IV), i.e., K_8k_{11}, has a value of 3.7×10^5 M^{-1} s^{-1}, similar to those measured for secondary alkyl radical oxidation by Ce(IV), Ti(IV), and Co(III) which presumably take place by a "direct" mechanism.[1,2] Electron delocalization above the reaction barrier involving the SOMO π orbital, the carbonyl π system, and the $4f_{5z^3-3zr^2}$ LUMO orbital of Ce(IV) seems to overcome distance effects for electron transfer in M_2.[9,10]

Experimental Section

Dicarboxymethyl radicals (M) were produced via reaction 1 by flowing solutions of malonic acid (MH) and Ce(IV) through an ESR mixing

$$Ce(IV) + MH = Ce(III) + M_1 + H^+ \qquad (1)$$

cell for aqueous media located in the TE_{102} cavity of a Bruker ER 200tt X-band ESR spectrometer.[6] A stopcock placed at the cell outlet was used to interrupt liquid circulation in stopped-flow kinetic experiments. Daily prepared solutions kept in 2-L containers were thoroughly deareated by bubbling high-purity nitrogen for about 4 h. The presence of O_2 traces led in all cases to the appearance of a broad doublet ($g = 2.0147$, $a(H_\gamma) = 3.8$ G) tentatively assigned to the peroxydicarboxylmethyl radical (MO_2). The g factors and $a(H_\alpha)$ hfs of the various radicals were determined against those of aqueous solutions of Fremy's salt, $NO(SO_3K)_2$.[6] Malonic acid (Merck) and perchloric acid (70%, p.a., Merck) were used as received. $Ce(ClO_4)_4$ solutions were prepared by electrolytic oxidation of $Ce(ClO_4)_3$. Rates of Ce(IV) decay were determined by kinetic absorption spectrophotometry at 317 or 397 nm in a Shimadzu 210A spectrophotometer. All experiments, performed at 298 K, were quite reproducible.

Results and Discussion

(1) Radical Identification. Two radicals M_1 and M_2 could be readily identified by ESR spectrometry in aqueous perchloric acid media at small steady flow rates (~0.7 cm^3/min) (Figure 1a). Their very similar ESR parameters, $g(M_1) = 2.0039$, $a(H_\alpha)(M_1) = 20.3$ G, $g(M_2) = 2.0035$, $a(H_\alpha)(M_2) = 19.6$ G, can be certainly ascribed to substituted alkyl radicals possessing a single α-proton.[11] On the basis of previous information, M_1 is identified as the free dicarboxymethyl radical.[7] A direct clue to the identity of M_2 as a metal-bound radical is provided by the observation that its signal dissappears upon addition of SO_4^{2-} (Figure 1b). This is interpreted as due to the fact that under such conditions dicarboxymethyl radicals are not able to compete with much larger concentrations of a doubly charged anion for positions in the coordination sphere of the metal ion.

Figure 1. ESR spectra: (a) free (1) and complexed (2) dicarboxymethyl radicals in $[HClO_4] = 0.84$ M, $[Ce(ClO_4)_4] = 3 \times 10^{-2}$ M and $[MH] = 0.3$ M under steady flow; (b) free dicarboxymethyl radical (M_1) in $[H_2SO_4] = 0.8$ M, $[Ce(SO_4)_2] = 3 \times 10^{-2}$ M, and $[MH] = 0.3$ M. Modulation frequency = 12.5 kHz.

The remarkably close g values and hfa's of the α-proton for M_1 and M_2 indicate both minimal spin–orbit coupling with the metal nucleus and negligible ground-state electron delocalization.[10]

(2) Equilibrium Measurements. An additional observation confirms the above view. Thus the ratio $r = [M_2]/[M_1]$, determined from the heights of the corresponding lower field peaks in the ESR spectra of both radicals recorded at steady flows, increases linearly with [Ce(IV)] and decreases with $[H^+]$. The scheme given in eq 2–11, which includes the various possible equilibria involving Ce(IV), H_2O, and malonic acid, is able to account for these facts.[8,12] MOH stands for tartronic acid.[13]

