

## OXIDATION OF SINGLET SUBSTRATES BY DIOXYGEN CATALYZED BY TRANSITION METAL IONS. EFFECT OF TEMPERATURE

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The effect of temperature on singlet substrate oxidations by dioxygen has been examined for both non-catalyzed reactions and reactions catalyzed by transition metal ions. The kinetics are discussed for various activation energies of catalyzed and non-catalyzed reactions and for various catalyst concentrations. It is shown that at sufficiently high temperatures trace amounts of transition metal ions present in reaction systems as impurities may become effective in catalyzing singlet substrate oxidations.

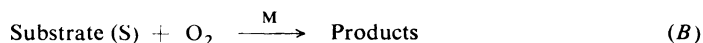
Oxidations of singlet substrates by dioxygen are spin-forbidden reactions, with high activation energies and extremely low rate constants.<sup>1,2</sup> Complex-forming reactions of transition metal ions with dioxygen and substrate provide a path that is spin-allowed and thus requires a substantially lower activation energy.

Let us suppose that a singlet substrate is oxidized by a mechanism involving cyclic generation of catalyst.<sup>3</sup> This mechanism consists of three processes which, to a first approximation, may be represented by reactions (A)–(C).

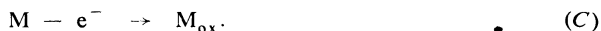
Generation of catalytically active ion in its lower oxidation state:



catalyzed oxidation of substrate:



catalyst deactivation:



Although each of the processes (A) to (C) is a complex reaction involving a series of steps, we shall introduce the simplifying assumption that the rate of process (A) is high and the rate of process (C) low enough for all of the catalyst precursor ( $M_{ox}$ ) to be converted into its catalytically active form (M). The substrate oxidation will then be controlled by the rate of process (B). This assumption is true for some real systems, for example for oxidations of sulphite<sup>4</sup> and ascorbic acid<sup>5</sup> catalyzed by cop-

per ions. Kinetic analysis of the effects of reactions (A) and (C) will be given in our next paper.<sup>3</sup> We shall further suppose that the rates of non-catalyzed and catalyzed reactions may be expressed by Eqs (1) and (2), respectively. Oxygen concentration is taken to be constant and

$$v_N = k_N[S][O_2] = A_N[S][O_2] \exp(-E_N/RT) \quad (1)$$

$$v_C = k_C[S][O_2][M] = A_C[S][O_2][M] \exp(-E_C/RT) \quad (2)$$

equal to  $1 \cdot 10^{-3} \text{ mol l}^{-1}$ , corresponding to oxygen solubility in aqueous solutions under conditions where the reaction mixture is continuously saturated with oxygen. Rate constants of non-catalyzed ( $k_N$ ) and catalyzed ( $k_C$ ) reactions are expressed by using Arrhenius equation;  $A_N$  and  $A_C$  have the meaning of rate constants at zero activation energy for non-catalyzed and catalyzed reactions, respectively.

## RESULTS AND DISCUSSION

It is clear that for  $E_N > E_C$  the rate of non-catalyzed reaction increases more rapidly with increasing temperature than does the rate of catalyzed reaction. Comparison of Eqs (1) and (2) reveals that for temperatures higher than  $T_1$  (Eq. 3) the rate of non-catalyzed reaction will exceed the rate of catalyzed

$$T_1^* = (E_N - E_C)/R \ln [A_N/([M] A_C)] \quad (3)$$

reaction. If activation energy of non-catalyzed reaction  $E_N \geq 120 \text{ kJ mol}^{-1}$ , which is a reasonable assumption, it follows that at room temperature there will be virtually no non-catalyzed reaction ( $v_N \leq A_N[S][O_2] \cdot 9.5 \cdot 10^{-22} \text{ mol l}^{-1} \text{ s}^{-1}$ ) and that the reaction can proceed at a measurable rate only on lowering the activation energy by added catalyst.

The more the activation energy is lowered by adding a catalyst (*i.e.* the lower the  $E_C$ ), the higher the sensitivity of the reaction system to the catalyst, and the lower catalyst concentration will be needed for the reaction to proceed at a measurable rate. Fig. 1 shows a plot of the initial rate of catalyzed reaction against catalyst concentration. Clearly, if activation energy for catalyzed reaction is very low, the reaction rate will be affected even by very small concentrations of catalyzing ions. In extreme cases, oxidation reactions may be catalyzed by transition metal ions and compounds present in reaction systems as trace impurities, *i.e.* at concentrations  $c_M < 10^{-7} \text{ mol l}^{-1}$ . Examples of reactions of this type are oxidations of sulphite,<sup>4-6</sup> benzaldehyde,<sup>7,8</sup> and ascorbic acid.<sup>5</sup>

If activation energy of catalyzed reaction is relatively high, the catalytic effect of transition metal ions and compounds is difficult to detect at room temperature.

