Kinetics of Degradation of Sorbic Acid in Aqueous Glycerol Solutions

C. C. Seow & P. B. Cheah

Department of Food Technology, School of Engineering Sciences & Industrial Technology, Universiti Sains Malaysia, Penang, Malaysia

(Received: 18 December, 1984)

ABSTRACT

Degradation of sorbic acid in aqueous glycerol solutions at pH 4·0 over the a_w range 0·71–1·00 and the temperature range 40°–60°C was found to follow first-order reaction kinetics and to conform to the Arrhenius equation. Activation energy values obtained were 5·8 kcal mol^{-1} and 7·8 kcal mol^{-1} for systems at 0·80 a_w with and without added Co^{++}, respectively. The rate of sorbic acid degradation was observed to increase with decreasing a_w (i.e. increasing glycerol concentration). The presence of added Co^{++} decreased the rate of sorbic acid breakdown at any particular a_w or temperature. Browning of sorbate solutions during storage was markedly inhibited by Co^{++}.

INTRODUCTION

Sorbic acid (*trans, trans*-2,4-hexadienoic acid) and its salts are used as preservatives in a wide variety of food products. The antimicrobial action and application of sorbates have been reviewed by Lück (1976) and Sofos & Busta (1981). Although very stable in the dry state, sorbic acid is known to be relatively unstable in aqueous solutions (Marx & Sabalitschka, 1965; Pekkarinen, 1969; Heintze, 1971; McCarthy & Eagles, 1976; Arya, 1980; Saxby *et al.*, 1982) and to undergo appreciable degradation in certain food products such as salted fish (Doesburg *et al.*, 1969), herring salad (Heintze, 1971), high moisture prunes (Bolin *et al.*, 1980) and orange squash (Vidyasagar & Arya, 1983).

Degradation of sorbic acid in foods and model systems can occur via

several mechanisms—i.e. oxidation, interactions with other food constituents or additives and microbial action. Being a di-unsaturated acid, sorbic acid can undergo autoxidation to yield malonaldehyde and other carbonyl compounds (Marx & Sabalitschka, 1965; Arya, 1980). The breakdown of sorbic acid in solutions of dilute sulphuric acid and sulphur dioxide appears to yield several volatile products, including α-angelica lactone and 2-methyl-5-acetylfuran (Saxby *et al.*, 1982). Degradation of sorbic acid in aqueous solutions has been reported to be accelerated by light (Marx & Sabalitschka, 1965; Saxby *et al.*, 1982) and inhibited by propyl gallate (Marx & Sabalitschka, 1965; Arya, 1980) and certain trace metal ions such as Cu^{++}, Fe^{++} and Mn^{++} (Arya, 1980). In general, the rate of sorbic acid degradation decreases with increasing pH (Arya, 1980; Saxby *et al.*, 1982).

Several studies have demonstrated the ability of sorbic acid to interact with a number of other food additives or constituents. For example, Salo (1963) has found that sorbic acid can react with parahydroxybenzaldehyde, vanillin or ethylvanillin in acid solutions to produce coloured compounds. Woo *et al.* (1967) have shown that sorbic acid can form complexes with gum acacia. The formation of mutagenic products (including ethylnitrolic acid and 1,4-dinitro-2-methylpyrrole) as a result of a reaction between sorbic acid and nitrite under certain conditions has been reported by several workers (Hayatsu *et al.*, 1975; Kito *et al.*, 1978; Namiki *et al.*, 1981). Aqueous solutions of sorbic acid have also been observed to brown during storage, the rate of browning being accelerated by the presence of amino acids (Arya, 1980). Sorbic acid can also be degraded or metabolized by certain micro-organisms (Melnick *et al.*, 1954; Marth *et al.*, 1966; Deak & Novak, 1972; Crowell & Guymon, 1975; Tahara *et al.*, 1977).

Sorbic acid or its potassium salt appears to be the preferred antimycotic agent used to enhance the shelf-life of intermediate moisture foods (IMF), a family of food products whose stability depends primarily on the control of water activity (a_w). Current literature contains little information on the reactivity and stability of sorbic acid in such foods. It seems pertinent, therefore, to study the kinetics of degradation of sorbic acid as a function of a_w in such systems. As a first step, the stability of sorbic acid in aqueous glycerol solutions, in the absence and presence of added Co^{++}, was investigated. The choice of glycerol was based on the fact that it is one of the most commonly used humectants in the development of new IMF.

