The OsO_4-catalysed Decomposition of Hydrogen Peroxide

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The decomposition of H_2O_2 has been investigated in the presence of OsO_4 as a catalyst. The rate of decomposition is proportional to the first power of the OsO_4 concentration and to the power 1—1.2 of the hydrogen peroxide concentration. The pH dependence of the decomposition rate is quite characteristic; a high maximum is attained at pH 10.6 and a much lower one at about pH 8.3. With the aid of appropriate free-radical reagents and by e.s.r. spectrometry, it is shown that hydroxyl and superoxide radicals are formed during the catalysed decomposition. The rate of formation of the OH radical depends on the concentrations of H_2O_2 and OsO_4, as well as on the pH. The rate of bleaching of *N*-dimethyl-*p*-nitrosoaniline and other dyes by the OH radical as a function of pH exhibits a maximum at pH 8.3. The OH radical is of both primary and secondary origin, and is involved in a chain reaction. The length of the chain is about 80—90 at pH < 8, while at pH > 9 this value drops to *ca.* 10 and is independent of the pH. The apparent activation energy of the reaction route involving the OH radical is 105—111 kJ mol^{-1} at pH < 9, 35—40 kJ mol^{-1} at pH > 10. Another decomposition route parallels that involving the OH radical, and predominates at pH > 9.5. In this case the catalysed decomposition can be approximated on the assumption that peroxo-osmate anion acts as a nucleophile towards the non-dissociated hydrogen peroxide molecule. The temperature dependence of this rate component gives an apparent activation energy of 60 kJ mol^{-1} at pH < 9, *ca.* 15 kJ mol^{-1} at pH > 10.

In weakly alkaline media osmium tetraoxide is a very efficient catalyst for the decomposition of hydrogen peroxide. Its catalase-like effectiveness has long been used for the quantitative removal of H_2O_2 in chemical analysis. In addition, a H_2O_2–OsO_4 mixture is frequently used in preparative organic chemistry as an hydroxylating agent, and consequently it is surprising that very little is known of the mechanism of the catalysed reaction.

Chugaev and Bikerman [1] found that the rate of the catalysed decomposition varied according to a curve with a maximum when different quantities of sodium hydroxide were added to the solution. The maximum was observed in the presence of 0.001—0.005 mol dm^{-3} sodium hydroxide. At lower concentrations the decomposition rate was proportional to the amount of OsO_4.

From a study of the γ-radiolysis of an acidic solution containing OsO_4 and H_2O_2, Dran [2] concluded that a catalysed decomposition reaction takes place, involving *O*-containing radicals and osmium(VII). Domka and Marciniec [3] followed the decomposition of H_2O_2 and the oxidation of indigo carmine catalysed by OsO_4 in a slightly acidic medium. They put forward alternative suggestions regarding the mechanism of the reaction. Lunenok-Burmakina [4] found that the dioxygen evolved during the catalysed decomposition of hydrogen peroxide arose solely from H_2O_2, and stated that the OH radical could be detected in the catalysed process at *ca.* pH 10.[5]

We have carried out investigations to try to shed light on the kinetics of the catalysed decomposition of hydrogen peroxide and on the role of osmium tetraoxide in this process. In the present paper some characteristic features of the catalysed reaction are elucidated.

EXPERIMENTAL

All reagents used were of analytical grade. The stock solutions of the catalyst were prepared from OsO_4 (Merck) dissolved in water (10^{-4} mol dm^{-3} OsO_4) or in 0.02 mol dm^{-3} sodium hydroxide solution (0.02 mol dm^{-3} OsO_4). They were stored in the dark in a refrigerator and were freshly diluted before use. The hydrogen peroxide solution was prepared from stabilizer-free Merck Perhydrol.

Ordinary distilled water was redistilled from alkaline permanganate, and was then passed through columns of Amberlite IR-120 and Dowex 50 ion-exchange resins in H^+ form. Afterwards it was boiled with potassium peroxodisulphate (1 g dm^{-3}) for *ca.* 30 min, neutralised with purified sodium hydroxide solution, and distilled from a Pyrex apparatus. Sodium hydroxide and sodium sulphate solutions were purified according to the method of D'Ans and Mattner.[6]

Methanol, ethanol, propan-2-ol, n-butanol, acrylonitrile, and methyl methacrylate were distilled twice before use. The stable free radical of 2,2,5,5-tetramethyl-4-phenylimidazolin-1-oxyl 3-oxide (denoted as tmpio) was prepared as described by Putirskaya and Matus.[7]

In preliminary experiments, attempts were made to remove insoluble impurities by filtering the solutions through a Millipore filter with a pore size of 0.2 μm, but since no difference was found between the rates of reaction of the filtered and unfiltered mixtures, this step was subsequently omitted.

Apparatus.—A Radiometer pH 26 pH-meter was used for pH measurements, and this meter combined with a Radiometer TTT Titrator and an ABU automatic syringe burette filled with acid was used as pH-stat. Spectrophotometric measurements were made with Unicam SP 500, SP 800, and Beckman DB-G spectrophotometers. A JEOL-JES-PE spectrometer was used for e.s.r. measurements.

Methods.—Concentrations of osmium tetraoxide solutions were determined spectrophotometrically with the aid of anthranilic acid [8] or thiourea [9] reagents, and by potentiometric titration using standard arsenite solution.[10]

The concentration of hydrogen peroxide was determined either spectrophotometrically or by titrimetry. In the former case the sample was added to a 15—50 fold excess of an acidified iron(II) solution, and after 30 min the absorbance of the iron(III) formed was measured at 304 nm. In other

cases the sample containing H_2O_2 was added to a known quantity of an acidified standard arsenite solution, the excess of which was titrated cerimetrically. The direct oxidimetric titration of hydrogen peroxide is not advisable in the presence of higher concentrations of OsO_4 ($>10^{-6}$ mol dm^{-3}), since the cerimetric (or permanganometric) titration is accompanied by an induced decomposition of H_2O_2.[11]

The volume of dioxygen evolved during the reaction was measured either with an automatic gas-measuring device [12] or with the simple apparatus shown in Figure 1. When

