METHANE FORMATION FROM THE REACTIONS OF HYDROXYL RADICALS AND HYDROGEN ATOMS WITH DIMETHYL SULFOXIDE (DMSO)

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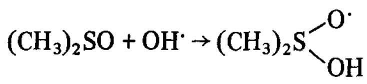
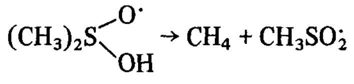
1. Introduction

DMSO is known to possess important radioprotective and anti-inflammatory properties which are generally associated with its rapid reaction with OH radicals. These may originate in chemical processes, for example: the Fenton reaction ($Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH + OH^-$); the Haber-Weiss reaction ($O_2^- + H_2O_2 \rightarrow OH + OH^- + O_2$); in biological processes such as microsomal electron-transfer reactions [1–3]; and in the radiolysis of aqueous systems. The rate constant of the reaction is $4.2 \times 10^9\ M^{-1}\ s^{-1}$ in neutral media [4]. It is generally accepted that the first step in the reaction mechanism is the formation of a radical adduct [5]:



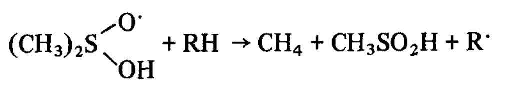
$$(CH_3)_2SO + OH^{\cdot} \rightarrow (CH_3)_2S\begin{matrix} O^{\cdot} \\ OH \end{matrix}$$

followed by, for example:



$$(CH_3)_2S\begin{matrix} O^{\cdot} \\ OH \end{matrix} \rightarrow CH_4 + CH_3SO_2^{\cdot}$$

or



$$(CH_3)_2S\begin{matrix} O^{\cdot} \\ OH \end{matrix} + RH \rightarrow CH_4 + CH_3SO_2H + R^{\cdot}$$

where RH may be another molecule of DMSO.

If the stoichiometry is simple, the methane yield should be equal to that of the OH radicals consumed. This formation of methane is important in biological research as it serves to estimate the OH production by liver microsomal reduction of oxygen and to determine the effect of other chemicals on this enzymatic process.

The radiolysis of aqueous DMSO solutions would appear to be a method well-suited for establishing this stoichiometry: the yield of OH radicals in water is known ($G_{OH} = 2.95$) [6] and by adding a second OH' scavenger such as the bromide ion it is possible to study the competition kinetics. The yield of methane should then vary according to the relation [7]:

$$G(CH_4)^{-1} = G_{OH}^{-1}\left(1 + \frac{k_1[Br^-]}{k_2[DMSO]}\right)$$

where k_1 and k_2 represent, respectively, the rate constants for the reactions of Br^- and DMSO with OH radicals.

In [8] methane was formed in pure DMSO by the reaction of hydrogen atoms and the question arises. Does this reaction also occur in the radiolysis of aqueous DMSO mixtures giving a second route to methane production?

We now study the effect of a second H-atom scavenger on the methane yield. Ethanol has been selected here since, in acidic media, it reacts with H to give H_2 but no CH_4 [9]. Conversely, the radiolysis of acidic aqueous solutions of DMSO leads to methane formation with only a constant low yield of (molecular) hydrogen ($G_{H_2} = 0.42$). Thus the hydrogen yield $G(H_2)$ formed by the competition between the 2 solutes for the radiolytic yield of H atoms will be given by:

$$\Delta G(H_2)^{-1} = G_H^{-1}\left(1 + \frac{k_3[DMSO]}{k_4[EtOH]}\right)$$

where $\Delta G(H_2) = G(H_2) - G_{H_2}$, k_3 and k_4 are the rate constants for the reaction of hydrogen with DMSO and EtOH, respectively.

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2. Experimental

Acidic, aqueous, deaerated solutions of pure DMSO, of DMSO–KBr and of DMSO–EtOH in completely filled glass ampoules were irradiated with a ^{60}Co γ source. The dose rate was 2.50×10^{21} ev . ℓ^{-1} . h^{-1}. The gases formed were extracted under vacuum and analysed by gas chromatography on 5 m columns packed with molecular seive 5A or 13X or Porapak Q. Argon and helium were used as carrier gases and the principal gaseous products were CH_4, H_2 and C_2H_6; traces of CO_2 and C_2H_4 were also detected.

