

The Mechanism of the Oxidation of Alcohols and Aldehydes with Peroxydisulphate Ion

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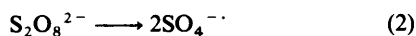
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The kinetics of the reactions of peroxydisulphate with alcohols (methanol, ethanol, propan-1-ol, propan-2-ol, and butanol) and with acetaldehyde have been studied. Their radical-chain behaviour has been established. Using a radical-scavenger method it has been shown that the chain-initiating step is the monomolecular homolysis of the peroxydisulphate anion. The 'limiting' concentration of the reducing agents, the mean kinetic chain length, and the overall energy of activation have been determined. The mechanism of the autoinhibition of the reaction of primary alcohol with peroxydisulphate has been discussed.

Analysis of literature data shows that there are two main and contradictory opinions on the mechanism of alcohol oxidation with peroxydisulphate ion, radical-chain and non-radical mechanisms. Bartlett and Cotman¹ have reported that in the presence of methanol the rate of peroxydisulphate decomposition increases 25-fold and the overall rate law is (1). These

$$R = k[P]^{3/2}[MeOH]^{1/2} \quad (1)$$

authors suppose that the reaction is radical-chain, and there are two parallel reactions for the chain initiation, monomolecular and bimolecular [reactions (2) and (3)]. Kolthoff *et al.*² have



proved the anti law (1) and found that only the reaction (2) takes place for chain initiation.

Edwards and his co-workers³⁻⁷ have attempted to elucidate the mechanism of alcohol oxidation with the peroxydisulphate ion. They have not been able completely to remove the inhibitory action of oxygen. For this reason the reaction has an initial slow rate. For the rapid region of the reaction they have established the rate law (4) and proposed a radical-chain

$$R = k[P][ROH]^{1/2} \quad (4)$$

mechanism including (2) as a chain-initiating step. A quadratic chain-termination reaction has been adopted. For high propan-2-ol concentrations the rate is independent of alcohol concentration [equation (5)].

$$R = k[P] \quad (5)$$

According to Bida *et al.*⁸ in oxygen-free medium the oxidation of propan-2-ol obeys the law (6).

$$R = k[P][Pr^iOH]^{3/2} \quad (6)$$

When u.v. light was used to initiate the oxidation, no reproducible results were obtained. This was due to traces of metal ion in the initial peroxydisulphate.

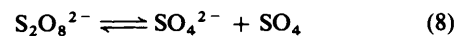
Stehlik and Fiala⁹ assumed that in the absence of Ag^+ there is no oxidation of MeOH and EtOH at low temperatures.

According to Subbaraman and Santappa¹⁰ the rate law of the oxidation of the alcohols and acetaldehyde is of the order of 3/2 for peroxydisulphate and 1/2 for the reducing agents. The occurrence of a negative salt effect has been established.

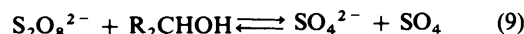
Levitt and Malinowski¹¹ have investigated the propan-2-ol oxidation at temperatures $\geq 50^\circ C$. They established the rate law (7) where $0 \leq n \leq 1$. n depends on the alcohol

$$R = k[P][Pr^iOH]^n \quad (7)$$

concentration. The overall energy of activation was 25 kcal mol⁻¹. SO_4^{2-} anions decreased the reaction rate. They put forward the heterolytic monomolecular cleavage (8) of $S_2O_8^{2-}$



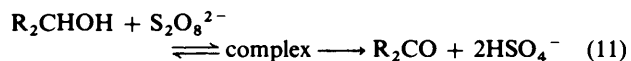
ion. These authors also proposed an alternative bimolecular mechanism (9),¹² leading to the rate law (10).



$$R = k[P][ROH]/(a + [P])(b + [ROH]) \quad (10)$$

Wiberg¹³ concluded that the mechanism proposed by Levitt and Malinowski was not probable. He assumes that the reaction is a radical-chain process and reaction (2) was the initiation step.

Levitt *et al.*^{14,15} did not accept the radical-chain mechanism and proposed a mechanism similar to enzymatic reactions [reaction (11)].