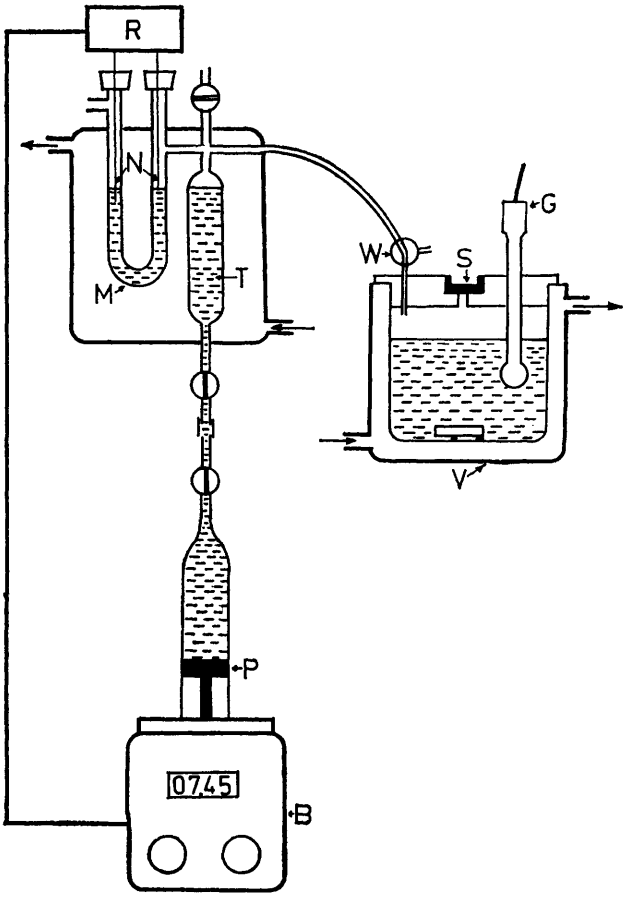

FIGURE 1 Outline of apparatus used for the determination of dioxygen formed. (V) = Pyrex reaction vessel; (S) = septum; (M) = manometer; (N) = platinum wire; (R) = relay and amplifier; (B) = syringe burette; (P) = plunger; (T) = thermostatted space filled with water at the start; (G) = glass electrode; (W) = three-way tap

dioxygen is evolved, the level of 1 mol dm^{-3} H_2SO_4 in the manometer (M) moves downwards and breaks the contact between the platinum wire (N) and the sulphuric acid; this actuates the relay (R) of the motor of a slightly modified (reversed-phase) Metrohm Dosimat E 415 syringe burette (B). The plunger (P) moves down, sucks water out of the space (T) to restore the level of the manometer, and the motor stops. The volume of gas evolved can be read off the meter of the Dosimat as a difference. The sensitivity is ± 0.02 cm^3.

Kinetic Measurements.—The measurements were made at 25 $\pm$ 0.05 °C, unless stated otherwise. The ionic strength was maintained at a constant value with the use of $Na_2[SO_4]$ or $Na[ClO_4]$ (1 mol dm^{-3} Na^+). Decomposition of hydrogen peroxide was followed by two methods: (*i*) by gas volumetry, and (*ii*) by measuring the concentration of H_2O_2 in samples taken from the reaction mixture at given time intervals.

In the gas-volumetric measurements 42 or 49 cm^3 buffered hydrogen peroxide solution were placed in the reaction vessel [Figure 1 (V)] and thermostatted for 20 min. The reaction was started by injecting 1.00 cm^3 OsO_4 catalyst solution through the septum (S) and the three-way tap (W) was turned in the manometer direction.

To minimize loss of OsO_4 by evaporation, in some experiments a 20-cm^3 all-glass syringe (fitted with a thermostat jacket) was used as reaction vessel. The buffered hydrogen peroxide solution was thermostatted in a separate beaker. The reaction was started by introduction of the catalyst, and reaction mixture was sucked into the syringe. The syringe was aligned vertically and the gas was displaced by the plunger. The tip of the syringe was connected by a Teflon tube to a pipette (1 cm^3) used for sampling. Some measurements were performed in a Teflon reaction vessel fitted with a thermostat jacket.

The rate of consumption of the inhibitor dyes was determined spectrophotometrically. To this end the pre-thermostatted components of the reaction mixture [solutions (1) and (2)] were mixed by a simple (two-jet) device made of glass, connected to the flow-through cell of appropriate light path in the thermostatted cell housing of a Beckmann DB-G spectrophotometer. The cells were supplied by two all-glass syringes (5 cm^3), the plungers of which were actuated manually *via* a common shaft. The syringes could be filled and emptied separately. The composition of solution (1) was buffer + OsO_4 solution, and that of solution (2) was buffer + H_2O_2 + dye solution. The change in absorbance was recorded at the appropriate wavelength and at a chart speed yielding satisfactory time resolution.

Evaluation of Kinetic Results.—Concentration *vs.* time curves were used to determine the initial rates. Initial rates were also obtained numerically. In some cases, when the gas volume *vs.* time curves showed short incubation periods due to the fact that the reaction mixture was not saturated with O_2, only the sufficiently linear parts of the curves were used to determine the initial rates.

RESULTS

Dependence on the Concentration of Hydrogen Peroxide.—When the logarithm of the hydrogen peroxide concentration or the logarithm of the volume of dioxygen evolved was plotted *vs.* time the curves obtained were virtually linear up to *ca.* 30% conversion (Figure 2). Departure from linearity indicates that the power of the hydrogen peroxide concentration in the rate equation is greater than one. It

$$R = -\mathrm{d}[H_2O_2]/\mathrm{d}t = k_{obs.}[H_2O_2]^n$$

was found that $n = \mathrm{d}(\log R)/\mathrm{d}(\log [H_2O_2])$ is in the range 1—1.2, and increases as the hydrogen peroxide concentration decreases during the run.

Loss of OsO_4.—When the decomposition was followed up to a conversion of at least 90%, and measurements were repeated after the initial concentration had been readjusted by adding concentrated hydrogen peroxide solution, observable departures between the first and the later runs were not found (see Figure 2). At concentrations of osmium tetraoxide higher than 10^{-5} mol dm^{-3} the concen-

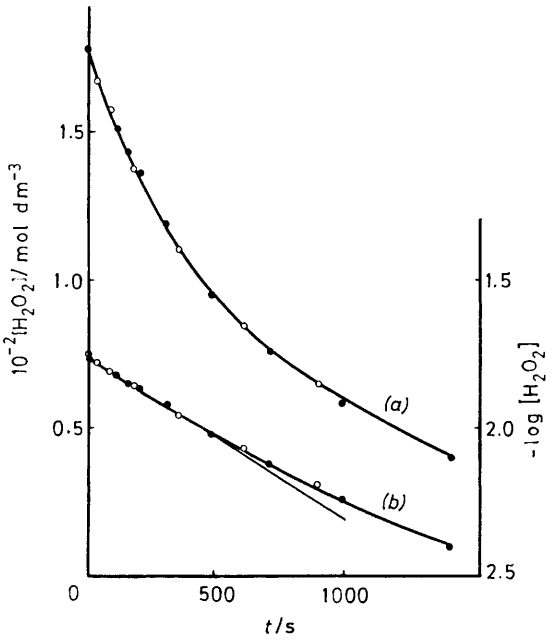

FIGURE 2 Kinetic curves for catalysed decomposition. Conditions: pH 9.65 maintained by pH-stat; 3×10^{-8} mol dm^{-3} OsO_4; 298 K; ionic strength: 1 mol dm^{-3} Na^+ adjusted with $Na_2[SO_4]$. Curves: (*a*) concentration *vs.* time curve, (○) first run, (●) second run, the initial concentration having been re-adjusted with concentrated H_2O_2; (*b*) log $[H_2O_2]$ *vs.* time

tration of the catalyst was estimated by spectrophotometry. The loss of the catalyst never exceeded 1—1.5%, even at pH 8.

