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Heterogeneous OH oxidation of isoprene-epoxydiol-derived organosulfates: kinetics, chemistry and formation of inorganic sulfate

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Tentative Reaction Mechanisms

Schemes S1–S5 show the reaction mechanisms tentatively proposed for the heterogeneous OH oxidation of 3-methyltetrol sulfate ester based on the aerosol mass spectra (Figs. 1 and 2) and well-known aerosol-phase reactions previously reported in the literature (George and Abbatt, 2010; Kroll et al., 2015). We acknowledge that more studies using different analytical techniques to characterize and quantify the reaction products in both aerosol and gas phase are needed in order to cross check the aerosol composition data obtained by DART and verify the proposed reaction mechanisms in this work.

Potassium methyltetrol sulfate ester likely dissociates and exists in its ionic form in the droplets. In the first oxidation step, the OH radical abstracts a hydrogen atom to form an alkyl radical which quickly reacts with oxygen to form a peroxy radical. No formation of alcohol or carbonyl functionalization product can be observed in aerosol mass spectra (Fig. 1), regardless of initial hydrogen abstraction site. The absence of functionalization products in the aerosol mass spectra may suggest that fragmentation processes are likely to have occurred. One possible explanation is that the multiple functional groups in the 3-methyltetrol sulfate ester (e.g. hydroxyl, methyl and sulfate groups, or a combination of these functional groups, depending on the initial OH reaction site), which are always located at positions vicinal to a peroxyl group, may sterically hinder the association of two peroxy radicals into the cyclic tetroxide intermediate proposed in the Russell mechanism (Russell, 1957) and Bennett–Summers reactions (Bennett and Summers, 1974). As the intermediate is essential for the formation of alcohol and carbonyl functionalization products, the steric effect may in turn favor the formation of alkoxy radicals (Cheng et al., 2015). Alkoxy radicals, once formed, may tend to undergo fragmentation due to the presence of vicinal hydroxyl groups, which lower the activation energy required for the decomposition of the alkoxy radicals (Wiegel et al., 2015; Jimenez et al., 2009). To gain more insights into this process, calculations are preformed using a structural–activity relationship (SAR) model developed for the decomposition of alkoxy radicals (Peeters et al., 2004; Vereecken and Peeters, 2009). For example, when the β-carbons are methyl groups (isopropoxyl radical), the barrier height, E_b, for the decomposition is calculated to be 15.6 kcal mol^{-1}. When one β-carbon bears a hydroxyl group (1-hydroxyisopropoxyl radical), E_b is lowered to 8.1 kcal mol^{-1}, implying a faster decomposition rate. However, the effect of vicinal sulfate on the decomposition of an alkoxy radical has not been estimated.

The fragmentation of alkoxy radicals can yield fragmentation products (without sulfate group), smaller organosulfates and sulfate radical anions ($SO_4^{\bullet-}$), as shown in Schemes S1–S5. However, like the functionalization products, these products have not been detected (Fig. 1). Only the intensity of HSO_4^- increases after oxidation (Fig. 2). On the basis of the proposed reaction pathways (Schemes S1–S5), one possibility is that fragmentation products are likely to be volatile and partition back to the gas phase. The high volatility of these products may contribute to the absence of fragmentation products in the aerosol mass spectra. We acknowledge the measurement of gas-phase products are needed to determine the significance of the volatilization of the fragmentation products. Fragmentation processes can also yield smaller organosulfates, which have low volatilities and remain in the particle phase. In our previous study, we have demonstrated that small organosulfates, such as sodium methyl sulfate (CH_3SO_4Na) and sodium ethyl sulfate

($C_2H_5SO_4Na$), the alcohol and carbonyl functionalization products of sodium ethyl sulfate can be detected by the DART ionization source (Kwong et al., 2018). If these small organosulfates are formed in a significant amount during the oxidation of methyltetrol sulfate, the DART ionization technique will likely be able to detect them. We acknowledge that the detection limits and possible matrix effects are not yet well understood. Further studies on the sensitivity of DART-MS to smaller organosulfates under different conditions are warranted.

