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Oxidation of sulphite in a caramel-containing system

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The Cu(II)-catalysed oxidation of sulphite by molecular oxygen in a caramel-containing model system is characterised by the induction time for browning to begin and the rate of loss of oxygen. Whilst caramel (ammonia-sulphite) and citric acid are both good antioxidants, the induction time is increased with caramel concentration to *c.* 0·05 wt%, but falls to zero at twice this concentration. As expected, sucrose acts as an antioxidant but saccharin and salt have no effect. Benzoic acid has some antioxidant behaviour.

INTRODUCTION

The stoichiometric equation for the reaction of sulphite ion with oxygen is straightforward,

$$SO_3^{2-} + \frac{1}{2}O_2 \longrightarrow 2SO_4^{2-}$$

but the mechanism reveals this to be a complex reaction. The most widely quoted mechanism is that originally proposed by Bäckström (1934) involving a transition-metal-catalysed initiation reaction (Hegg & Hobbs, 1978),

$$SO_3^{2-} + M^{+} \longrightarrow SO_3^{\cdot -} + M$$

followed by the formation of intermediates such as $SO_5^{\cdot -}$ in radical chain propagating steps. Modifications to this scheme (Hayon *et al.*, 1972) include additional steps to explain the proven formation of species such as $O_2^{\cdot -}$, $\cdot OH$ and $SO_4^{\cdot -}$. These are known oxidising agents and it is a feature of sulphite oxidation reactions that they are able to cause the oxidation of unsaturated organic compounds, e.g. unsaturated fatty acids, essential oils and β-carotene (Yang, 1984). The free-radical sulphonation of alkenes is very well known (Kharasch *et al.*, 1939) and is the result of the addition of $SO_3^{\cdot -}$ to the double bonds.

The extensive reactivity of the chain-propagating radicals means that the oxidation of sulphite is easily inhibited by a wide range of organic compounds, e.g. ethanol, sugars and other polyols. The need for a transition metal ion catalyst means that chelating agents are also good inhibitors of oxidation; EDTA is often added to protect solutions of sulphite species, S(IV).

Despite the presence of many naturally occurring and added antioxidants, there is evidence to suggest that S(IV) is oxidised to some extent in many sulphited foods (Wedzicha & Herrera-Viloria, 1991). Here we report the effects of citric acid, caramel (negative) and other components of a caramel-containing soft drink on the Cu(II)-catalysed oxidation of S(IV).

EXPERIMENTAL

Ammonia-sulphite caramel (15748, 73·2% solids, pH 2·8–3·4) was obtained from CPC (UK) Ltd. All other chemicals were from BDH Chemicals Ltd, Poole and were of AnalaR grade.

The concentration of oxygen was measured using the Clark-type polarographic electrode (Rank Brothers). Reaction mixtures were prepared by placing the solution (1 ml) of all reactants except S(IV) (25 μM $Cu(NO_3)_2$; pH 5·7 acetate buffer (50 mM sodium acetate + 5 mM acetic acid); citric acid, caramel, sucrose) into the electrode cell, allowing for thermal equilibrium to be reached (25°C), and adding 50 μl of a solution of $NaHSO_3$ (0·25 M) to start the reaction.

RESULTS AND DISCUSSION

Reaction mixtures contained 25 μM Cu(II) to swamp the catalytic effects of stray transition metal ions and to increase the rate of oxidation to a conveniently measurable value. The oxidation of S(IV) was measured in terms of the rate of loss of oxygen and was characterised by an induction period (initial rate of oxidation = zero) and a near-constant rate of loss of oxygen over the major part of the reaction. When present at a concentration of 4 wt%, sucrose reduced the rate of oxidation 40-fold. Saccharin (50–250 mg $litre^{-1}$) had no effect whilst benzoic acid (300 mg $litre^{-1}$), added as sodium benzoate, reduced the rate to one-third.