It is important to establish the final products of the alcohol oxidation. Bartlett and Cotmann¹ showed that MeOH oxidizes to HCHO. According to Kolthoff *et al.*², the final product of MeOH oxidation was formic acid which increased the rate of peroxydisulphate decomposition. Propan-2-ol was oxidized to acetone, which is subject to further oxidation.¹⁰

Schröder and Griffith¹⁶ reported that the products of alcohol and aldehyde oxidation with oxygen in the presence of peroxydisulphate were the corresponding acids. Walling and Camaioni¹⁷ showed that the products of the oxidation of 2-methylbutan-2-ol are ethanol, acetone, and 2-methylbutane-2,3-diol. Menghani and Bakore¹⁸ identified acetaldehyde when butane-2,3-diol was oxidized in the presence of Ag^+ . But Srivastava and Gupta^{19,20} did not report the C-C cleavage when diols are oxidized. The reaction is of first order for peroxydisulphate and catalyst and zero order for alcohols.

From analysis of the literature data it becomes obvious that different kinetic laws have been established and different

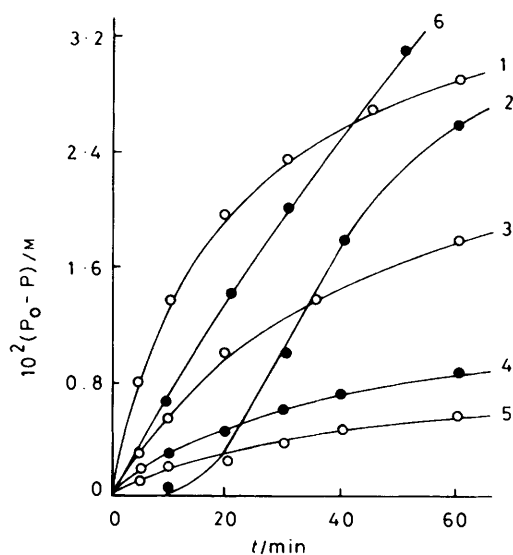


Figure 1. The kinetic curves of the peroxydisulphate consumption in the presence of oxygen (1 and 2), methanol (3), propan-1-ol (4), butanol (5), and propan-2-ol (6) at 45 °C.

mechanisms proposed for the oxidation of alcohols and aldehydes with peroxydisulphate. We think the main reasons for such dissonance are the following: (1) the reaction mixtures are not completely free from dissolved oxygen; (2) the influence of reagent concentrations on the reaction rate has not been studied over a wide range. (3) each elementary reaction has not yet been sufficiently studied. This refers mainly to the mechanism of the chain-initiation step.

Experimental

Potassium peroxydisulphate recrystallized five times from bidistilled water was used. Alcohols were distilled twice in an oxygen-free medium and the purity was checked chromatographically. Bidistilled water was stored in Pyrex apparatus.

An aqueous solution of peroxydisulphate was purified using oxygen-free nitrogen at 10^{-2} Torr after freezing and refreezing the solution with liquid nitrogen 4–5 times (0.002% oxygen nitrogen). Alcohol was degassed with nitrogen and was then injected into the reaction vessel immersed in a thermostat (± 0.05 °C). The rate dependence on the initial concentrations of peroxydisulphate and alcohols was studied in the range $0.005 \leq [P]_0 \leq 0.05M$ and $0.002 \leq [ROH]_0 \leq 0.02M$ correspondingly. The study of the effect of acetic acid ($[CH_3COOH]_0 \leq 0.02M$) on the rate of the reaction $P + EtOH$ shows that it has no influence on the overall rate of peroxydisulphate decomposition.

The rate of peroxydisulphate disappearance was determined iodometrically. Aldehydes were quantitatively identified polarographically and carbonic acids chromatographically as their ethyl esters.

Using this method no sigmoid kinetic curves were obtained. When traces of oxygen were present in the reaction mixture, an autocatalytic run was registered (see Figure 1, curve 2).

Results and Discussion

The Macrokinetic Law.—The investigation of the reaction of peroxydisulphate with ethanol at 35 °C in the absence of oxygen²¹ shows that the rate law of peroxydisulphate (P) decomposition is (12) where $n = 1/2$ in the range $0 < [EtOH]_0$

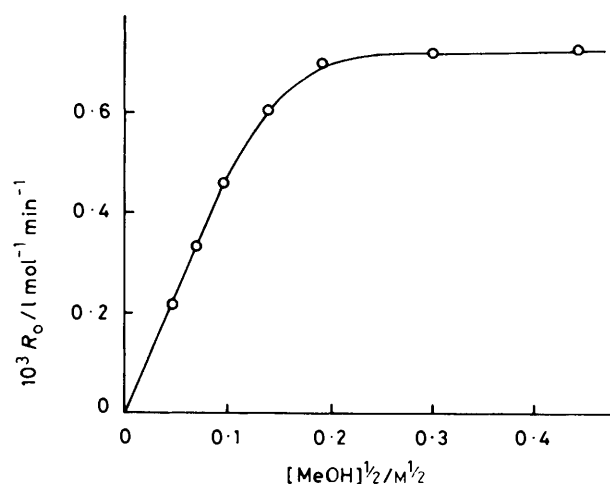


Figure 2. The dependence of the initial rate of the peroxydisulphate-methanol reaction on the concentration of methanol at 45 °C

