Methylperoxyl Radicals:

A Study of the γ -Radiolysis of Methane in Oxygenated Aqueous Solutions

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A product study has been made of the γ -radiolysis of aqueous methane solutions that also contained nitrous oxide and oxygen. Formaldehyde ($G = 2.8$), hydrogen peroxide ($G = 2.1$), methanol ($G = 1.5$), methylhydroperoxide ($G = 0.8$), formic acid ($G = 0.3$), and dimethylperoxide ($G = 0.1$) were found. In alkaline solutions (pH 8, 10^{-3} M phosphate buffer), the formaldehyde yield rises to $G = 3.2$, while the formic acid yield falls to almost zero ($G = 0.05$). The initial precursor of the carbon-containing products is the methylperoxyl radical. The methylperoxyl radicals decay through a short-lived tetroxide along various pathways. The most prominent one leads to formaldehyde, methanol and oxygen. Methoxyl radicals (and oxygen) are also formed and, after rearrangement into hydroxymethyl radicals and their conversion into hydroxymethylperoxyl radicals, eventually yield formic acid and probably further formaldehyde. A route to formaldehyde and hydrogen peroxide is also envisaged. Methylhydroperoxide is formed in the reaction of methylperoxyl radicals with HO_2/O_2^- radicals (from radiolytic H atoms and the unimolecular decay of the hydroxymethylperoxyl radical).

Introduction

In the presence of oxygen, carbon-centered radicals are readily converted into the corresponding peroxyl radicals. In systems where it has been possible to measure the rate of this reaction it has been found to be close to diffusion-controlled ($k \approx 2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) (e.g. Ref. [1]). Thus, because of the omnipresence of oxygen, peroxyl radicals will play a more important role in non-artificial systems than the alkyl radicals themselves. The reactions of the prototype, $\text{CH}_3\text{O}_2^\cdot$, have therefore been studied in some detail in the gas phase [2–4, and references cited therein]. Much less, however, is known about its behaviour in solution [5–7].

To study the reactions of methyl peroxyl radicals in aqueous solution, radiation techniques can be advantageously used. The γ -radiolysis of aqueous solutions yields as reactive intermediates OH radicals, solvated electrons (e_{aq}^-) and H atoms (reaction (1)). In the presence of N_2O the solvated electrons yield further OH radicals (reaction (2)). The OH radicals can be converted into methyl radicals either by reacting them with methane (reaction (3); $k_3 = 1.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) [8], or with dimethylsulfoxide (reaction (4); $k_4 = 7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) [9].

In solutions that contain methane, N_2O and oxygen ($\geq 2 \times 10^{-4} \text{ M}$), the methyl radicals are converted into methylperoxyl radicals (reaction (5)) while the H atoms (from reaction (1)) which show only a low reactivity towards methane ($k < 10^5 \text{ M}^{-1} \text{ s}^{-1}$ [10]) are largely scavenged by oxygen (reaction (6); $k_6 = 2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ [11]). The $\text{HO}_2^\cdot$ radical is in equilibrium with its unprotonated form ($\text{pK} = 4.7$ [12]).

For many purposes the methane method to generate methyl radicals is not advisable because of the low solubility of methane in water [13], and the dimethylsulfoxide method might be of advantage. However, in a product study such as undertaken in this work, dimethylsulfoxide, methylsulfinic acid and other radiation products interfere with the analysis of the products. Thus, the methane method was used, but in order to prevent the products from being attacked by the OH radicals, larger substrate concentrations were employed by using methane at an elevated pressure. Since the earlier work on methane

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radiolysis in aqueous solutions, there has been an improvement of the analytical techniques, as well as a considerable progress in the general knowledge of peroxyl radical chemistry. This allows to give now a more complete picture of the products and, to some extent, of the mechanistic aspects of methylperoxyl radical chemistry.

