E.S.R. Evidence for the Formation of New Vinyl Radicals in Solution

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The new vinyl radicals $HC(SO_3^-)=\dot{C}CMe_2OH$, $HC(SO_3^-)=\dot{C}CH_2OH$, and $HC(SO_3^-)=\dot{C}CH(Me)OH$ were observed during the reactions of the SO_3^- radical with the corresponding alkynes 3-methylbut-1-yn-3-ol, prop-2-ynyl alcohol, and but-1-yn-3-ol, respectively, by use of an e.s.r. method coupled with a rapid-mixing flow technique which allows the detection of radicals having life-times of 5—100 ms.

In continuation of our work[1–4] on the reactivities of the SO_3^- radical which is generated from the Ce^{4+}–$NaHSO_3$ system, we have investigated the additions of the SO_3^- radical to C=C[3] or C=S[4] double bonds. Since there are few reports that e.s.r. spectroscopy has been employed in studies of radical intermediates formed in the reactions of alkynes, we have examined the reactions of the SO_3^- radical with alkynes in an aqueous flow system and we now report that new vinyl radicals are formed as intermediates.

The e.s.r. measurements were carried out on a JEOL-PE-1X

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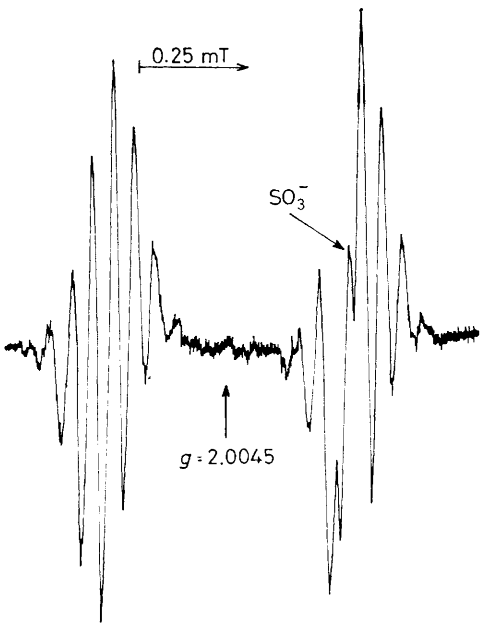
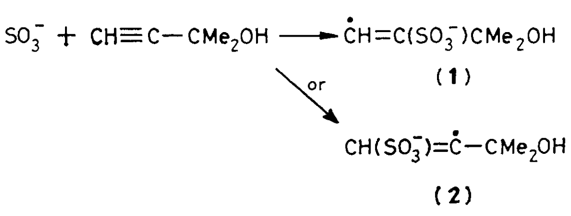


Figure 1. E.s.r. spectrum observed during the reaction of the SO_3^- radical with 3-methylbut-1-yn-3-ol in aqueous solution at room temperature.

e.s.r. spectrometer (X-band) with 100 kHz field modulation in conjunction with a JEOL mixing chamber. This apparatus enabled us to detect radicals having a lifetime of 5—100 ms. The hyperfine coupling constants and g-factors were calibrated by comparison with an aqueous solution of Fremy's salt (g = 2.0055, a^N = 1.30 mT)[5] kept in a capillary tube attached to the sample. For the generation of the SO_3^- radical, commercial samples of $Ce(NO_3)_4 \cdot 2NH_4NO_3$ and $NaHSO_3$ were used without further purification. Two solutions were prepared: (a) contained 0.01 M Ce^{4+} acidified with sulphuric acid and (b) 0.1 M $NaHSO_3$. To investigate the reactions of the SO_3^- radical with alkynes, the following alkynes (0.1 M) were added to solution (b): 3-methylbut-1-yn-3-ol, prop-2-ynyl alcohol, but-2-yne-1,4-diol, and but-1-yn-3-ol.

When solutions (a) and (b) were mixed, in the absence of alkyne, in the cavity of the e.s.r. spectrometer, a singlet line was observed, as expected (g = 2.0022) which has been assigned to the SO_3^- radical by us.[1] When 3-methylbut-1-yn-3-ol was added to solution (b) and the mixture allowed to react with solution (a), the intensity of the signal due to the SO_3^- radical was reduced considerably, and a new e.s.r. signal appeared at g = 2.0045 (Figure 1). This new signal was not detectable in the absence of either Ce^{4+} ion or $NaHSO_3$, suggesting that the SO_3^- radical participates in the formation of the secondary radical.

The g-factor (2.0045) of the new radical is somewhat higher than those of carbon radicals, which implies that the spectrum is not due to a carbon radical, but instead to a sulphur radical which are known to show a fairly large spin–orbit coupling constant.[6] Furthermore, since we have shown that the SO_3^- radical is rather inactive towards hydrogen abstraction,[3] the new radical species observed is presumably formed by the addition of the SO_3^- radical to the triple bond of the alkyne (Scheme 1). Two types of vinyl radicals (**1**) and (**2**) may be formed. The e.s.r. spectrum of the new radical species is analysed as follows: $a^H(1)$ = 0.510 mT, $a^H(6)$ = 0.043 mT.



$$SO_3^- + CH{\equiv}C{-}CMe_2OH \longrightarrow \dot{C}H{=}C(SO_3^-)CMe_2OH \ (\mathbf{1}) \quad \text{or} \quad CH(SO_3^-){=}\dot{C}{-}CMe_2OH \ (\mathbf{2})$$

Scheme 1

Since the SO_3^- radical is large, we suggest that its addition is subject to steric hindrance. This suggestion was supported by the following experiments. But-2-yne-1,4-diol ($HOH_2CC{\equiv}CCH_2OH$) having bulky substituents on either side of the triple bond did not give a secondary radical on reaction with the SO_3^- radical, whereas prop-2-ynyl alcohol ($HC{\equiv}CCH_2OH$) having a bulky substituent on one side of the triple bond only gave a secondary radical [$a^H(1)$ = 0.587 mT, $a^H(2)$ = 0.223 mT, g = 2.0048]. Accordingly, it is reasonable to consider that the new radical species has the structure (**2**). The new radical species from prop-2-ynyl alcohol is assigned the analogous structure $HC(SO_3^-){=}\dot{C}CH_2OH$. The hyperfine coupling constants for β-protons of vinyl radicals have been reported to be in the range 3.5—7.0 mT.[7,8] The fact that the β-proton couplings are smaller than those reported previously may be due to extensive delocalization of the electron density on the sulphur atom of the new radical (**2**).

A similar vinyl radical $HC(SO_3^-){=}\dot{C}CH(Me)OH$ [$a^H(1)$ = 0.574 mT, a^H (1) = 0.268 mT, a^H (3) = 0.062 mT, g = 2.0048] was observed during the reaction of the SO_3^- radical with but-1-yn-3-ol.

It is well known that vinyl radicals are too unstable to be detected by the usual e.s.r. measurements.[9] However, indirect evidence for the involvement of vinyl radials has been presented for their intermolecular addition, and intramolecular abstraction reactions.[9,10] The observation of vinyl radicals during the reactions of the SO_3^- radical with alkynes suggests that the SO_3^- ion stabilizes the vinyl radicals formed.

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