We postulate that upon oxidation the reaction intermediates may tend to decompose and eventually yield $SO_4^{\bullet -}$. $SO_4^{\bullet -}$ is a strong oxidant in aqueous phase and can react with a variety of organic compounds (e.g. alcohols, ethers, alkanes and aromatic compounds) (Neta et al., 1988; Clifton and Huie, 1989; Padmaja et al., 1993). For the OH reaction with 3-methyltetrol sulfate ester, $SO_4^{\bullet -}$ can abstract a hydrogen atom from a neighboring organic molecule (e.g. unreacted 3-methyltetrol sulfate ester) to form HSO_4^- (R1) or react with particle-phase water to yield a HSO_4^- and an OH radical (R2) (Tang et al., 1988) as illustrated below. It is noted that $SO_4^{\bullet -}$ or OH radical recycled from R2 can react with 3-methyltetrol sulfate ester, contributing to the secondary chain reactions.

$$\mathrm{C_5H_{11}O_7}S^- + \mathrm{SO_4}^{\bullet -} \rightarrow \mathrm{C_5H_{10}O_7}S^{\bullet -} + \mathrm{HSO_4}^- \qquad (R1)$$

$$\mathrm{SO_4}^{\bullet -} + \mathrm{H_2O} \rightleftharpoons \mathrm{OH}^{\bullet} + \mathrm{HSO_4}^- \qquad (R2)$$

Since 3-methyltetrol sulfate ester is unlikely to hydrolyze (Darer et al., 2011), the formation of the HSO_4^- upon OH oxidation could be best explained by the formation and subsequent reactions of $SO_4^{\bullet -}$. For instance, the OH-initiated oxidation by hydrogen abstraction at the terminal secondary carbon site (Scheme S1) can yield a peroxy radical. The formation of alkoxy radicals through the self-reactions of two peroxy radicals might be favored due to the steric effect induced by the presence of methyl and hydroxyl groups near the peroxyl group. The resultant alkoxy radical likely undergoes β-scission, attributing to the hydroxyl group located near the alkoxy group could lower the energy barrier height (Jimenez et al., 2009). It is postulated that an alkyl radical of methyl sulfate ion could be formed after multiple reaction steps proposed in the reaction scheme. Our recent work on the heterogeneous OH oxidation of sodium methyl sulfate has demonstrated that further reactions of this alkyl radical can lead to the formation of a formaldehyde and a $SO_4^{\bullet -}$, which subsequently abstract a hydrogen atom to form HSO_4^- (Scheme S5) (Kwong et al., 2018). At the same time, fragmentation products formed during β-scission (e.g. formic acid and acetic acid) are volatile and likely to partition back to the gas phase. It is noted that decomposition of α-hydroxylperoxy radical to carbonyl and HO_2 is a dominant pathway in gas phase (Neta et al., 1990). In our previous study, we have also found that this intramolecular HO_2 elimination process is an important reaction pathway during the heterogeneous OH oxidation of tartaric acid (Cheng et al., 2016). However, the carbonyl functionalization products have not detected in the aerosol mass spectra. Given the similarity in structures as compared to the parent compound (i.e. methyltetrol sulfate), the ionization issue might not be the primary reason for the absence of carbonyl products in the mass spectra. However, further investigations on the ionization efficiency and detection limit of reaction products are needed to better understand the reaction pathways and the significance of the decomposition of α-hydroxyperoxy radicals through HO_2 elimination process during oxidation.

