A Comparative Reduction of 18-Molybdodiphosphate by α-Tocopherol in Micellar and Isotropic Media

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Micelles are considered as the simplest models [1] of biological membranes, and therefore the investigation of certain reactions such as redox reactions in micellar media could approximately mimick analogous processes occurring in biological systems. In this communication we report the reduction of $[P_2Mo_{18}O_{62}]^{6-}(Mo_{18}{}^{6-})^2$ with α-tocopherol. The Mo polyoxometalate containing several metal ions and capable of reversible multi-electron reduction (reversible in the sense that reoxidation leaves the anion intact) can be approximated to the active centers of molybdenum enzymes [3], while α-tocopherol, the major component of Vitamin E, due to its lipophilic character acts primarily as an efficient inhibitor of lipid peroxidation [4]. Furthermore, as has been previously discussed [5], 'chemical evidence' concerning the solubilization site of reactants, determined by studying their reactivity, provides information concerning solubilization in addition to spectroscopic methods.

Triton X-100, a non-ionic surfactant of cmc 2×10^{-4} [6a, 6b] and aggregation number 140–150 [6a], was used for the formation of the micellar medium. A cationic surfactant such as CTAB (Cetyltrimethylammonium bromide) could not be used since its bromide counterions are replaced by the bulky negatively charged $Mo_{18}{}^{6-}$ ions causing precipitation. On the other hand, anionic surfactants such as SDS (Sodium dodecyl sulfate) are not appropriate since polyoxometalates will be repelled into the bulk phase. Solubilization of α-tocopherol in the surfactant was rather difficult; it was accomplished by stirring for several hours the appropriate amount of α-tocopherol in the

micellar solution. The concentrations of the solubilizates were kept low since, in general, the catalytic effectiveness of micelles falls off very rapidly with increasing concentration of the solubilizate [7]. α-Tocopherol concentration was always in excess of that of $Mo_{18}{}^{6-}$ in order that pseudo-first order dependency could be observed in all cases. A typical micellar experiment was performed as follows: to a Triton X-100 micellar solution α-tocopherol was solubilized, and this solution was interacted with an aqueous solution of $Mo_{18}{}^{6-}$ in $HClO_4$. The reaction was monitored at 756 nm, which is the characteristic absorption of the 2e-reduced molybdate blue. Reduction of $Mo_{18}{}^{6-}$ under isotropic conditions was performed in ethanol, since α-tocopherol is insoluble in H_2O, and the rates in this case were determined by the stop-flow technique. Rate constants and experimental conditions are shown in Table I.

Triton X-100 micelles seem to exert a large inhibitory effect on the rate of reduction of $Mo_{18}{}^{6-}$ by α-tocopherol as compared to the respective reactions in isotropic media; *i.e.*, a difference of three orders of magnitude is observed (Table I). α-Tocopherol with its strongly lipophilic character is anchored into the micellar core, while its polar phenolic hydroxylic group responsible for the reduction of $Mo_{18}{}^{6-}$ is located, at least, in the interior of the so-called Stern region. On the other hand, since there is no charge barrier (the surfactant is non-ionic) it may be assumed that an equilibrium is established between the $Mo_{18}{}^{6-}$ located in the Stern region and the one in the bulk phase. Thus, the hydroxylic group of α-tocopherol is approached by polyoxometalate and reduction occurs. As far as the extent of reduction of $Mo_{18}{}^{6-}$ by α-tocopherol is concerned, it seems that there is only a minor difference in the extent of reduction in both media. For all practical purposes, and under the same relative concentration of α-tocopherol to $Mo_{18}{}^{6-}$, reduction proceeds to the addition of about 4 e$^-$. The latter is in accordance with literature data for α-tocopherol reporting $E(1/2) \sim 0.53$ (*vs.* NHE) at pH 3.9 [9]. It is known that reduction of $Mo_{18}{}^{6-}$ is pH-dependent, the reduction potential becoming more and more negative, *i.e.*, more diffi-

TABLE I. Rate Constants of $Mo_{18}{}^{6-}$ by α-Tocopherol in Triton X-100 Micellar and Isotropic Media
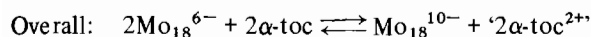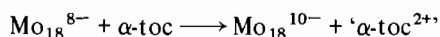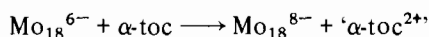
$Mo_{18}{}^{6-} \times 10^{-5}$ M	α-Toc. $\times 10^{-3}$ M	Medium	Triton $\times 10^{-2}$ M	$HClO_4$ (M)	k^a (M^{-1} s^{-1})
(1–10)	(0.8–1.0)	micellar	2	0.05	12.2[b]
3.0	(1.3–2.5)	C_2H_5OH		0.05	6.6×10^3 [c]

[a]k refers to initial reduction up to 2 e$^-$. In calculating k, A_∞ was considered the calculated absorption of 2 e$^-$ reduction product.
[b]Measured spectrophotometrically at 756 nm. Values within 15%.   [c]Measured with the stop-flow technique; values within 30%.

cult to reduce, as the pH increases. We have verified the influence of pH in the extent of reduction of Mo_{18}^{6-} by α-tocopherol by performing experiments in ethanol at pH ~ 0.5 with $HClO_4$, and pH ~ 5 in otherwise identical solutions of Mo_{18}^{6-} (5×10^{-5} M) and α-tocopherol (1×10^{-3} M). Reduction by ~ 4 e^- and less than ~ 0.5 e^- was observed, respectively, in agreement with reported redox potentials [2]. Under these conditions α-tocopherol, being a phenol with pK_a [8] of the order of 10, is fully protonated and no change in its redox properties is anticipated with pH. The fact that no change in the extent of reduction is observed in isotropic and micellar media under the same H^+ indicates that the pH in the Stern region is not affected, due to limited protonation of polyoxyethylene moieties. This in agreement with literature pK_a values, for instance, for diethyl ether in the range of -0.30 to -10.2 depending on the experimental method [8], thus making protonation under the experimental conditions used highly unfavorable.

It should also be noted here that because of the vicinity of half-wave potentials, an equilibrium is established according to the scheme below in which protonation has been omitted for clarity.

$$Mo_{18}^{6-} + \alpha\text{-toc} \longrightarrow Mo_{18}^{8-} + \text{`}\alpha\text{-toc}^{2+}\text{'}$$

$$Mo_{18}^{8-} + \alpha\text{-toc} \longrightarrow Mo_{18}^{10-} + \text{`}\alpha\text{-toc}^{2+}\text{'}$$

Overall: $2Mo_{18}^{6-} + 2\alpha\text{-toc} \rightleftharpoons Mo_{18}^{10-} + \text{`}2\alpha\text{-toc}^{2+}\text{'}$

The extent of reduction is therefore a matter of relative concentration of α-toc to Mo_{18}^{6-}. For instance, for a ratio of α-toc:Mo_{18}^{6-} of 10:4 reduction proceeds to $\sim 85\%$, 2 e^- and 15%, 4 e^-, whereas for a 100:4 ratio reduction proceeds to 100%, ~ 4 e^-.

Acknowledgements

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