Results and Discussion

In the radiolysis of $\text{N}_2\text{O}/\text{O}_2$ -containing aqueous solutions of methane (for conditions see Experimental) the major products are formaldehyde, methanol, hydrogen peroxide and methylhydroperoxide. Some formic acid and dimethylperoxide are also formed. The yield of these products increases linearly with dose up to 500 Gy and only at higher doses deviations from linearity have been observed. From such dose-yield plots G values have been calculated. They are shown in Table I. Under the given conditions

Table I. Product G values* from the γ -radiolysis of aqueous solutions of methane in the presence of N_2O and O_2 .

	pH ≤ 6 unbuffered	8 buffered
CH_2O	2.8	3.2
CH_3OH	1.5	n.d.
CH_3OOH	0.8	0.7
HCOOH	0.3	0.0 ₅
CH_3OOCH_3	0.1	n.d.
H_2O_2	2.1	2.3

* Possible error $\pm 10\%$, n.d. = not determined.

$G(\text{OH}) = 5.3$ is to be expected [14]. In reactions (3) and (5) these OH radicals are converted into methylperoxyl radicals. The carbon atom balance ($G(\text{carbon atoms in products}) = 5.6$, cf. Table I) indicates that chain reactions are insignificant. In particular, the reaction $\text{CH}_3\text{O}_2^\cdot + \text{CH}_4 \rightarrow \text{CH}_3\text{OOH} + \text{CH}_3$ is unable to compete effectively with the self-reaction of the methylperoxyl radical (cf. [15]). Because of the formation of some H atoms in reaction (1) ($G(\text{H}) = 0.55$) $\text{HO}_2^\cdot/\text{O}_2^\cdot$ radicals from reaction (6) and from other sources (see below) also contribute to some extent to the product spectrum.

The primary peroxyl radical, $\text{CH}_3\text{O}_2^\cdot$, can participate only in bimolecular processes and reactions (7)–(10) must be taken into consideration. A tetroxide is usually assumed to be a short lived intermediate. Reactions (7)–(9) are well-documented for the

vapour phase [2–5]. Reactions of this type are also recognized

in liquid systems [16–18]. Even though no reference seems to have been made regarding the importance of reaction (10) in the gas phase, there are cases where an analogous reaction is of major importance in the liquid phase [18–20]. Accordingly, reaction (10) must also be considered a possibility in the present system.

All the products observed except formic acid and methylhydroperoxide can be accounted for qualitatively (though not quantitatively) in terms of the foregoing reactions. Formic acid presupposes a precursor more highly oxidised than the methyl peroxyl radical, while for the formation of methylhydroperoxide a hydrogen donor is required.

Rearrangement of the methoxyl radical; hydroxymethylperoxyl radical as precursors of formic acid

The rearrangement of primary and secondary alkoxyl radicals in aqueous medium is a well-known process [21–23].

Reaction (11) has been observed in the UV (185 nm) photolysis of dimethyl ether in oxygen-free aqueous solution [23], where it competes with the hydrogen abstraction reaction $\text{CH}_3\text{O}^\cdot + \text{CH}_3\text{OCH}_3 \rightarrow \text{CH}_3\text{OH} + \text{CH}_2\text{OCH}_3$. Assuming for this reaction a rate constant of approximately $3 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ (cf. [24]); $k_{11} \approx 5 \times 10^5 \text{ s}^{-1}$ may be estimated from the data in Ref. [23]. Because the rate constant of hydrogen abstraction by methoxyl from methane will be lower than the above value, this reaction cannot effectively compete with reaction (11) in the system under study. In the presence of oxygen the hydroxymethyl radicals are readily converted into the corresponding peroxyl radicals (reaction (12)); $k_{12} = 4.9 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ [1]).

The reactions of hydroxymethyl peroxyl radicals have already been investigated in some detail (for a

review see Ref. [25]). They are known to decompose unimolecularly (reaction (13); $k_{13} \leq 10 \text{ s}^{-1}$) and to undergo an OH^- -induced O_2^- elimination (reaction (14); $k_{14} = 1.5 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$).

In competition with these two processes which are kinetically of first order in peroxyl radicals the hydroxymethylperoxyl radicals undergo a bimolecular decay with two main routes, reaction (15) being four times more important than reaction (16) [20].

Nothing is known about the decay of the primary methylperoxyl radicals with the hydroxymethylperoxyl radicals, but one should formulate reactions (17)–(20), two of which would lead to formic acid (reactions (18) and (20)). The rate of $\text{HO}_2^-/\text{O}_2^-$ elimination of the hydroxymethylperoxyl radical is speeded up by buffer which acts similarly to the hydroxide ion (*cf.* reaction (14)). In the pH 8 buffered experiments, hardly any formic acid was found. This indicates that under those conditions reactions (15)–(20) largely fall away.