Dependence on the Neutral-salt Concentration.—When decompositions were carried out at different ionic strengths (maintained by $Na_2[SO_4]$ or $Na[ClO_4]$ in the range 0.05—1.0 mol dm^{-3}), the decomposition curves coincided exactly.

Dependence on the pH *and Influence of Buffers.*—The rate of decomposition depends strongly on the pH. A plot of the initial rate *vs.* pH exhibits two maxima; a high maximum at *ca.* pH 10.6 and a considerably lower one at *ca.* pH 8.3 (Figure 3). The height of the lower maximum depends greatly on the quality (phosphate, borate, carbonate, *etc.*) and the quantity of the buffering substances, while the larger one does not show such a dependence. The smaller maximum, superimposed on the ascending arm of the larger maximum, appears as an increase of a few percent of the local decomposition rate in the absence of buffers. Otherwise, in the ascending part of the rate *vs.* pH curve, the rate is proportional to $1/[H^+]$ (Table 1).

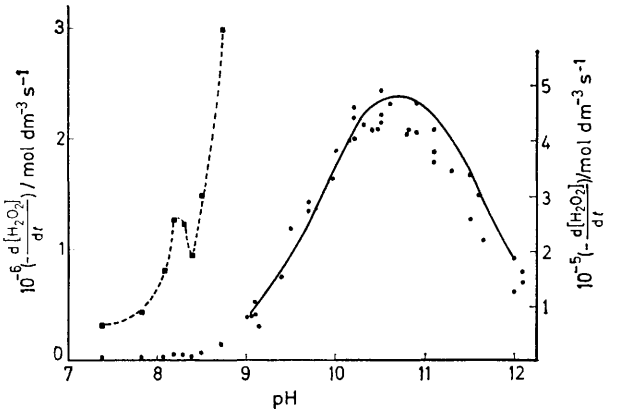

FIGURE 3 pH Dependence of the initial rate of catalysed decomposition. Conditions: 1.8×10^{-2} mol dm^{-3} H_2O_2; 3×10^{-8} mol dm^{-3} OsO_4; 298 K; ionic strength: 1 mol dm^{-3} Na^+ adjusted with $Na_2[SO_4]$; pH maintained by pH-stat by adding H_2SO_4. (●) and (■), measured values; (——), calculated *via* equation (8)

Dependence on the Concentration of OsO_4.—In the range pH 9—12 the initial rate was proportional to the concentration of the catalyst in the interval 10^{-9}—10^{-6} mol dm^{-3}. At lower pH and higher concentrations of OsO_4 the power of the catalyst concentration m in the rate equation (i) is

$$R = k[OsO_4]^m[H_2O_2]^n \qquad \text{(i)}$$

less than one. When the concentration of osmium tetraoxide reaches or exceeds 10^{-3} mol dm^{-3} the rate becomes independent of the catalyst concentration. In such cases the reproducibility of the decomposition reaction is poorer.

Effect of Radical Scavengers at pH > 9.5.—The rate is not observably affected by acrylonitrile (10^{-5}—10^{-3} mol dm^{-3}, methyl methacrylate (10^{-4}—10^{-2} mol dm^{-3}), ethanol (10^{-1} mol dm^{-3}), or H_4edta (ethylenediaminetetra-acetic acid, 10^{-3} mol dm^{-3}) at pH > 9.5. In the presence of acrylonitrile or methyl methacrylate no polymer precipitation was observed. It should be noted, however, that polymer precipitation could not be observed either when an dioxygen-saturated solution containing 0.2 mol dm^{-3} acrylonitrile at pH 10.6

TABLE 1

Values of the exponents of the concentrations (mol dm^{-3}) in the rate equation for the catalysed decomposition, Rate = constant . $[OsO_4]^m[H_2O_2]^n[H^+]^p$

Range of variation	Fixed parameters		Exponent [a]		
			m	*n*	*p*
$[OsO_4]$	$[H_2O_2]_0$	pH			
5×10^{-5}—1×10^{-3}	5×10^{-2}	5.4 [b]	0.62 (10)		
6×10^{-7}—8×10^{-6}	2×10^{-2}	7.7 [b]	0.81 (9)		
1×10^{-8}—8×10^{-8}	2×10^{-2}	10.8 [c]	0.98 (7)		
$[H_2O_2]_0$	$[OsO_4]$	pH			
9×10^{-3}—9×10^{-2}	3×10^{-8}	10.8 [c]		1.11 (8)	
pH	$[OsO_4]$	$[H_2O_2]_0$			
4.3—6.3 [d]	2.7×10^{-3}	5×10^{-2}			−1.00 (11)
6.2—7.5 [b]	1.6×10^{-5}	2×10^{-2}			−1.05 (10)
9.0—9.5 [c]	3×10^{-8}	2×10^{-2}			−1.01 (6)

[a] The figures in brackets are the numbers of experiments from which the exponents were determined. [b] By using 0.1 mol dm^{-3} phosphate buffers. [c] Maintained with the aid of a pH-stat using dilute H_2SO_4. [d] Adjusted by adding acid or alkali at the beginning.

was irradiated with (cobalt-60) γ-rays for 30 min or longer at a dose rate of 2.5×10^{14} eV dm^{-3}.*

Detection of the OH *Radical.*—Because of the high reactivity of the OH radical its direct detection by e.s.r. spectroscopy was not attempted. However, the stable radical tmpio is a selective reagent for the OH radical in the presence of O_2^-, H_2O_2, and O_2.[7] As the adduct formed in the interaction between tmpio and the OH radical is e.s.r.-inactive, the e.s.r. signal decreased in proportion with the quantity of the OH radical formed. Further evidence for the presence of the OH radical in the reaction mixture was obtained with the aid of an α-phenyl-*N*-t-butylnitrone, PhCH=N(O)Bu^t. The hyperfine splitting of the e.s.r. spectrum suggests the simultaneous presence of OH and O_2^- radicals. Both radicals furnished the corresponding e.s.r.-active *N*-oxyl radical.[13] When the OH radical was

