

A New Approach to the Kinetics of Beer Oxidation: From Physical Chemistry to Industrial Brewing

Jean-Claude André, *G. R. A. P. P. de l' U. A., 328 du Centre National de la Recherche Scientifique, E. N. S. I. C., I. N. P. L., 54042 Nancy, France, and Manfred Moll, TEPRAL, Centre de Recherches et de Développement, Branche Boissons BSN, 54250 Champigneulle, France*

ABSTRACT

The concentration of antioxidants in beer, expressed in equivalents of ascorbic acid, was determined by oxidizing the beer at constant pressure. Among other things, these studies showed that antioxidants are responsible for the oxidation chains relating to oxidizable substances. A kinetic study of beer oxidation before the primary antioxidants were completely consumed (the rapid oxidation phase), led to the conception of a reasonable mechanism for the chains of oxidation involved. Phenomenological analysis allowed the reaction to be described in a mathematical model, which enabled us to calculate the duration of consumption of the head-space oxygen at the moment of packaging.

Beer comprises many substances, more than 850 of which have been described in the literature (11).

The role of oxygen during the making of malt and of beer is still insufficiently understood. The degrees of oxygenation of beer (cold) or of oxidation of wort (hot) remain completely unknown because on the one hand, a certain amount of oxygen is required by the yeast for the exponential growth phase, and if this is not available the fermentation does not proceed properly; on the other hand, it is undesirable to oxidize or oxygenate the wort too much, because there is a risk of inhibiting the formation of many of the reducing agents naturally present in the medium and thus limiting its protection against oxygen.

It has long been known that oxygen plays a deleterious role after the main fermentation, when the beer is no longer protected by the yeast, which assimilates oxygen rapidly (9,12). Thus, during beer storage oxygen is responsible for: the decline of colloidal stability (13), degradation of flavor (4,6,9,19), and increase in color.

To limit these unwanted consequences, various methods of filtration or stabilization of beer after storage have been suggested, such as: reducing the concentration of oxygen (10), and the use of artificial antioxidants such as reductones, sulphites, and/or ascorbic acid (8,12,18). In France, legislation authorizes the use of ascorbic acid in beer to prevent too rapid an oxidation. Presumably, its rate of oxidation is greater than that of normal constituents of beer.

Quantities of ascorbic acid (AH₂) were added to various beers, previously treated with AH₂ or untreated, to raise its concentration in each to 50 mg/L. When the beers were exposed to air, the rate of AH₂ disappearance was found to follow curves having different slopes (Fig. 1). The ascorbic acid might disappear in a few hours, or be stable for more than 24 hr. This observation led us to make a kinetic study of the oxidation of beer from which we were able to show that this natural product underwent oxidation much faster if it contained increased amounts of an antioxidant such as ascorbic acid. Then, when all the antioxidant was consumed, the beer was further oxidized but much more slowly.

With the goal of understanding the stages of these antioxidants, we studied the kinetics of beer oxidation and the effects of ascorbic acid on it.

EXPERIMENTAL

Equipment

The experimental unit, analogous to one set up in the laboratory (4,5), was modified to achieve satisfactory adaptation for studying the kinetics of beer oxidation (Fig. 2). It consisted of: a vacuum

system comprising an oil pump, a mercury diffusion pump, and a Macleod gauge; a thermostatted room in which a fixed temperature could be maintained during the manipulations; a thermometer for the room; a supply of oxygen-nitrogen gas mixture, three containers each of 6 L; and gas burettes for measuring the concentration of oxygen. The system was provided with three graduated burettes of 200-, 50-, and 10-ml capacity, respectively; the one used was chosen in relation to the rate of oxidation to be measured. Other equipment included a carbon dioxide trap consisting of wet sodium hydroxide pellets, a magnetic stirrer to provide perfect mixing of oxygen in the reactor (the rate of stirring was adjustable), a manometer for reading the pressure inside the unit, and a platinum electrode in a cell containing a saturated solution of oxalic acid. Electrolysis of this set led to a mixture of carbon monoxide and carbon dioxide which was used to achieve constant pressure despite the consumption of oxygen during an experiment. A cylindrical reactor, water jacketed for temperature control, had provision for insertion of temperature probes and for introduction of the catalyst (Fig. 3). A Colara thermostat maintained constant water temperature. This

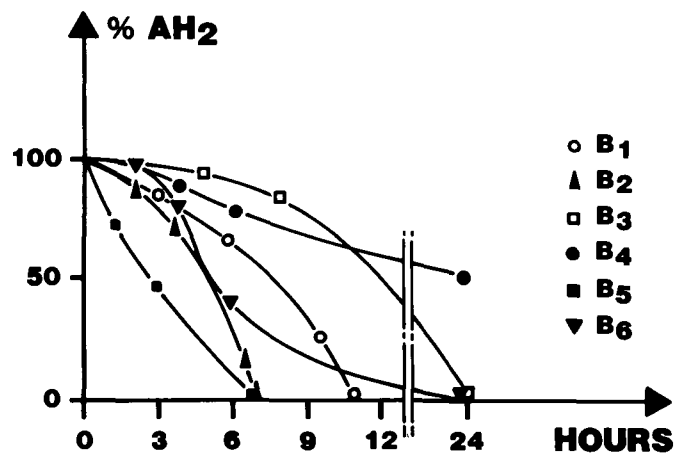


Fig. 1. Disappearance of ascorbic acid (AH₂) over time. The ascorbic acid content of each beer was measured, and then ascorbic acid was added to each to bring the concentration to 50 mg/L. B₁-B₄, French beers treated with ascorbic acid; B₅, alcohol-free beer; B₆, German beer (pilsner type) not treated with ascorbic acid.

