Reaction of 1-propanol with Ozone in Aqueous Media

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Abstract: The main aim of this work is to substantiate the mechanism of 1-propanol oxidation
by ozone in aqueous solution when the substrate is present in large excess. Further goals are
assessment of the products, their formation yields as well as the kinetic parameters of the considered
reaction. The reaction of ozone with 1-propanol in aqueous solution occurs via hydride transfer,
H-abstraction and insertion. Of these three mechanisms, the largest share is for hydride transfer.
This implies the extraction of an hydride ion from the activated C−H group by O 3 according to
reaction: (C 2 H 5 ) (H)(HO)C−H + O 3 → [(C 2 H 5 ) (H)(HO)C + + HO 3 ] cage → (C 2 H 5 ) (H)(HO)C + + HO 3 −.
The experimentally determined products and their overall formation yields with respect to ozone
are: propionaldehyde—(60 ± 3)% , propionic acid—(27.4 ± 1.0)% , acetaldehyde—(4.9 ± 0.3)% , acetic
acid—(0.3 ± 0.1)% , formaldehyde—(1.0 ± 0.1)% , formic acid—(4.6 ± 0.3)% , hydrogen peroxide—
(11.1 ± 0.3)% and hydroxyl radical—(9.8 ± 0.3)% . The reaction of ozone with 1-propanol in aqueous
media follows a second order kinetics with a reaction rate constant of (0.64 ± 0.02) M −1 · s −1 at pH = 7
and 23 °C. The dependence of the second order rate constant on temperature is described by the equation:
ln k II = (27.17 ± 0.38) −(8180 ± 120) × T −1 , which gives the activation energy, E a = (68 ± 1) kJ mol −1
and pre-exponential factor, A = (6.3 ± 2.4) × 10 11 M −1 s −1 . The nature of products, their yields and the
kinetic data can be used in water treatment. The fact that the hydride transfer is the main pathway in
the 1-propanol/ozone system can probably be transferred on other systems in which the substrate is
characterized by C−H active sites only.

Keywords: ozone; 1-propanol; hydride transfer; H-abstraction; insertion; kinetic data

1. Introduction

This paper is one of a series that tries to shed some light on ozone reactions with compounds
characterised by C−H active sites only, compounds known as less reactive. In this context, the main
aims are to elucidate the mechanism of 1-propanol reaction with ozone in aqueous media and to provide
kinetic parameters that characterize this reaction (activation energy and pre-exponential factor).

To the best of our knowledge, there are only a few data in the literature on 1-propanol/ozone
aqueous system and these refer mainly to the rate constants of 1-propanol reactions with oxidants such
as O 3 , HO• , and O•− at temperatures between 20 and 25 °C. This information is given in Table 1.
Table 1. Second order rate constants for the reactions of 1-propanol with various oxidising agents in aqueous media.

| Oxidising Agent | K (M$^{-1}$ s$^{-1}$) | Working Conditions | References |
|-----------------|------------------------|--------------------|------------|
| O$_3$ | (0.37 ± 0.04) | pH = 2, t = (20 ± 0.5) °C | [1] |
| | (0.64 ± 0.02) | pH = 7, t = 23 °C | this work |
| HO• | 2.8 × 10$^9$ | pH = 7 | [2] |
| | 1.5 × 10$^9$ | pH = 10.7 | [3] |
| | 1.5 × 10$^9$ | pH = 7 | [3] |
| | 2.7 × 10$^9$ | | [4] |
| O•$^-$ | 1.5 × 10$^9$ | pH = 14 | [4] |

The reason why the mechanism of this reaction is of such great interest is the assumption that hydride transfer plays an important role when ozone attack occurs at a C–H bond. This pattern has already been reported for aqueous systems such as 2-propanol/ozone [5], tert-butanol/ozone and formate/ozone [6]. The elementary reaction that triggers this mechanism can be written as follows [5–7]:

\[
R_3C−H + O_3 \rightarrow R_3C+ + HO_3− \quad (a)
\]

where R stands for hydrogen, organic or functional groups, identical or different.

The interpretation of experimental data for the system 2-propanol/ozone in organic media has led to the conclusion that ozone attack at C–H bond occurs via H-abstraction [8–10]:

\[
R_3C−H + O_3 \rightarrow R_3C• + HO_3• \quad (b)
\]

The mechanism triggered by reaction (b) is not ruled out in aqueous media, but it plays a secondary role at least in the previously mentioned systems.

Other two possible interactions between ozone and substrate are insertion (reaction (c)) and electron transfer (reaction (d)):

\[
R_3C−H + O_3 \rightarrow R_3C−O−O−O−H \quad (c)
\]

\[
R_3C−H + O_3 \rightarrow [R_3C−H]• + O_3•− \quad (d)
\]

In order to determine which of the four mentioned pathways is the most probable, Gibbs energies of the constituent reactions and overall formation yields of the products with respect to ozone were taken into consideration.

The results of this study, mainly the kinetic data and information about the nature and yields of products can also serve practical purposes, such as the treatment of wastewaters containing 1-propanol (1-propanol may be used as a solvent or as an ingredient of degreasing agents, anti-freezes, disinfectants, inks, toners, dye solutions and also as a raw material for herbicides, insecticides, cosmetics and pharmaceuticals).

2. Results

2.1. Products

2.1.1. Hydroxyl Radical

As described in Materials and Methods Section, HO• formation yield with respect to ozone was determined indirectly by assessing formaldehyde formation yields with respect to ozone in the
1-propanol/O$_3$ system in the absence and presence of tert-butanol acting as a scavenger. In order to use this method, the reaction between substrate and O$_3$ should definitely prevail over that one between tert-butanol and O$_3$. In addition, the reaction of the substrate with HO• should be negligible with respect to that one between tert-butanol and HO•. Under our working conditions: [1-propanol] = 0.1 M and [tert-butanol] = 1 M, 98% of O$_3$ reacted with 1-propanol (k(1-propanol + O$_3$) = (0.64 ± 0.02) M$^{-1}$ s$^{-1}$ (this work) and k(tert-butanol + O$_3$) = 1.1 × 10$^{-3}$ M$^{-1}$ s$^{-1}$ [6]) and 69% of HO• was scavenged by tert-butanol (k(1-propanol + HO•) = 2.7 × 10$^9$ M$^{-1}$ s$^{-1}$ [4]) and k(tert-butanol + HO•) = 6 × 10$^8$ M$^{-1}$ s$^{-1}$ [11,12]). Practically, HO• formation yield with respect to ozone was calculated with the following formula:

$$\eta(\text{HO}•) = 2 \frac{(a - 0.31 \cdot b)}{0.69} \%$$

where: the factor 2 comes from the 50% formaldehyde formation yield with respect to HO• (more details are given in the Materials and Methods section), $a$ and $b$ are the formaldehyde formation yields with respect to ozone in the presence and absence of tert-butanol, 0.69 is the part of HO• that reacts with tert-butanol and 0.31 the part of HO• that reacts with 1-propanol in systems that contains both substrates next to ozone. The formaldehyde formation yields with respect to ozone, $a$ and $b$, are derived from the slopes of the straight lines in the graphic representation of the formed formaldehyde concentration vs. the added ozone concentration, as shown in Figure 1. Under these circumstances HO• formation yield was (9.8 ± 0.3)%.

![Figure 1. Main graph: determination of HO• formation yield with respect to ozone by using the formaldehyde formation yields in 1-propanol/ozone system in the absence (triangles) and presence of tert-butanol (circles) used as scavenger. Formaldehyde was determined spectrophotometrically with the Hantzsch method. [1-propanol] = 0.1 M, [tert-butanol] = 1 M. Inset: dependence of the formed hydrogen peroxide vs. added ozone concentrations. Hydrogen peroxide was determined spectrophotometrically by using Allen’s method. [1-propanol] = 0.1 M.](image)

This value indicates that the substrate is oxidized by both O$_3$ (direct reaction) and HO• (indirect reaction). Due to the fact that some of the products arise on both channels and that
one cannot make a clear distinction between the two contributions, the experimentally determined formation yields are called “overall formation yields”.

