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The autoxidation of sodium salicylate in aqueous solution

C. B. BEYNON* AND K. C. JAMES

The induction period of the auto-oxidation of aqueous alkaline solutions of sodium salicylate has been examined by following the oxygen concentrations polarographically. The reaction is photochemical, and is catalysed by copper, iron and manganese, although the increase in rate is less than 150% of the rate of the uncatalysed reaction. Bicarbonate ions are not necessary for reaction, which is first order with respect to light intensity and oxygen and salicylate concentrations.

THE darkening of aqueous alkaline solutions of sodium salicylate is due to oxidation. Changes in extinction of aerated sodium salicylate solutions with time have been measured and the process shown to be dependent on the aeration rate (Beynon & James, 1964). The form of the plot of extinction against time suggested autoxidation, but the procedure used had the disadvantages that the reaction was heterogeneous, and extinction could not be linked directly with reactant concentration. We have further investigated oxygenated solutions of salicylate and determined their oxygen concentrations polarographically.

Experimental

Determination of oxygen. The polarographic determination of oxygen has been summarized in several reviews (for example, Page, 1952). There are two reduction steps: at $E_{0\cdot5} = -0\cdot1$ V (vs. standard calomel electrode) representing reduction to hydrogen peroxide, and at $E_{0\cdot5} = -0\cdot9$ V due to reduction of hydrogen peroxide. Determinations were made at $-0\cdot1$ V using a Cambridge recording polarograph with mercury anode and direct current. A complete reduction step was traced in each determination to ensure that measurements were made on the limiting current plateau. Preliminary experiments showed that the diffusion current was not affected by the presence of sodium bicarbonate, sodium salicylate or changes in pH. Sodium chloride (0·1 M) was used as indifferent electrolyte in most determinations; when the molar concentration was varied between 0·08 and 0·13 M, or sodium chloride substituted in part by sodium bicarbonate or sodium hydroxide, the diffusion current remained constant. No polarographic maxima were seen. The calibration curve of diffusion current against oxygen concentration, using Krogh's (1935) modification of Winkler's method, was a straight line passing through the origin.

Rate determinations. Three ml of a solution containing all the components required for the reaction except sodium salicylate was placed in a polarograph cell, protected from the atmosphere by a mercury seal, and suspended in a constant temperature bath at 50°. Oxygen was bubbled

The Welsh School of Pharmacy, Welsh College of Advanced Technology, Cathays Park, Cardiff.

* Present address: Merck, Sharpe & Dohme, Nederland N.V. Postbus 581, Haarlem, Netherlands.

through to a predetermined concentration, indicated by the diffusion current, and if exceeded was reduced with a current of nitrogen. Concentrations were arranged to give the required composition when the reaction was started by adding 3 ml of a salicylate solution to the polarograph cell. Blank determinations were made. Initial rates of disappearance of oxygen were obtained from the tangent of the plot of oxygen concentration against time at zero time. Initial rates were used to formulate the rate equations in order to avoid complications occurring later in the autoxidation chain. The kinetic curves over the complete 80 min runs followed a similar pattern.

Effect of ultraviolet irradiation. The constant temperature bath was coated with black paint and covered with a black cardboard lid. One glass side of the bath was left unpainted and faced onto a light-tight tunnel normal to it. A rail along the axis of the tunnel carried a Hanovia medium pressure arc in quartz with a spectrum range from 1850 Å to the near infrared. The source was mounted on a trolley which could be moved along the rail, and its distance from the mixture measured by means of a rule attached to the track. The polarograph cell was placed near to and at a fixed distance from the irradiated side.

To examine the effect of the irradiation, rates were measured with the light source at varying distances from the reaction. Quantum output was measured using potassium ferrioxalate (Hatchard & Parker, 1956). The radiation was confined to the 3025 and 3125 Å wavebands. A solution of nickel chloride, placed in the beam, absorbed the longer wavebands and the glass side of the tank absorbed the shorter wavebands All other determinations were made with the lamp 30 cm from the polarograph cell, and without the nickel chloride filter.

Effect of metallic ions. Neither sodium edetate nor sodium cyanide had any effect on reaction rate.

Measured quantities of manganic sulphate were added to the indifferent electrolyte solution before passing oxygen, and the concentration of manganese confirmed from the diffusion current at −1·51 V (vs. standard calomel electrode). The salicylate solution was then added and the rate of uptake of oxygen determined as before. A similar procedure was carried out with ferric and cupric ions. The effects of these are shown in Fig. 1.