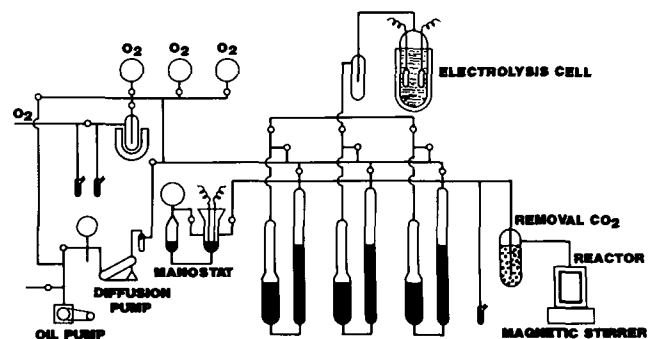


Fig. 2. General layout of the experimental equipment design.

was linked to a pump for recirculating the water from the thermostat to the jacket of the reactor. The reactor containing the solution to be oxidized was connected to the installation, and observations were made at a predetermined oxygen pressure.

The onset of the reaction was brought about by introducing the catalyst (Cu^{2+} ions) into the reactor. Any partial consumption of oxygen by the liquid phase led to a reduction of pressure inside the equipment; the mercury rose in the manostat attached to the reactor until it contacted the tungsten wire; closure of relays started the electrolysis of the oxalic acid. The initial pressure was thus reestablished. Therefore, it was possible to read the consumption of oxygen over time, at constant temperature and pressure. Corrections were made to express oxygen consumption as at 760 torr and 21°C.

Reagents

The reagents used in this work were ascorbic acid; copper sulfate hydrate, analytical grade; 3-octanol, quality purum (serves as antifoam at 1 ml/L of beer); sodium hydroxide pellets; and gaseous oxygen.

Equipment Testing

Fifty milliliters of degassed beer was introduced into the reactor, and 3-octanol was added to serve as an antifoaming agent; slight agitation dispersed the emulsion. The temperature probe and the means of introducing the catalyst were fixed on the reactor.

TABLE I
Reproducibility of Measurement of Initial Rate^a

Type of Beer	Trials (n)	V_0 (ml/min)	Standard Deviation (ml/min)	Coefficient of Variation (%)
Pale	10	3.80	0.212	10.5
Dark	10	4.00	0.182	8.8

^aOperating conditions: temperature of the liquid phase, 20°C; concentration of Cu^{2+} ions, 0.4 mg/L; oxygen pressure, 223–230 torr; agitation, 300 rpm; beer volume, 50 ml. The initial rate was measured during the first 4 min of the oxidation (ml O_2 /min, 50 ml of beer at 760 torr, 21°C).

TABLE II
Effects of Stirring on Initial Rate V_0^a

Type of Beer	Rate of Stirring (rpm)		
	300	600	900
Pale	3.67 (P = 235 torr)	3.97 (P = 232 torr)	3.72 (P = 232 torr)
Dark	3.82 (P = 230 torr)	4.20 (P = 228 torr)	4.0 (P = 224 torr)

^aOperating conditions: beer volume, 50 ml; temperature of the liquid phase, 20°C; concentration of Cu^{2+} ions, 0.4 mg/L.

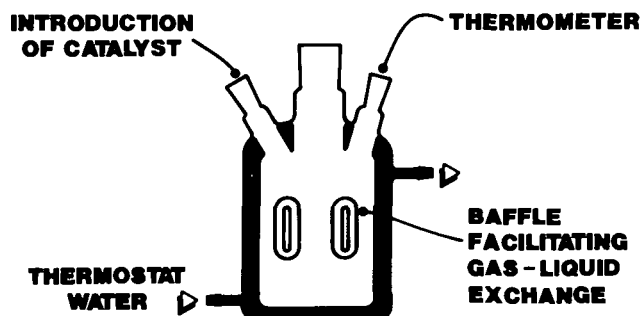


Fig. 3. Schematic representation of the reactor.

After the rest of the installation was emptied, oxygen was introduced into the system until it reached a predetermined pressure for measuring the oxidation kinetics. The reactor was linked to this system, and circulation of water was started in the reactor jacket. The reaction began when copper ions were introduced into the reactor.

The consumption of oxygen over time was read on the graduated burette.

Reproducibility of Measurements

To establish the reliability of the results, oxidation kinetics of two types of beer were studied. The reproducibilities of the initial rates of oxidation of these beers were estimated as $\pm 10\%$ (Table I). Also, the effect of stirring in the oxidation reactor was studied, and it was shown to have no effect on the kinetics of beer oxidation (Table II). Thus, the apparatus shown schematically in Figure 2 allows the consumption of oxygen by beer at constant oxygen pressure to be measured during a period of time.