$$Ce^{4+} + H_2O \rightleftharpoons HOCe^{3+} + H^+ \qquad (2)$$

$$Ce^{4+} + MH \rightleftharpoons CeMH^{4+} \qquad (3)$$

$$HOCe^{3+} + MH \rightleftharpoons HOCeMH^{3+} \qquad (4)$$

$$CeMH^{4+} \rightarrow Ce^{3+} + H^+ + M_1 \qquad (5)$$

$$HOCeMH^{3+} \rightarrow Ce^{3+} + H_2O + M_1 \qquad (6)$$

$$Ce^{4+} + M_1 \rightleftharpoons CeM^{4+} \ (M_2) \qquad (7)$$

$$HOCe^{3+} + M_1 \rightleftharpoons HOCeM^{3+} \ (M_2) \qquad (8)$$

$$2M_1 + H_2O \rightarrow MH + MOH \qquad (9)$$

$$H_2O + CeM^{4+} \rightarrow Ce^{3+} + MOH + H^+ \qquad (10)$$

$$HOCeM^{3+} \rightarrow Ce^{3+} + MOH \qquad (11)$$

Reactions 5 and 6 are essentially irreversible since radical concentrations were found to be independent of the aggregate of Ce^{3+}.[14] On the other hand, the products of reactions 7 and 8

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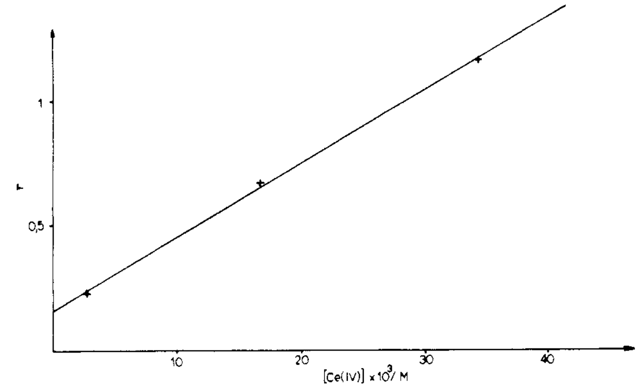


Figure 2. Ratio of concentrations of complexed (M_2) and free (M_1) dicarboxymethyl radicals $r = [M_2]/[M_1]$ vs [Ce(IV)] at $[H^+] = 0.8$ M and [MH] = 0.1 M.

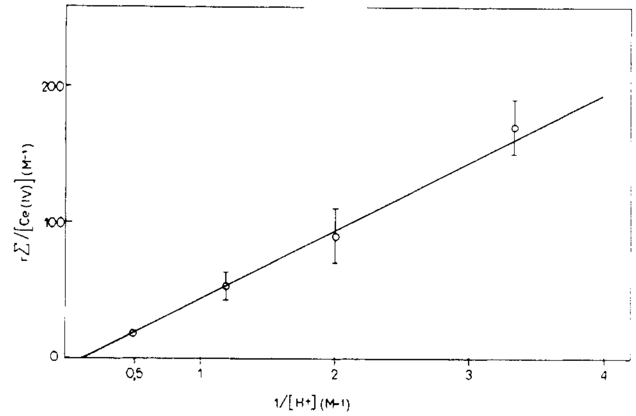


Figure 3. Ratio $r\Sigma/[\mathrm{Ce(IV)}]$ vs $[H^+]^{-1}$ at [MH] = 0.1 M, $r = [M_2]/[M_1]$, and $\Sigma = 1 + K_3[\mathrm{MH}] + K_2[H^+]^{-1}(1 + K_4[\mathrm{MH}])$.

are collectively assigned to species M_2. This may be an oversimplification since ESR spectra recorded under high resolution (12.5-kHz modulation frequency, Figure 1a) reveal additional, albeit unresolved, satellites of the main peaks. Finally it is further assumed that complexing reactions are faster than radical redox or termination processes. In particular, self-reaction of complexed radicals was excluded on the basis of electrostatic arguments.[15] Analysis of the above scheme can be conveniently carried out in two stages.