The effects of citric acid and caramel are illustrated in Figs 1–4. Low concentrations of both compounds markedly reduce the rate of oxidation. In the case of citric acid (≤ 1 mM), the rate of reaction depends on the concentration of free Cu(II), calculated assuming that Cu(II) forms a 1 : 1 complex with citric acid (dissociation constant = 0·25 mM). Citric acid also extends the induction

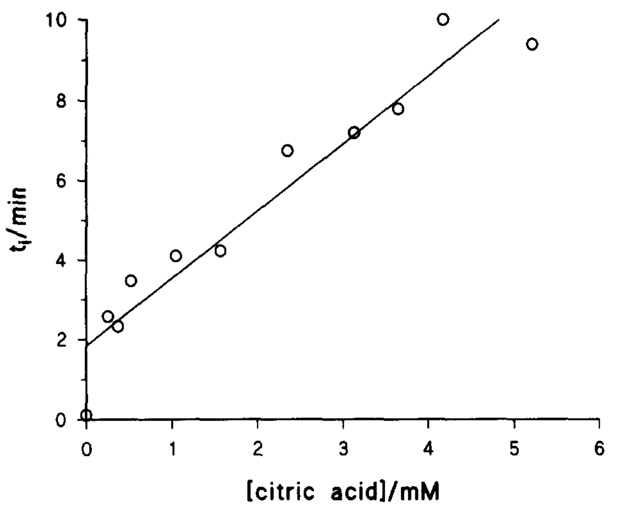

Fig. 1. Effect of citric acid concentration on the induction time t_i for the loss of oxygen in the Cu(II)-catalysed oxidation of S(IV). Reaction conditions: [Cu(II)] = 25 μM; [S(IV)] = 12·5 mM; pH 5·7; 25°C.

period for oxidation to begin. This is consistent with the inhibition of the initiating step and, therefore, necessitating a longer time for chain-propagating radicals to become established. On the other hand, the effect of caramel on the induction period is more complicated. An increase of induction time at low concentrations could be explained in the same terms as for citric acid, i.e. the caramel forms an unreactive complex with metal ion catalysts. The reduction of induction time at high concentration suggests that the caramel might be a source of initiating radicals. It is known that the products of the Maillard browning of reducing sugars with primary amino compounds show ESR signals indicative of the presence of free radicals (Hayashi *et al.*, 1977); it is not unreasonable to presume that the caramel might also contain free radicals. Irrespective of the effect of the caramel on the induction time, the overall effect, of the addition of any amount of caramel, is one of inhibition of the oxidation of S(IV).

Combinations of citric acid and caramel were much

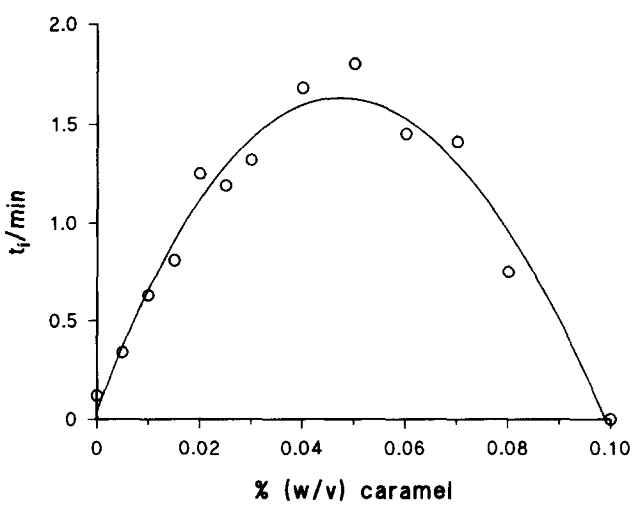

Fig. 2. Effect of citric acid concentration on the rate of loss of oxygen during the Cu(II)-catalysed oxidation of S(IV). Reaction conditions: [Cu(II)] = 25 μM; [S(IV)] = 12·5 mM; pH 5·7; 25°C.