RESULTS AND DISCUSSION

Beer Oxidation Kinetics and Antioxidant Concentration

In general, the rate of oxidation of beer is slow and may vary significantly in relation to the presence of catalysts. To assure a more rapid result and to remove any confusion from catalysts already present in low concentrations, the behavior of reducing substances was studied in beer to which a known quantity of Cu^{2+} ions had been added.

At present, colorimetric methods are mainly used for measuring the kinetics of the oxidation of beer. These give only a partial idea of the behavior of beer during storage, because they use artificial oxidants, and it is not certain that the reactions of these are comparable with the oxidations brought about by molecular oxygen. Therefore, in this work a volumetric method was used to measure the kinetics of oxidation by molecular oxygen. The equipment used for the work described in the experimental section was based on that of André et al (1–3) modified for the purpose.

In the general system used, 50 ml of degassed beer was studied for the effects of temperature, concentration of ascorbic acid, and concentration of catalyst on the rate of uptake of oxygen. The reproducibility of the results was satisfactory ($\pm 10\%$).

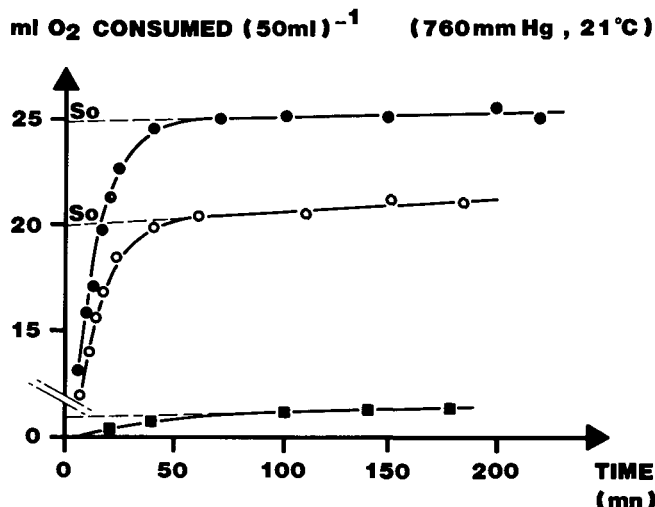


Fig. 4. Evolution of the consumption of oxygen during aging of a pale beer: ● = at start; ○ = 48 hr later; and ■ = seven days later. Oxygen pressure, 300 mmHg; liquid temperature, 30°C; Cu^{2+} , 2 mg/L; stirring speed, 600 rpm. S_0 = zone of rapid oxidation.

Effects of Time of Beer Contact with Air on the Consumption of Oxygen

Figure 4 illustrates the evolution of the oxidation kinetics of a pale beer with time: the oxidation curve has a short phase in which consumption is rapid, followed by a phase of slow oxidation that is relatively long. After leaving the same beer in contact with air, these measurements were repeated, and it was shown qualitatively that the longer the contact time the shorter the duration of the phase of rapid oxidation. The reactivity of beer towards molecular oxygen depends on its content of reducing agents. Among the substances able to react relatively rapidly are ascorbic acid and reductones that would be expected to be involved in the first phase of rapid oxidation.

In the absence of stirring, beer kept under air oxidizes slowly, and these primary antioxidants must disappear, which explains the reduction of the zone of rapid oxidation represented by S_0 (Fig. 4), the ordinate at $t = 0$ (sec), and the slope of the line representing the rate of oxidation.

Measuring the Concentration of Primary Reducing Agents

These studies showed that the reducing agents capable of being oxidized in beer could be divided into the group of primary reducing agents reacting during the first rapid phase, and the secondary reducing agents active in the slow phase. Among the primary reducing agents, AH_2 is an artificial antioxidant used to protect beer against molecular oxygen. Oxidation reduces the organoleptic quality of beer, and some natural constituents of beer may also participate in the oxidation buffering of beer, i.e., maintaining its stability towards oxidation. For this study, a sample of beer not treated with added antioxidants was used.

Figure 5 shows the kinetics of oxygen consumption with time by this beer with various quantities of added ascorbic acid. The addition of ascorbic acid did not significantly change the rate of the