2.1.2. Aldehydes

As part of this category, propionaldehyde was formed by oxidation, while acetaldehyde and formaldehyde resulted from oxidative cleavage of 1-propanol.

Acetaldehyde and propionaldehyde were determined by means of high performance liquid chromatography (HPLC) and formaldehyde by spectrophotometric method. Details can be found in the Materials and Methods section.

The formation yield of propionaldehyde was $(60 \pm 3)\%$ and it was obtained from the plot of the formed propionaldehyde versus the added ozone concentrations, as shown in Figure 2.

The formation yields for formaldehyde and acetaldehyde were one order of magnitude lower than the one for propionaldehyde. Thus, the formation yield of formaldehyde was $(1.0 \pm 0.1)\%$ and that one for acetaldehyde was $(4.9 \pm 0.3)\%$. These results were based on data from Figure 1 (for formaldehyde; triangles in the main graph) and the inset of Figure 2 (for acetaldehyde).

2.1.3. Acids

Of this category, propionic, acetic and formic acids formed within our system. Their concentrations were determined by way of ion chromatography (IC) as described in Materials and Methods section. The formation yields with respect to ozone were as follows $(27.4 \pm 1.0)\%$—propionic acid, $(0.3 \pm 0.1)\%$—acetic acid and $(4.6 \pm 0.3)\%$—formic acid. These values were obtained based on data in Figure 3, which shows the dependence of the formed acid on opposing ozone concentrations.
2.1.4. Hydrogen Peroxide

The overall $\text{H}_2\text{O}_2$ formation yield with respect to ozone was determined from the plot of the formed $\text{H}_2\text{O}_2$ concentration versus added ozone, as shown in the inset of Figure 1. The resulted value was $(11.1 \pm 0.3)\%$. The $\text{H}_2\text{O}_2$ concentration was determined spectrophotometrically, as shown in Section 4.

2.1.5. Overview

Table 2 summarizes overall product formation yields in 1-propanol/O$_3$ system. Firstly, these data show that the material balance is nearly closed, i.e., the sum of products formation yields with respect to O$_3$ is 93%. The remaining 7% is due to the practically unmeasurable low concentration of certain products (hydroxyacetone, hydroxyacetaldehyde and 1,2-propanediol), experimental errors, values used for molar absorption coefficients, etc. Secondly, one can notice that the sum of formation yields of compounds with one carbon atom (5.6%—resulted from 1.0% for formaldehyde and 4.6% for formic acid) equals that one corresponding to compounds with two carbon atoms (5.2%—obtained from 4.9% for acetaldehyde and 0.3% for acetic acid).

Table 2. Overview of the products formed in 1-propanol/O$_3$ aqueous system and their overall formation yields with respect to O$_3$.

| Product          | Propionic Aldehyde | Propionic Acid | Acetaldehyde | Acetic Acid | Formic Aldehyde | Formic Acid | Hydroxyl Radical | Hydrogen Peroxyde |
|------------------|--------------------|----------------|--------------|-------------|-----------------|-------------|------------------|-------------------|
| Yield (%)        | 60 ± 3             | 27.4 ± 1.0     | 4.9 ± 0.3    | 0.3 ± 0.1   | 1.0 ± 0.1       | 4.6 ± 0.3   | 9.8 ± 0.3        | 11.1 ± 0.3        |

2.2. Kinetic Data

The first part of this section refers to determining the second order rate constant of the reaction between 1-propanol and ozone at 23 °C and comparing it with corresponding data in the literature and also with values reported for other alcohols.
The determination of the second order rate constant is based on graphic representation of the pseudo-first order rate constant, $k_{obs}$, versus 1-propanol concentration, which practically remained unchanged throughout the reaction (Figure 4, main graph). To get the pseudo-first order rate constant, the variation of ozone absorbance at 260 nm was recorded as the reaction went on (Figure 4, upper inset), the natural logarithm of the ratio between current and initial absorbance was plotted versus time (Figure 4, lower inset) and finally the slope of the straight line was calculated ($\tan \alpha = k_{obs}$).

![Figure 4](image)

**Figure 4.** Main graph: Determination of the second order rate constant for the reaction of ozone with 1-propanol. Correlation of pseudo-first order rate constant (observed rate constant, $k_{obs}$) with 1-propanol concentration at $t = 23 \, ^\circ \text{C}$ and $pH = 7$ (as 1-propanol is in large excess with respect to ozone, the concentration of 1-propanol can be considered constant during reaction). Upper inset: exponential decrease of ozone concentration (measured as absorbance at 260 nm) versus time for [1-propanol] = 36 mM. Lower inset: the corresponding linear decrease of $\ln (A/A_0)$ versus time.

The resulting value for the second order rate constant at pH = 7 and 23 °C is $(0.64 \pm 0.02) \, \text{M}^{-1} \cdot \text{s}^{-1}$. Table 3 shows second order rate constants for reactions among O$_3$ and various alcohols.

By comparing the second order rate constants as determined by Hoigné and Bader at 20 °C for primary alcohols [1], one can notice the increase of the reaction rate within series, from methanol to 1-octanol, following the increase of the electron repelling inductive effect as the number of carbon atoms within the organic chain increases. As expected, the rate constant also increases when the number of methyl groups that show electron repelling inductive effect increases. Table 3 highlights this influence for the switch from ethanol (one methyl group) to 2-propanol (two methyl groups).

The second part of this section deals with Arrhenius graphic representation in order to derive the second order rate constants at any given temperature within the considered range and also of the activation energy and pre-exponential factor. To get this information, the second order rate constants were determined for temperatures between 10 and 45 °C and the natural logarithm of the second order rate constant was plotted against the inverse of absolute temperature, as in Figure 5. The explicit forms of dependencies $\ln k_{II} = f(T^{-1})$ and $k = f(T)$ are:

$$\ln k_{II} = (27.17 \pm 0.38) - (8180 \pm 120) \times T^{-1}$$

and

$$k_{II} = (6.3 \pm 2.4) \times 10^{11} \cdot e^{-(681 \pm 10^3)/R T}$$
As expected, the rate constant also increases when the reaction is carried out at higher temperatures.

The second part of this section deals with Arrhenius graphic representation in order to derive the activation energy, Ea, and pre-exponential factor, A. Dependence between the natural logarithm of the second order rate constant and inverse of absolute temperature (Arrhenius plot).

These relations lead to $(68 \pm 1) \text{kJ mol}^{-1}$ activation energy and $(6.3 \pm 2.4) \times 10^{11} \text{M}^{-1} \text{s}^{-1}$ pre-exponential factor.
The second order rate constant at 20 °C and pH = 7 derived from the dependence \( k = f(T) \) was \((4.7 \pm 0.2) \times 10^{-1} \text{M}^{-1} \text{s}^{-1}\) and it was in agreement with that reported by Hoigné and Bader of \((3.7 \pm 0.4) \times 10^{-1} \text{M}^{-1} \text{s}^{-1}\) at the same temperature and pH = 2 [1].