Effect of hydroxyl and bicarbonate ion concentrations. Rate determinations were made at a series of different pH values. The ionic strength was kept constant with sodium chloride, and the pH varied by adding different quantities of sodium hydroxide. pH values were measured on an E.I.L. pH meter using glass and calomel electrodes. In similar experiments, sodium bicarbonate concentration was varied and pH and ionic strength kept constant. Substituted salicylic acids were examined in the same way.

Absorptiometer measurements. This procedure has been described previously (Beynon & James, 1964).

Results and discussion

The rapid darkening of sodium salicylate—sodium bicarbonate solutions has been attributed to traces of metal impurity in the sodium bicarbonate. Mesnard & Marzar (1950) proposed iron as the catalyst, Zwikker & Weber (1940) manganese, and Liberelli (1935) iron and copper. Fig. 1 shows that all these catalysed the uptake of oxygen, rapidly reaching a limiting value less than 50% greater than the uncatalysed rate. The polarograms suggested that metallic impurity in the reactants could not be greater than 0·3 parts per million, and the failure of sodium edetate or sodium cyanide (for copper) to retard the reaction shows that these ions, if present as impurity below this level, have no effect under the conditions described. These results do not necessarily contradict the opinions of the above authors, in fact, absorptiometer measurements with more

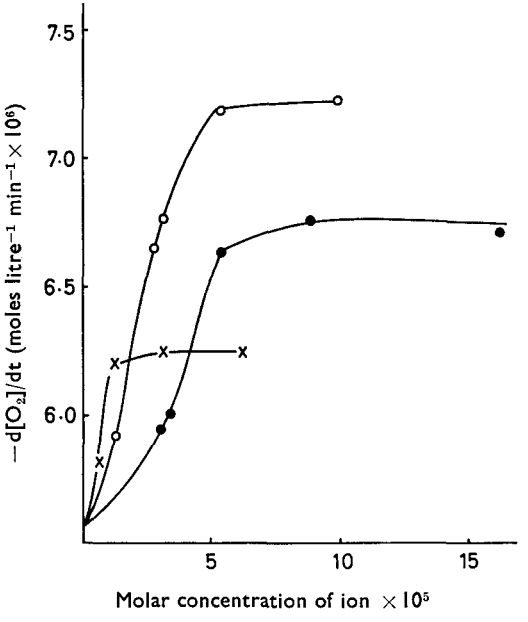

FIG. 1. Effect of metallic ions on reaction rate. $[C_7H_5O_3Na]_0 = 1{\cdot}5 \times 10^{-3}$. $[O_2]_0 = 7{\cdot}35 \times 10^{-4}$. ●, Mn^{2+}; ×, Cu^{2+}; ○, Fe^{3+}.

concentrated mixtures have indicated that sodium edetate has a marked effect on retarding discolouration (Beynon & James, 1964). In that work the rate of increase in extinction was shown to pass through three stages typical of auto-oxidation processes—an induction period with very little colour development, followed by a rapid increase in extinction which subsequently slowed down. The induction period lasted for 100 min, hence the observations in this communication, which were made for 80 min, belong to this period. Metal ion catalysis of auto-oxidation usually affects the second stage (Ingold, 1961), and it is probable that it is this stage of the salicylate oxidation which is markedly influenced by metal ions.

Hilton & Bailey (1938) have stated that light has very little effect on the reaction, but most workers (for example Grill, 1932; Ernst & Menashi, 1963) agree that it is light sensitive, although no attempt has been made to relate rate with light intensity. This we did by observing the effect of ultraviolet light on the extinction of 0·3M sodium salicylate solutions. Under these conditions the length of the induction period was proportional to, and the rate inversely proportional to the distance of the energy source from the reaction mixture. In determining the order of the reaction with respect to the radiation intensity, we found it was important to ensure that the mixture was uniformly illuminated throughout. The 3025 and 3125 Å emission bands of mercury were used because wavelengths lower than 3025 Å are absorbed by glass, and wavebands higher than 3125 Å are not absorbed by salicylic acid. Extinction measurements at the two emission wavelengths revealed that the concentrations used in the preliminary experiments absorbed most of the radiation in less than the first mm. Since this would result in a reaction with diffusion as a complicating factor, subsequent polarographic determinations were made with $2{\cdot}0 \times 10^{-5}$ M solutions of sodium salicylate, which absorbed less than 10% of the incident radiation. Order with respect to radiation intensity was calculated by plotting log intensity against log initial rate. A straight line of slope 1·00 was obtained (Fig. 2). Similar graphs (Fig. 3) gave slopes of 0·90 for salicylate and 0·92 for oxygen, indicating that the rate equation for the main reaction at constant pH is probably,

$$\frac{-d[O_2]}{dt} \propto I_0[O_2] \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (1)$$

where I_0 is incident radiation intensity, at constant salicylate concentration, and

$$\frac{-d[O_2]}{dt} \propto [O_2]\,[C_7H_5O_3Na] \quad \ldots \quad \ldots \quad \ldots \quad (2)$$

at constant radiation intensity.