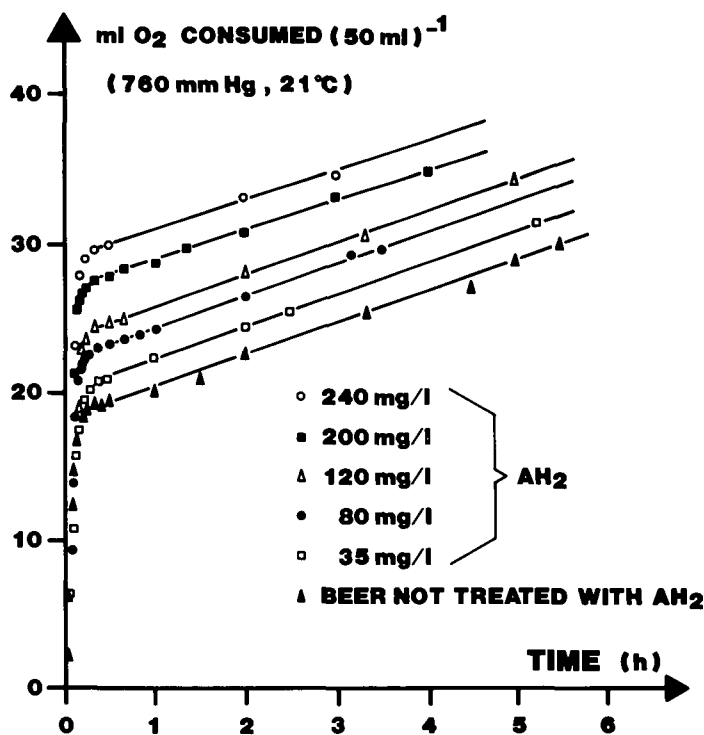


Fig. 5. Oxygen consumption by beers treated with different amounts of ascorbic acid (AH_2). Cu^{2+} concentration, 0.4 mg/L; temperature of the liquid phase, 35°C; oxygen pressure, 300 mmHg; stirring speed, 300 rpm.

slow phase of oxidation, whereas, as shown in Figure 6, the value of S_0 , characterizing the phase of rapid oxidation, was increased linearly by stepwise additions of ascorbic acid. This process of standard additions allows the concentration of antioxidants present in the beer itself to be calculated, as shown in Figure 6, at approximately 409 mg/L of AH_2 equivalent.

The Mechanism of Oxidation

It is evident that the added ascorbic acid participates in the consumption of oxygen. From the concentrations of ascorbic acid and the values of S_0 , it can be calculated that about 10 to 50 molecules of oxygen are consumed for each molecule of ascorbic acid, which implies the existence of oxidation by relatively short chain reactions. A possible mechanism to explain these observations is developed below.

Phenomenological Analysis of Beer Oxidation

If $S(t)$ represents the difference between the intercept S_0 at $t = 0$ and the curve representing the consumption of oxygen, we attempted to determine whether there is an "order" with time, i.e., a relationship between the rate of reaction $dS(t)/dt$ and the macroscopic factors varying in the system (Fig. 7). If n be the order, a factor K should exist such that $dS/dt = -KS^n$, leading to: $1/(n-1) \cdot S^{-n+1} = Kt + \text{constant}$.

From the experimental results, the most probable value of n was determined by a parametric adjustment method. The value $n = 0.5$ was found, leading to:

$$S_0^2 - S_t^2 = Kt/2, \quad (A)$$

where S_0 represents the value of $S(t)$ at $t = 0$. Taking into consideration the substantial effect of antioxidants such as ascorbic acid on the reaction (particularly over a short time), this relationship allows for the occurrence of a chain reaction, in accord with other work (12-21). In the experiments described later, the variation of K with macroscopic factors of the system has been calculated for beers both treated and not treated with added antioxidants.

Using relationship (A), the values of K were calculated for various conditions in which a single experimental parameter (oxygen pressure, temperature, or concentration of catalyst and ascorbic acid) was varied. The results of these calculations are summarized in Table III. Among the metal ion catalysts which could be involved in beer oxidation, Cu^{2+} ions have a non-

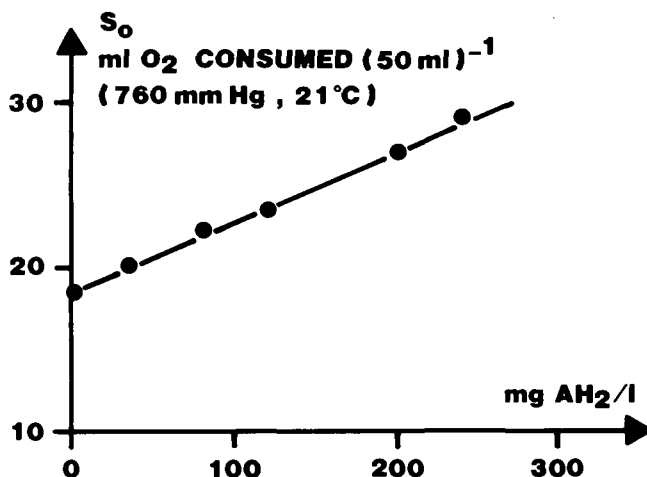


Fig. 6. Effect of ascorbic acid (AH_2) on the ordinate at the origin in slow oxidation curves.

negligible effect. This effect is related to the concentration of ions in the solution, and is difficult to separate from effects of other metal ions that may be present, or from those of organic catalysts. The effect of the partial pressure of oxygen on the kinetics of beer oxidation is such that the rate of oxidation decreases with decreasing oxygen pressure. Thus, it is desirable to remove oxygen from the headspace in packages, but the overall effect on the kinetics of the reaction is relatively small.

Finally, in this perfectly mixed system the effect of temperature on the kinetics of oxidation is negative. It may be that the solubility of oxygen in beer is the determining factor. However, the rate of deterioration of beer is known to be positively correlated with the storage temperature (7). Higher temperatures would be expected to increase the rate of oxygen diffusion through beer and thus compensate for the lower rate of dissolution of the oxygen.