$\leq 0.2M$. $n < 1/2$ when $[EtOH]_0 > 0.2M$. In the temperature range 25–45 °C the overall energy of activation is 17.7 kcal mol⁻¹.

$$(-d[P]/dt)_{t=0} = k[P]_0[EtOH]_0^n \quad (12)$$

As we have mentioned above, when oxygen traces are present, the kinetic curves have a sigmoid shape. In the steady-state region the rate may be expressed by equation (13) with an

$$(-d[P]/dt)_{t=0} = k[P]_0^{3/2}[EtOH]_0^{1/2} \quad (13)$$

overall energy of activation of 24.0 kcal mol⁻¹. Such deviations have been reported in refs. 1, 2, and 14.

In the case of methanol oxidation the order in alcohol changes from 1/2 to 0 (see Figure 2). When $[CH_3OH]_0 \geq 0.04M$, the rate does not depend on alcohol concentration. Similar data have been obtained for propan-1-ol, propan-2-ol, and butanol oxidation. The order of the reaction for peroxydisulphate also changes from 1 to 3/2 when its initial concentration increases for all the cases investigated.²²

So we have to deal with a similar phenomenon which does not depend on the nature of the alcohol. At low initial alcohol concentrations we have equations (14) and at high initial concentrations, when the concentration of alcohol is 'limiting', (15). Some kinetic parameters are in Table 1. It is of interest that

$$(-d[P]/dt)_0 = k'[P]_0[Alc]_0^{1/2} \quad (14)$$

$$(-d[P]/dt)_0 = k''[P]_0^{3/2} \quad (15)$$

the overall energy of activation is virtually independent of the nature of the alcohol (see Table 1).

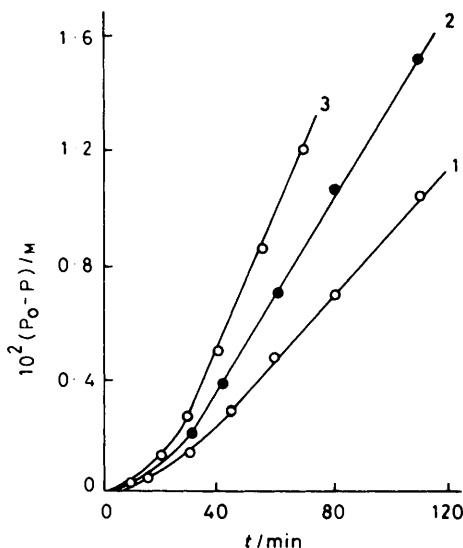
Only the peroxydisulphate-propan-2-ol reaction proceeds normally to high conversions. There is autoinhibition in the case of the oxidation of primary alcohols with peroxydisulphate due to the aldehydes, which are the initial products of alcohol oxidation.²³

Our experimental data undoubtedly show that peroxydisulphate-alcohol reactions are radical-chain as has previously been mentioned.^{3,5,7}

Kinetics and the Mechanism of the Chain-initiation Step.—It has already been shown that the mechanism of the initiation step is unclear. The reason is the absence of rigorous kinetic

Table 1. Some kinetic parameters for peroxydisulphate-alcohol reactions

Alcohols	MeOH	EtOH	PrOH	BuOH	[Pr ¹ OH]
'Limiting' concentration of alcohol (M)	0.04	2	0.04	0.08	0.04
Overall E_a /kcal mol ⁻¹	17.1	17.7	16.9	18.7	
Initial rate $10^4/R_0$ l mol ⁻¹ min ⁻¹	7.06	15.60	4.60	2.70	8.20
Mean kinetic chain length	247	546	161	95	288

**Figure 3.** Kinetic curves for the consumption of peroxydisulphate in the peroxydisulphate-ethanol reaction in the presence of inhibitor (1×10^{-5} M) and at $[P]_0$ 0.04 M, $[EtOH]_0$ 0.05 (1), 0.2 (2), and 0.4 M (3) (θ 35 °C)

data. Using the inhibitory method, we have investigated the kinetics and the mechanism of primary radical formation. As a radical scavenger the stable nitroxide free radical has been used. The concentration of the scavenger was *ca.* 10^{-5} M. The initiation rate has been calculated using formula (16), where f is

$$R_0 = f[InH]_0/\tau \quad (16)$$

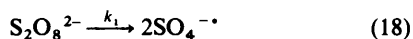
the stoichiometric coefficient of the inhibition, $[InH]_0$ is the initial scavenger concentration, and τ is the induction period. It must be noted that in the presence of InH there is complete inhibition of the reaction.