MATERIALS AND METHODS

Different glycerol–water mixtures at different water activities were prepared by varying the concentration of glycerol used (0, 48 and 60 % w/w). Potassium sorbate (ICN Pharmaceuticals) was dissolved in each solution to a level of 0·3 % w/v. The effect of Co^{++} on the degradation of sorbate was studied by using another set of solutions with cobaltous nitrate being added to give a Co^{++} concentration of 100 mg litre^{-1}. All solutions were adjusted to pH 4·0 using hydrochloric acid. The actual a_w of each solution at 40 °C was determined using a NOVA-SINA equi-Hygroscope comprising a DAL-20 digital humidity indicator and an enZFBA-4 sensor.

Each solution was then apportioned (*ca.* 6-ml aliquots) into airtight, rubber-lined, screw-capped Universal bottles with adequate headspace and stored in the dark at the desired temperatures (40°, 50° and 60 °C). At suitable intervals, duplicate bottles of each solution were withdrawn and analysed for sorbic acid by measuring the absorbance at 258 nm after appropriate dilution with distilled water. Calculation of the concentration of unreacted sorbic acid was based on an $E_{1cm}^{1\%}$ value of 2150 (Arya, 1980).

In a separate experiment, the intensity of browning of samples after 35 days' storage at 40 °C was determined, in triplicate, by measuring the absorbance at 420 nm. All chemicals used were of analytical grade.

RESULTS AND DISCUSSION

The degradation of sorbic acid in aqueous glycerol solutions was found to follow first-order reaction kinetics, as indicated by the linear relationships obtained in the semi-logarithmic plots of per cent retention of sorbic acid versus storage time (Figs 1 and 2). This is in agreement with the findings of Arya (1980) who similarly observed first-order degradation of sorbic acid in aqueous solutions. In the present study, the degradation data at all a_w levels and storage temperatures, and both in the absence and presence of added Co^{++}, conform to the first-order rate function:
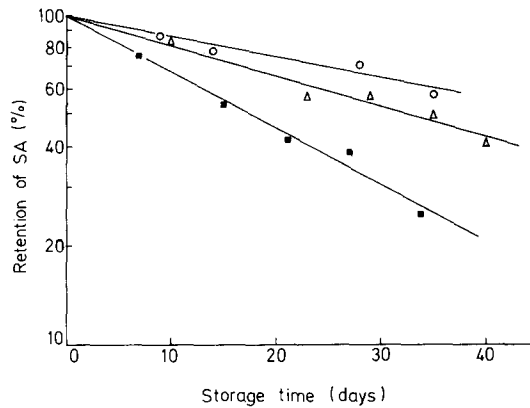
$$-\frac{d(SA)}{dt} = k(SA)$$

Fig. 1. Degradation of sorbic acid in aqueous glycerol–sorbate solutions during storage at 40 °C as a function of a_w (○, 1·00; △, 0·80; ■, 0·71).

where (SA) represents concentration of sorbic acid, k represents the first-order rate constant, t is the reaction time and $d(SA)/dt$ is the rate of change of reactant concentration. Calculated k values are presented in Tables 1 and 2. The results show that the rate of sorbic acid degradation increased with decreasing a_w (i.e. with increasing glycerol concentration). In general, unless other factors predominate, a decrease in a_w from a high to an intermediate level would be expected to decrease the rate of sorbic acid degradation as a result of an increase in viscosity of the system which, in turn, would lead to an increase in diffusion resistance, thereby inhibiting reactant mobility. A possible explanation for the reverse effect
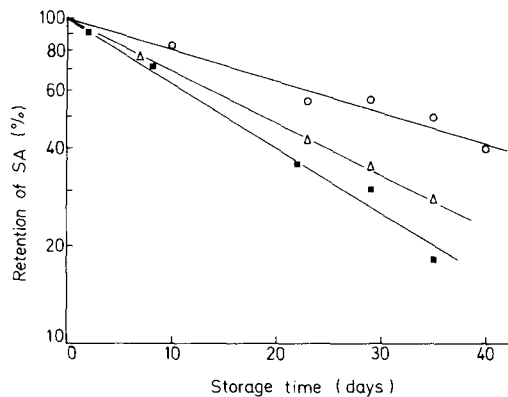

Fig. 2. Effect of temperature (○, 40 °; △, 50 °; ■ 60 °C) on sorbic acid degradation in aqueous glycerol–sorbate solutions at $0·80\,a_w$.