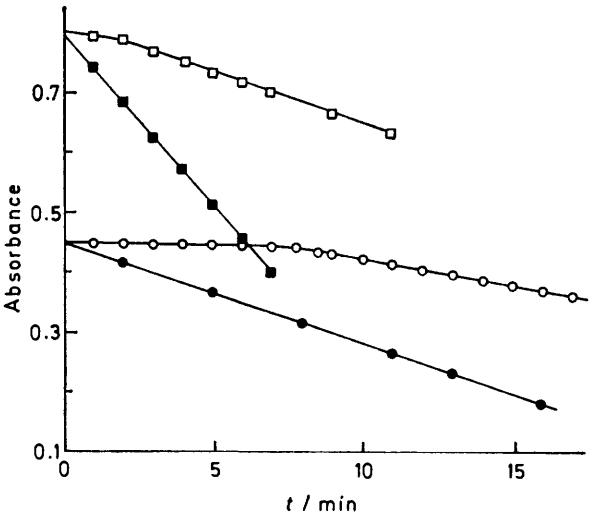

FIGURE 4 Influence of tnm on the bleaching of RNO at different pH values. Conditions: 298 K; light path length 0.1 cm, wavelength 420 nm. Curves: (□), pH 8.0, 1.0×10^{-6} mol dm^{-3} OsO_4, 3.1×10^{-2} mol dm^{-3} H_2O_2, 2.4×10^{-4} mol dm^{-3} RNO, 2.3×10^{-4} mol dm^{-3} tnm; (■), pH 8.0, 1.0×10^{-6} OsO_4, 3.1×10^{-2} H_2O_2, 2.4×10^{-4} RNO, 0.0 tnm; (○), pH 7.55, 2.20×10^{-6} OsO_4, 2.92×10^{-2} H_2O_2, 1.31×10^{-4} RNO, 3.02×10^{-4} tnm; (●), pH 7.55, 2.26×10^{-6} OsO_4, 2.92×10^{-2} H_2O_2, 1.31×10^{-4} RNO, 0.0 tnm

removed with *N*-dimethyl-*p*-nitrosoaniline (denoted RNO),[14] *N*-oxyl radical production was observed, although in a lower yield. The *N*-chloro- and *N*-bromo-derivatives of 4-hydroxy-2,2,6,6-tetramethylpiperidine [15, 16] could not be used successfully for detection of the O_2^- radical.

Further, the bleaching of RNO was measured as a function of the concentration of various competitor molecules (comp). The corresponding relative rate constants were determined by plotting $1/\Delta$[RNO] *vs.* [comp]/[RNO], and using the value $k_{OH+RNO} = 1.25 \times 10^{10}$ dm^3 mol^{-1} s^{-1},[17] the absolute rate constants were also calculated. The data obtained were compared with those in the literature and furnished further evidence for the participation of the OH radical in the OsO_4-catalysed decomposition of hydrogen peroxide.

Effect of Tetranitromethane (tnm) *on the Bleaching of* RNO.—In order to learn whether OH or O_2^- radicals are the primary species in the reaction route involving the OH radical, the bleaching of RNO was investigated in the presence of increasing quantities of tnm. It was found that the bleaching of RNO can be considerably inhibited by tnm. When the tnm has been consumed quantitatively, the bleaching of RNO immediately sets in with a higher rate (Figure 4).

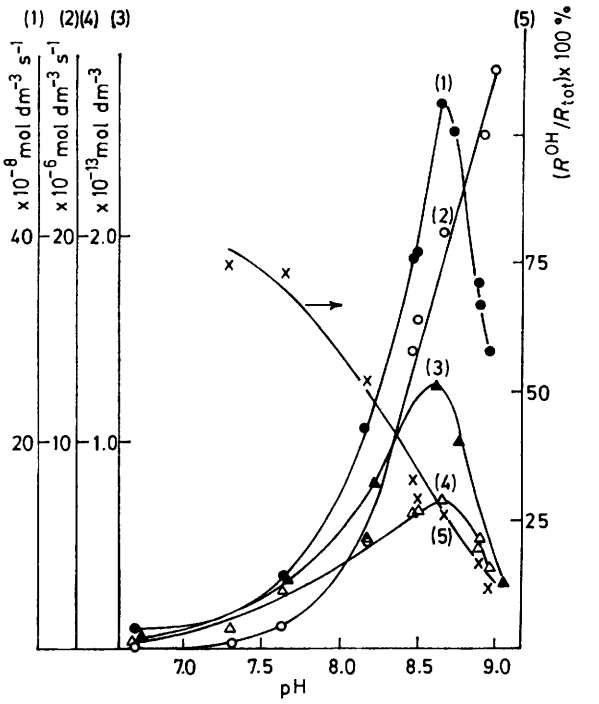

FIGURE 5 pH Dependence of the rate components for the decomposition of hydrogen peroxide. Conditions: 298 K; 1.74×10^{-7} mol dm^{-3} OsO_4; 8.2×10^{-2} mol dm^{-3} H_2O_2. Curves: (1), rate of initiation involving OH radical, R_i^{OH}; (2), remaining rate; (3), steady-state concentration of OH radical, $[OH]_{stat.}$; (4), rate of reaction *via* OH radical, R^{OH}; (5), 100 R^{OH}/R_{total} *vs.* pH

Estimation of the Steady-state Concentration of the OH *Radical.*—An attempt was made to determine the stationary-state concentration of the OH radical by measuring the rate of bleaching of RNO. It was assumed that this concentration is not influenced appreciably when RNO is added to the reaction mixture in low concentrations ($\approx 10^{-5}$ mol dm^{-3}); then, with the known value of the bleaching rate of RNO ($\Delta A/dt$) and accepting that Δ[RNO]/Δ[OH] = 0.5 for the bleaching reaction,[17] $[OH]_{stat.}$ can be calculated as in (ii) where ΔA is the change in the

$$[OH]_{stat.} = \frac{\Delta A}{dt} \cdot \frac{2}{l\varepsilon k_{OH+RNO}[RNO]_0} \qquad \text{(ii)}$$

absorbance at 420 nm, l the path length, $[RNO]_0$ the initial concentration of the dye, and $\varepsilon = 3.42 \times 10^4$ dm^3 mol^{-1} cm^{-1},[14] the molar absorbancy of RNO at 420 nm. The values obtained can be seen in Figure 5, curve (3).

pH *Dependence of* OH *Radical Formation.*—Besides RNO, a series of dyes of different types were applied in the catalysed decomposition of hydrogen peroxide, such as xylenol orange, *p*-ethoxychrysoidine, methyl red, methylene blue, par [4-(2′-pyridylazo)resorcinol], erythrosine, Congo red, neutral red, and erioglaucin-A. Figure 6 shows that the dyes behave similarly, *i.e.* all are bleached as a function

* Throughout this paper: 1 eV = $1.602\,18 \times 10^{-19}$ J.