The variation in reaction rate with pH, shown in Fig. 4 supports the observations of Greenish & Beesely (1915) and of Hilton & Bailey (1938) that the rate reaches a maximum around pH 10·3, but the fact that mixtures containing sodium bicarbonate follow the same pattern as those without sodium bicarbonate is contrary to the supposition of these authors that the bicarbonate ion is necessary for the reaction to proceed. The broken lines in Fig. 4 represent the effect of pH on the rates of oxidation of two substituted salicylic acids and indicate that there is a connection between the pH at which the maximum rate occurs and the pK_a value of the phenol group. This suggests that the reacting species is the ion R(OH)COO′, and that the rise and fall in the reaction rate with pH are due to the equilibria,

$$R(OH)COOH \overset{K_1}{\rightleftharpoons} R(OH)COO' + H^+ \quad \ldots \quad \ldots \quad (3)$$

$$R(OH)COO' \overset{K_2}{\rightleftharpoons} R(O')COO' + H^+ \quad \ldots \quad \ldots \quad (4)$$

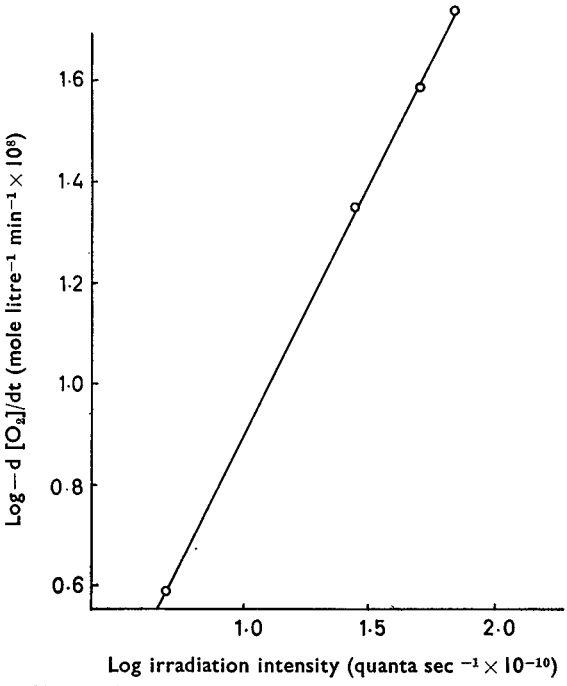

FIG. 2. Effect of irradiation intensity on reaction rate. $[C_7H_5O_3Na]_o = 2{\cdot}0 \times 10^{-5}$. $[O_2]_o = 8{\cdot}0 \times 10^{-5}$.

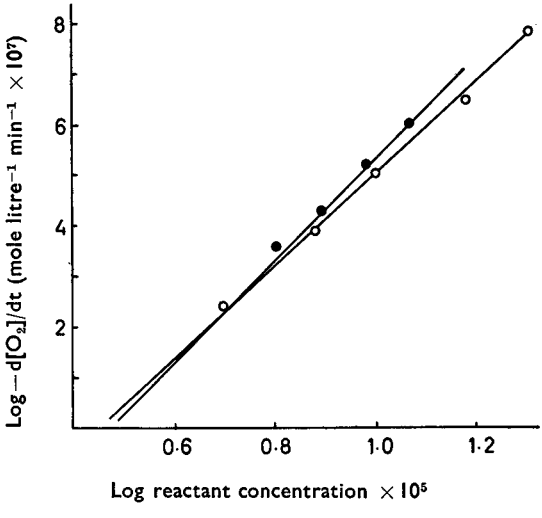

FIG. 3. Effect of reactant concentration on reactant rate. ○ Salicylate ($[O_2]_o = 1{\cdot}02 \times 10^{-4}$); ● oxygen ($[C_7H_5O_3Na]_o = 1{\cdot}25 \times 10^{-4}$).