3. Discussion

3.1. Mechanism Initiated by the Direct Reaction of O₃ with 1-propanol

3.1.1. Hydride Transfer

In the first step, O₃ extracts a hydride ion from the activated C–H group thereby forming a carbocation and a hydrogen trioxide anion, HO₃⁻; this ion couple is kept together for some time within the solvent cage (reaction (1)). Further, these ions can recombine in the solvent cage forming α-hydroxyalkylhydrotrioxide (reaction (2), overall Gibbs energy for reactions (1) and (2), \( \Delta G = -192 \text{kJ mol}^{-1}\)), or they can escape from the cage (reaction (3), overall Gibbs energy for reactions (1) and (3), \( \Delta G = -167 \text{kJ mol}^{-1}\)).

\[
\begin{align*}
(C_2H_5)(H)(HO)C−H + O_3 &\rightarrow [(C_2H_5)(H)(HO)C^+ + HO_3^-]_{cage} \quad (1) \\
[(C_2H_5)(H)(HO)C^+ + −O_3H]_{cage} &\rightarrow (C_2H_5)(H)(HO)C−O−O−OH \quad (2) \\
[(C_2H_5)(H)(HO)C^+ + HO_3^-]_{cage} &\rightarrow (C_2H_5)(H)(HO)C^+ + HO_3^- \quad (3)
\end{align*}
\]

One can notice that both successions of reactions ((1) plus (2) and (1) plus (3)) are highly exergonic and thus thermodynamically favoured. The fate of trioxide will be discussed as part of the paragraph that deals with the insertion mechanism.

The carbocation resulted following reaction (3) might rearrange by forming protonated propionaldehyde (reaction (4), \( \Delta G = 0 \text{kJ mol}^{-1}\)), a species that is likely to lead to propionaldehyde by deprotonation (reaction (5), \( \Delta G = -40 \text{kJ mol}^{-1}\)).

\[
\begin{align*}
(C_2H_5)(H)(HO)C^+ &\rightarrow (C_2H_5)(H)C=OH^+ \quad (4) \\
(C_2H_5)(H)C=OH^+ &\rightarrow (C_2H_5)(H)C=O + H^+ \quad (5)
\end{align*}
\]

At the circumneutral pH of our experiments, hydrogen trioxide anion that resulted in reaction (3) will protonate forming hydrogen trioxide (reaction (6), \( \text{pKa}(H_2O_3^-) = (9.5 \pm 0.2) \) at 20 °C, \( k_− = 9.2 \text{s}^{-1}\), \( k_+ = 10^{10} \text{M}^{-1} \text{s}^{-1}\) [13–15]), an unstable species in water, which decays by acid catalysis (reaction (7), \( k = 6 \text{M}^{-1} \text{s}^{-1}\) [13–15], \( \Delta G = -234 \text{kJ mol}^{-1}\)). The hydrogen trioxide anion itself undergoes decay to singlet oxygen and hydroxide ion (reaction (8), \( \Delta G = -40 \text{kJ mol}^{-1}\) [13].

\[
\begin{align*}
\text{HO}_3^- + \text{H}^+ &\rightarrow \text{H}_2\text{O}_3 \quad (6) \\
\text{H}_2\text{O}_3 + \text{H}^+ &\rightarrow \text{H}_3\text{O}^+ + \text{O}_2 \quad (7) \\
\text{HO}_3^- &\rightarrow \text{HO}^- + ^1\text{O}_2 \quad (8)
\end{align*}
\]

Given the reaction sequence initiated by a hydride ion transfer from 1-propanol to ozone (reactions (1), (3)–(8)), it follows that the sole stable product is propionaldehyde (except for oxygen). As the overall formation yield for propionaldehyde is \((60 \pm 3)\%\), it means that maximum \((60 \pm 3)\%\) of ozone has reacted with 1-propanol according to this mechanism (practically, by hydride transfer followed by ions escaping from the solvent cage).

3.1.2. Insertion

This mechanism involves the intercalation of one O₃ molecule between carbon and hydrogen atoms of an activated C–H group, when α-hydroxyalkylhydrotrioxide forms (reaction (9),

\[
\begin{align*}
(C_2H_5)(H)(HO)C−O−O−OH &\rightarrow [(C_2H_5)(H)(HO)C−O−O−OH]_{cage} \quad (9)
\end{align*}
\]
$\Delta G = -192 \text{ kJ mol}^{-1}$. This trioxide might also form within the solvent cage via a hydride transfer mechanism (by recombination of the previously formed ion pair) and/or via H-abstraction (by recombination of the radical pair).

$$\text{(C}_2\text{H}_3\text{)(H)(HO)}\text{C}−\text{H} + \text{O}_3 \rightarrow \text{(C}_2\text{H}_3\text{)(H)(HO)}\text{C}−\text{O}−\text{O}−\text{OH} \quad (9)$$

The resulted $\alpha$-hydroxyalkylhydrotrioxide is likely to cleave to a secondary $\alpha$-hydroxyalkyloxy radical and a hydroperoxyl radical (reaction (10), $\Delta G = -14 \text{ kJ mol}^{-1}$) or to a secondary $\alpha$-hydroxyalkylperoxyl radical and a hydroxyl radical (reaction (11), $\Delta G = 46 \text{ kJ mol}^{-1}$). Both Gibbs energies of reactions and lengths of O–O bonds (1.442 Å for O–OOH and 1.426 Å for OO–OH) indicate that reaction (10) is favored over reaction (11).

$$\text{(C}_2\text{H}_3\text{)(H)(HO)}\text{C}−\text{O}−\text{OH} \rightarrow \text{(C}_2\text{H}_3\text{)(H)(HO)}\text{C}−\text{O}−\text{O}−\text{OH} + \text{HO}_2\bullet \quad (10)$$

$$\text{(C}_2\text{H}_3\text{)(H)(HO)}\text{C}−\text{O}−\text{O}−\text{OH} \rightarrow \text{(C}_2\text{H}_3\text{)(H)(HO)}\text{C}−\text{O}−\text{O}−\text{O}−\text{O}−\text{OH} + \text{HO}\bullet \quad (11)$$

The $\alpha$-hydroxyalkyloxy radical might undergo 1,2-H shift (reaction (12), $\Delta G = -30 \text{ kJ mol}^{-1}$) or $\beta$-fragmentation (reaction (13), $\Delta G = -82 \text{ kJ mol}^{-1}$)

$$\text{(C}_2\text{H}_3\text{)(H)(HO)}\text{C}−\text{O}−\text{O}−\text{O}−\text{O}−\text{O}−\text{OH} \rightarrow \text{(C}_2\text{H}_3\text{)(H)(HO)}\text{C}−\text{O}−\text{O}−\text{O}−\text{O}−\text{O}−\text{OH} + \text{C}_2\text{H}_5 + \text{HCOOH} \quad (12)$$

$$\text{(C}_2\text{H}_3\text{)(H)(HO)}\text{C}−\text{O}−\text{O}−\text{O}−\text{O}−\text{O}−\text{OH} \rightarrow \text{C}_2\text{H}_5 + \text{HCOOH} \quad (13)$$

When O$_2$ is present, as in our system, it reacts with the dihydroxyalkyl radical formed in reaction (12), leading to a $\alpha$-hydroxyalkylperoxyl radical (reaction (14), $\Delta G = -101 \text{ kJ mol}^{-1}$), which itself is in equilibrium with the corresponding radical anion (reaction (15)).

$$\text{(C}_2\text{H}_3\text{)(H)(HO)}\text{C}−\text{O}−\text{O}−\text{O}−\text{O}−\text{O}−\text{OH} + \text{O}_2 \rightarrow \text{(C}_2\text{H}_3\text{)(H)(HO)}\text{C}−\text{O}−\text{O}−\text{O}−\text{O}−\text{O}−\text{OH} + \text{O}_2\bullet \quad (14)$$

$$\text{(C}_2\text{H}_3\text{)(H)(HO)}\text{C}−\text{O}−\text{O}−\text{O}−\text{O}−\text{O}−\text{OH} + \text{HO}− \rightarrow \text{(C}_2\text{H}_3\text{)(H)(HO)}\text{C}−\text{O}−\text{O}−\text{O}−\text{O}−\text{O}−\text{O}−\text{OH} + \text{H}_2\text{O} \quad (15)$$

The literature shows that as a general rule, $\alpha$-hydroxyalkylperoxyl radicals, R$_2$(HO)C−O−O•, eliminate HO$_2$• following a first order reaction that may be slow, the reaction rate constant depending on the nature of substituents [16–18]. The corresponding radical anions, R$_2$(O−)C−O−O•, eliminate O$_2$• very fast, following a second order process. Actually, this process consists of the equilibrium between the protonated and deprotonated species and O$_2$• elimination from deprotonated species, where the first step is the rate limiting one [7,19]. More details about HO$_2$•/O$_2$• elimination are provided in Supplementary Materials.