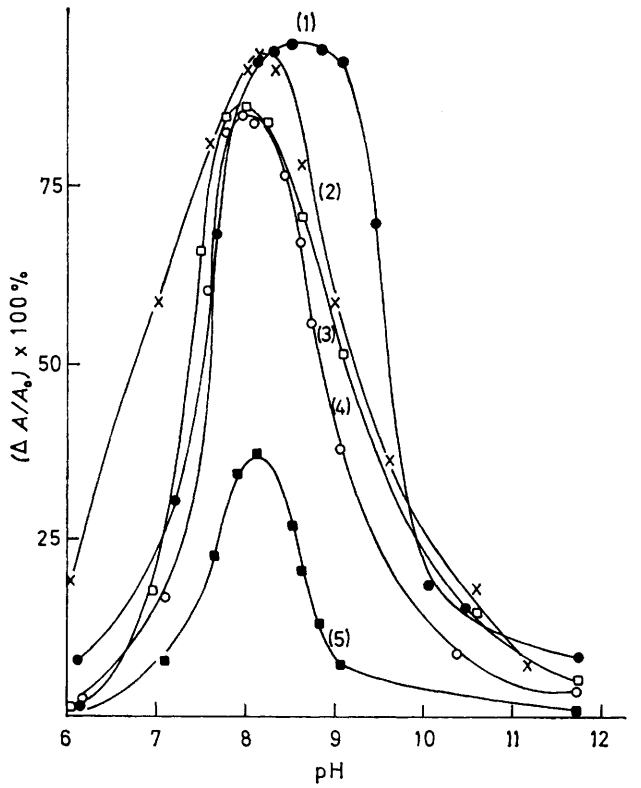

FIGURE 6 Bleaching of different dyes as a function of pH. Conditions: 298 K; 1.43×10^{-7} mol dm^{-3} OsO_4; 1.0×10^{-2} mol dm^{-3} H_2O_2; 0.1 mol dm^{-3} phosphate buffer. Absorbance was measured at the appropriate wavelength after 45 min. Curves: (1), 1.43×10^{-5} mol dm^{-3} methylene blue at 665 nm; (2), 3.32×10^{-5} mol dm^{-3} par at 415 nm; (3), 1.43×10^{-4} mol dm^{-3} erythrosine at 520 nm; (4), 1.85×10^{-5} mol dm^{-3} RNO at 440 nm; (5), 1.43×10^{-6} mol dm^{-3} Congo red at 490 nm

of pH according to a curve which exhibits a maximum. Independently of the structures of the dyes, all the maxima are in the pH range 8.2—8.6.

Rate of Production of OH *Radical.*—The rate of decomposition of H_2O_2 decreases and reaches a lowest limiting value (remaining rate) when RNO or another OH inhibitor is added in increasing quantities to the reaction mixture. At the same time the rate of bleaching of the dye increases and reaches an upper limiting rate. Twice the limiting rate was considered to be the rate of initiation (R_i^{OH}) of the OH radical; R_i^{OH} depends on the pH according to a curve with a maximum at pH 8.6 [Figure 5, curve (1)]. The remaining rate of hydrogen peroxide decomposition or the reduced rate of O_2 evolution shows clearly that the decomposition has another independent route, which is not stopped when all the OH radicals are scavenged [Figure 5, curve (2)].

The difference between the total rate of decomposition (R_{total}) and the remaining rate in the presence of a sufficient quantity of the appropriate scavenger gives the rate of that reaction component which proceeds *via* the OH radical [Figure 5, curve (4)]. The percentage contribution of the OH radical route ($100\ R^{OH}/R_{total}$) is large at low pH and decreases considerably as the pH is increased [Figure 5, curve (5)]; at pH > 9.5 this contribution amounts to only 1—2%.

Dependence of the Rate of Bleaching of RNO *on the Concentrations of* OsO_4 *and* H_2O_2.—The relationship (iii) was

$$R_i^{OH} = \text{constant} \cdot [H_2O_2]^p[OsO_4]^q \qquad \text{(iii)}$$

found, where q was always 1, independent of the pH, while $p = 0.86$ at pH 6.8 and 0.53 at pH 8.3. Similar information is presented in Figure 7, where the changes in the initial rate of decomposition of H_2O_2 and in that of the initiation are plotted as functions of (*a*) the hydrogen peroxide concentration and (*b*) the catalyst concentration on logarithmic scales.

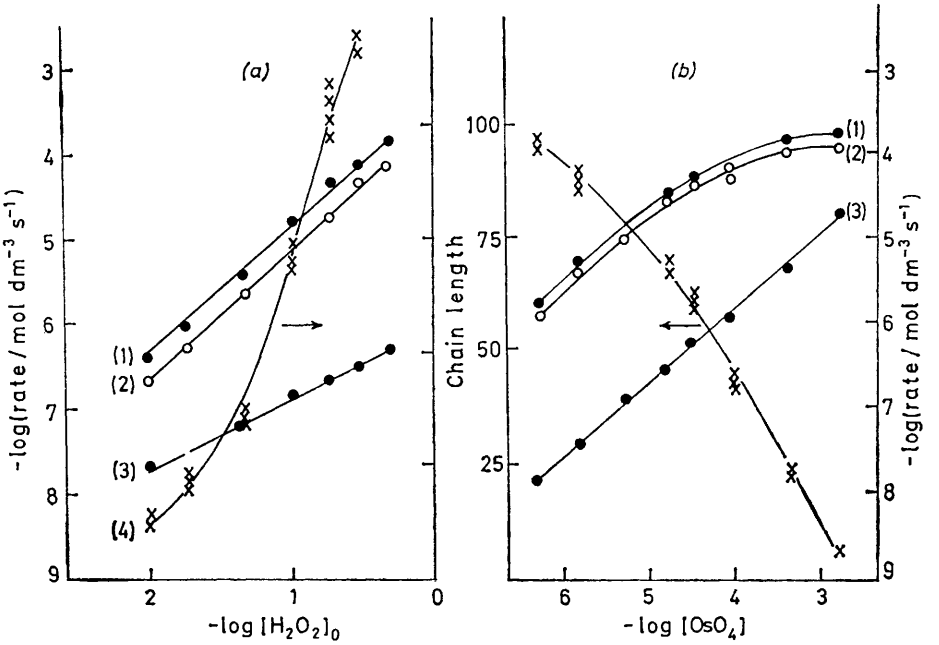

FIGURE 7 Dependence of log rates and of the chain length on the log concentrations of H_2O_2 (*a*) and OsO_4 (*b*), respectively. Conditions: 298 K; pH 6.80; 2.2×10^{-6} mol dm^{-3} OsO_4; and 8.2×10^{-2} mol dm^{-3} H_2O_2, respectively. Curves: (1), log initial overall rate of decomposition of H_2O_2; (2), log initial rate of decomposition of H_2O_2 *via* OH radical; (3), log rate of initiation (log R_i^{OH}); (4), length of reaction chain involving OH radical