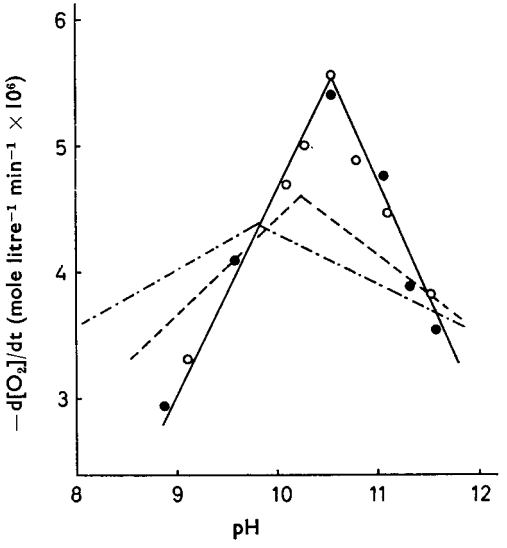

FIG. 4. The effect of pH on reaction rate. — Sodium salicylate, pK_{a_2} $2{\cdot}56 \times 10^{-14}$ at 25°: ○ with HCO_3'; ● without HCO_3'. —·— Sodium 5-nitrosalicylate, pK_{a_2} $4{\cdot}58 \times 10^{-13}$ at 25°. – – – Sodium 5-bromosalicylate, pK_{a_2} $1{\cdot}46 \times 10^{-13}$ at 25°. $[O_2]_o = 2{\cdot}35 \times 10^{-4}$. $[\text{Salicylate}]_o = 1{\cdot}5 \times 10^{-3}$.

The pH independent rate equation would then be,

$$\frac{-d[O_2]}{dt} = k[O_2]\,[R(OH)COO'] \quad .. \quad .. \quad .. \quad (5)$$

at constant irradiation intensity.

It can be calculated that,

$$[\text{Total phenolic acid}] = [R(OH)COO']\left\{1 + \frac{[H^+]}{K_1} + \frac{K_2}{[H^+]}\right\} \quad .. \quad (6)$$

and substitution for $[R(OH)COO']$ from (5) gives,

$$[\text{Total phenolic acid}] = \frac{-d[O_2]}{dt}\left\{1 + \frac{[H^+]}{K_1} + \frac{K_2}{[H^+]}\right\}\Big/ k[O_2] \quad .. \quad (7)$$

Table 1 shows the initial rates of oxygen consumption at various pH values. Substitution of these in equation (7) gave 6 simultaneous equations, which on least squares analysis, using an Elliot 803 electronic computer, yielded the values,

$$K_1 = 2{\cdot}04 \times 10^{-10}; \quad K_2 = 8{\cdot}36 \times 10^{-14} \quad .. \quad ..$$

Table 1 shows the second order constants obtained by substituting these dissociation constants in equation (7). They are reasonably constant in comparison with the $-d[O_2]/dt$ results and do not appear to pass through a maximum.

TABLE 1. THE EFFECT OF HYDROGEN ION CONCENTRATION ON REACTION RATE

$[O_2]_o = 8{\cdot}0 \times 10^{-5}$ $[C_7H_5O_3Na]_o = 2{\cdot}0 \times 10^{-5}$

	pH					
	10·1	10·6	10·8	11·1	11·6	12·6
$-d[O_2]/dt \times 10^7$ (mole litres^{-1} min^{-1})	4·19	4·54	5·89	6·66	5·45	4·40
k (calc. from eqn 7) litres mole^{-1} min^{-1}	377	325	398	437	356	370

The first dissociation constant of salicylic acid of $1{\cdot}06 \times 10^{-3}$ is much higher than K_1 ($2{\cdot}04 \times 10^{-10}$). Hermans, Leach & Scheraga (1963) have reported a second pK_a of 12·48 at 45° and an enthalpy of ionization of 10·5 kcal/mole. Substitution of these values in the van't Hoff isochore gave a dissociation constant of $4{\cdot}32 \times 10^{-13}$ at 50°, which does not agree with the second dissociation constant (K_2) calculated above. Weller (1961) has reported that the excited states of organic acids have vastly different pK_a values from the ground states. In general, phenols are more dissociated in the excited state, and carboxy acids more dissociated in the ground state. There is no information on the behaviour of molecules in which phenol and carboxy are conjugated, but it is possible that the dissociation constants calculated above are those of the excited state of salicylic acid, and that in this reaction the most reactive form is either $C_6H_4(OH)COO'^*$ or $C_6H_4(COOH)O'^*$, where * denotes activated state.

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