The hydroxymethoxyl radical formed in reaction (19) is expected to rearrange rapidly (*cf.* reaction (11)). The resulting dihydroxymethyl radical adds oxygen and eliminates $\text{HO}_2^\cdot$ ($k \geq 10^6 \text{ s}^{-1}$) to give formic acid [26].

Routes to methylhydroperoxide

It is commonly assumed (*cf.* Ref. [6]) that in the radiolysis of oxygenated aqueous solutions of organic compounds the organic hydroperoxide is formed in the reaction of the organic peroxyl radical with $\text{HO}_2^-/\text{O}_2^-$ (*cf.* reaction (21))

One of the sources of the required $\text{HO}_2^-/\text{O}_2^-$ is the radiolytically formed H atom (reaction (6)). In the

present system further $\text{HO}_2^-/\text{O}_2^-$ radicals are expected from reactions (13) and (14). Despite the low rate of reaction (13) and the low $[\text{OH}^-]$ at pH ≈ 5.5 that prevails under the present irradiation conditions, the $\text{HO}_2^-/\text{O}_2^-$ elimination competes on comparable terms with the bimolecular decay of the peroxyl radicals at the dose rate used for these experiments ($2 \text{ k}(\text{peroxyl radicals}) \approx 10^9 \text{ M}^{-1}\text{s}^{-1}$ [18, 27]). It has also been proposed [28] (see however Ref. [29]) that primary peroxyl radicals react as indicated for the methylperoxyl radical in reaction (22), whereby the hydroperoxide (reaction (22)) and the readily hydrolysable (reaction (23)) Criegee intermediate [30, 31] is formed. Under experimental conditions such as ours the hydroxymethylhydroperoxides yield the aldehyde and hydrogen peroxide (reaction (24)) [32].

To distinguish between these two possible processes (reaction (21) vs. reaction (22)) some experiments using superoxide dismutase (SOD) which eliminates O_2^- by disproportionating it into hydrogen peroxide and oxygen have been done. SOD does not react, however, with alkylperoxyl radicals. In a solution buffered at pH 8 with 10^{-3} M phosphate containing SOD (5 mg l^{-1}) the methylhydroperoxide yield was reduced to 1/6 of its value in the absence of SOD. Concomitantly the loss of methylhydroperoxide was balanced by an increase in hydrogen peroxide, as well as to a large extent, by formaldehyde. This is an indication that methylhydroperoxide is largely formed according to reaction (21). In competition with reaction (21) the self-termination of $\text{HO}_2^-/\text{O}_2^-$ radicals will occur (reaction (25)).

At first sight, the yield of H_2O_2 observed in the present study seems very high. But this fact can be rationalized. Besides H_2O_2 from reactions (10), (20) and (25) there is always some H_2O_2 from spur reactions (*cf.* reaction (1)). This value normally is assumed to be 0.7, but on saturation with N_2O at atmospheric pressure $G(\text{H}_2\text{O}_2)$ increases to at least 0.85 [33]. Increasing the N_2O saturation pressure leads to further spur production of OH radicals [34] and hence one expects that this value must exceed 0.85 under our experimental conditions.

Quantitative aspects

Despite the complexities outlined above some quantitative conclusions might be drawn. One may infer from $G(\text{methanol}) = 1.5$ that *ca.* 56% of the methylperoxyl radicals follow reaction (7) (Russell mechanism) or its free radical equivalent, the cage disproportionation of two methoxyl radicals which are formed in reaction (8). Reaction (9), the cage combination of two methoxyl radicals is a very minor process ($\sim 4\%$). A larger percentage of the methoxyl radicals will escape the cage and rearrange (reaction (11)). $G(\text{formic acid}) = 0.3$ provides a lower limit, but because of reactions (13) and (14) and termination reactions such as (16) and (17) one would suspect that the yield of free methoxyl radicals (reaction (8)) is considerably higher than $G = 0.3$ (6%). Methylperoxyl radicals that end up as methyl hydroperoxide ($G = 0.8$) amount to *ca.* 15%. That leaves for reaction (10) at the most 19%, a value that could be lower due to a possibly higher contribution of reaction (8).