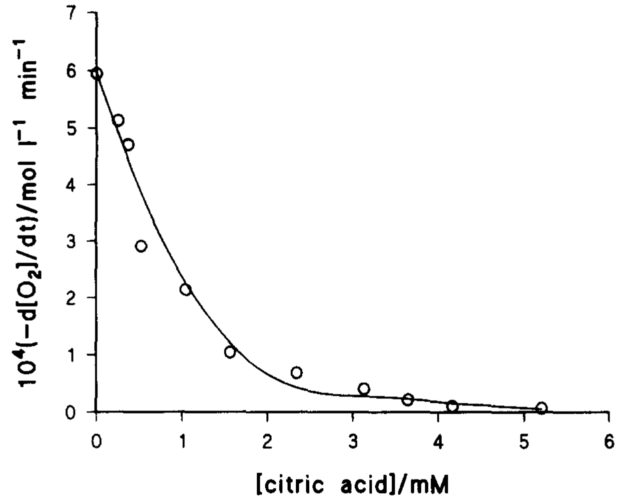

Fig. 3. Effect of caramel concentration on the induction time t_i for the loss of oxygen in the Cu(II)-catalysed oxidation of S (IV) . Reaction conditions: [Cu(II)] = 25 μM; [S(IV)] = 12·5 mM; pH 5·7; 25°C.

more effective in reducing the rate of oxidation (data not shown). For example, the rate of 0·6 mmol litre^{-1} min^{-1}, in the absence of any additive, was reduced to 0·3 μmol litre^{-1} min^{-1} in the presence of only 0·027 wt% caramel + 0·003 wt% citric acid; the mixture is 130 times more effective than expected for the two substances acting independently, i.e. they act synergistically.

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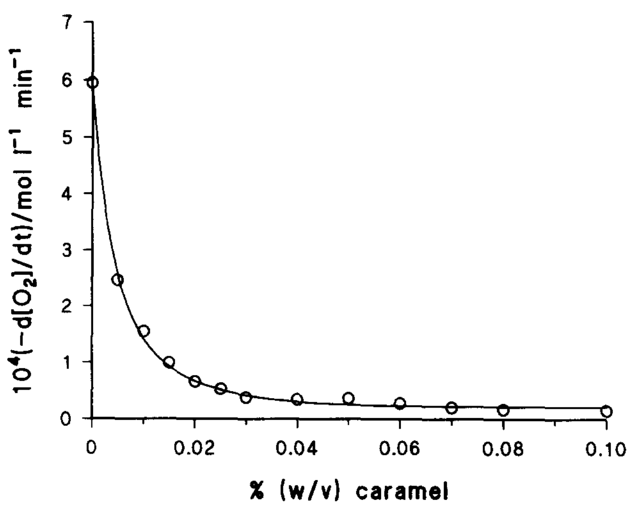

Fig. 4. Effect of caramel concentration on the rate of loss of oxygen in the Cu(II)-catalysed oxidation of S(IV). Reaction conditions: [Cu(II)] = 25 μM; [S(IV)] = 12·5 mM; pH 5·7; 25°C.

REFERENCES

Bäckström H. L. J. (1934). The chain mechanism in the autoxidation of sodium sulphite solutions. *Z. Phys. Chem.*, **B25**, 122–38.

Hayashi, T., Ohta, Y. & Namiki, M. (1977). Electron spin resonance spectral study on the structure of the novel free radical products formed by the reactions of sugars with amino acids or amines. *J. Agric. Food Chem.*, **25**, 1282–7.

Hayon, E., Treinin, A. & Wilf, J. (1972). Electronic spectra, photochemistry and autoxidation mechanism of sulphite–bisulphite–pyrosulphite systems. The SO_2^-, SO_3^-, SO_4^- and SO_5^- radicals. *J. Amer. Chem. Soc.*, **94**, 47–57.

Hegg, D. A. & Hobbs, P. A. (1978). Oxidation of sulphur dioxide in aqueous systems with particular reference to the atmosphere. *Atmospheric Environment*, **12**, 241–53.

Kharasch, M. S., May, E. M. & Mayo, F. R. (1939). The peroxide effect in the addition of reagents to unsaturated compounds. XVIII. The addition and substitution of bisulphite. *J. Org. Chem.*, **3**, 175–92.

Wedzicha, B. L. & Herrera-Viloria, J. C. (1991). The formation of sulphate ion during the dehydration of sulphited vegetables. *Food Add. Cont.*, **8**, 683–92.

Wedzicha, B. L. & Johnson, M. K. (1979). A variation of the Monier Williams distillation technique for the determination of sulphur dioxide in ginger ale. *Analyst (London)*, **104**, 694–6.

Yang, S. F. (1984). Reactions of oxidation intermediates of sulphite species with some cellular components of plants. *Food Chem.*, **15**, 113–24.