From the data of Table 2 we can deduce equation (17). It has

$$R_0 = k_1[P] \quad (17)$$

been shown that R_0 is zero order in EtOH (see Figure 3).

Similar data have been obtained for other alcohols. So the chain-initiation step is the monomolecular homolysis of P [reaction (18)]. The temperature dependence of k_1 has been



studied in the range 30–45 °C. From Table 3 we can derive equation (19).

$$k_1/\text{min}^{-1} = \frac{1}{2}k_1 \times 3.0 \times 10^{15} \exp(-29\,000 \pm 1\,000)/RT \quad (19)$$

The values of k_1 and E_a are in good accord with Kolthoff's and Miller's data obtained for the decomposition of peroxydisulphate in neutral aqueous solutions.²⁵

Table 2. The dependence of τ on the peroxydisulphate concentration at $[EtOH]_0$ 0.2 M and 35 °C²⁴

$10^2[P]_0/M$	2.0	3.0	4.0	4.9
τ/min	34	24	18	13

Table 3. Dependence of k_1 on temperature

$\theta/^\circ\text{C}$	30	35	40	45
$10^5 k_1/\text{min}^{-1}$	0.35	0.75	1.52	3.55

Table 4. Dependence of the initial rate of peroxydisulphate decomposition in the presence of ethanol and different amounts of added aldehyde: $[P]_0$ 0.04 M, $[EtOH]_0$ 0.2 M, θ 35 °C

$[Aldehyde]_0/M$	0	0.02	0.05	0.1	0.2
$10^4 R_0/\text{l mol}^{-1} \text{min}^{-1}$	6.3	4.6	3.4	2.5	2.5

The mean kinetic chain length has been calculated from the values of overall and initial reaction rates ($\bar{\nu} = R_0/R_0$). These values have been reported in ref. 22. The values for 45 °C are in Table 1.

For the initial period of the reaction when it is not complicated by products, the mechanism (20)–(24) is valid. In the case of propan-2-ol oxidation acetone is formed in place of aldehyde. When $\bar{\nu} \gg 1$ we can write equation (25). It is easy to show that equations (14) and (15) are particular cases of the general equation (25).



$$R_0 = -d[P]/dt = k_3(2k_1k_2)^{1/2}[P]^{3/2} [Alc]^{1/2}/(2k_3k_4[P] + k_2k_5[Alc])^{1/2} \quad (25)$$

When the concentration of alcohol is low, we have equation (26). When the concentration of alcohol is equal to or more than the 'limiting' values, equation (27) holds. It is obvious that the mechanism of chain termination depends on the initial concentration of alcohol.

$$-d[P]/dt = (k_1k_2k_3/k_4)^{1/2}[P][Alc]^{1/2} \quad (26)$$

$$-d[P]/dt = (2k_1/k_5)^{1/2}[P]^{3/2} \quad (27)$$

Mechanism of the Autoinhibition of the Oxidation of the Primary Alcohols.—Autoinhibition is due to the action of the

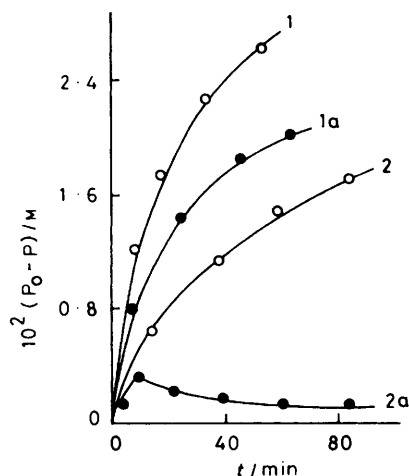


Figure 4. Kinetic curves of peroxydisulphate consumption (1 and 2) and acetaldehyde accumulation (1a and 2a) at $[P]_0$ 0.04M, $[\text{EtOH}]_0$ 0.2M (1); $[P]_0$ 0.02M, $[\text{EtOH}]_0$ 0.02M (2) (θ 40 °C)

aldehyde, the initial product of alcohol oxidation, on the overall rate of peroxydisulphate decomposition. From Table 4 we can conclude that R_0 diminishes with an increase of the amount of the aldehyde which is added to the initial reaction mixture P + alcohol.