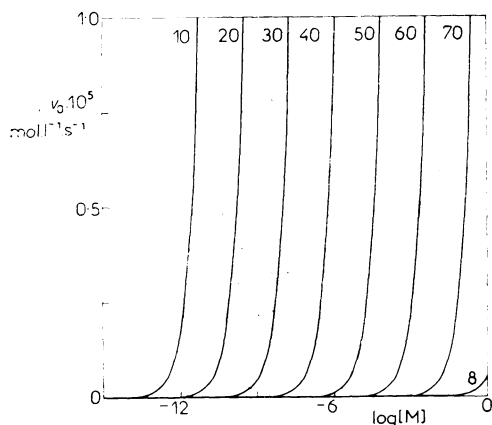


FIG. 1

Initial rate of catalyzed reaction ( $v_0$ ) as a function of concentration of catalytically active ions at various activation energies of catalyzed reaction.  $v_0 = A_C[S]_0[O_2][M] \exp(-E_C/RT)$ ;  $A_C = 1 \cdot 10^{11} \text{ l mol}^{-1} \text{ s}^{-1}$ ;  $T = 293.15 \text{ K}$ ;  $[S]_0 = 1 \text{ mol l}^{-1}$ ;  $[O_2] = 1 \cdot 10^{-3} \text{ mol l}^{-1}$ ; values of  $E_C$  ( $\text{kJ mol}^{-1}$ ) are quoted at the curves

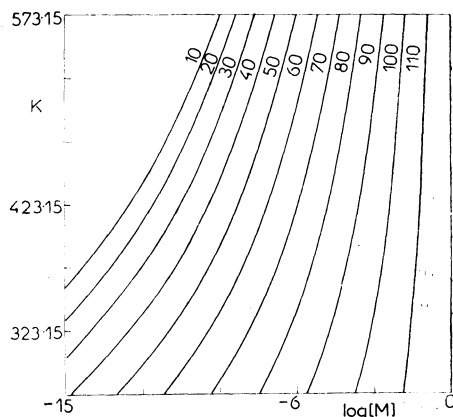


FIG. 2

Limiting temperature  $T = (E_N - E_C)/R \cdot \ln[(A_N E_N)/([M] A_C E_C)]$  as a function of concentration of catalytically active ions at various activation energies of catalyzed reaction.  $A_N = A_C$ ;  $E_N = 120 \text{ kJ mol}^{-1}$ ; values of  $E_C$  ( $\text{kJ mol}^{-1}$ ) are quoted at the curves

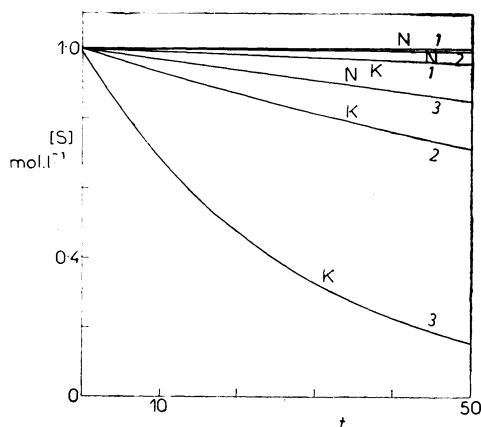


FIG. 3

Kinetics of catalyzed and non-catalyzed oxidations at various temperatures. Kinetic equations considered: a) non-catalyzed reaction  $[S] = [S]_0 \exp[-A \cdot \exp(-E_N/RT) \cdot [O_2] t]$ ; b) catalyzed reaction  $[S] = [S]_0 \cdot \exp[-A \cdot \exp(-E_C/RT) [M] [O_2] t]$ ;  $t$  in hours;  $E_N = 95 \text{ kJ} \cdot \text{mol}^{-1}$ ;  $E_C = 54 \text{ kJ} \cdot \text{mol}^{-1}$ ;  $[M] = 1 \cdot 10^{-5} \text{ mol} \cdot \text{l}^{-1}$ ;  $[S]_0 = 1 \text{ mol l}^{-1}$ ;  $A = 1 \cdot 10^{11} \text{ mol}^{-2} \cdot \text{l}^2 \text{ s}^{-1}$ ; N non-catalyzed reaction; K catalyzed reaction;  $T$ : 1 293.15 K; 2 323.15 K; 3 353.15 K

In this case, the difference in reaction rates of catalyzed and non-catalyzed reactions,  $y = v_C - v_N$ , will be the point of interest in experimental studies of catalytic effects.

$$y = A_C[S][O_2][M] \exp(-E_C/RT) - A_N[S][O_2] \exp(-E_N/RT) \quad (4)$$

It is readily seen that  $y$  will increase with increasing temperature provided inequality (5) and the condition  $[M] A_C E_C < A_N E_N$  are satisfied (this condition is met with most real systems). For temperatures satisfying condition (5), an increase of temperature

$$T < (E_C - E_N)/R \ln \left( \frac{[M] A_C E_C}{A_N E_N} \right) \quad (5)$$

will enhance the difference in rates of catalyzed and non-catalyzed reactions; thus, on elevating the temperature, we shall observe a greater catalytic effect of added catalyst.

Fig. 2 shows a plot of the limiting values of  $T$  corresponding to inequality (5) for  $E_N = 120 \text{ kJ mol}^{-1}$  and  $A_C = A_N$  against  $\log [M]$  at various values of  $E_C$ . It is seen that for  $E_C < 100 \text{ kJ mol}^{-1}$  and  $[M] > 1 \cdot 10^{-9} \text{ mol l}^{-1}$ ,  $y$  will increase with increasing temperature over the whole range of temperatures ordinary in liquid-phase reactions ( $T < 570 \text{ K}$ ).

The increase in catalytic activity is illustrated in Fig. 3, where kinetics of catalyzed and non-catalyzed oxidations are shown at different temperatures. Such enhancement of catalytic activity (*i.e.*, an increase in  $y = v_C - v_N$ ) with increasing temperature has been observed experimentally in thermal and photoinitiated oxidations of tetraline by dioxygen.<sup>9</sup>

## CONCLUSIONS

Catalytic effects of transition metal ions and compounds whose additions affect reaction rates at room temperature but little may be markedly promoted by elevating the temperature. At sufficiently high temperatures, trace amounts of transition metal ions present in reaction systems as impurities may become effective in catalyzing singlet substrate oxidations.

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