Mechanism of the First Order Decay of 2-Hydroxy-propyl-2-peroxyl Radicals and of O_2^- Formation in Aqueous Solution

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(Z. Naturforsch. **32b**, 886–889 [1977]; received March 16, 1977)

Photo Flash Conductivity, ESR, Peroxyl Radicals, Isotope Effect

Using time resolved ESR spectroscopy and photoflash conductivity the uncatalysed, first order decay of 2-hydroxy-propyl-2-peroxyl radicals and the uncatalysed, first order generation of O_2^- and H^+ were measured to have the same rate constants. The formation of O_2^- and H^+ was measured in H_2O and D_2O and a kinetic isotope effect of $k_H/k_D = 3.5$ was obtained. Comparing the rate constants of the peroxyl radicals derived from methanol, ethanol and 2-propanol it was shown that the rate constant increases with increasing methyl-substitution. In 2-propanol water mixtures the rate constant of the 2-hydroxy-propyl-2-peroxyl radical increases only slightly with increasing polarity of the solvent. The experimental results are in accord with a mechanism which involves a cyclic transition state leading to a concerted elimination of $HO_2\cdot$ followed by dissociation into H^+ and O_2^- .

Introduction

Previously, it had been found by pulse-radiolytic and photo flash conductivity studies, that 2-hydroxy-propyl-2-peroxyl radicals (1) decay into H^+ and O_2^- in a first order process (eq. (1))^{1,2}. In the present paper we wish to present the results of some experiments, which were performed in order to obtain information about the detailed mechanisms of this reaction.

Besides the first order decay the peroxyl radicals may under suitable conditions disappear by a second order process^{1,2} which is not considered here. Furthermore they can decompose in an OH^- catalysed reaction^{2,3} (eq. (2)).

Below $pH = 5.7$ and at temperatures above $20^\circ C$ there is only negligible contribution of reaction (2)

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in the case of radical 1. At pH values greater than 8, 1 reacts predominantly *via* pathway (2).

Experimental Results

In a flash photolysis apparatus the rate constants of eqs. (1) and (2) were determined in aqueous

Fig. 1. Build up of conductivity in an oxygen-saturated aqueous solution of 2-propanol ($5 \cdot 10^{-2}$ M) and H_2O_2 (10^{-3} M) after a $10 \mu sec$ flash. Horizontal line indicates baseline in the absence of the flash. $pH = 6.7$, $T = 22^\circ C$; sweep: 1 ms/division. Ordinate: change of conductivity (relative units); concentration of flash-produced radicals: $9 \cdot 10^{-8}$ M.

solutions by measuring the rates of conductivity build up due to the production of H^+ and O_2^- . In addition to this, the rate constant k_1 for the peroxyl radicals **1** was determined by carrying out time dependent ESR measurements. As examples, the results of two experiments are shown in Fig. 1 and Fig. 2. Within the limits of experimental error, both methods gave the same results which are presented in this section.

Fig. 2. Formation and decay of radicals $(\text{CH}_3)_2\text{C}(\text{OH})\text{OO}^\cdot$ (**1**).

as observed by time resolved (fixed field) ESR signals, extending to full period of chopping UV irradiation. During 1/3 of each period ($\uparrow$) irradiation was "turned on" at fixed time delay. Figure obtained from signal averaging of 10^4 cycles of 50 msec periods at continuous flow of solution. Aqueous solution of 0.3 M 2-propanol, 0.2 M H_2O_2 and $4 \cdot 10^{-4}$ M O_2 at 12.3° , flow rate: $0.2 \text{ cm}^3 \text{ s}^{-1}$, spectrometer response: 10^{-4} s .

1. The measured rate constants of reactions (1) and (2) for three peroxyl radicals derived from simple aliphatic alcohols are shown in Table I.

Table I. Rate constants for the first order formation of H^+ and O_2^- from $\text{R}'\text{R}''\text{C}(\text{OH})\text{OO}^\cdot$ radicals (k_1) and for the OH^- catalysed reaction (k_2) in aqueous solutions.