3. Results

Fig.1 shows the CH_4 yield from water–DMSO mixtures plotted against the DMSO concentration. One observes that $G(CH_4)$ does not reach a true plateau but continues to increase gently at higher [DMSO]. The curve giving $G(C_2H_6)$ is similar in form but the values are much lower and less precise as the yields decrease with the total dose absorbed. The plateau values are slightly lower than the values obtained in [10] for neutral media, $G(CH_4) = 2.25$; $G(C_2H_6) = 0.45$.

Both hydrogen and methane yields were measured in the DMSO–EtOH mixtures. In fig.2, $\Delta G(H_2)^{-1}$ is plotted against [DMSO]/[EtOH]. The points are fairly well aligned and the plot leads to values of $G_H = 3.65$ and $k_3/k_4 = 0.57$. The former agrees with the literature value for G_H in acid solution and the latter leads to $k_3 = 2.6 \pm 0.3 \times 10^7$ M^{-1} . s^{-1} taking $k_4 = 4.6 \times 10^7$ M^{-1} . s^{-1} [11]. Thus DMSO is a relatively efficient H-atom scavenger. However, it is evident from the difference between the plateau value $G(CH_4) = 1.8$ (fig.1) and $G_H = 3.65$ that all the hydrogen atoms captured by DMSO do not give rise to methane formation. Moreover, the plot of $G(CH_4)^{-1}$ *vs* [EtOH]/[DMSO] is not linear, showing that the methane production mechanism is more complex than the simple reaction of H atoms with DMSO.

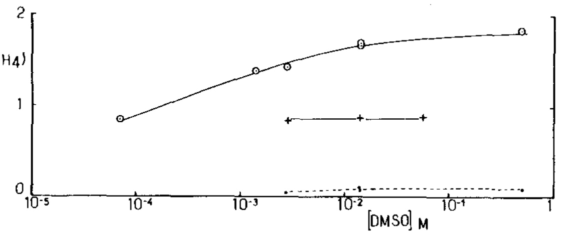

Fig.1. (⊙) CH_4 yield; (+) CH_4 yield (in presence of 7×10^{-2} M Br^-); (•) C_2H_6 yield *vs* DMSO concentration.

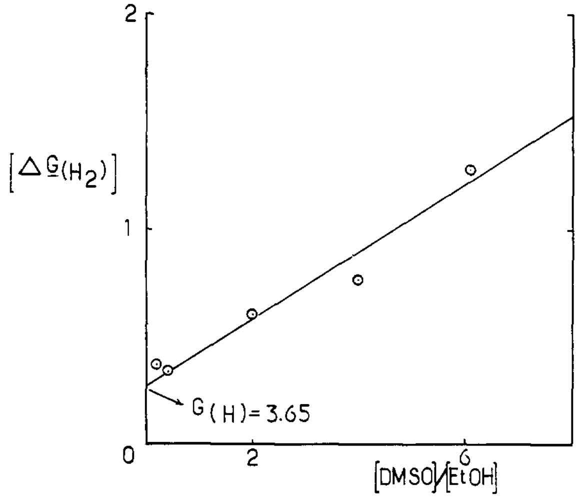

Fig.2. Reciprocal of $G(H_2) - 0.42$ *vs* [DMSO]/[EtOH].

The other possible source of CH_4 being the OH radical reaction with DMSO [1,10], in order to determine the contribution of this process the methane yields were measured at different DMSO concentrations in the presence of 7×10^{-2} M KBr. The rate constants of the reactions $OH + Br^- \rightarrow Br + OH^-$ and $OH + DMSO \rightarrow$ products, being, respectively, 2×10^{10} M^{-1} . s^{-1} in acid solution (extrapolated from values given in [12]) and 7×10^9 M^{-1} . s^{-1} in neutral solution [13] the former process is probably largely favoured for [DMSO] $\leqslant 6 \times 10^{-2}$ M.