Thus, the $\alpha$-hydroxyalkylperoxyl radical formed in reaction (14) is likely to eliminate HO$_2$• according to reaction (16) ($\Delta G = -98 \text{ kJ mol}^{-1}$) and the corresponding $\alpha$-hydroxyalkylperoxyl radical anion might eliminate O$_2$• as shown in reaction (17) ($\Delta G = -11 \text{ kJ mol}^{-1}$). Both reactions lead to propionic acid as a product.

$$\text{(C}_2\text{H}_3\text{)(HO)}\text{C}−\text{O}−\text{O}−\text{O}−\text{O}−\text{OH} \rightarrow \text{(C}_2\text{H}_3\text{)(HO)}\text{C}−\text{O}−\text{O}−\text{O}−\text{O}−\text{OH} + \text{HO}_2\bullet \quad (16)$$

$$\text{(C}_2\text{H}_3\text{)(HO)}\text{C}−\text{O}−\text{O}−\text{O}−\text{O}−\text{O}−\text{OH} \rightarrow \text{(C}_2\text{H}_3\text{)(HO)}\text{C}−\text{O}−\text{O}−\text{O}−\text{O}−\text{O}−\text{OH} + \text{O}_2\bullet \quad (17)$$

Between HO$_2$• and O$_2$•, as formed in reactions (16) and (17), one can write equilibrium (18) characterized by pK$_a = (4.8 \pm 0.1)$, which indicates that in our system (pH ~ 7), O$_2$• is the predominant species [20]. This could react with O$_3$ in excess, according to reaction (19), thus forming O$_3$•, which is a precursor of HO•. Given that in our experiments the substrate is in large excess ([2-propanol] = 10$^{-1}$ M,
with $\Delta G$ (reaction (26)). Both the protonated and deprotonated species lead to propionaldehyde by elimination (reaction (25), (reaction (24), overall Gibbs energy for reactions (22) and (24), \[ \Delta G = -192 \, \text{kJ mol}^{-1} \]) thereby forming $\text{H}_2\text{O}_2/\text{HO}_2^-$ [20]. However, a bimolecular decay of $\text{O}_2\bullet^-$ does not take place to any significant extent [7].

\[
\begin{align*}
2 \text{HO}_2\bullet & \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \\
\text{HO}_2\bullet + \text{O}_2\bullet^- & \rightarrow \text{HO}_2^- + \text{O}_2
\end{align*}
\]

According to reactions (9)–(21), it follows that the products resulted by the insertion mechanism are: propionic acid, formic acid, hydrogen peroxide, acetaldehyde and acetic acid (the last two compounds result following the oxidation of ethyl radical as a product of reaction (13)). The overall formation yields of these products are: (27.4 ± 1.0)%—propionic acid, (4.6 ± 0.3)%—formic acid, (11.1 ± 0.3)%—hydrogen peroxide, (4.9 ± 0.3)%—acetaldehyde and (0.3 ± 0.1)%—acetic acid. From these formation yields it follows that trioxide is formed. However, this finding does not clarify whether trioxide forms following the insertion mechanism or by recombination of the ions formed by hydride transfer or of the radicals resulted from H-abstraction.

3.1.3. H-abstraction

This mechanism involves taking away one hydrogen atom from the activated C–H group as shown in reaction (22), when $\alpha$-hydroxyalkyl and hydrogen trioxide radicals are likely formed. The radical pair is kept together for some time by the solvent cage where they can recombine to form trioxide (reaction (23), overall Gibbs energy for reactions (22) and (23), $\Delta G = -192 \, \text{kJ mol}^{-1}$), or they can escape (reaction (24), overall Gibbs energy for reactions (22) and (24), $\Delta G = -19 \, \text{kJ mol}^{-1}$). One can notice that both pathways are exergonic and thus thermodynamically possible; the formation of trioxide is thermodynamically favored given the one order of magnitude higher Gibbs energy (absolute value) than that for the formation of free radicals.

\[
\begin{align*}
\text{(C}_2\text{H}_3)(\text{H})(\text{HO})\text{C}^- + \text{O}_3 & \rightarrow [\text{(C}_2\text{H}_3)(\text{H})(\text{HO})\text{C}^- + \text{HO}_2\bullet]_{\text{cage}} \\
[\text{(C}_2\text{H}_3)(\text{H})(\text{HO})\text{C}^- + \text{O}_3\text{H}]_{\text{cage}} & \rightarrow (\text{C}_2\text{H}_3)(\text{H})(\text{HO})\text{C}^- + \text{HO}_2\bullet \\
[\text{(C}_2\text{H}_3)(\text{H})(\text{HO})\text{C}^- + \text{HO}_2\bullet]_{\text{cage}} & \rightarrow (\text{C}_2\text{H}_3)(\text{H})(\text{HO})\text{C}^- + \text{HO}_2\bullet
\end{align*}
\]

The fate of $\alpha$-hydroxyalkyltrioxide has already been presented in the paragraph that deals with insertion mechanism (reactions (10)–(17)).

The $\alpha$-hydroxyalkyl radical formed in reaction (24) might further reacts with oxygen that is in high concentration in our system, thereby most likely leading to $\alpha$-hydroxyalkylperoxyl radical (reaction (25), $\Delta G = -95 \, \text{kJ mol}^{-1}$). This species is in equilibrium with the corresponding radical anion (reaction (26)). Both the protonated and deprotonated species lead to propionaldehyde by elimination of $\text{HO}_2\bullet$ and $\text{O}_2\bullet^-$, respectively (reaction (27) characterized by $\Delta G = -27 \, \text{kJ mol}^{-1}$ and reaction (28) with $\Delta G = -31 \, \text{kJ mol}^{-1}$).

\[
\begin{align*}
\text{(C}_2\text{H}_3)(\text{H})(\text{HO})\text{C}^- + \text{O}_2 & \rightarrow (\text{C}_2\text{H}_3)(\text{H})(\text{HO})\text{C}^- + \text{O}^- \\
(\text{C}_2\text{H}_3)(\text{H})(\text{HO})\text{C}^- + \text{H}_2\text{O}^- & \rightarrow (\text{C}_2\text{H}_3)(\text{H})(\text{HO})\text{C}^- + \text{H}_2\text{O} \\
(\text{C}_2\text{H}_3)(\text{H})(\text{HO})\text{C}^- + \text{HO}_2\bullet & \rightarrow (\text{C}_2\text{H}_3)(\text{H})(\text{HO})\text{C}^- + \text{H}_2\text{O}_2\bullet
\end{align*}
\]
As has already been shown at the insertion mechanism:

- There is an acid-base equilibrium between HO$_2^-$ and O$_2^-$ (reaction (18));
- At the circumneutral pH within our system, O$_2^-$ is the predominant species (pKa(HO$_2^-$) = (4.8 ± 0.1));
- Reaction between two HO$_2^-$ moles or between one HO$_2^-$ and one O$_2^-$ moles leads to the formation of H$_2$O$_2$ and HO$_2^-$, respectively (reactions (20) and (21));
- Given the large excess of substrate up against ozone within our system, reaction between O$_2^-$ and O$_3$ is not important and it follows that O$_3^-$ (as a precursor of HOO•) does not form practically via this pathway.