TABLE III
Factors Affecting the Variation of K

Factor	K Value
Temperature (°C)	
10	0.31
25	0.20
35	0.19
50	0.13
60	0.12
Cu ²⁺ (mg/ml)	
0	0.16
0.1	0.18
0.2	0.22
0.3	0.28
0.4	0.30
0.5	0.35
0.6	0.40
Oxygen pressure (torr)	
60	0.04
130	0.19
200	0.25
260	0.33
300	0.35
390	0.37
550	0.39

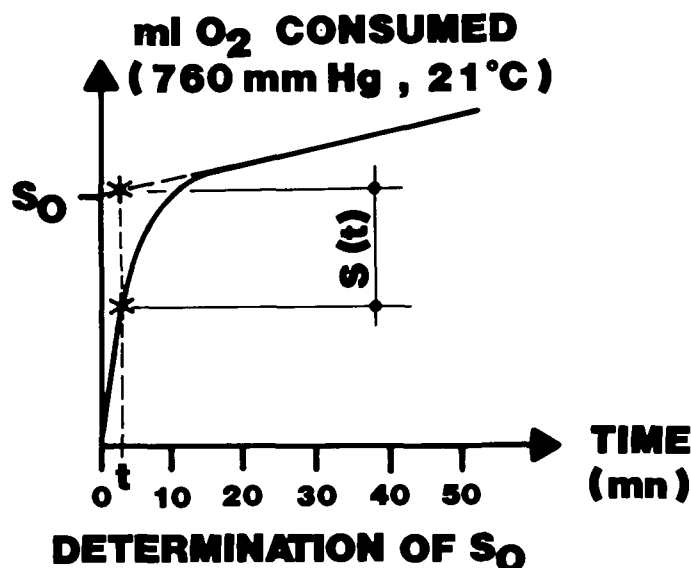


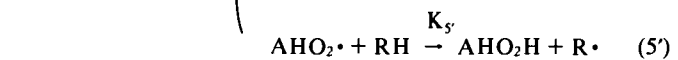
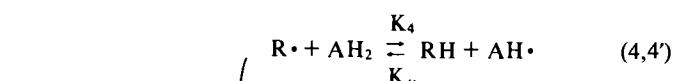
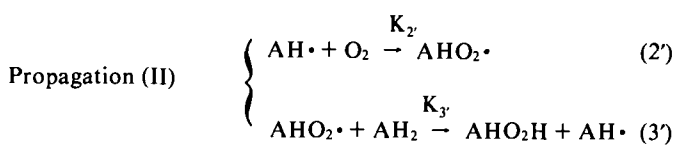
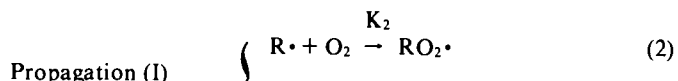
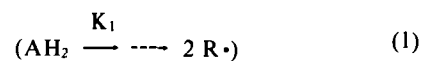
Fig. 7. Schematic representation of the kinetics of oxidation of beer. S₀ = zone of rapid oxidation; S(t) represents the difference between the intercept S₀ at t = 0 and the curve representing oxygen consumption.

Possible Reaction Mechanism

Because in this work it was found that the quantity of ascorbic acid that was lost from the system was, in molar terms, about one-fiftieth of the amount of oxygen used, it is reasonable to consider that chain reactions each some 10–50 in length, are involved.

Let us designate RH as an oxidizable molecule and assume, for simplicity, the involvement of free radicals rather than radical ions. In these circumstances, RH will be oxidized according to the classical mechanism at the start of the reaction, in the presence or in absence of AH₂ (3).

Initiation: production of free radical chains transferring R• at a rate of 2v.



Termination: destruction in pairs of radicals R•, AH•, RO₂•, and AHO₂•.

The study of the kinetic effects of AH• in general is very complex, but it can be simplified if one considers possible limiting conditions. Thus, if it is assumed that the free radicals derived from AH₂ are not able to remove hydrogen atoms from RH or from AH₂, equations 3' and 5' need not be considered, and the system is simplified to the kinetic expression previously published (2):

$$\frac{v}{v_{\text{O}_2}} \approx 1 + \frac{v}{2v} \cdot \frac{K_3[\text{AH}_2]}{K_3[\text{RH}]},$$

where, other things being equal, v represents the rate of oxidation of RH alone (d[RH]/dt) and v_{O₂} the rate of consumption of oxygen (d[O₂]/dt). Because the second term of this equation is much greater than unity, one can write:

$$v_{\text{O}_2} \approx 2v \cdot \frac{K_3[\text{RH}]}{K_3[\text{AH}_2]} = \frac{2K_1K_3[\text{RH}]}{K_5},$$

where v = K₁[AH₂]; where K₁ is the initiation rate constant which, as it is independent of AH₂, would explain the stability of the initial rate of oxidation in relation to AH₂ shown in Figure 5.

AH₂ can play a double role, being involved in the initiation of the reaction (v) and in the modification of the kinetics of the chain reaction.

