Kinetics and Mechanism of the Oxidation of the Calcium Complex of Ethylenediaminetetra-acetic Acid by Perbenzoic Acids

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The rate of oxidation of ethylenediaminetetra-acetic acid (EDTA) by perbenzoic acids in aqueous acetate buffers is retarded by added calcium ions. The oxidation of CaEDTA^{2-} proceeds *via* parallel pathways involving dissociation and subsequent oxidation of the ligand and direct nucleophilic attack of the nitrogen atom of the complex on the outer peroxidic oxygen of the peracid respectively. The mechanism of the latter pathway is discussed. An application of the Ca–EDTA system as a reservoir of EDTA for the inhibition of interfering trace-metal-ion catalysed reactions of peracids is suggested.

Perbenzoic acids react with ethylenediaminetetra-acetic acid (EDTA) and related chelating agents, to form *N*-oxides *via* nucleophilic attack of the nitrogen atom of the chelator on the outer peroxidic oxygen of the peracid.[1] Protonation of the nitrogen atoms of the chelator[1] or co-ordination of metal ions, for example Cu(II) to EDTA,[2] stabilizes the ligand with respect to oxidation by the peracid. The goal of the present work is to establish to what extent, and how, metal ions suppress the reactions of EDTA and perbenzoic acids. To this end we have studied CaEDTA^{2-} since the reactions of peroxides and transition-metal complexes such as FeEDTA^{-} are complicated by redox cycling of the metal between oxidation states and accompanying chemical reactions.[3,4]

Experimental

Materials.—Chemicals were AnalaR grade (BDH) except for *m*-chloroperbenzoic acid (MCPBA, 85%, BDH) and *p*-nitroperbenzoic acid (PNPBA, 40%, provided by Interox Chemicals) which contained the parent acid as the only significant impurity. Solutions were made up in distilled water.

Kinetic Measurements.—Absorbances were measured using a Hewlett–Packard HP8451A spectrophotometer with a thermostatted cell holder at 25 °C. The reduction of MCPBA and PNPBA was monitored at 242 and 260 nm respectively. Kinetic runs were carried out as described previously[1] with EDTA in large excess over peracid. Sodium acetate–acetic acid buffers, ionic strength 0.1 mol dm^{-3}, were used with 1×10^{-3} mol dm^{-3} EDTA and $2\text{–}5 \times 10^{-3}$ mol dm^{-3} $\mathrm{Ca(NO_3)_2}$; the total ionic strength was held constant at 0.115 mol dm^{-3} with $\mathrm{NaNO_3}$. The gradients of plots of ln $(A\text{–}A_\infty)$ *vs.* time gave the observed pseudo-first-order rate constant, k_{obs}.

Results and Discussion

The reduction of peracid is first order for at least four half-lives and k_{obs} is independent of the initial concentration of peracid. The dependence of k_{obs} on the total calcium-ion concentration is shown in Table 1. The results are consistent with the mechanism shown in equations (1)–(3), in which ionic charges are omitted and where P and Y respectively represent all the forms of peracid and EDTA present at a given pH and CaY represents CaEDTA^{2-}, since, from thermodynamic data[5–7] it can be shown that the concentrations of $\mathrm{Ca_2EDTA}$ and $\mathrm{CaHEDTA}^{-}$ are negligible under the present experimental conditions.

$$\mathrm{CaY} \overset{K_1}{\rightleftharpoons} \mathrm{Ca} + \mathrm{Y} \qquad (1)$$

$$\mathrm{Y} + \mathrm{P} \xrightarrow{k_2} \text{products} \qquad (2)$$

$$\mathrm{CaY} + \mathrm{P} \xrightarrow{k_3} \text{products} \qquad (3)$$

The product of reaction (2) is EDTA *N*-oxide[1] and we can safely assume that *N*-oxidation results from reaction (3) since $\mathrm{Ca^{II}}$ is redox inactive. From the most appropriate thermodynamic data[7] it can be shown that under the present conditions the degree of dissociation of CaY, reaction (1), is less than 0.06 and 0.008 respectively at pH 5.1 and 5.6 and hence the mechanism given in equations (1)–(3) leads to the rate law shown in equation (4) in which $[\mathrm{Y}]_\mathrm{T}$ and $[\mathrm{Ca}]_\mathrm{T}$ represent the total concentrations of EDTA and calcium and K_1, k_2, and k_3 are constant at any given pH as defined in equations (1)–(3), and k_{obs} is defined in equation (5).

$$-\mathrm{d}[\mathrm{P}]/\mathrm{d}t = \{K_1k_2([\mathrm{Ca}]_\mathrm{T} - [\mathrm{Y}]_\mathrm{T})^{-1} + k_3\}\,[\mathrm{Y}]_\mathrm{T}[\mathrm{P}] \qquad (4)$$

$$K_1k_2([\mathrm{Ca}]_\mathrm{T} - [\mathrm{Y}]_\mathrm{T})^{-1} + k_3 = k_{\mathrm{obs}}/[\mathrm{Y}]_\mathrm{T} \qquad (5)$$