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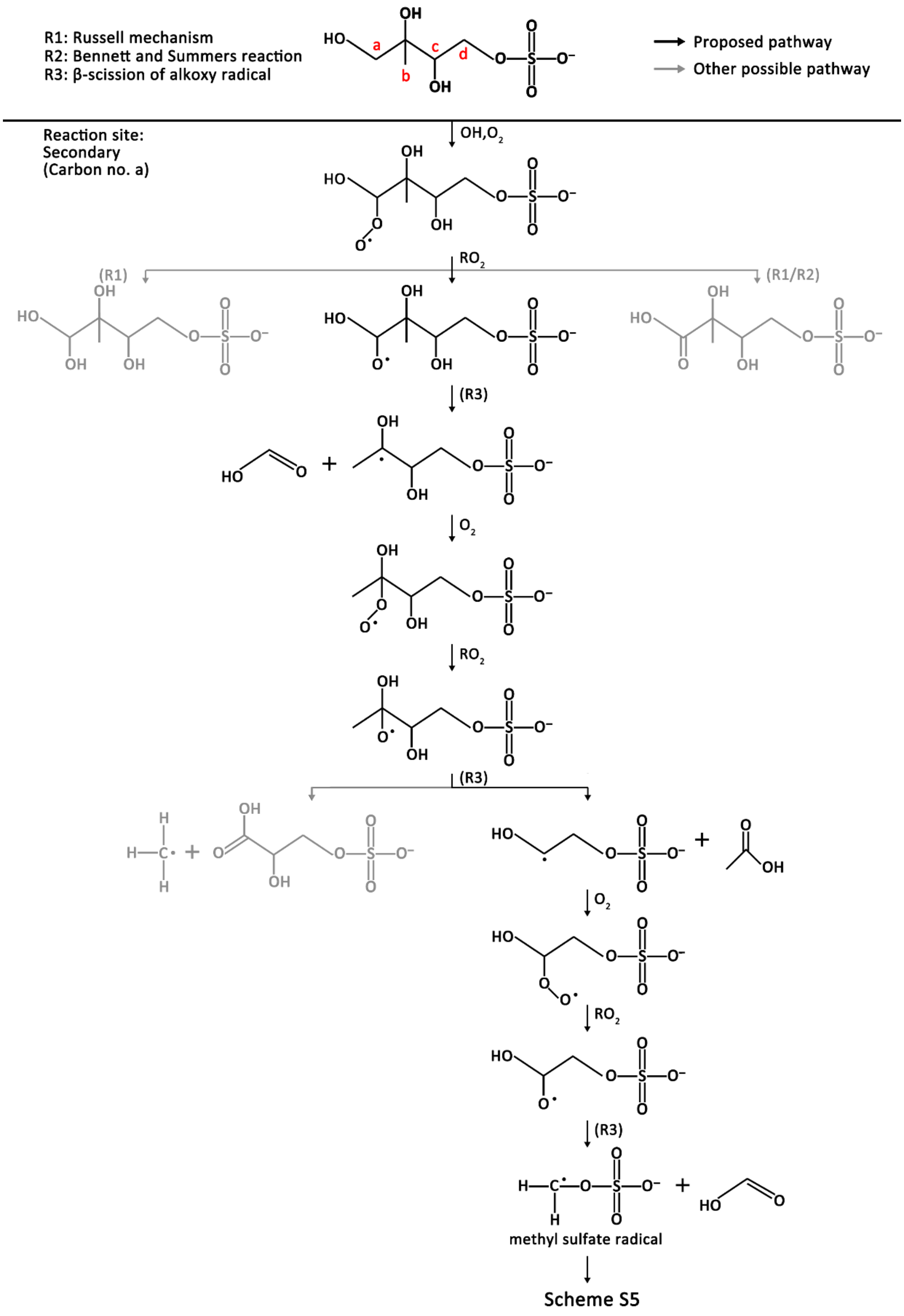
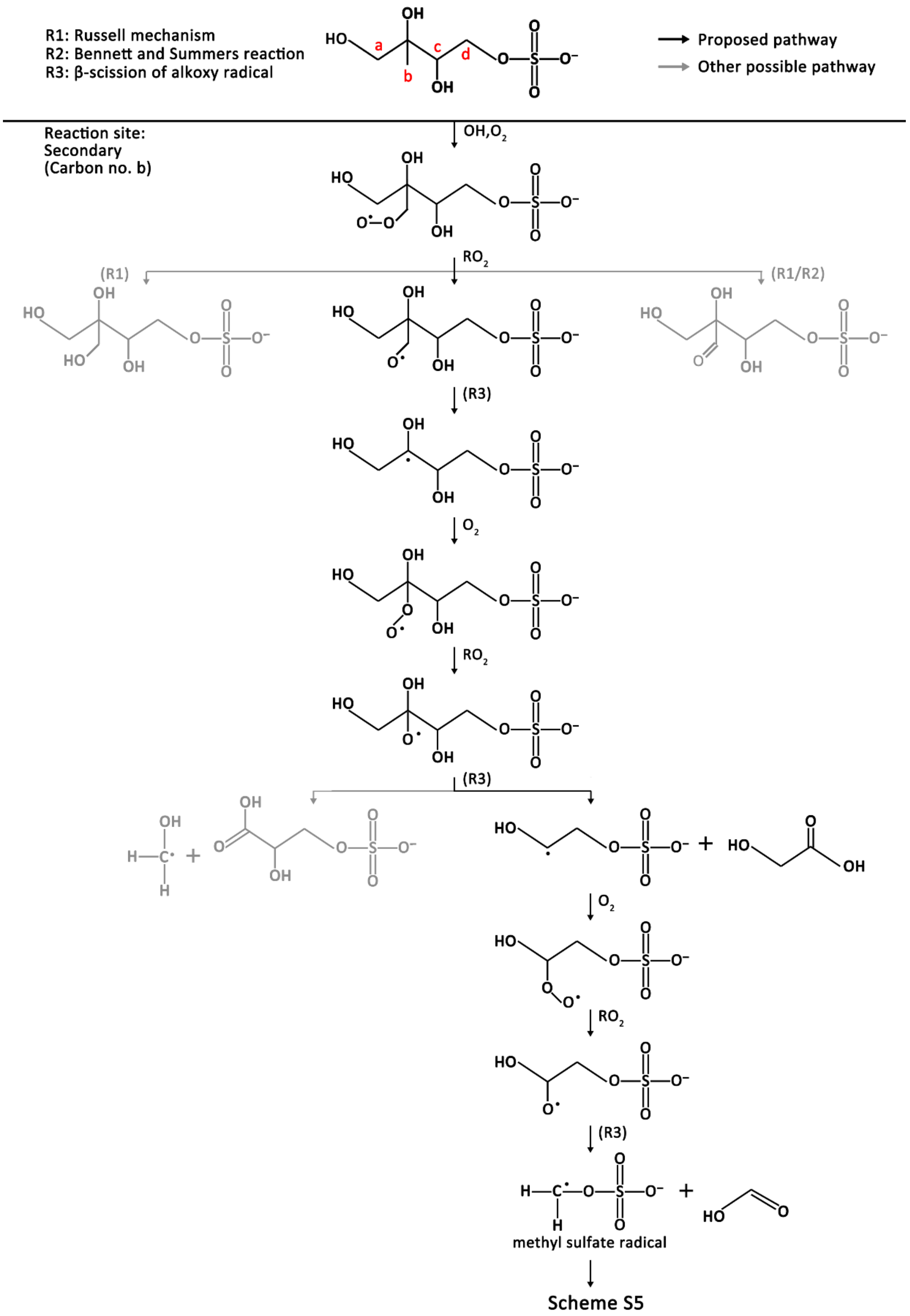
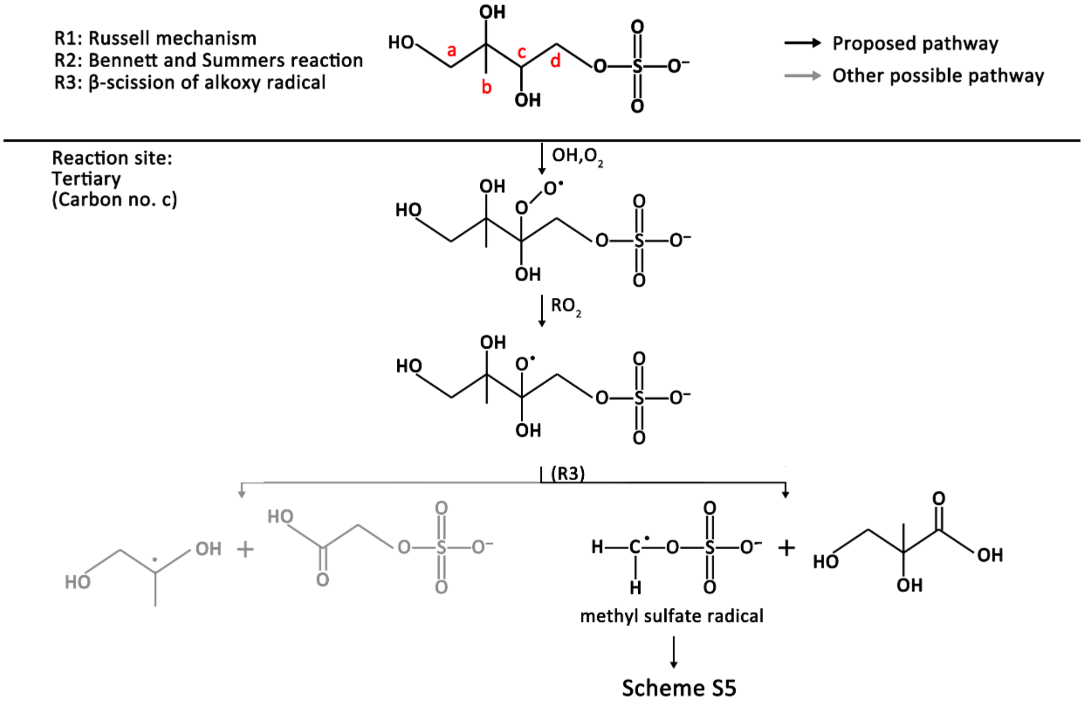