If AH₂ only initiated chains, then the evolution over time of its concentration could be expressed by an exponential law as:

$$[AH_2] = [AH_2]_{t=0} \cdot \exp(-K_1 t)$$

If we now assume that peroxy radicals react with AH₂ leading to nonreactive radicals, then each RO₂• leads to the disappearance of an AH₂ molecule. From one AH₂ molecule two free radicals are formed in the initiation step, and three AH₂ molecules disappear. Under these conditions the kinetics of the consumption of AH₂ molecules is:

$$[AH_2] = [AH]_{t=0} \cdot \exp(-3K_1 t)$$

A more sophisticated calculation leads from

$$d[AH_2]/dt = -K_1[AH_2] - K_5[RO_2\cdot][AH_2],$$

to

$$d[AH_2]/dt = -K_1[AH_2] \cdot \left[1 + \frac{2K_5[AH_2]}{K_5[AH_2] + 2K_6^{1/2} K_1^{1/2} [AH_2^{1/2}]} \right]$$

where K₆ corresponds to the recombination rate constant of two peroxy radicals. This complex expression is close to an exponential form. Then, in a first approximation, we have introduced a parameter α₁, which is between 1 when K₅ is small and 3 when K₅ is large. According to this assumption, the evolution of AH₂ over time is now:

$$[AH_2] = [AH_2]_{t=0} \exp(-\alpha_1 K_1 \cdot t)$$

Following this relationship and the oxidation rate of the beer, which is defined by

$$V_{O_2} = \frac{-d[O_2]}{dt} = \frac{d[RH]}{dt} = \frac{d[AH_2]}{dt} = (K_3[RH] + K_5[AH_2])[RO_2\cdot],$$

where

$$[RO_2\cdot] = \frac{2K_1[AH_2]}{2K_6^{1/2} K_5^{1/2} [AH_2^{1/2}] + K_5[AH_2]}$$

we obtain the analytical expression of S(t).

Using the first part of V_{O₂} above,

$$S(t)_i = \int_0^t V_{O_2} dt$$

$$A_1 = \frac{2K_6^{1/2} K_5^{1/2}}{K_5[AH_2]_{t=0}^{1/2}}$$

$$B_1 = \frac{2K_3 K_1 [RH]}{K_5}$$

$$V_{O_2} = \frac{B_1}{1 + A_1 \exp(\alpha_1 K_1 t / 2)}$$

S(t) is expressed by:

$$S(t) = (2B_1 / \alpha_1 K_1) \ln(1 + 1 / A_1) \exp(-\alpha_1 K_1 t / 2)$$

and

$$S(0) = S_0 = (2B_1 / \alpha_1 K_1) \ln(1 + 1 / A_1)$$

Figure 8 shows for particular values of A₁ that it is possible to express semiquantitatively the linear variation of √S(t) with time. These results are in good agreement with experimental results.

In Figure 9 it is possible to illustrate the quasi linear variation of S(0) = S₀ versus [AH₂] in a large domain of antioxidant concentration.

Prediction of the Consumption of Oxygen After Bottling

Although the kinetic mechanisms discussed above show the double role of the antioxidant as an initiator of the chain reaction and an inhibitor of oxidation, it does not appear to be possible at present to describe this type of oxidation more fully. In fact, it seems especially difficult to understand the mechanisms of

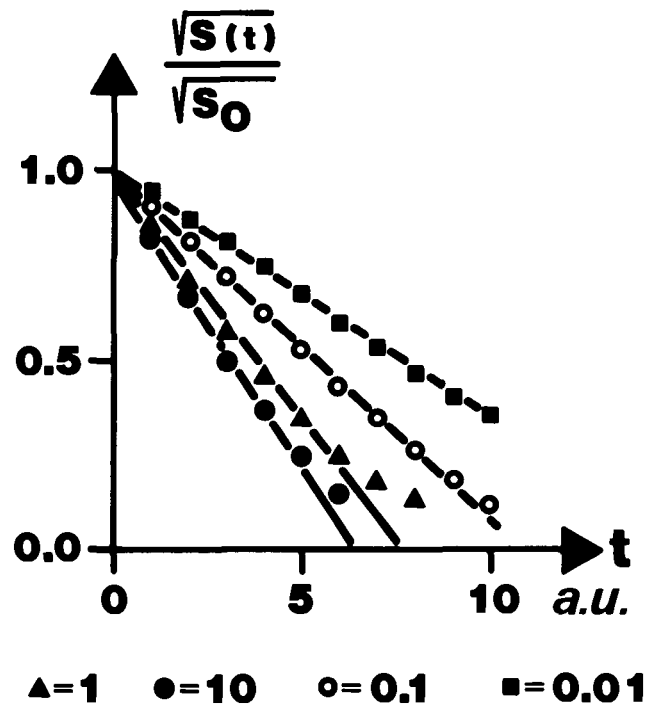


Fig. 8. Changes in the content of reducing substances during the rapid phase. a.u. = Arbitrary units.