Due to the fact that α-hydroxyalkylperoxy radical, formed in reaction (25), is a secondary peroxyl radical, it might also dimerize (reaction (29), $\Delta G = 94$ kJ mol$^{-1}$):

$$2 (C_2H_5)(H)(HO)C-O-O• \rightleftharpoons (C_2H_5)(H)(HO)C-O-O-O-O-O-C(OH)(H)(C_2H_5)$$

(29)

The formed tetroxide is actually a short lived intermediate that further might:

- Reform the α-hydroxyalkylperoxy radical (reverse of reaction (29), $\Delta G = -94$ kJ mol$^{-1}$);
- Eliminate O$_2$, thus forming two α-hydroxyalkoxy radicals (reaction (30), $\Delta G = -180$ kJ mol$^{-1}$) whose fate is described by the succession of reactions (12)–(17) at insertion mechanism;

$$(C_2H_5)(H)(HO)C-O-O-O-O-C(OH)(H)(C_2H_5) \rightarrow 2 (C_2H_5)(H)(HO)C-O• + O_2$$

(30)

- Decay via Russel reaction that involves a transition state with a six-membered ring (reaction (31), $\Delta G = -583$ kJ mol$^{-1}$) [7,21]. Given that the diol formed in reaction (31) eliminates one water molecule intramolecularly according to reaction (32) ($\Delta G = -52$ kJ mol$^{-1}$), the products are propionaldehyde, propionic acid, and oxygen in a 1:1:1 ratio;

$$(C_2H_5)(H)(HO)C-O-O-O-O-C(OH)(H)(C_2H_5) \rightarrow (C_2H_5)(H)(HO)2C + (C_2H_5)COOH + O_2$$

(31)

$$2 (C_2H_5)(H)(HO)2C \rightarrow (C_2H_5)(H)C=O + H_2O$$

(32)

- Decay via Bennett reaction that involves a transition state with two five-membered rings (reaction (33), $\Delta G = -752$ kJ mol$^{-1}$) [7,17,22]. The products that form via this reaction are propionic acid and hydrogen peroxide in a ratio of 2:1.

$$(C_2H_5)(H)(HO)C-O-O-O-O-C(OH)(H)(C_2H_5) \rightarrow 2 (C_2H_5)COOH + H_2O_2$$

(33)

The Supplementary Materials describes α-hydroxyalkylperoxy radicals’ transformation to products, according to Russel and Bennett mechanisms and the corresponding energy diagram. As already suggested, these processes occur in accordance with the following succession: Reactants $\rightarrow$ First Transition State $\rightarrow$ Intermediate (Tetroxide) $\rightarrow$ Second Transition State $\rightarrow$ Products.

Between HO$_3^•$ formed in reaction (24) and the corresponding anion, O$_3$$-$, one can write the equilibrium (34). Given the pKa = −2 of this reaction, it follows that HO$_3^•$ is a very strong acid and O$_3$$-$ is the predominant species in our system [7,15,23–26]. The deprotonation occurs in the timescale of $10^{-12}$ s (reaction (34), $k_s = 10^{12}$ s$^{-1}$) [23,24]. Under the same timescale, i.e., in competition with deprotonation, HO$_3^•$ decays to HO• and O$_2$ (reaction (35)) [7].

$$\text{HO}_3^• \rightleftharpoons \text{O}_3^- + \text{H}^+$$

(34)

$$\text{HO}_3^• \rightarrow \text{HO}^• + \text{O}_2$$

(35)
O$_3$$^{•-}$ formed by deprotonation also acts as HO$•$ precursor, but it decays in a larger timescale [6,24,25]. In the first step, O$_3$$^{•-}$ cleaves to O$^{•-}$ and O$_2$ (reaction (36), characterized by K = $5.5 \times 10^{-7}$ M, $k_+ = (1.94 \pm 0.16) \times 10^3$ s$^{-1}$, $k_- = 3.5 \times 10^9$ M$^{-1}$ s$^{-1}$) [7,24,25,27] and then O$^{•-}$ is protonated (reaction (37), pKa = (11.84 ± 0.08)) [27].

$$O_3$$^{•-} \rightleftharpoons O_2 + O$$^{•-}$$ \hspace{1cm} (36)$$O$$^{•-} + H^+ \rightleftharpoons HO$$•$$ \hspace{1cm} (37)$

Hydroxyl radicals could undergo bimolecular decay thus leading to hydrogen peroxide (reaction (38), $k = 7.7 \times 10^{9}$ M$^{-1}$ s$^{-1}$ [28]). Due to the fact that the substrate is in very large concentration in our system ([1-propanol] = 0.1 M) it can be expected that HO$•$ reacts mainly with the substrate and that reaction (38) is negligibly. The interaction of hydroxyl radical with the substrate is discussed at the paragraph no. 3.2. Mechanism initiated by the reaction of HO$•$ with 1-propanol. It is also shown in Figure 7.

$$2 \text{HO}• \rightarrow \text{H}_2\text{O}_2 \hspace{1cm} (38)$$

The products according to this mechanism are as follows: propionaldehyde, propionic acid, acetaldehyde, acetic acid, formic acid, hydrogen peroxide and hydroxyl radical. The overall formation yields, as experimentally determined, are as follows: propionaldehyde—(60 ± 3)%, propionic acid—(27.4 ± 1.0)%, acetaldehyde—(4.9 ± 0.3)%, acetic acid—(0.3 ± 0.1)%, formic acid—(4.6 ± 0.3)%, hydrogen peroxide—(11.1 ± 0.3)% and hydroxyl radical—(9.8 ± 0.3)%.

Due to the fact that HO$•$ practically forms only via this mechanism, ozone consumption yield according to H-abstraction is expected to be equal to HO$•$ formation yield, about 10%.

3.1.4. Electron Transfer

Ozone might also react with 1-propanol by withdrawing one electron when a radical cation and an ozonide anion are likely formed (reaction (39), $\Delta G = 100$ kJ mol$^{-1}$).

$$(\text{C}_2\text{H}_5)\text{H}_2\text{C}$$−$$\text{OH} + O_3 \rightarrow [(\text{C}_2\text{H}_5)\text{H}_2\text{C}$$−$$\text{OH}]$$^{•+} + O_3$$^{•−} \hspace{1cm} (39)$$

The radical cation might lose one proton (reaction (40), $\Delta G = −41$ kJ mol$^{-1}$) and the resulting alkylxyl radical is likely to undergo $\beta$-fragmentation (reaction (41), $\Delta G = −19$ kJ mol$^{-1}$) and 1,2-H shift (reaction (42), $\Delta G = −48$ kJ mol$^{-1}$).

$$[(\text{C}_2\text{H}_5)\text{H}_2\text{C}$$−$$\text{OH}]$$^{•+} \rightarrow (\text{C}_2\text{H}_5)\text{H}_2\text{C}$$−$$\text{O}$$• + H$^+$ \hspace{1cm} (40)$$$(\text{C}_2\text{H}_5)\text{H}_2\text{C}$$−$$\text{O}$$• \rightarrow •\text{C}_2\text{H}_5 + \text{H}_2\text{C}=\text{O} \hspace{1cm} (41)$$(\text{C}_2\text{H}_5)\text{H}_2\text{C}$$−$$\text{O}$$• \rightarrow (\text{C}_2\text{H}_3)(\text{H})(\text{HO})$$• \hspace{1cm} (42)$

The hydroxyalkyl radical resulted following 1,2-H shift (reaction (42)), would further react according to the sequence formed from reactions (25)–(33).

The ozonide anion formed in reaction (39) would lead to HO$•$ according to reactions (34)–(37).

Practically, the mechanism triggered by the electron transfer is ruled out, as suggested by the fact that the first step is strongly endergonic ($\Delta G = 100$ kJ mol$^{-1}$). One can notice that all products that could form via electron transfer also form through other mechanisms.