It should, however, be noted that the values given above should not be taken literally but rather present a likely picture. The error margins of product determinations have always to be considered. They can deviate into different directions, especially in cases where different determination techniques have to be employed for different products, as in the present study. Except for dimethyl peroxide which is a minor product there is no other product that can be formed unambiguously by one single route. Furthermore, pulse radiolysis studies that have been very helpful in elucidating mechanistic details of peroxyl radical chemistry [12, 18, 20, 25–27, 32] have not been possible here, because of the low solubility of methane.

Experimental

Triply distilled water saturated with methane (Messer Griesheim, stated purity 99.995%) at 50 bar ($[\text{CH}_4] = 0.08 \text{ M}$ at 15°C) and $\text{N}_2\text{O}/\text{O}_2$ (4:1) at 4 bar ($[\text{N}_2\text{O}] = 0.10 \text{ M}$, $[\text{O}_2] = 1.2 \times 10^{-3} \text{ M}$) were irradiated at a dose rate of $0.3 \text{ Gy} \cdot \text{s}^{-1}$ (obtained by Fricke-dosimetry). In most cases, doses were between 90 and 530 Gy; the highest dose received was 2100 Gy.

The samples were prepared as follows. A glass vessel capable of holding 100 ml of liquid and equipped with a teflon-coated magnetic stirring bar was placed in a stainless steel autoclave with a total capacity of

$\sim 150 \text{ ml}$, and charged with 100 ml of triply distilled water (pH 5.6). The open autoclave with its charge was then placed in an icebath, and $\text{N}_2\text{O}/\text{O}_2$ mixture (4:1) bubbled through for 30 min. Then the autoclave was closed and further loaded with $\text{N}_2\text{O}/\text{O}_2$ at 4 bar for 1 h, under ice cooling and stirring. Subsequently the methane was pressed in up to a partial pressure of 50 bar. The fully charged autoclave was left overnight and the solution stirred to ensure saturation. The pH of these solutions was about 6 (before irradiation). Some experiments were also carried out with solutions buffered to pH 8 with $1 \times 10^{-3} \text{ M}$ phosphate buffer, with as well as without superoxide dismutase (bovine blood, Sigma) (concentration $5 \mu\text{g/ml}$).

The combustible gas mixture present in the headspace of the autoclave did not represent a safety risk, considering the radiation intensities to be used (*cf.* [35, 36]).

After irradiation the valve of the autoclave was opened slightly to allow the solution to decompress without frothing. The solution was then removed and the products determined. Formaldehyde was measured spectrophotometrically, using the acetylacetone/ammonium acetate method [37]. Total hydroperoxide ($\text{H}_2\text{O}_2 + \text{CH}_3\text{OOH}$) was measured spectrophotometrically using the iodide method [38], employing a molar extinction coefficient of ϵ (350 nm) $= 2.5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ for the triiodide. The methylhydroperoxide was measured in the same way after destruction of the hydrogen peroxide by catalase (Boehringer Mannheim) (concentration $0.8 \mu\text{g/ml}$). This catalase concentration sufficed to destroy essentially all the H_2O_2 within a contact time of 5 min, after which the reading remained practically unchanged for a couple of hours. (A very slight activity of catalase toward methylhydroperoxide was nevertheless observed, such that after a day's standing the reading decreased to about half its initial value). The H_2O_2 yield is represented by the difference between hydroperoxide total and CH_3OOH . The acid formed was determined by ion chromatography (Dionex; model 2000i) as well as from the pH of the irradiated unbuffered solutions. Methanol and dimethylperoxide were determined by gas chromatography, with the assumption that the molar GC response for dimethylperoxide is twice that of methanol. The column used was a carbowax 400-coated glass capillary, 143 m long, operated at 70°C , with hydrogen as the carrier gas. Authentic dimethylperoxide was synthesized from dimethyl sulfate and hydrogen peroxide [39]. Dilute dimethylperoxide is comparatively stable, and does not react under the conditions of the hydroperoxide determination employed here [39, 40].