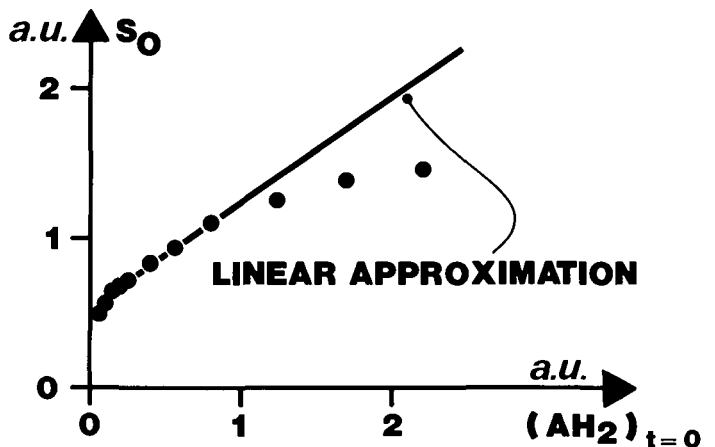


Fig. 9. Influence of ascorbic acid (AH₂) on S₀. a.u. = Arbitrary units.

initiation and the various reactivities of the substances (RH) involved, whether proteins, polyphenols, or others. Further, in solution in water, the peroxy radicals in particular are partly solvated, which substantially changes their reactivity (3,5). In view of this, despite the existence of a plausible mechanism, it is necessary for the kinetic analysis to be limited to a global description such as that presented above. In this situation, it can be shown experimentally that the rate V , measured in milliliters of oxygen per minute at 760 torr and 21°C, for 50 ml of beer, can be represented by an empirical equation of the form:

$$V = (P/(A + BP)) \sqrt{15.6 + 0.000156 P - Q}$$

where P is the partial pressure of oxygen (measured in torr), A and B are two coefficients determined from the kinetic model by parametric adjustment ($A = 531$ and $B = 1.315$), and Q is the quantity of oxygen in milliliters at 760 torr and 21°C consumed in time t by 50 ml of beer.

Consumption of Oxygen After Packaging

When beer is packaged, it is generally considered to contain from 0.4 to 0.8 ppm of oxygen in solution, corresponding to a partial pressure of 10 torr. Assuming that the closed bottle is perfectly sealed, two particular conditions have been considered: 1) The beer is sufficiently mixed, for instance during transport, for the contents of the bottle to be considered to be perfectly mixed. The concentration of oxygen is then considered constant throughout the beer. 2) The beer is not mixed. In these circumstances, if the liquid itself was free of oxygen at the moment of packaging, the rate of diffusion of the oxygen would limit its consumption.

Perfectly Stirred Reactor

At low oxygen pressures, which correspond approximately to industrial conditions, the expression giving V can be greatly simplified:

$$V_{O_2} \approx (P/A) \sqrt{15.6 - Q - KS}$$

where $S = 15.6 + 0.000156P - Q$.

From the experimental values of K obtained earlier, the value of K , expressed in $\text{mol}^{1/2} \cdot \text{L}^{1/2} \cdot \text{s}^{-1}$ is obtained by:

$$K \text{ mol}^{1/2} \cdot \text{L}^{1/2} \cdot \text{s}^{-1} = 4.82 \times 10^{-4} \text{ units per milliliter of } O_2 \text{ (760 torr, } 21^\circ\text{C for 50 ml of beer, } t \text{ in minutes),}$$

$$\text{and } V_{O_2} = - \frac{d o_2}{dt} \approx + 5.5 \times 10^{-6} P/A = 1.04 \times 10^{-2} (O_2).$$

As predicted by Henry's Law relating the solubility of oxygen to its partial pressure, the consumption of oxygen resulting from the presence of protective agents will be rapid and follow a largely exponential form:

$$[O_2] = [O_2]_{t=0} \exp(-1.04 \times 10^{-2} t)$$

where t is in seconds.

Note: In order for this result to be realistic, however, it would be necessary to be sure that the mechanism operating at higher pressures (>60 torr) is substantially identical to that at lower pressures. Only a study conducted under industrial conditions would allow full verification of these calculations. Some laboratory trials have been made at present; however, with the equipment available, the measurements were inexact because of frothing that limited the oxygen-beer exchange and because of the relatively high water pressure. Thus, the necessary further work requires equipment that operates on a different principle.

Reactor Working in the Diffusion Mode

In a system such as that shown in Figure 10, the liquid of depth x is contained below a gas-space of volume V containing oxygen at pressure p . The cross-sectional area of the reactor is ES .

The concentration of oxygen in solution in the liquid just below the gas-liquid interface is governed by Henry's Law, so that no increase of transfer is related to the chemical reaction.

If C be the concentration of oxygen in solution and D its diffusion coefficient in beer, then the change in C as a function of x (Fig. 10) is given by the classical equation:

$$\partial C/\partial t = D \nabla^2 C - KC,$$

where K is the constant determined previously just above ($1.04 \times 10^{-2} \text{sec}^{-1}$). D in solution is of the order of $10^{-5} \text{cm}^2 \text{sec}^{-1}$; on the other hand, in the gas phase D is much greater. In fact, the gas has a uniform oxygen pressure, i.e., the gas phase is assumed to be in a perfectly stirred reactor.