TABLE 1

Rate Constants (k) of Sorbic Acid Degradation at 40 °C as a Function of
Water Activity

System	$k \times 10^2$ (per day)		
	$0.71\,a_w$	$0.80\,a_w$	$1.00\,a_w$
Glycerol–Sorbate	3·96	2·21	1·45
Glycerol–Sorbate–Co^{++}	2·89	1·51	0·89

observed in the present study is that glycerol could have a significant pro-oxidant, or catalytic, effect on the autoxidation of sorbic acid, as suggested by Arya (1980) who found that glycerol, at the 1 % and 5 % levels, increased the rate of sorbic acid degradation in aqueous model systems. It is likely that, under the present experimental conditions, the pro-oxidant effect of glycerol predominates over the inhibitory effect (if any) of a_w lowering *per se*.

From Tables 1 and 2, it is apparent that the presence of added Co^{++} has a stabilising effect on sorbic acid at any particular a_w or temperature. This is consistent with the findings of Pekkarinen (1972) that oxidation of sorbic acid by molecular oxygen in acetic acid was strongly inhibited by cuprous acetate, manganese acetate and cobalt acetate at concentrations as low as 10^{-5}M, whilst autoxidation of sorbic acid in water was slightly retarded by high cobalt concentrations ($> 10^{-2}$M).

Heavy metal ions generally accelerate the rate of autoxidation of organic compounds (Ingold, 1961). However, under certain conditions, they may act as inhibitors. For example, Betts & Uri (1966) have shown that certain cobalt compounds, which are autoxidation catalysts at low concentrations, become inhibitors in the same system at high concentrations. It has been suggested (Ingold, 1961; Betts & Uri, 1966) that such inhibition occurs as a result of the formation of free radical–metal
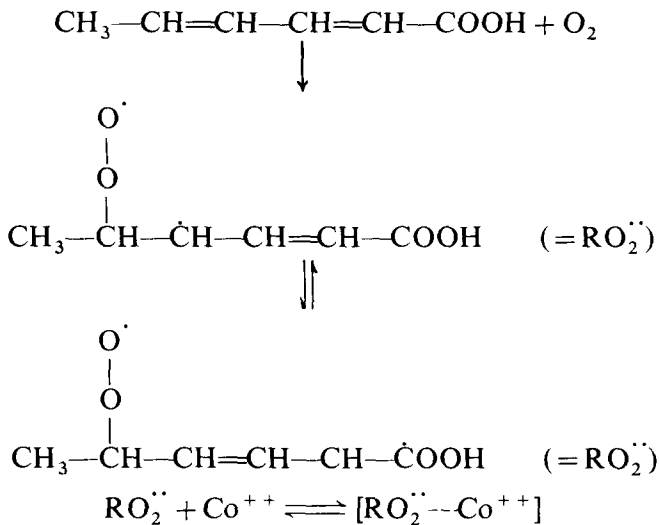
TABLE 2

Rate Constants (k) of Sorbic Acid Degradation at $0.80\,a_w$ as a Function of Temperature

System	$k \times 10^2$ (per day)			E_a (kcal mol^{-1})
	40°C	50°C	60°C	
Glycerol–Sorbate	2·21	3·63	4·67	7·8
Glycerol–Sorbate–Co^{++}	1·51	1·96	2·65	5·8

ion complexes which are relatively inactive and/or the consumption of free radicals via termination reactions such as:

$$RO^{\cdot} + Co^{++} \longrightarrow RO^{-} + Co^{3+}$$
$$RO^{\cdot} + Co^{++} \longrightarrow RO_2^{-} + Co^{3+}$$
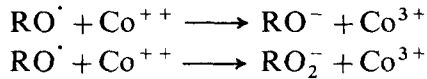
It is likely that similar mechanisms operate to decrease the rate of sorbic acid degradation in the presence of Co^{++} as well as other metal ions. In this case, inhibition probably arises as a result of the formation of labile complexes between the metal ions and peroxy biradicals (which are produced on autoxidation of compounds with conjugated double bonds), as suggested by Pekkarinen (1972). The reaction scheme may be represented as follows:

$$CH_3-CH\!=\!CH-CH\!=\!CH-COOH + O_2$$

$$\downarrow$$

$$CH_3-\overset{\overset{\overset{\displaystyle O^{\cdot}}{|}}{\overset{\displaystyle O}{|}}}{C}H-\overset{\cdot}{C}H-CH\!=\!CH-COOH \qquad (= RO_2^{\cdot\cdot})$$

$$\updownarrow$$

$$CH_3-\overset{\overset{\overset{\displaystyle O^{\cdot}}{|}}{\overset{\displaystyle O}{|}}}{C}H-CH\!=\!CH-CH-\overset{\cdot}{C}OOH \qquad (= RO_2^{\cdot\cdot})$$

$$RO_2^{\cdot\cdot} + Co^{++} \rightleftharpoons [RO_2^{\cdot\cdot}\!-\!-Co^{++}]$$