Determination of the Length of the Reaction Chain involving the OH *Radical.*—If the difference between the number of moles of hydrogen peroxide decomposed in the absence and in the presence of a scavenger, applied in a quantity sufficient to remove all the OH radical formed, is calculated and divided by twice the number of moles of scavenger oxidised by the OH radical during the same period of time, the length of the chain involving the OH radical can be obtained. The chain length increases as the concentration of H_2O_2 increases but decreases with increasing concentration of OsO_4 [Figure 7(*a*), (*b*), curve (4)]. The values obtained by using different scavengers are in good agreement (Table 2).

TABLE 2

Length of the chain determined by different inhibitors at 298 K, 8.2×10^{-2} mol dm^{-3} H_2O_2, and 5.80×10^{-6} mol dm^{-3} OsO_4

Inhibitors	*n* (pH 6.80)			*n* (pH 8.10)			
Erioglaucin-A	75	70	69	13.5	13	15	15
Safranine T	73	70	70				
Thymine	78	73	70				
		73					
RNO	77	75	75	12.5	12	10.5	

The chain length was dependent on the pH: at pH 6 it has a value of 80—90, while at pH > 9 it is *ca.* 10 and no longer depends on the pH (Figure 8).

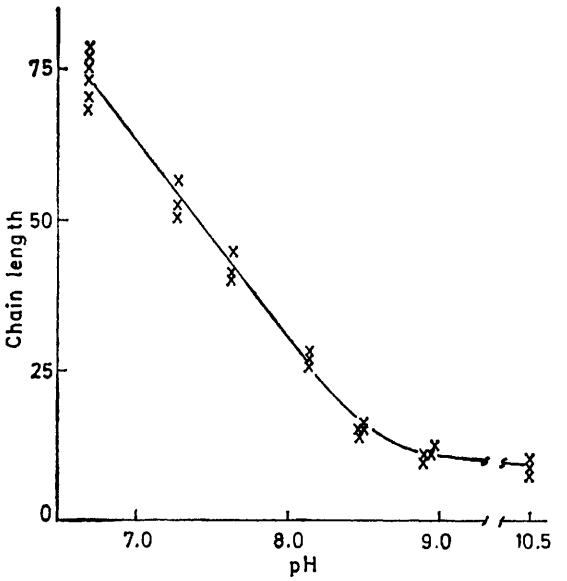

FIGURE 8 Dependence of chain length on pH. Conditions: 298 K; 1.7×10^{-7} mol dm^{-3} OsO_4; 8.2×10^{-2} mol dm^{-3} H_2O_2

Temperature Dependence of the Decomposition Routes of Hydrogen Peroxide.—The temperature dependence of the catalysed decomposition of H_2O_2 was determined in the absence and in the presence of inhibitors (RNO, propan-2-ol, tnm, thymine, *etc.*) by measuring the rate of O_2 evolution and the rates of disappearance of hydrogen peroxide and of the dye molecule. The data obtained (Figure 9) indicate that the apparent energy of activation of the disappearance of inhibitor, *i.e.* of the reaction component involving the OH radical, has a value of 105—110 kJ mol^{-1} at pH < 9, which drops to 35—40 kJ mol^{-1} at pH > 10. The remaining rate component in the presence of radical scavenger also has a temperature dependence of sigmoidal character: the apparent activation energy changes from 60 to *ca.* 15 kJ mol^{-1} when the pH is altered as above. The overall temperature dependence can be calculated from the actual temperature dependences of the reaction components, taking into consideration the actual contributions of the different reaction routes.

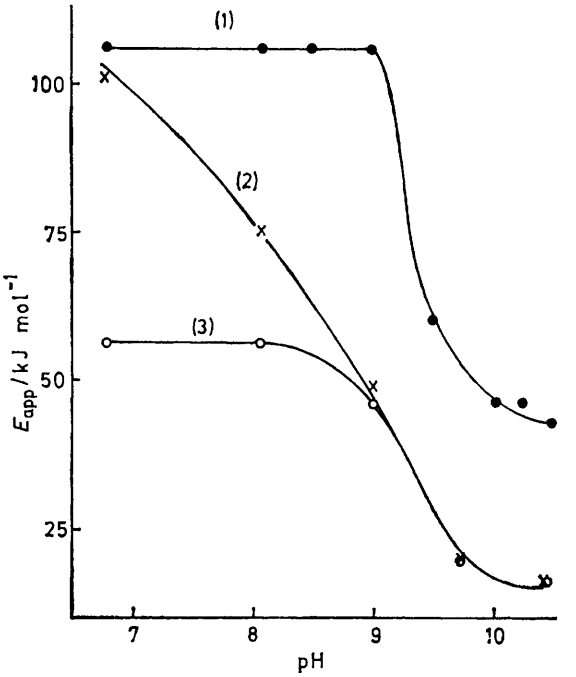

FIGURE 9 pH Dependence of the apparent activation energies. Curves: (1), temperature dependence of bleaching of RNO; (2), temperature dependence of decomposition of H_2O_2; (3), temperature dependence of remaining rate component (total rate minus that of the radical route)

Detection of Osmium(VI).—At pH > 10 osmium(VIII) is reduced by H_2O_2 to an extent depending on the pH. Osmium(VI) was detected by its u.v. absorption spectrum and also by polarography. The formation of different osmium species in the OsO_4–H_2O_2 system will be discussed in a subsequent paper.

DISCUSSION

In the absence of catalyst the decomposition of hydrogen peroxide was found to be very slow and a homogeneous process; the extent of the background (uncatalysed) reaction never exceeded 1% of that of the catalysed one, *i.e.* the contribution of the uncatalysed process can be neglected.

The fact that the dependence of the rate on the concentration of H_2O_2 can be expressed by an exponent of 1—1.2 indicates that the decomposition is a complex process. However, it was shown that this fractional exponent did not arise from the volatility of the OsO_4 or from the purging effect of dioxygen evolution.