3.1.5. Overview

The possible pathways initiated by the direct reactions of ozone with 1-propanol are shown in Figure 6.
Based on the above-mentioned discussion, it follows that of the four pathways by which ozone can react with 1-propanol directly, hydride transfer, insertion and H-abstraction are confirmed both by the thermodynamic data and quite high formation yields of the expected products. In the case of electron transfer, the highly positive value of Gibbs energy (ΔG = 100 kJ mol⁻¹) suggests that this reaction does not occur, which is also confirmed by the low overall formation yield of HO•, which actually forms via H-abstraction (for the first step, when HO₃• (HO• precursor) forms, Gibbs energy is ΔG = −19 kJ mol⁻¹).

By H-abstraction, 10% of the available ozone react and this percentage is given by HO• formation yield. The stable products as part of this pathway are propionaldehyde, propionic acid, acetaldehyde, acetic acid, formic acid and hydrogen peroxide. One can notice that although the overall formation yield with respect to ozone for propionic acid and propionaldehyde are (27.4 ± 0.5)%, respectively, maximum 10% of the available ozone leads to the formation of these products by H-abstraction.

Hydride transfer mechanism leads only to propionaldehyde and due to the very high overall formation yield of this species, (60 ± 3)%, it means that, although it might also form by other pathways (H-abstraction and HO• attack at 1-propanol), hydride transfer is the main mechanism to a maximum 60% share of the studied mechanisms.

Insertion mechanism is likely to lead to propionic acid, acetic acid, acetaldehyde, formic acid and hydrogen peroxide. Given that the overall formation yield of propionic acid with respect to ozone is (27.4 ± 1.0)%, it follows that insertion is an important pathway, although this product can form also through H-abstraction and HO• attack at 1-propanol.

One must note that the three thermodynamically possible pathways are interconnected. Thus, the radical pair resulting from H-abstraction might undergo electron transfer, leading to the ion-pair resulting from hydride transfer (ΔG = −148 kJ mol⁻¹). Also the radical pair might recombine to form the trioxide (ΔG = −173 kJ mol⁻¹). In addition, an equilibrium is likely to be possible between the caged ion pair formed by hydride transfer and the trioxide formed after insertion. The reason for this is that the solvation energies of the ions might be underestimated by more than the difference between the

Figure 6. Pathways triggered by the direct reactions of ozone with 1-propanol.
Gibbs energies of the two reactions ($\Delta G = -167$ kJ mol$^{-1}$ for hydride transfer and $\Delta G = -192$ kJ mol$^{-1}$ for insertion).

3.1.6. Comparison between 1-propanol/ozone and 2-propanol/ozone systems

The most important similarities or dissimilarities between the two aqueous systems are as follows:

- Carbonyl compounds with three carbon atoms formation yields with respect to ozone was very high for 2-propanol/ozone system (acetone formation yield was 87%) and decreased by 30% for the 1-propanol/ozone system (propionaldehyde formation yield was 60%). In the case of the 1-propanol/ozone system, propionic acid was also formed with a yield of 27%.

- Hydride transfer played a very important role for both systems, however the share of this mechanism was higher for the 2-propanol/ozone system (around 90% as opposed to maximum 60% for 1-propanol/ozone). The overall share of H-abstraction and insertion for 1-propanol/ozone system was higher or equal to 27% (propionic formation yield) and only a few percent for 2-propanol/ozone system.

- The second order rate constant of the reaction between 2-propanol and O$_3$ at 23 $^\circ$C, $k_{II} = (2.7 \pm 0.1)$ M$^{-1}$ s$^{-1}$, was roughly four times higher than that between 1-propanol and O$_3$, $k_{II} = (6.4 \pm 0.2) \times 10^{-1}$ M$^{-1}$ s$^{-1}$.

- Hydroxyl radicals formation yield was about four times higher for 1-propanol/ozone system, (9.8 $\pm$ 0.3)%, than that for 2-propanol/ozone, (2.4 $\pm$ 0.5)%. This information showed that the H-abstraction share was roughly four times higher in 1-propanol/ozone system than in 2-propanol/ozone (H-abstraction share was equal to HO• formation yield) and highlighted the increase of the importance of reactions between HO• and substrate for 1-propanol/ozone as against 2-propanol/ozone.

3.2. Mechanism Initiated by the Reaction of HO• with 1-propanol

Asmus and co-workers have found as part of their pulse radiolysis studies, that HO• attack on 1-propanol occurs at C($\alpha$)—53.4%, C($\beta$)—46% and OH—less than 0.5% [29]. The corresponding reactions are (43), (44) and (45), characterized by the following Gibbs energies: $-123$ kJ mol$^{-1}$, $-107$ kJ mol$^{-1}$ and $-76$ kJ mol$^{-1}$, respectively. The attack of HO• on hydroxyl group will be neglected in the following discussion due to the low occurrence yield.

\[
\begin{align*}
(C_3H_8)(H)(HO)C-H + HO\bullet &\rightarrow (C_3H_8)(H)(HO)C\bullet + H_2O \quad (43) \\
((HO)CH_2)(CH_3)(H)C-H + HO\bullet &\rightarrow ((HO)CH_2)(CH_3)(H)C\bullet + H_2O \quad (44) \\
(C_2H_5)H_2C-OH + HO\bullet &\rightarrow (C_2H_5)H_2C-O\bullet + H_2O \quad (45)
\end{align*}
\]

One can notice that the radical resulted in reaction (43) is the same as the one formed after H-abstraction (reactions (22) and (24)) and its fate can be followed in the paragraphs that deals with H-abstraction mechanism (reactions (25)–(33)) and insertion mechanism (reactions (12)–(17)). The resulting products (from the reaction of 1-propanol with both O$_3$ and HO•) and the corresponding overall formation yields are: propionaldehyde—(60 $\pm$ 3)%, propionic acid—(27.4 $\pm$ 1.0)%, acetaldehyde—(4.9 $\pm$ 0.3)%, acetic acid—(0.3 $\pm$ 0.1)%, formic acid—(4.6 $\pm$ 0.3)% and hydrogen peroxide—(11.1 $\pm$ 0.3)%.

The radical formed in reaction (44) might add O$_2$, which is in high concentration in our system, thereby leading to a peroxyl radical (reaction (46), $\Delta G = -100$ kJ mol$^{-1}$).

\[
((HO)CH_2)(CH_3)(H)C\bullet + O_2 \rightarrow ((HO)CH_2)(CH_3)(H)C-O-O\bullet \quad (46)
\]
Given that this peroxy radical does not contain the hydroxyl group in α-position, it cannot eliminate HOO•/O2• but, as a secondary peroxy radical, it might dimerise (reaction (47), $\Delta G = 85$ kJ mol$^{-1}$).

$$
2 \text{(HO(CH$_2$)$_2$)(CH$_3$)(H)C-O-O•} \rightleftharpoons \text{(HO(CH)$_2$)(CH$_3$)(H)C-O-O-O-C(H)(CH$_3$)(CH$_2$)(OH)) (47)}
$$

The formed tetroxide is a short-lived intermediate that might: (a) reform the peroxy radical (reverse of reaction (47), $\Delta G = -85$ kJ mol$^{-1}$), (b) eliminate oxygen (reaction (48), $\Delta G = -134$ kJ mol$^{-1}$ and the Russel reaction (49), $\Delta G = -505$ kJ mol$^{-1}$) and (c) eliminate H$_2$O$_2$ (Bennett reaction (50), $\Delta G = -627$ kJ mol$^{-1}$).