R'	R''	$k_1 [\text{s}^{-1}]$ at 22°C	$k_2 [\text{M}^{-1} \text{s}^{-1}]$
H	H	<10	$1.5 \cdot 10^{10}$
H	CH_3	52	$8 \cdot 10^9$
CH_3	CH_3	665	$5 \cdot 10^9$

2. On replacing H_2O by D_2O and comparing the rates of the conductivity build up at $\text{pH} = 5.5$ for both solvents in the case of peroxyl radicals **1**, we found a kinetic isotope effect $k_{\text{H}}/k_{\text{D}} = 3.5$ at 22°C .

3. Replacing 2-propanol by di-2-propyl ether, the rate of conductivity build up was lower by a factor of at least $5 \cdot 10^2$ in comparison with k_1 for **1**.

4. Varying the temperature of the solutions in the range $-2^\circ \text{C} < T < 50^\circ \text{C}$ we found a straight line (Fig. 3), on plotting k_1 on a logarithmic scale versus T^{-1} . The activation parameters derived from the plot were $E_A = 13.5 \text{ kcal} \cdot \text{mol}^{-1}$ and $\Delta S^\ddagger =$

$-3 \text{ cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ for a 2-propanol concentration of $5 \cdot 10^{-2} \text{ M}$.

5. If the concentration of 2-propanol is increased from 1 to 50 Vol.%, the rate constant k_1 for **1** decreases by a factor of 1.6, independently of temperature (Fig. 3). Using E_T^4 values and the equation $\log k_1 = a E_T + b$ to describe the influence of the solvent polarity, we obtained values of $a = +0.02$ and $b = +1.5$.

Discussion

At least six mechanisms of reaction (1) seem possible:

a) A slow dissociation of a proton followed by a fast elimination of O_2^- from the radical anions (eq. (3)).

The mechanism can be ruled out since it is known that the rate constants for proton dissociation are increased with decreasing methyl substitution, the observed sequence k_1 , however, is just the opposite (Table I).

b) A $\text{S}_{\text{N}}2$ mechanism could be possible (eq. (4)), which consists of a reaction of **1** with H_2O .

This kind of mechanism can be rejected, since k_1 should be greater with decreasing methyl substitution for steric reasons, but the opposite is observed. Furthermore, one would expect that the peroxyl radicals derived from di-2-propyl ether should show an O_2^- elimination with a rate constant similar to those measured in case of the radicals **1**. This was not observed (see point 3 of the Experimental Results).

c) An elongation of the $\text{C}-\text{OO}^\cdot$ bond leading to the formation of an ion-pair could be the rate determining step followed by fast elimination of H^+ from the intermediate highly acidic cation (eq. (5)).

In this case a small or vanishing deuterium effect would be expected. The measured ratio $k_{\text{H}}/k_{\text{D}} = 3.5$ is too high to be in agreement with reaction (5).

d) Another possible mechanism is the formation

of an ion pair as shown in eq. (5), however, with a fast back reaction.

If it is assumed that the elongation of the O-H bond is an immediate consequence of the strength of the positive charge at the central carbon atom which itself is a result of the charge separation induced by the elongation of the C-OO $\cdot$ bond, then the described mechanism is less probable. In fact, the observed influence of the solvent polarity is too small⁴ to make an ion-pair like intermediate likely. For typical monomolecular nucleophilic substitution reactions *via* ion pairs values of $a = 0.197$ – 0.355 and values of $b = -13.26$ up to -25.29 are found⁴ whereas the a value found in the present work is much lower (see point 5 of the Experimental Results).

e) Still another possibility is the elimination of O $_2^{\cdot-}$ and H $^+$ by simultaneous C-OO $\cdot$ and O-H bond breaking leading to a polar, possibly ion-pair like, transition state (eq. (6)).

Again, the argument of the small influence of the solvent polarity bears on this and makes the mechanism according to eq. (6) less probable. Furthermore, it is known⁵ that the proton is not formed without a considerable decrease in entropy, greater than the observed value of $-3 \text{ cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ (see point 4 of the Experimental Results).

f) Further, the decay of 1 could occur *via* a cyclic transition state (eq. (7)) leading to HO $_2^{\cdot}$ which subsequently dissociates in a fast step into H $^+$ and O $_2^{\cdot-}$.