Investigations using hydrogen peroxide doubly-labelled with oxygen-18 [4] proved that the dioxygen evolved during the OsO_4-catalysed reaction at pH 10.6 is derived exclusively from hydrogen peroxide molecules,

and neither scrambling of the oxygens of $H_2{}^{16}O_2$ nor admixture of oxygen atoms of the water molecules with the dioxygen was observed. This finding may be used in support of a two-electron mechanism, however, it must be noted that a series of one-electron reactions is possible which also do not require breaking of the O–O bond.

The Non-radical Mechanism pH > 9.5.—From the observation that the rate of decomposition of H_2O_2 is hardly influenced by the addition of radical scavengers, it can be concluded that the decomposition does not take place (or predominantly not) in one-electron steps involving the OH radical. Therefore, an attempt is made below to explain part of the experimental facts assuming two-electron reactions.

As a plausible explanation one may assume that the catalysis occurs *via* a two-equivalent redox cycle in which osmium(VIII) and osmium(VI) species are involved alternately. If it is accepted that the non-dissociated hydrogen peroxide is the more oxidizing species and its anion is the more reducing species, we can write * equations (1)—(3). According to equation (3) the rate

$$OsO_4 + HO_2^- \longrightarrow OsO_3 + O_2 + OH^- \quad (1)$$

$$OsO_3 + H_2O_2 \longrightarrow OsO_4 + H_2O \quad (2)$$

$$-d[H_2O_2]_{anal.}/dt = k_1[OsO_4][HO_2^-] + k_2[OsO_3][H_2O_2] \quad (3)$$

of decomposition will increase with increasing pH. An increase of the peroxide anion concentration is accompanied by an increase in the first rate component. On further increase of the pH the rate of decomposition will decrease, because the reoxidation of OsO_3 will be decreased. From this it follows that the rate of decomposition should show a maximum, but this mechanism cannot account for the experimentally observed dependence of the rate on the concentration of hydrogen peroxide, *i.e.* $n > 1$.

The observed phenomena can be better explained by assuming the formation of peroxo-osmic acid which, being a strong oxidant, attacks free hydrogen peroxide. There is no reference in the literature to the formation of peroxo-osmic acid; its existence can be inferred from the polarographic behaviour of the OsO_4–H_2O_2 system,[18] and the occurrence of an induced reaction when hydrogen peroxide is oxidized by a one-equivalent oxidant [cerium(IV), permanganate] in the presence of osmium tetraoxide.[11] On the other hand, the formation of peroxo-acids is a general phenomenon for the transition metals, and thus this assumption appears to be reasonable by analogy.

In our view, the initial step of the reaction is the formation of peroxo-osmic acid [equation (4)]. At

$$OsO_4 + H_2O_2 \rightleftharpoons O_3Os\begin{matrix}OH\\O(OH)\end{matrix} \quad (4)$$

suitable pH values, this dissociates as an acid [equation (5)]. The rate of decomposition of H_2O_2 does not

$$O_3Os\begin{matrix}OH\\O(OH)\end{matrix} + H_2O \rightleftharpoons O_3Os\begin{matrix}OH\\O^-\end{matrix} + H_3O^+ \quad (5)$$

depend on the ionic strength. In the range pH 10.4—10.9, however, where the maximum rate of decomposition was found, the vast majority of the free hydrogen peroxide is present in the non-dissociated form and this leads us to consider that the peroxo-osmate anion reacts as a nucleophile with non-dissociated hydrogen peroxide [equation (6)]. Taking into consideration the dissociation of hydrogen peroxide [equation (7)], rate equation (8) is obtained.

$$O_3Os(OH)O^- + H_2O_2 \rightleftharpoons [X] \longrightarrow O_2 + OsO_4 + H_2O + OH^- \quad (6)$$

$$H_2O_2 + H_2O \rightleftharpoons HOO^- + H_3O^+ \quad (7)$$

$$-d[H_2O_2]/dt = k_6[OsO_4]_{anal}\,[H_2O_2]_{anal}\,Q \quad (8)$$

where $Q = \frac{f}{1+f} \cdot \frac{1}{1+j+\{j(1+f)/K_4 f[H_2O_2]_{anal}\}}$

with $f = [H_3O^+]/K_7$ and $j = [H_3O^+]/K_5$

It is clear from this equation that the rate of decomposition of hydrogen peroxide is proportional to the analytical concentration of OsO_4 and to that of H_2O_2 raised to a power somewhat greater than one. If the terms not containing hydrogen peroxide are collected together into suitable constants, a simplified rate equation (9) results. By integration of this, the values of

$$-\frac{d[H_2O_2]}{dt} = \frac{[H_2O_2]_{anal}{}^2}{a + b[H_2O_2]_{anal}} \quad (9)$$

a and b giving the best fit to the kinetic curves were determined with a minimizing program. Satisfactory agreement can be attained with this approximation up to about 60—70% conversion (Figure 3 solid line curve).

This mechanism satisfactorily reflects most of the observations in the ranges pH 9.5—12 and $[OsO_4] = 10^{-9}$—10^{-6} mol dm^{-3} up to 60—70% conversion. The remaining experimental facts, *e.g.* that there is another rate maximum at pH 8.3, and the formation of the OH radical, require, however, a more complete explanation.

The Free-radical Mechanism, pH < 9.5.—By using the free-radical reagents tmpio and α-phenyl-*N*-t-butylnitrone, it was demonstrated that the OH radical is formed during the catalysed decomposition. This was supported by experiments with different dyes. It was also found that only restricted formation of the OH radical (RNO bleaching) took place when the superoxide radical was removed with tnm from the reaction mixture. This finding indicates that the OH radical is of both primary and secondary origin. It is assumed that the homolytic fission of the O–O bond of the peroxo-osmic acid is the primary source of the OH radical [equation (10)].

$$O_3Os\begin{matrix}OH\\O(OH)\end{matrix} \longrightarrow O_3Os\begin{matrix}OH\\O^\bullet\end{matrix} + OH \quad (10)$$

* The various rate and equilibrium constants k_1, k_2, *etc.* are defined by the correspondingly numbered equations.