First, by neglecting the amount of Ce(IV) complexed to free radicals (M_2), one can express the concentration of the several cerium-containing species in terms of [Ce(IV)], [MH], and $[H^+]$: $[\mathrm{Ce}^{4+}] = [\mathrm{Ce(IV)}]/\Sigma$, $[\mathrm{HOCe}^{3+}] = K_2\ [\mathrm{Ce(IV)}]/([H^+]\Sigma)$, $[\mathrm{CeMH}^{4+}] = K_3[\mathrm{MH}][\mathrm{Ce(IV)}]/\Sigma$ and $[\mathrm{HOCeMH}^{3+}] = K_2K_4[\mathrm{MH}][\mathrm{Ce(IV)}]/([H^+]\Sigma)$, where [Ce(IV)] is the analytical concentration of tetravalent cerium and $\Sigma = 1 + K_3[\mathrm{MH}] + K_2[H^+]^{-1}(1 + K_4[\mathrm{MH}])$. Assuming now that M_1 and M_2 are at a steady state, we get

$$[\mathrm{CeM}^{4+}] = k_7[\mathrm{Ce}^{4+}][M_1]/(k_{-7} + k_{10})$$

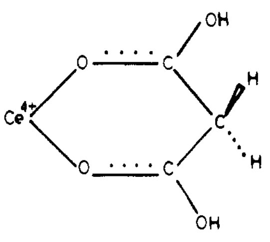
$$[\mathrm{HOCeM}^{3+}] = k_8[\mathrm{HOCe}^{3+}][M_1]/(k_{-8} + k_{11})$$

From the above it follows that

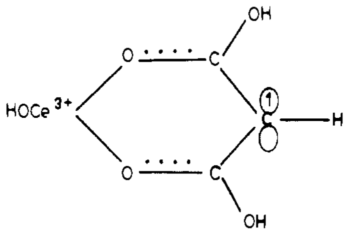
$$r = [M_2]/[M_1] = (K_7 + K_2K_8[H^+]^{-1})[\mathrm{Ce(IV)}]/\Sigma \qquad \text{(I)}$$

$$r\Sigma/[\mathrm{Ce(IV)}] = K_7 + K_2K_8/[H^+] \qquad \text{(II)}$$

These relationships are satisfied by experimental data as shown in Figures 2 and 3, from which we obtain $K_7 = (-8.1 \pm 9.7) \sim 0$, and $K_8 = 242 \pm 31$ by using $K_2 = 0.21$, $K_3 = 2.03$, and $K_4 = 1.14$ as given by Amjad and McAuley.[8] Notice that K_8 is more than 200 times larger than K_4, although both equilibria involve the formation of similar six-center chelates, A and M_2. This is supported by the fact that direct interaction of the half-filled molecular orbital with the metal center can be disregarded since it would lead to larger differences in the magnetic parameters of M_1 and M_2 at variance with experimental observations.[11] Actually the relief of some 3.3 kcal/mol of ring strain in going from A to M_2 due to the formation of a planar trigonal radical center is able to account for the greater stability of M_2. Finally, the possible participation of dimeric Ce(IV) species was considered and discarded since it led to a $r = a[\mathrm{HOCe}^{3+}] + b[\mathrm{HOCe}^{3+}]^2$ dependence that is not borne out by present data (Appendix).[12,16]



A



M_2

Kinetic Measurements. Upon flow interruption the ESR signals corresponding to M_1 and M_2 decayed at markedly different rates.[6] Actually the ratio S of the initial slopes of log $[M_2]$ and log $[M_1]$ vs time plots always had a value larger than 3. To begin with we observe that omission of reactions 10 and 11 leads immediately to a $[M_1] \propto [\mathrm{Ce(IV)}]^{1/2}$ dependence, which follows from the second-order termination, reaction 9. Since $[M_2] \propto [M_1][\mathrm{Ce(IV)}]$ (eq I), then $[M_2] \propto [\mathrm{Ce(IV)}]^{3/2}$, and the pseudo-first-order decay of [Ce(IV)] found in ref 8 and verified here effectively implies $S = 3$. In general it can be shown that at steady state

$$[M_1] = (-p + (p^2 + q)^{1/2})[\mathrm{Ce(IV)}] \qquad \text{(III)}$$

$$[M_2] = K_2K_8/(\Sigma[H^+])(-p + (p^2 + q)^{1/2})[\mathrm{Ce(IV)}]^2 \qquad \text{(IV)}$$