$$
\text{(HO(CH)$_2$)(CH$_3$)(H)C-O-O-O-C(H)(CH$_3$)(CH$_2$)(OH))} \rightarrow 2 \text{(HO(CH)$_2$)(CH$_3$)(H)C-O•} + \text{O} \tag{48}
$$

$$
\text{(HO(CH)$_2$)(CH$_3$)(H)C-O-O-O-C(H)(CH$_3$)(CH$_2$)(OH))} \rightarrow \text{(HO(CH)$_2$)(CH$_3$)(H)C-OH} + \text{(HO(CH)$_2$)(CH$_3$)C=O + O}_2 \tag{49}
$$

$$
\text{(HO(CH)$_2$)(CH$_3$)(H)C-O-O-O-C(H)(CH$_3$)(CH$_2$)(OH))} \rightarrow 2 \text{(HO(CH)$_2$)(CH$_3$)C=O + H}_2\text{O}_2 \tag{50}
$$

The oxyl radical which occurred in reaction (48) is likely to decay by β-fragmentation (reaction (51), $\Delta G = -21$ kJ mol$^{-1}$ and reaction (52), $\Delta G = -60$ kJ mol$^{-1}$) and it might undergo 1,2-H shift (reaction (53), $\Delta G = -48$ kJ mol$^{-1}$).

$$
\text{(HO(CH)$_2$)(CH$_3$)(H)C-O•} \rightarrow \text{(HO(CH)$_2$)(H)C=O + \bullet\text{CH}_3} \tag{51}
$$

$$
\text{(HO(CH)$_2$)(CH$_3$)(H)C-O•} \rightarrow \text{(HO)$_2$C• + (CH$_3$)(H)C=O} \tag{52}
$$

$$
\text{(HO(CH)$_2$)(CH$_3$)(H)C-O•} \rightarrow \text{(HO(CH)$_2$)(CH$_2$)(HO)C•} \tag{53}
$$

Reaction (53) is followed by an O$_2$ addition to the alkyl radical, when α-hydroxalkylperoxy radical forms (reaction (54), $\Delta G = -69$ kJ mol$^{-1}$). This is in equilibrium with the corresponding radical anion, according to reaction (55). Further, both protonated and deprotonated species form hydroxyacetone by eliminating HO$_2$•/O$_2$• (reaction (56) characterised by $\Delta G = -46$ kJ mol$^{-1}$ and reaction (57) with $\Delta G = -45$ kJ mol$^{-1}$).

$$
\text{(HO(CH)$_2$)(CH$_3$)(HO)C•} + \text{O}_2 \rightarrow \text{(HO(CH)$_2$)(CH$_3$)(HO)C-O-O•} \tag{54}
$$

$$
\text{(HO(CH)$_2$)(CH$_3$)(HO)C-O-O•} + \text{H}^+ \rightleftharpoons \text{(HO(CH)$_2$)(CH$_3$)(HO)C-O-O•} + \text{H}_2\text{O} \tag{55}
$$

$$
\text{(HO(CH)$_2$)(CH$_3$)(HO)C-O-O•} \rightarrow \text{(HO(CH)$_2$)(CH$_3$)C=O + HO$_2$•} \tag{56}
$$

$$
\text{(HO(CH)$_2$)(CH$_3$)(HO)C-O-O•} \rightarrow \text{(HO(CH)$_2$)(CH$_3$)C=O + O$_2$•} \tag{57}
$$

The products that might form via HO• attack on 1-propanol in β position are: 1,2-propanediol, hydroxyacetone, acetaldehyde, hydroxyacetalddehde, formaldehyde, formic acid and hydrogen peroxy. Out of these products, only the overall formation yields with respect to ozone of a few were determined, as follows: acetaldehyde—$(4.9 \pm 0.3)\%$, formaldehyde—$(1.0 \pm 0.1)\%$, formic acid—$(4.6 \pm 0.3)\%$ and hydrogen peroxy—$(11.1 \pm 0.3)\%$.

Due to the relatively low HO• formation yield with respect to ozone, $(9.8 \pm 0.3)\%$, and taking into account that the yields of HO• attack at C(α) and C(β) are $53.4\%$ and $46\%$, respectively, it results that the products formation yields with respect to ozone might be a few percent at most for this pathway.

Figure 7 shows the succession of reactions triggered by the attack of HO• on 1-propanol.
hydroxyacetone by eliminating HO$_2$•/O$_2$• (reaction (56) characterised by $\Delta G = -46$ kJ mol$^{-1}$) and reaction (57) with $\Delta G = -45$ kJ mol$^{-1}$).

$$((\text{HO})\text{CH}_2)(\text{CH}_3)(\text{HO})\text{C}• + \text{O}_2 \rightarrow ((\text{HO})\text{CH}_2)(\text{CH}_3)(\text{HO})\text{C}^-\text{O}^-\text{O}•$$  (54)

$$((\text{HO})\text{CH}_2)(\text{CH}_3)(\text{HO})\text{C}^-\text{O}^-\text{O}• + \text{HO}^- \rightleftharpoons ((\text{HO})\text{CH}_2)(\text{CH}_3)(\text{HO})\text{C}^-\text{O}^-\text{O}• + \text{H}_2\text{O}$$  (55)

$$((\text{HO})\text{CH}_2)(\text{CH}_3)(\text{HO})\text{C}^-\text{O}^-\text{O}• \rightarrow ((\text{HO})\text{CH}_2)(\text{CH}_3)\text{C}=\text{O} + \text{HO}_2•$$  (56)

$$((\text{HO})\text{CH}_2)(\text{CH}_3)(\text{HO})\text{C}^-\text{O}^-\text{O}• \rightarrow ((\text{HO})\text{CH}_2)(\text{CH}_3)\text{C}=\text{O} + \text{O}_2•$$  (57)

The products that might form via HO• attack on 1-propanol in $\beta$ position are: 1,2-propandiol, hydroxyacetone, acetaldehyde, hydroxyacetaldehyde, formaldehyde, formic acid and hydrogen peroxide. Out of these products, only the overall formation yields with respect to ozone of a few were determined, as follows: acetaldehyde — $(4.9 \pm 0.3)$%, formaldehyde — $(1.0 \pm 0.1)$%, formic acid — $(4.6 \pm 0.3)$% and hydrogen peroxide — $(11.1 \pm 0.3)$%.

Due to the relatively low HO• formation yield with respect to ozone, $(9.8 \pm 0.3)$%, and taking into account that the yields of HO• attack at C(α) and C(β) are 53.4% and 46%, respectively, it results that the products formation yields with respect to ozone might be a few percent at most for this pathway.

Figure 7 shows the succession of reactions triggered by the attack of HO• on 1-propanol.

4. Materials and Methods

All chemicals were p.a. grade from: Merck (Merck Millipore, Darmstadt, Germany), Fluka (Fluka Chemie GmbH, Buchs, Switzerland), Fischer (Fischer Scientific GmbH, Schwerte, Germany), Alfa Aesar (Alfa Aesar, Karlsruhe, Germany) or Sigma Aldrich (Sigma Aldrich Chemie GmbH, München, Germany) and they were used without further purification. More information is given in Supplementary Materials.

Ozone solutions were prepared by bubbling ozone containing oxygen stream in type I Millipore water. Ozone containing gas was obtained by means of a Sander 300.5 ozone generator (Erwin Sander Elektroapparatebau GmbH, Uetze-Eltze, Germany) fed with oxygen 6.0 from Linde (Linde A.G., München, Germany). The type I water came from a Milli Q device (Merck Millipore, Darmstadt, Germany). Ozone and 1-propanol solutions were mixed in various proportions. The concentration of ozone in both freshly prepared ozone solutions and in those that resulted after mixing with 1-propanol was determined spectrophotometrically at 260 nm by using $\varepsilon(260) = 3200 \text{ M}^{-1} \text{cm}^{-1}$ [7]. All spectrophotometric measurements were carried out with a Shimadzu UV 1800 device (Shimadzu Europa GmbH, Duisburg, Germany).