The temperature dependency of sorbic acid degradation was studied at a single intermediate a_w level (0·80) over the temperature range 40°–60 °C. The loss of sorbic acid was temperature dependent and conformed to the Arrhenius equation. Activation energy (E_a) values, calculated from the slopes of the Arrhenius plots as shown in Fig. 3, are given in Table 2. The E_a values obtained (5·8 and 7·8 kcal mol^{-1} for systems with and without added Co^{++}, respectively) are relatively low compared with those of many other reactions of significance to foods. The effect of temperature on the degradation of sorbic acid is thus not very great. Degradation of sorbic acid appeared to be less sensitive to temperature change in the presence of Co^{++}.
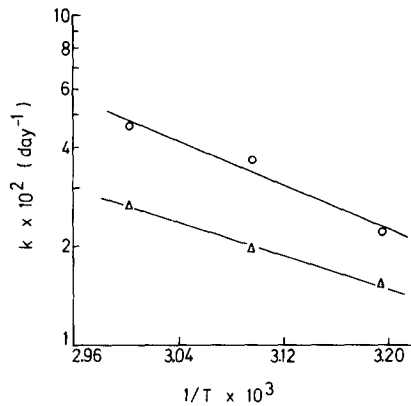
Fig. 3. Arrhenius plots of sorbic acid degradation in aqueous glycerol–sorbate ($\bigcirc$) and glycerol–sorbate–Co^{++} ($\triangle$) systems at $0 \cdot 80\, a_w$.

Browning of sorbate solutions (with or without added Co^{++}) was observed to occur during storage, the rate generally decreasing with increasing a_w, as shown in Table 3. It is interesting to note that this trend appears to resemble that of the glucose–glycine browning reaction in aqueous glycerol solutions as observed by Eichner & Karel (1972) who attributed the decrease in browning rate with increasing moisture content or a_w primarily to product-inhibition by water operating through the law of mass action. Whether a similar mechanism operates in the case of sorbate browning is a matter of conjecture at this point. It is now generally well known that non-enzymatic browning in most systems occurs at some intermediate a_w, and any increase in a_w beyond this point leads to a decrease in browning rate (Eichner, 1975; Labuza & Saltmarch, 1981). It is evident from Table 3 that sorbate browning was markedly inhibited by Co^{++}, although the mechanism of action remains to be elucidated. Loss of sorbic acid thus appears to be related to the

TABLE 3
Relative Browning Rates of Sorbate Solutions at 40 °C

System	Absorbance at 420 nm[a]		
	0·71 a_w	*0·80 a_w*	*1·00 a_w*
Glycerol–Sorbate	0·11	0·13	0·05
Glycerol–Sorbate–Co^{++}	0·08	0·05	0·03

[a] Mean of triplicate samples.

development of brown pigments, both processes occurring at higher rates at the lower a_w levels and both being inhibited by Co^{++}.

No brown pigment formation was detected in aqueous glycerol solutions in the absence of sorbate over the time span of the present experiment. In model system studies of this nature, glycerol has always been regarded as an inert humectant or diluent. However, the direct participation of glycerol in browning reactions involving sorbate cannot be totally dismissed in the light of findings obtained by Obanu *et al.* (1977) regarding the reactivity and browning potential of glycerol itself, especially on prolonged storage at elevated temperatures. Sorbate browning, therefore, warrants further investigation, especially with regard to its mechanism and significance in intermediate moisture systems containing glycerol.

REFERENCES

Arya, S. S. (1980). Stability of sorbic acid in aqueous solutions. *J. Agric. Food Chem.*, **28**, 1246–9.

Betts, A. T. & Uri, N. (1966). The conversion of metal catalysts into inhibitors of autoxidation, *Makromol. Chemie*, **95**, 22–39.

Bolin, H. R., King, A. D. & Stafford, A. E. (1980). Sorbic acid loss from high moisture prunes, *J. Food Sci.*, **45**, 1434–5.

Crowell, E. A. & Guymon, I. F. (1975). Wine constituents arising from sorbic acid addition and identification of 2-ethoxyhexa-3,5-diene as a source of geranium-like off-odor, *Am. J. Enol. Vitic*, **26**, 97–102.

Deak, T. & Novak, E. K. (1972). Assimilation of sorbic acid by yeasts, *Acta Aliment.*, **1**, 87–104.

Doesburg, J. J., Lamprecht, E. C., Elliot, M. C. & Reid, D. A. (1969). The use of sorbic acid in salted fish, *J. Food Technol.*, **4**, 339–52.

Eichner, K. (1975). The influence of water content on non-enzymic browning reactions in dehydrated foods and model systems and the inhibition of fat oxidation by browning intermediates. In: *Water relations of foods.* (Duckworth R. B. (Ed.)), London, Academic Press, 417–34.