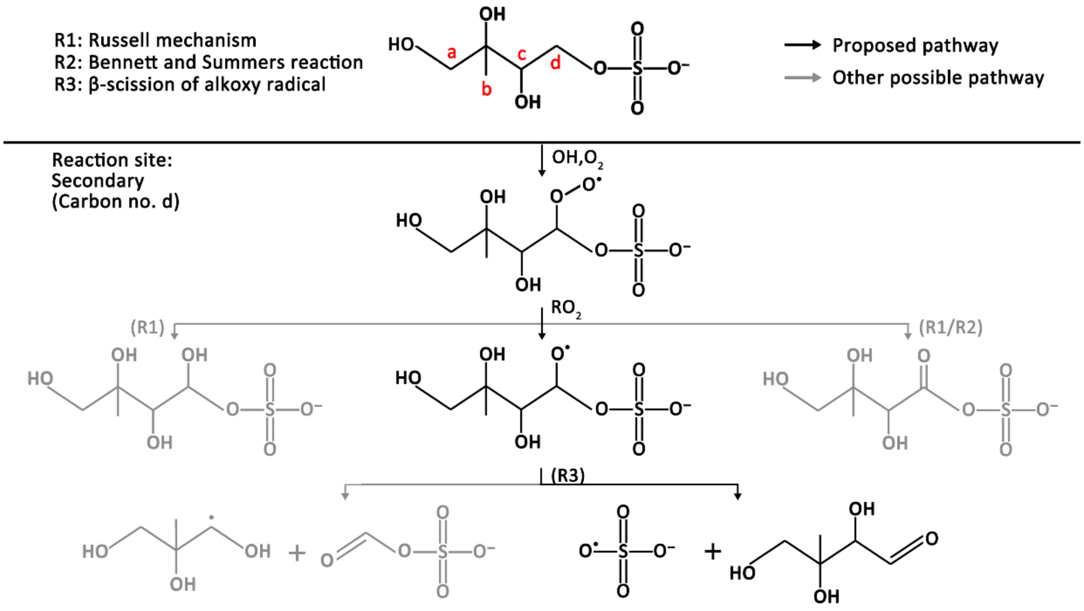
Scheme S1. Proposed reaction mechanisms for the heterogeneous OH oxidation of potassium 3-methyltetrol sulfate ester at the carbon labelled a.



