

THE INFLUENCE OF SOME STRUCTURALLY RELATED PLURONICS ON THE AEROBIC OXIDATION OF ASCORBIC ACID

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The aerobic oxidation of ascorbic acid has been studied in a variety of aqueous solutions and a range of pH values. Attempts to stabilize ascorbic acid in aqueous solution by incorporating micellar concentrations of non-ionic surfactants has resulted normally in protection. However, in one study, Pluronic F68 was used as the surfactant, at very low concentrations, and an increase in oxidation rate was observed (Blaug & Hajratwala, 1974). Little information is available about the effect of change of surfactant structure on oxidation rate. In this work, three pluronics (polyoxyethylene-polyoxypropylene block polymers) have been included in aqueous solutions of ascorbic acid and the rate of oxidation measured in both the presence and absence of copper sulphate, as catalyst. The pluronics used, L64, P65 and F68, were structurally related, having the same hydrophobe and an increasing hydrophilic content.

Degradation studies were carried out in the dark at pH 1.0 and 37^o C. In all cases the aerobic oxidation of ascorbic acid followed first order kinetics.

The rate of oxidation of ascorbic acid is increased in the presence of all three Pluronics. As the Pluronic concentration is increased, so there is an increase in the oxidation rate. However, at the same concentration, L64 is more effective at increasing the oxidation rate than P65, and P65 is more effective than F68. These results are summarised in Table 1.

Table 1. First order rate constants ($\text{min}^{-1} \times 10^4$) in aqueous solution at pH 1.0

% w/v Pluronic	L64	P65	F68	In presence of 1×10^{-4} M Cu ⁺⁺⁺		
				L64	P65	F68
0	0.49	0.49	0.49	71.68	71.68	71.68
1	9.28	3.10	0.99	48.00	44.5	45.7
3	14.02	6.40	1.81	45.40	38.2	36.2
5	21.21	13.07	2.39	49.2	32.9	33.3

When copper sulphate (1×10^{-4} M cupric ions) is included as a catalyst, then the oxidation rate of ascorbic acid is dramatically increased, but increased to a lesser extent in the presence of pluronics, as shown in Table 1. It can be seen that in all cases the oxidation rate is much greater than in the absence of a catalyst. However, whereas, in the absence of catalyst the oxidation rate is increased by Pluronics in the ascending order F68, P65 and L64, in the presence of a catalyst the oxidation rate is reduced by the Pluronics, in the reverse order.

This protective mechanism of the Pluronics in the presence of catalyst could be due to either the catalyst being solubilized by the Pluronics or the Pluronics being "salted out" by the ionic effect of the catalyst. When the oxidation of ascorbic acid in Pluronic solutions was followed in the absence of catalyst, but in the presence of sodium chloride, at the same ionic strength as the catalyst, then the oxidation rate was identical to solutions without the catalyst.

Blaug, S.M. & Hajratwala, B. (1974) J. Pharm. Sci. 63, 1240-1243