Table 2 shows the best-fit values and standard deviations of K_1k_2 and k_3 obtained from weighted (inverse variance of k_{obs}) linear regression of $k_{\mathrm{obs}}/[\mathrm{Y}]_\mathrm{T}$ against the left-hand side of equation (5). The dependence of k_2 upon the pH and the nature of the peracid has been reported previously and the decrease in K_1k_2 for MCPBA between pH 5.1 and 5.6 is consistent with the increase in k_2[1] being offset by the larger decrease in K_1[7] over this pH range. Similarly, at pH 5.1, the inverse dependence of K_1k_2 upon the pK_a of the peracid simply reflects the effect of peracid substituents upon k_2. In equation (5) the K_1k_2 term represents the pathway that involves dissociation of CaEDTA^{2-} followed by oxidation of the unco-ordinated chelating agent. The finite values of k_3 shows that there is a parallel pathway involving a direct reaction of the peracid and CaEDTA^{2-}. The value of k_3 is independent of pH and inversely proportional to the pK_a of the peracid which indicates that the reaction takes place *via* a nucleophilic attack of a nitrogen atom of CaEDTA^{2-} on the outer peroxidic oxygen of the conjugate acid form of the peracid. This is similar to the mechanism of the

Table 1. Dependence upon Ca^{2+} concentration of the observed first-order rate constants (25 °C) for the reaction of 1×10^{-3} mol dm^{-3} EDTA with substituted perbenzoic acids in acetate buffers, ionic strength 0.115 mol dm^{-3}.

	MCPBA						PNPBA		
	pH 5.1			pH 5.6			pH 5.1		
$[Ca^{2+}]_T$/ 10^{-3} mol dm^{-3}	k_{obs}/ 10^{-4} s^{-1}	$\hat{k}_{obs}$[a]/ 10^{-4} s^{-1}	k_{calc}[b]/ 10^{-4} s^{-1}	k_{obs}/ 10^{-4} s^{-1}	$\hat{k}_{obs}$[a]/ 10^{-4} s^{-1}	k_{calc}[b]/ 10^{-4} s^{-1}	k_{obs}/ 10^{-4} s^{-1}	$\hat{k}_{obs}$[a]/ 10^{-4} s^{-1}	k_{calc}[b]/ 10^{-4} s^{-1}
0	291	—	—	—	—	—	—	—	—
2.0	8.70	8.88	7.91	4.23	4.07	4.01	17.76	17.91	15.95
2.5	6.04	6.08	5.69	3.05	2.87	2.85	12.70	12.18	11.38
3.0	4.93	4.68	4.46	2.05	2.27	2.26	9.13	9.33	8.88
3.5	4.03	3.84	3.71	1.92	1.91	1.90	—	—	—
4.0	3.20	3.28	3.12	1.82	1.67	1.66	6.03	6.44	6.26
4.5	2.84	2.88	2.81	1.51	1.50	1.50	5.80	5.63	5.49
5.0	—	—	—	—	—	—	5.10	5.01	4.91

[a] The value of $\hat{k}_{obs}$ is calculated from equation (5) using the best-fit kinetic parameters shown in Table 2. [b] The value of k_{calc} is calculated from the exact form of the rate equation, $k_{obs} = K_1k_2[CaY]/[Ca] + k_3[CaY]$ using the best-fit kinetic parameters shown in Table 2 and values of [CaY] and [Ca] calculated from the most appropriate thermodynamic data.[7] The systematic deviation of k_{calc} from $\hat{k}_{obs}$ is small, which shows that the approximation $[CaY] = [Y]_T$ used to derive equation (5) is justified.

Table 2. Kinetic parameters calculated from the data shown in the previous table.

Peracid (pK_a)[a]	pH	$K_1k_2/10^{-4}$ s^{-1}	$k_3/10^{-2}$ dm^3 mol^{-1} s^{-1}
MCPBA (7.53)	5.1	8.4 ± 0.4	4.8 ± 1.7
MCPBA	5.6	3.6 ± 0.4	4.7 ± 1.7
PNPBA (7.14)	5.1	17.2 ± 0.8	7.1 ± 3.3

[a] Taken from D. M. Davies and P. Jones, *J. Org. Chem.*, 1978, **43**, 769.

reaction between $EDTA^{4-}$ and peracid,[1] although this has a rate constant 544 dm^3 mol^{-1} s^{-1}, in the case of MCPBA, which is four orders of magnitude larger than the value of k_3 reported here for the reaction between MCPBA and $CaEDTA^{2-}$. The Ca–N bonds in $CaEDTA^{2-}$ are weak and predominantly electrostatic[8] and so the nitrogen atoms of $CaEDTA^{2-}$ may retain their nucleophilic character, albeit of reduced strength compared with free EDTA. Alternatively, the reaction could involve a pre-equilibrium in which one of the iminodiacetate groups of EDTA dissociates from the calcium, to give a structure analogous to that suggested[6,7] for $CaHEDTA^{-}$, prior to attack of the nitrogen on the peracid.

Chelating agents such as EDTA are commonly used to sequester trace metal ions and thus suppress undesired metal-catalysed side reactions of peroxides. The reduced reactivity towards peracid of $CaEDTA^{2-}$ compared with free EDTA suggests the use of $CaEDTA^{2-}$ as a reservoir of EDTA that is relatively inert with respect to oxidation by the peracid but nevertheless is available to sequester those metal ions that bind to EDTA more strongly than does calcium.

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