The dissociation of HO $_2^{\cdot}$ into H $^+$ and O $_2^{\cdot-}$ cannot be the rate determining step in the build up of conductivity. The pK-value of HO $_2^{\cdot}$ is ~ 4.7 ^{2,6} from which a k value of $1 \cdot 10^6 \text{ s}^{-1}$ is estimated for the last step of eq. (7), if a rate constant of $5 \cdot 10^{10} \text{ M}^{-1}\text{sec}^{-1}$ is assumed for the recombination reaction of H $^+$ and O $_2^{\cdot-}$. This has to be compared with the rate constants k_1 of Table I which are more than three orders of magnitude smaller.

We believe, that the decay of 1 occurs according to eq. (7) since that mechanism is in agreement with the presently known experimental results. The

cyclic transition state explains the small influence of the solvent. Activation entropies in the order found have been observed for cyclic transition states⁷ and kinetic isotope effects of the observed magnitude are expected for cyclic transition states⁸. Long lived intermediates, *e.g.* hydroxy hydroperoxides and tetroxides have not been observed since the decay of 1 as measured by ESR has the same rate constant as the formation of O $_2^{\cdot-}$ and H $^+$ (Fig. 3).

Fig. 3. Rate constant k_1 for the first order decay of the peroxyl radicals 1 measured by ESR and build up of conductivity as a function of temperature.

○ ○ ○ ○ = photoflash conductivity measurements, pH = 5.5, [2-prop.] = $5 \cdot 10^{-2} \text{ M}$;
□ □ □ □ = photoflash conductivity measurements, pH = 5.5, [2-prop.] = 6.5 M ;
+ + + + = ESR-measurements, [2-prop.] = 0.3 M .

The following question still remains open with regard to mechanism eq. (7): Why do the rate constants k_1 increase in going from R=H to R=CH $_3$ (Table I)? One reason for this may be the stabilisation of the carbonyl group effected by substituting CH $_3$ for H. According to BENSON's method of group increments⁹ the stabilisation of the carbonyl group thus obtained amounts to $\sim 1.9 \text{ kcal/mol}$ per H substituted by a methyl group. Using this value and assuming a) that the configuration of the transition states resembles that of the reaction products and b) that the pre-exponential factors remain the same in going from R'=H, R''=CH $_3$ to R'=R''=CH $_3$, k_1 is calculated to increase by a factor of ~ 25 which has to be compared with the experimental increase of ~ 13 (Table I). A similar argument has been used¹⁰ to explain the influence of methyl substituents on the rates of fragmentation of α -alkoxy alkyl radicals.

Another reason for the increase of k_1 with higher

degree of methylation could be found in the formation of a more pronounced intramolecular hydrogen bond of the OH group in the higher methylated radicals. This is suggested by the decrease of k_2 to values considerably lower than diffusion controlled (Table I). In studies of similar reactions it was observed¹¹ that in the presence of hydrogen bonds OH⁻ catalysed reactions have rate constants lower than $2 \cdot 10^{10} \text{ M}^{-1}\text{s}^{-1}$.

Experimental Section

The rate of formation of H⁺ and O₂⁻ (reaction (1)) was measured using a flash photolysis-conductivity apparatus described earlier². The aqueous solutions were saturated with oxygen and contained H₂O₂ (10^{-3} — $4 \cdot 10^{-2} \text{ M}$) and an aliphatic alcohol (10^{-2} —

6.5 M). The UV light of the flash (duration $10 \mu\text{s}$) was absorbed by H₂O₂ producing OH radicals. The OH radicals abstract H atoms from the alcohols leading preferentially to α -hydroxy alkyl radicals (e.g. (CH₃)₂COH in the case of 2-propanol)¹². The α -hydroxy alkyl radicals add oxygen and form α -hydroxy alkyl peroxyl radicals. The concentrations of the α -hydroxy-peroxyl radicals were held below $1 \cdot 10^{-7} \text{ M}$ in order to avoid bimolecular reactions².

The decay of the peroxyl radicals was measured with time resolved in situ ESR spectroscopy at constant field. The time dependence of the ESR signal was obtained by periodically repeated real time measurements using chopped UV irradiation of the H₂O₂ in the solution. The ESR signals thus obtained were sampled and averaged to improve the signal/noise ratio.

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