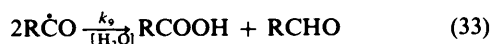
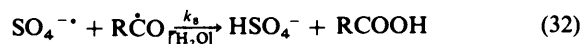
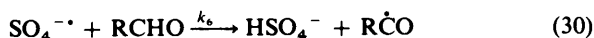
In ref. 23 it has been shown that the aldehyde is oxidized as well. When the ratio $[P]/[\text{EtOH}]$ increases, the rate of aldehyde accumulation diminishes (see Figure 4).

There is no doubt that RCHO may be further oxidized to the corresponding carboxylic acid. It has been established that there is apparent decomposition of peroxydisulphate in aqueous solutions of aldehydes at 40 °C. These reactions are also radical-chain processes. Oxygen inhibits the reaction. There is a 'limiting' concentration for RCHO. When its value is more than the 'limiting' concentration, the reaction P + RCHO is zero order in regard to RCHO. The overall rate law in this case is (28). The chain-initiation step is monomolecular homolysis of $\text{S}_2\text{O}_8^{2-}$.²³ At 40 °C $\bar{\nu} = 350$ for the reaction P + AcH.

$$-d[P]/dt = k[P]^{3/2} \quad (28)$$

Assuming that the product of RCHO oxidation is RCOOH and the latter has practically no effect on the overall reaction rate,²⁶ a linear relationship must hold between $([P] - x)^{1/2}$ and time, as found.²³

So for the RCHO oxidation we have the mechanism (29)—(33). At high aldehyde concentration equations (34) holds, which is similar to the empirical law (28).



$$-d[P]/dt = k_7(2k_1/k_9)^{1/2}[P]^{3/2} \quad (34)$$

So in order fully to describe the oxidation of alcohols with peroxydisulphate it is indispensable to take into account reactions (20)—(33).

The following question arises logically. If RCHO also induces radical-chain decomposition of persulphate, why does it inhibit the reaction P + RCH₂OH? The reason lies in the values of the mean chain length of both reactions: $\bar{\nu}_{\text{P}+\text{RCHO}} < \bar{\nu}_{\text{P}+\text{RCH}_2\text{OH}}$. This may be explained by assuming that the free radical R $\dot{\text{C}}\text{O}$ is less reactive toward $\text{S}_2\text{O}_8^{2-}$ than the corresponding R $\dot{\text{C}}\text{HOH}$ radical. So in the course of the reaction more reactive radicals are displaced by less reactive ones. It means that $R_{\text{R}\dot{\text{C}}\text{O}+\text{S}_2\text{O}_8^{2-}} < R_{\text{R}\dot{\text{C}}\text{HOH}+\text{S}_2\text{O}_8^{2-}}$.

The kinetic rate law which is derived from all the probable reactions (20)—(33) is (35). From this equation one can easily derive equations corresponding to all cases which are experimentally established.

$$-d[P]/dt = \frac{k_2k_3k_7[\text{Alc}] + k_3k_6k_7[\text{Ald}]}{k_3k_6[\text{Ald}] + k_2k_7[\text{Alc}]} (2k_1/k_9)^{1/2}[P]^{3/2} \quad (35)$$

If this hypothesis is true, then upon adding methanol to a P + EtOH mixture the rate of the latter reaction is diminished because $\bar{\nu}_{\text{P}+\text{CH}_2\text{OH}} < \bar{\nu}_{\text{P}+\text{EtOH}}$. This assumption is experimentally affirmed.

Using this hypothesis it is possible to explain the result postulated in ref. 14 according to which the addition of butan-2-ol diminishes the rate of the reaction between peroxydisulphate and propan-2-ol. This result was explained by assuming complex formation between peroxydisulphate and butan-2-ol which is not experimentally proved.

Thus in summary we can affirm that alcohols and aldehydes are oxidized with peroxydisulphate by a similar radical-chain mechanism as above at various temperatures with different rates.

In ref. 27 it is shown that compounds with ionization potentials > 9.5–10 eV are unable to react directly with peroxides, particularly with peroxydisulphate. The ionization potentials are: for acetone 9.7 eV, for alcohols and aldehydes 10–11 eV. So theoretically they do not react directly with peroxydisulphate which is in complete agreement with predictions expressed in ref. 27.

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