The OH radical can be formed, however, in a greater quantity as a consequence of the appearance of the superoxide radical in the reaction mixture. The appearance of the superoxide radical suggests that in alkaline media the peroxo-anion decomposes in a one-electron redox reaction furnishing osmium(VII) and the superoxide radical [equation (11)]. Further, the OH

$$O_3Os\langle^{OH}_{OO^-} \longrightarrow O_3Os^{OH} \text{ (or simply } Os^{VII}) + O_2^- \quad (11)$$

radical can be formed in two parallel reactions [equations (12) and (13)].

$$O_2^- + H_2O_2 \longrightarrow O_2 + OH + OH^- \quad (12)$$

$$Os^{VII} + H_2O_2 \longrightarrow Os^{VIII} + OH + OH^- \quad (13)$$

The OH radical produced can react either with hydrogen peroxide, resulting in the superoxide radical, again, or with osmium(VII) [equations (14) and (15)].

$$OH + H_2O_2 \longrightarrow H_2O + O_2^- + H^+ \quad (14)$$

$$OH + Os^{VII} + H^+ \longrightarrow H_2O + Os^{VIII} \quad (15)$$

As regards the reliability of the use of the RNO reagent for the determination of the concentration of OH radicals, the following should be considered. According to Baxendale and Khan [17] RNO is transformed by the OH radical (produced by pulse radiolysis of an RNO solution saturated with N_2O) into an adduct the formation of which results in the immediate bleaching of the dye (band at 440 nm) and the appearance of a new band at 350 nm. This band shows second-order decay kinetics in which half of the lost intensity at 440 nm is recovered with a rate constant of 7.0×10^8 dm^3 mol^{-1} s^{-1}. Accordingly the equations below can be written.

$$RNO + OH \longrightarrow RNO{\cdot}OH \text{ (loss of band at 440 nm)}$$

$$2\ RNO{\cdot}OH \longrightarrow RNO + RNO_2 + H_2O$$

Dainton and Wiseall [19] proved by thin-layer chromatography that besides the main product, RNO_2 (*NN*-dimethyl-*p*-nitroaniline), other substances are formed during the pulse radiolysis of an RNO solution. It should also be added that Holcman and Sehested [20] pointed out the possibility of the addition of the OH radical to the aromatic ring, and in the case of *NN*-dimethylaniline showed that the hydroxycyclohexadienyl radicals formed not only decay in a second-order radical–radical process, but also take part in a competitive first-order water-elimination reaction. There are no data in the literature indicating how RNO and its reaction products with OH are influenced by the constituents of the reaction mixture investigated here. In this context, the roles of hydrogen peroxide and the superoxide radical should be considered. If the adduct of RNO were to undergo reactions with H_2O_2, the radical yield of the catalysed decomposition of hydrogen peroxide would be altered as shown below.

$$RNO{\cdot}OH + H_2O_2 \longrightarrow \begin{cases} RNO + H_2O + HO_2 \\ RNO_2 + H_2O + OH \end{cases}$$

One has to recollect, however, that the pulse radiolysis of an RNO solution saturated with dioxygen gives a simpler product distribution and an almost complete recovery of RNO bleached, due to the following reactions.

$$RNO{\cdot}OH + O_2^- \longrightarrow \begin{cases} RNO + OH^- + O_2 \\ RNO_2 + HO_2^- \end{cases}$$

Since we do not know enough about the probability of the above reactions involving hydrogen peroxide, we can state only that the figures obtained for the stationary-state concentration of the OH radical by this method are merely of informative value and serve as upper estimates of the true values.

It was found that the steady-state concentration of OH passes through a maximum as the pH is increased. This may be interpreted in that the radical species formed in step (11) react with one other before they can diffuse out of the solvent cage [equation (16)] and Os^{VII} is reduced

$$O_2^- + Os^{VII} \xrightarrow{OH^-} O_2 + Os^{VI} \quad (16)$$

by hydrogen peroxide with an increasing rate when the pH is increased [equation (17)]. Because of the pH

$$Os^{VII} + HO_2^- \longrightarrow Os^{VI} + O_2^- + H^+ \quad (17)$$

dependence of steps (16) and (17) the production of the OH radical decreases as the pH increases. The formation of osmium(VI) was observed by different independent methods at pH > 10.

The osmium(VI) formed will be reoxidized by hydrogen peroxide in a presumably two-electron step [equation (18)]. The rate of regeneration of osmium(VIII) is

$$Os^{VI} + H_2O_2 + 2\ H^+ \longrightarrow Os^{VIII} + 2\ H_2O \quad (18)$$

proportional to the square of the hydrogen ion concentration of the reaction mixture.

The length of the chain ν is defined as the number of moles of H_2O_2 protected from decomposition by removing the OH radical divided by the number of moles of OH radical captured ($=2\ [RNO]_{bleached}$). It follows from this definition that the value of ν decreases with increasing concentration of osmic acid. The rate of step (19)

$$O_2^- + Os^{VIII} \longrightarrow O_2 + Os^{VII} \quad (19)$$

increases with the increase of the concentration of osmium tetraoxide, resulting in an increase in the quantity of the end-product, *i.e.* a decrease in the number of moles of hydrogen peroxide protected from decomposition. At the same time osmium(VII) is obtained in higher concentration, which gives rise to a higher concentration of OH *via* step (13). The latter enhances the RNO bleaching, *i.e.* the value of the denominator of ν is increased. The effect of hydrogen peroxide is just the opposite. On increasing the concentration of H_2O_2, reaction (11) furnishes O_2^- and osmium(VII) intermediates in increased quantities, while steps (12) and (13) yield a higher OH radical concentration, thereby giving back O_2^- by step (14) at a higher rate, *etc.* The higher

concentration of hydrogen peroxide enhances the rate of step (14) and competes with the reaction between OH and RNO; this results in a decrease of the denominator, *i.e.* the value of ν increases.

At higher pH where osmium(VII) is reduced rapidly by O_2^- [step (16)] and by the peroxide anion [step (17)] the length of the chain is reduced because the re-oxidation of Os^{VI} by hydrogen peroxide [step (18)] is slower.

The overall apparent activation energy (E_{app}) and the temperature dependence of the bleaching of RNO are rather complicated parameters. The parameter E_{app} contains the temperature dependence of all steps involved in the decomposition $E_{app} = E_{10} + E_{11} + E_{12} + \ldots + E_{19}$. In the presence of OH scavengers, *e.g.* RNO or propan-2-ol, the apparent energy of activation of the remaining reaction would be determined by the steps which do not involve the OH radical; $E_{app}^{rem} = E_{app} - (E_{10} + E_{14} + E_{15})$. The energy required for breaking the O–O bond of the peroxo-complex is fairly high in comparison with that of steps (14) and (15). In contrast, the energy requirement of step (11) seems to be less than that of (10), if it is considered that, on the one hand, the transfer of an electron from the peroxide oxygen to osmium(VIII) results in an increase of the O–O bond strength from *ca.* 210 to *ca.* 370 kJ mol^{-1}, and, on the other hand, the bond between osmium(VII) and the superoxide ion formed is weakened because of the decrease in electronegativity of the core due to the reduction of osmium(VIII).

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