Kinetic studies were carried out in the presence of large 1-propanol excess with respect to ozone to secure half-life times of minutes. Under these circumstances, the ozone decay via HO• was negligible. More details are provided in Supplementary Materials. Practically, 1 mL ozone solution (about 15 °C) was added to 14 mL 1-propanol solution, previously brought to the required temperature, in a 5 cm thermostated quartz cuvette. The temperature of the solution was measured with a dipped thermocouple before ozone addition and after completion of the reaction. The difference between the two temperatures did not exceed 0.4 °C. Ozone decay was followed spectrophotometrically by using the time-drive mode.

The formed acids (formic, acetic and propionic acids) were quantified by means of IC with conductometric detection. The analyses were carried out by using a Metrohm 883 Basic IC plus device (Metrohm, Herisau, Switzerland) equipped with a Metrosep Organic Acids 250/7.8 column...
The absorption coe... against a blank. The molar

The concentration of the formed aldehydes (formaldehyde, acetaldehyde and propionaldehyde) was determined by HPLC-DAD. To that end, derivatization of the aldehydes with 2,4-dinitrophenyl hydrazine (2,4-DNPH) to 2,4-dinitrophenylhydrazones was used [30]. Practically, a solution resulted by adding 0.2 mL 2,4-dinitrophenylhydrazine in acetonitrile (6 mM) and 0.1 mL perchloric acid in acetonitrile (1 M) to 1.7 mL sample, which was kept in dark for 45 min, was injected in a Shimadzu LC 20 chromatograph (Shimadzu Europa GmbH, Duisburg, Germany). The separation of hydrazones was carried out by using a C18 (NC-04, 250 mm × 4.0 mm ID, 5.0 µm, Prontosil) column (Bischoff Analysentechnik und Geräte GmbH, Leonberg, Germany). The eluent was acetonitrile in water (35%—2 min, 45%—3 min, 100%—20 min and 35%—15 min) at a flow rate of 0.5 mL min⁻¹. The retention times and wavelengths used for detection were 18.0 min/350 nm for formaldehyde, 18.8 min/359 nm for acetaldehyde and 19.7 min/360 nm for propionaldehyde. Under the above-mentioned conditions, the derivatization was considered as a quantitative process.

Formaldehyde was also determined spectrophotometrically by using the Hantzsch method. This is based on the reaction among formaldehyde, acetylacetone and ammonium acetate, when the product is a yellow compound that has an absorption maximum at 412 nm of ε(412) = 7700 M⁻¹ cm⁻¹ [31]. The technique consists of adding 2 mL Hantzsch reagent (25 g ammonium acetate, 3 mL glacial acetic acid and 0.2 mL acetylacetone brought to 100 mL with water) to 10 mL sample, keeping the obtained mixture for 30 min at 50 °C, and measuring the absorbance of the suddenly cooled sample against a blank.

The assessment of hydroxyl radical formation yield with respect to ozone was based on formaldehyde formation following the reaction between tert-butanol (acting as a scavenger) and hydroxyl radicals in the presence of oxygen [32]. For the systems where ozone occurs together with oxygen, Flyunt et al. have reported a 50% formaldehyde formation yield with respect to hydroxyl radicals [33].

Given that in our system formaldehyde also resulted following the reaction of 1-propanol with hydroxyl radicals, the calculation of hydroxyl radicals’ formation yield with respect to ozone involves knowing formaldehyde formation yields with respect to ozone in the presence and absence of tert-butanol.

Formaldehyde formation yields in the two systems can be derived from the slopes of straight lines in the graphic representation of the formed formaldehyde concentration versus the introduced ozone concentration. An aspect that had to be taken into consideration with this method was the fact that usually isobutene may be present as impurity in tert-butanol, which could lead to formaldehyde following the reaction with ozone: (H₃C)₂C=CH₂ + O₃ + H₂O → (H₃C)₂C=O + H₂C=O + H₂O₂ [34,35]. Given the fact that this reaction was fast, formaldehyde formed at the beginning and thus it did not exert influence on the slopes, but only on the y-intercepts.

Hydrogen peroxide quantification was carried out by using Allen’s method [36]. This was based on the reaction between compounds such as R−O−O−H (R can be an H atom or an organic group) and I⁻, in excess, whereby I₃⁻ is formed. Given that this is usually a slow reaction, a catalyst, namely ammonium heptamolybdate, is introduced in the system. In the case of H₂O₂, the catalyst led to the increase of reaction rate constant from 1.8 × 10⁻³ M⁻¹ s⁻¹ [33] to 2.1 M⁻¹ s⁻¹ [34]. Practically, 1 mL Allen’s A (1 g NaOH, 33 g KI and 0.1 g (NH₄)₆Mo₇O₂₄·4H₂O dissolved in Millipore water and brought to 500 mL), 1 mL Allen’s B (10 g potassium hydrogen phthalate dissolved in Millipore water and brought to 500 mL) and 1 mL sample were mixed in a 1 cm cuvette (in between additions the cuvette was strongly stirred). The absorbance of the mixture was read at 350 nm against a blank. The molar absorption coefficient of I₃⁻ was ε(350) = 25500 M⁻¹ cm⁻¹ [36].

Quantum chemical calculations were done by using the Density Functional Theory method (DFT) B3LYP [37,38], as implemented in Jaguar program [39]. The structures of the studied molecules were...
optimized in water with Jaguar’s Poisson-Boltzmann solver (PBF) [40] at B3LYP/6-311+G(d,p)/PBF level of theory. The frequency analysis was carried out to characterize the stationary points on the potential surface and to obtain Gibbs energy (G) at 298 K. The Gibbs energy of reactions (ΔG) were derived from the calculated Gibbs energies of reactants and products. The calculated Gibbs energies give some insight in the feasibility of the reactions. Actually the competition of pathways and product formation are determined by kinetics (for thermodynamically feasible reactions). Calculations of charged species as required for the Gibbs energy of equilibrium are inherently poorer. It was shown [23], that via B3LYP/6–311+G(d,p)/PBF method values comes closest to the experimental ones.

5. Conclusions

This study confirms the supposition that ozone reacts with 1-propanol in aqueous media mainly by hydride transfer as expected based on the results for 2-propanol/ozone aqueous system. In contrast to 2-propanol/ozone system, where insertion and H-abstraction have a share of a small percentage, ozone reacts with 1-propanol with yields of one order of magnitude higher as part of the afore-mentioned mechanisms. This is an important finding that linked to the fact that the nature of products depends on mechanism. Thus, the hydride transfer leads to aldehyde and ketone with the same number of carbon atoms as alcohols, while by insertion and H-abstraction, the result is a mix of acids and carbonyl compounds. This means that the same ozone consumption lead to a higher degree of oxidation and to fragmentation of the initial molecule for insertion and H-abstraction (other oxidants such as HO•, HO2• and H2O2 are also formed). In addition, one can notice that the reaction rate between 1-propanol and ozone is four times lower than that between 2-propanol and ozone. The two second order rate constants are: (6.4 ± 0.2) × 10⁻¹ M⁻¹ s⁻¹ for 1-propanol and (2.7 ± 0.1) M⁻¹ s⁻¹ for 2-propanol. This finding is also correlated with the share of mechanisms.

The comparison between the 2-propanol/ozone and 1-propanol/ozone aqueous systems clearly shows that a small change in the structure of the molecule (in our case switching from a secondary alcohol to a primary one with the same number of carbon atoms) leads to significant variations in the nature and share of the reaction products and also on the reaction rate. This has a great impact, for example, in the treatment of waters. In this context, one may foresee that the water treatment will rely less on the use of some overall parameters and that it will be more and more specific, based on the knowledge of the exact composition of certain waters and the interaction with various chemicals used for water treatment.

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