where $p = k_{11}K_2K_8/(4k_9[H^+]\Sigma)$ and $q = k_5K_3[\mathrm{MH}]/(2k_9[\mathrm{Ce(IV)}]\Sigma)$ if we disregard CeM^{4+} complexes based on the small value of K_7 derived above and recall that $k_6 \sim 0$.[8] Time derivatives of log $[M_1]$ and log $[M_2]$ can be directly obtained from eq III and IV, namely

$$\frac{d(\ln [M_1])}{dt} = \left(1 - \frac{1}{2}f\right)\frac{d(\ln [\mathrm{Ce(IV)}])}{dt} \qquad \text{(V)}$$

$$\frac{d(\ln [M_2])}{dt} = \left(2 - \frac{1}{2}f\right)\frac{d(\ln [\mathrm{Ce(IV)}])}{dt} \qquad \text{(VI)}$$

where $1 \leqslant f = (1 + pq^{-1}[p - (p^2 + q)^{1/2}])^{-1} \leqslant 2$.

From the definitions of p and q it can be easily found that if $q \rightarrow \infty$, i.e. if [MH]/[Ce(IV)] is large, then $f \rightarrow 1$. On the other hand the reverse condition, i.e. $q \rightarrow 0$, leads to $f \rightarrow 2$. Also notice that if $k_{11} = 0$ then $p = 0$, $f = 1$, and $S = d(\ln [M_2])/d(\ln [M_1]) = 3$. In other words, as mentioned above, S values larger than 3 imply a finite rate of intramolecular decomposition of chelated radicals. From eq V and VI one gets

$$S = [2 - \tfrac{1}{2}f]/[1 - \tfrac{1}{2}f] \qquad \text{(VII)}$$

or $f = (2S - 4)/(S - 1)$, and from the definitions of f, p, and q above

$$J = [H^+]\Sigma^{1/2}(2k_5K_3[\mathrm{MH}]/[\mathrm{Ce(IV)}])^{1/2}/(K_2K_8) = (k_{11}/k_9^{1/2})(S - 2)^{1/2}/(S - 3) \qquad \text{(VIII)}$$

can be derived. Experimental data closely verify eq VIII (Figure 4), from which an estimate of $k_{11} = (1.5 \pm 0.3) \times 10^3$ can be

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(14) Försterling, H. D.; Pachl, R.; Schreiber, H. *Z. Naturforsch., A: Phys. Sci.* **1987**, *42A*, 963. However, these authors found an inhibiting effect by Ce(III) in sulfate media that can be rationalized as arising from the lower oxidation potential of $\mathrm{CeSO_4}^{2+}$ relative to Ce^{4+}.

(15) Repulsion energies between (CeOH^{3+}–CeOH^{3+}) and (Ce^{4+}–Ce^{4+}) pairs at the distances of 8.3 Å imposed by six-membered dicarboxymethyl chelates amount to 4.2 and 7.5 kcal/mol, leading to rates about 8×10^{-4} and 3×10^{-6} times slower than reaction 9.

(16) Hardwich, T. J.; Robertson, E. *Can. J. Chem.* **1951**, *29*, 818.

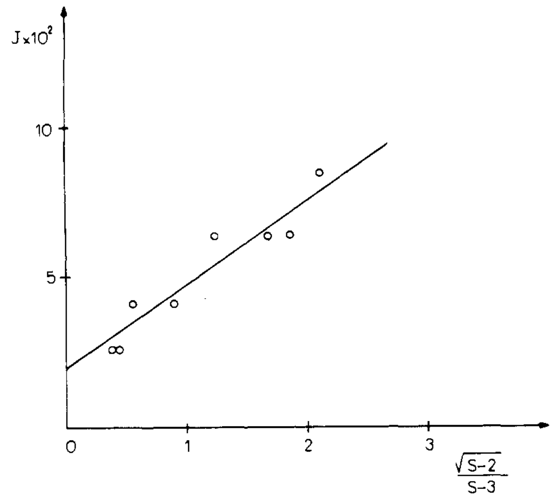

Figure 4. J (see eq VIII in the text) vs $(S-2)^{1/2}/(S-3)$, where S is the ratio of initial slopes of ln $[M_1]$ and ln $[M_2]$ vs time plots. The slope is $(k_{11}/K_9^{1/2})$.