The results are shown in fig.1. The methane yield has been reduced to a constant value of 0.85 which therefore represents the contribution of the H + DMSO reaction to CH_4 production. The difference between the total CH_4 yields and those measured in the presence of 7×10^{-2} M KBr corresponds to the contribution furnished by the OH + DMSO reaction. Thus in neither case, H nor OH, does the total radical yield lead to methane production, which would otherwise have a maximum value equal to $G_H + G_{OH} = 2.95 + 3.65 = 6.6$, much greater than the value $G(CH_4) = 1.8$ observed.

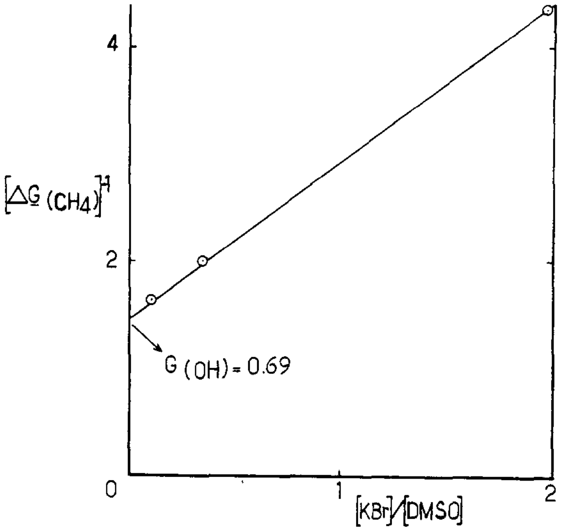

Fig.3. Reciprocal of $G(CH_4) - 0.85$ *vs* $[Br^-]/[DMSO]$.

In order to determine k_2 in acid media methane yields were determined in solutions containing 1.4×10^{-2} M DMSO, 1.5×10^{-3} M < KBr < 7×10^{-2} M, and 5×10^{-1} M sulfuric acid. Fig.3 represents the function $\Delta G(CH_4)^{-1}$ *vs* $[Br^-]/[DMSO]$ where $\Delta G(CH_4) = G(CH_4) - 0.85$. From the linear plot one obtains $G(OH) = 0.69$ and $k_4 = 2.0 \pm 0.2 \times 10^{10}$ $M^{-1} . s^{-1}$ in acid solution. This value of the rate constant is 5-times greater than that found in neutral solution: A similar increase in the rate constant of the reaction OH + Br^- is observed in going from neutral to acid medium ($k_1 = 2 \times 10^9$ $M^{-1} . s^{-1}$ at pH 7: 2×10^{10} $M^{-1} . s^{-1}$ at pH 0).

Thus whereas both H and OH radicals react with DMSO to give methane, only a fraction of each species captured leads to this product (0.69/2.95 = 23% of OH radicals; 0.85/3.65 = 23% of H atoms). These results suggest that the radical adducts $(CH_3)_2S\begin{smallmatrix}O^{\cdot}\\OH\end{smallmatrix}$ and $(CH_3)_2S^{\cdot}OH$ react in several different ways, methane production being a relatively unimportant path.

It is also evident that the maximum methane yield deriving from the H atom and OH radical reactions (0.85 + 0.69 = 1.54) is significantly less than the experimental value ($G(CH_4) = 1.8$) suggesting the existence of another source of methane [8].

These results thus show that, taken alone, methane production is not a reliable or sufficient test for the identification of OH radicals in biological systems.

4. Conclusion

Both hydrogen atoms and hydroxyl radicals react with dimethylsulfoxide in aqueous acid solution to produce methane. In both cases however only a fraction of the radicals captured (~23% of each under the experimental conditions employed) gives rise to this product. Thus methane formed in the reaction of DMSO with biological systems is not unequivocal proof of the presence of OH radicals; nor is the yield of methane a direct measure of an OH yield.

The rate constants $k(H + DMSO) = 2.6 \times 10^7$ $M^{-1} . s^{-1}$ and $k(OH + DMSO) = 2.1 \times 10^{10}$ $M^{-1} . s^{-1}$ have been determined in the presence of 5×10^{-1} M sulfuric acid.

Acknowledgements

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