The relevant equations can be developed by taking into account the fact that the total amount of oxygen remaining in the reactor is equal to the initial amount less that which has been lost by reaction. If n_0 be the total number of milliliters of oxygen at 760 torr and 21°C for 50 ml of beer at $t = 0$, and n the value when t is greater than 0, the relationship between n and n_0 can be calculated (Appendix I) for long times as:

$$\frac{n}{n_0} \sim \frac{B}{2K^2} \cdot \frac{\exp(-Kt)}{t \sqrt{\pi t}}$$

with $K \approx 10^{-2} \text{sec}^{-1}$, and $B \approx 0.2$, which corresponds under the chosen experimental conditions to

$$n/n_0 < 0.1 \text{ for } t < 130 \text{ sec.}$$

Thus, it appears that oxygen in the bottle is consumed in a few minutes, whether the bottle is shaken or not. Nevertheless, although the calculations appear to show that the beer may be protected from the first moments of its entry into the bottle, too great a significance should not be attached to the actual figures now presented, as the presence of foam at the gas-liquid interface could be responsible for a reduction of the rate of transfer and thus affect the oxidation kinetics.

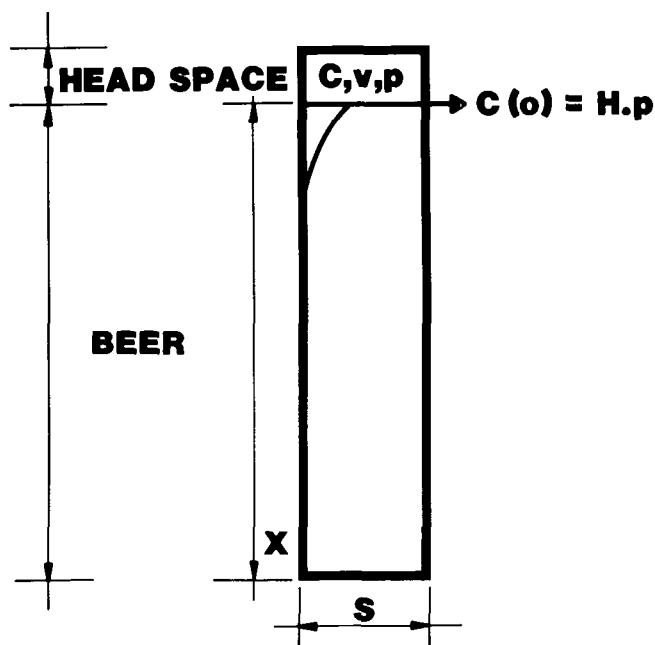


Fig. 10. Reactor working in the diffusion mode.

CONCLUSION

Kinetic studies of the oxidation of beer at constant pressure in the presence of copper ions as catalyst demonstrated that two distinct temporal phases can be observed: one over short time, linked to a rapid rate of oxidation and dependent on the concentration of antioxidant and on time; and the other characteristic of long times, at a slow rate that is almost independent of time and the quantity of antioxidant in the beer. The phase of rapid oxidation involves chain reactions in which the primary antioxidants act as both initiators and inhibitors of the oxidation reaction.

From a phenomenological kinetic analysis, it has been possible to write equations describing the oxidation of beer by oxygen present in the head-space at the moment of packaging. If we hypothesize that foams that would retard the transfer of oxygen at the gas-liquid interface do not interface in this reaction, the oxygen would be almost completely consumed in a few minutes.

ACKNOWLEDGMENT

The authors wish to thank F. Djeuhon for technical help.

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APPENDIX I

Variation of n/n_0 with Time for Nonmixed Reactions

As shown in the text, if C be the concentration of oxygen in solution and D its diffusion coefficient in beer, then the change in C as a function of x (Fig. 10) is given by the classical equation

$$\partial C / \partial t = D \nabla^2 C - KC.$$

Thus, applying a Laplace transformation to C (let it be y) one can write:

$$y(s) = \int_0^\infty \exp(-st) C(t) dt$$

$$sy = Dy'' - Ky$$

where y'' is the second derivative of y relative to the space. This leads, for a system sufficiently deep to be considered infinite, to

$$y = \alpha \exp\left(-\frac{\sqrt{s+k}}{D} \cdot x\right)$$

where α is a coefficient that depends on the limiting conditions.

If n_0 be the number of milliliters of O_2 at 760 torr and $21^\circ C$ for 50 ml of beer at $t=0$, and n the number at $t>0$, the change of n/n_0 after various manipulations from Laplace space into real space is given by:

$$\begin{aligned} n/n_0 = & (1/4E) \left[(B+2E) \exp\left[\frac{B+2E}{2}t\right] \cdot \operatorname{Erfc}\left[\frac{B-2E}{2}\sqrt{t}\right] \right. \\ & \left. - (B-2E) \exp\left[\frac{B-2E}{2}t\right] \cdot \operatorname{Erfc}\left[\frac{B-2E}{2}\sqrt{t}\right] \right] \end{aligned}$$

$$B = \sqrt{D} \frac{H \cdot P \cdot V \cdot S}{v},$$

where P is the atmospheric pressure, v is the volume of oxygen in the head-space, V is the molecular volume, S is the area of the gas-liquid interface, and

$$E = \left[K + \frac{B^2}{4} \right]^{1/2}$$

$$K = 10^{-2} \text{sec}^{-1}.$$

In particular, when t tends to infinity,

$$\frac{n}{n_0} \sim \frac{B}{2K^2} \cdot \frac{\exp(-Kt)}{t \sqrt{\pi t}}$$