obtained, by using the known values of k_5, k_9, K_2, K_3, and K_8. Obviously the variable $(S-2)^{1/2}/(S-3)$ would vanish under present experimental conditions only if $S \rightarrow \infty$, i.e. if k_{11} becomes very large. In that case the assumption that complexing equilibria reactions are much faster than irreversible steps would no longer be valid, and therefore the plot is not expected to go through the origin as eq VIII apparently predicts. Clearly oxidation of dicarboxymethyl radicals in this system takes place by prior formation of metal–radical complexes followed by the very favorable intramolecular one-electron oxidative substitution, reaction 11.

$$\mathrm{HOCe(HOOC)_2\dot{C}H^{3+} \rightarrow (HOOC)_2C(H)OH + Ce^{3+}} \qquad (11)$$

The effective rate constant for radical oxidation would be given by $K_8k_{11} = 3.7 \times 10^5$ M^{-1} s^{-1}, which is comparable to the one measured for the oxidation of 2-hydroxyisopropyl radical by Co $(NH_3)_6^{3+}$ (4.1×10^5 M^{-1} s^{-1}) or by TiO^{2+} (1.1×10^6 M^{-1} s^{-1}).[1,2] Further work is under way.

Conclusion

Direct evidence has been presented for the formation and decay of paramagnetic chelates of Ce(IV) with dicarboxymethyl radicals during the oxidation of malonic acid by Ce(IV) in perchloric acid media. The very similar magnetic parameters of free and complexes radicals reveal that the latter do not involve metal–carbon bond formation. The rates of oxidation of malonyl radicals via complex formation are very similar to the direct oxidations of secondary alkyl radicals by other cations, revealing the absence of discernible distance effects. This is ascribed to extensive electron delocalization in the transition state.

Appendix

A detailed analysis of the possible involvement of dimeric tetravalent cerium has been carried out based on the following scheme:

$$\mathrm{Ce^{4+} + H_2O \rightleftharpoons HOCe^{3+} + H^+} \qquad (2)$$

$$\mathrm{Ce^{4+} + MH \rightleftharpoons CeMH^{4+}} \qquad (3)$$

$$\mathrm{HOCe^{3+} + MH \rightleftharpoons HOCeMH^{3+}} \qquad (4)$$

$$\mathrm{HOCe^{3+} + M_1 \rightleftharpoons HOCeM^{3+}} \qquad (8)$$

$$\mathrm{HOCe^{3+} + H_2O \rightleftharpoons (HO)_2Ce^{2+} + H^+} \qquad (12)$$

$$\mathrm{2HOCe^{3+} \rightleftharpoons H_2O + OCe_2{}^{6+}} \qquad (13)$$

$$\mathrm{(HO)_2Ce^{2+} + MH \rightleftharpoons (HO)_2CeMH^{2+}} \qquad (14)$$

$$\mathrm{OCe_2{}^{6+} + MH \rightleftharpoons OCe_2MH^{6+}} \qquad (15)$$

$$\mathrm{(HO)_2Ce^{2+} + M_1 \rightleftharpoons (HO)_2CeM^{2+}} \qquad (16)$$

$$\mathrm{OCe_2{}^{6+} + M_1 \rightleftharpoons OCe_2M^{6+}} \qquad (17)$$

Under typical experimental conditions the most abundant cerium species comes out to be $HOCe^{3+}$ in the absence of MH by using the K_2 and K_{13} values given by Hardwick and Robertson.[16] In this connection, it should be emphasized that these values have been questioned by a number of authors, particularly by Offner and Skoog, who suggest a much lower value of both K_2 and K_{13}.[12] In this sense, it is fair to say that although the question of the extent of dimerization in ceric ion solutions has not been settled, our choice of Hardwick and Robertson's parameters represents an extreme test of the role of the dimer.

At the steady state and after some tedious algebra one arrives at the expression

$$r/[\mathrm{HOCe^{3+}}] = (K_8 + K_{16}K_{12}[\mathrm{H^+}]^{-1}) + K_{13}K_{15}[\mathrm{HOCe^{3+}}] \qquad \text{(IX)}$$

which is not verified by our data. We conclude that either K_{13} or K_{15} or both are negligible and can be ignored in the present work.