Eichner, K. & Karel, M. (1972). The influence of water content and water activity on the sugar-amino browning reaction in model systems under various conditions, *J. Agric. Food Chem.*, **20**, 218–23.

Hayatsu, H., Chung, K. C., Kada, T. & Nakajima, T. (1975). Generation of mutagenic compound(s) by a reaction between sorbic acid and nitrite, *Mut. Res.*, **30**, 417–9.

Heintze, K. (1971). Stability of sorbic acid, *Lebensm.-Wiss. Technol.*, **4**, 64–5. (*Chem. Abstr.*, 1971, **75**, 62264w).

Ingold, K. U. (1961). Inhibition of the autoxidation of organic substances in the liquid phase, *Chem. Rev.*, **61**, 563–89.

Kito, Y., Namiki, M. & Tsuji, K. (1978). A new *N*-nitropyrrole, 1,4-dinitro-2-methylpyrrole, formed by the reaction of sorbic acid with sodium nitrite, *Tetrahedron*, **34**, 505–8.

Labuza, T. P. & Saltmarch, M. (1981). The non-enzymatic browning reactions as affected by water in foods. In: *Water activity: Influences on food quality*. (Rockland, L. B. & Stewart, G. F. (Eds)), New York, Academic Press, 605–50.

Lück. E. (1976). Sorbic acid as a food preservative, *Int. Flavors Food Additiv.*, **7**, 122–4, 127.

Marth, E. H., Capp, C. M., Hasenzahl, L., Jackson, H. W. & Hussong, R. V. (1966). Degradation of potassium sorbate by *Penicillium* species, *J. Dairy Sci.*, **49**, 1197–205.

Marx., H. & Sabalitschka, T. (1965). Instability of sorbic acid. IV. Stabilization of sorbic acid with propyl gallate, *Seifen-Oele-Fette-Wachse*, **91**, 720–2. (*Chem. Abstr.* 1966, **64**, 7271f).

McCarthy, T. J. & Eagles, P. F. K. (1976). Further studies on glass-stored sorbic acid solutions, *Cosmet. Toiletries*, **91**, 33–4, 36.

Melnick, D., Luckmann, F. H. & Gooding, C. M. (1954). Sorbic acid as a fungistatic agent for foods. VI. Metabolic degradation of sorbic acid in cheese by molds and the mechanism of mold inhibition, *Food Res.*, **19**, 44–58.

Namiki, M., Osawa, T., Ishibashi, H., Namiki, K. & Tsuji, K. (1981). Chemical aspects of mutagen formation by sorbic acid–sodium nitrite reaction, *J. Agric. Food Chem.*, **29**, 407–11.

Obanu, Z. A., Ledward, D. A. & Lawrie, R. A. (1977). Reactivity of glycerol in intermediate moisture meats, *Meat Sci.*, **1**, 177–83.

Pekkarinen, L. (1969). Uber die autoxydation der sorbinsaure in citronensaurehaltiger, wassriger losung, *Z. Lebensmittelunters. u-Forsch.*, **139**, 23–9.

Pekkarinen, L. (1972). The influence of metal acetates on the oxidation of sorbic acid by molecular oxygen in acetic acid and comparison of the results with those for eleostearic acids, *Acta Chem. Scand.*, **26**, 2367–71.

Salo, T. (1963), Komarowsky color reaction of sorbic acid, *Suomen Kemistilehti*, **36**, Pt. B. (1), 1–5. (*Chem. Abstr.*, 1963, **58**, 9634d).

Saxby, M. J., Stephens, M. A. & Reid, R. G. (1982). Degradation of sorbic acid in model food systems, *Food Chem.*, **9**, 283–7.

Sofos, J. N. & Busta, F. F. (1981). Antimicrobial activity of sorbate, *J. Food Prot.*, **44**, 614–22, 647.

Tahara, S., Kurogochi, S., Kudo, M. & Mizutani, J. (1977). Fungal metabolism of α, β-unsaturated carboxylic acids. Part II. Fungal metabolism of sorbic acid, *Agric. Biol. Chem.*, **41**, 1635–42.

Vidyasagar, K. & Arya, S. S. (1983). Stability of sorbic acid in orange squash, *J. Agric. Food Chem.*, **31**, 1262–4.

Woo, C. H., Kim, S. K. & Min, S. H. (1967). Complex interaction of acacia and sodium alginate with certain preservatives (spectrophotometric studies), *Yakhak Hoeji*, **11**, 27–32. (*Chem. Abstr.*, 1969, **71**, 5353v).