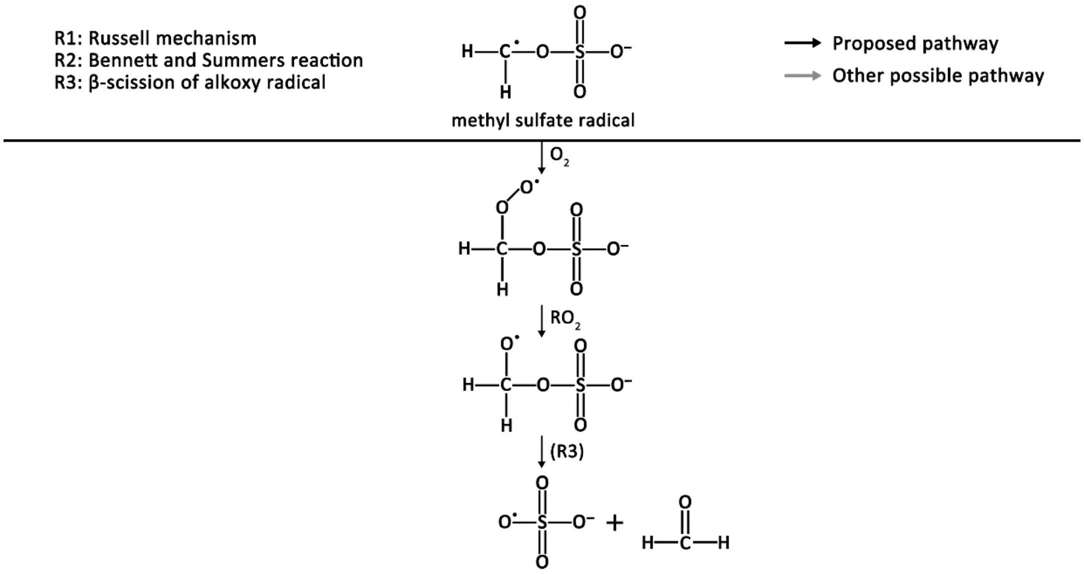
Scheme S2. Proposed reaction mechanisms for the heterogeneous OH oxidation of potassium 3-methyltetrol sulfate ester at the carbon labelled b.



Scheme S3. Proposed reaction mechanisms for the heterogeneous OH oxidation of potassium 3-methyltetrol sulfate ester at the carbon labelled c.



Scheme S4. Proposed reaction mechanism for the heterogeneous OH oxidation of potassium 3-methyltetrol sulfate ester at the carbon labelled d.



Scheme S5. Proposed reaction mechanism for the reactions of alkyl radical of methyl sulfate anion.