- [1] G. E. Adams and R. L. Willson, *Trans. Faraday Soc.* **65**, 2981 (1969).
- [2] D. A. Parkes, *Int. J. Chem. Kinet.* **9**, 451 (1977).
- [3] K. Selby and D. J. Waddington, *J. Chem. Soc. Perkin Trans. II* **1979**, 1259.
- [4] C. S. Kan, J. G. Calvert, and J. H. Shaw, *J. Phys. Chem.* **84**, 3411 (1980).
- [5] S. P. Sander and R. T. Watson, *J. Phys. Chem.* **85**, 2690 (1981).
- [6] R. C. A. Johnson and J. Weiss, *Chem. Ind.* **1955**, 358.
- [7] M. Ahmad, *Sci. Ind.* **6**, 57 (1968).
- [8] G. C. Stevens, R. M. Clarke, and E. J. Hart, *J. Phys. Chem.* **76**, 3863 (1972).
- [9] D. Veltwisch, E. Janata, and K.-D. Asmus, *J. Chem. Soc. Perkin II* **1980**, 146.
- [10] P. Neta, R. W. Fessenden, and R. H. Schuler, *J. Phys. Chem.* **75**, 1654 (1971).
- [11] M. Anbar, Farhataziz, and A. B. Ross, NSRDS-NBS 51, U.S. Dept. of Commerce, Washington, D.C. 1975.
- [12] B. H. J. Bielski, *Photochem. Photobiol.* **28**, 645 (1978).
- [13] D'Ans-Lax, *Taschenbuch für Chemiker und Physiker*, Vol. 1. Springer Verlag, Berlin, Heidelberg, New York 1964, p. 1205.
- [14] R. H. Schuler, A. Hartzell, and B. Behar, *J. Phys. Chem.* **85**, 192 (1981).
- [15] J. A. Howard, in J. K. Kochi (ed.): *Free Radicals*, Vol. II, Wiley, New York 1973, pp. 3–62.
- [16] F. R. Mayo, *Acc. Chem. Res.* **1**, 193 (1968).
- [17] J. A. Howard, in W. A. Pryor (ed.): *Organic Free Radicals*, ACS Symposium Ser. 69, Am. Chem. Soc., Washington, D.C. 1978, p. 413.
- [18] M. N. Schuchmann and C. von Sonntag, *J. Phys. Chem.* **83**, 780 (1979).
- [19] J. E. Bennett and R. Summers, *Can. J. Chem.* **52**, 1377 (1974).
- [20] E. Bothe and D. Schulte-Frohlinde, *Z. Naturforsch.* **33b**, 786 (1978).
- [21] V. M. Berdnikov, N. M. Bazhin, V. K. Fedorov, and O. V. Polyakov, *Kinet. Katal.* **13**, 1093 (1972).
- [22] B. C. Gilbert, R. G. G. Holmes, and R. O. C. Norman, *J. Chem. Res. (S)* **1977**, 1.
- [23] H.-P. Schuchmann and C. von Sonntag, *J. Photochem.* **16**, 289 (1981).
- [24] D. H. Ellison, G. A. Salmon, and F. Wilkinson, *Proc. Roy. Soc. London A* **328**, 23 (1972).
- [25] E. Bothe, M. N. Schuchmann, D. Schulte-Frohlinde, and C. von Sonntag, *Photochem. Photobiol.* **28**, 639 (1978).
- [26] E. Bothe and D. Schulte-Frohlinde, *Z. Naturforsch.* **35b**, 1035 (1980).
- [27] M. N. Schuchmann and C. von Sonntag, *J. Phys. Chem.* **86**, 1995 (1982).
- [28] P. S. Nangia and S. W. Benson, *Int. J. Chem. Kinet.* **12**, 43 (1980).
- [29] J. T. Herron, R. I. Martinez, and R. E. Huie, *Int. J. Chem. Kinet.* **14**, 225 (1982).
- [30] R. Criegee and G. Wenner, *Liebigs Ann. Chem.* **564**, 9 (1949).
- [31] P. S. Bayley, *Ozonation in Organic Chemistry*, Vol. 1, Academic Press, New York 1978, p. 57 and 111.
- [32] E. Bothe, M. N. Schuchmann, D. Schulte-Frohlinde, and C. von Sonntag, *Z. Naturforsch.* **38b**, 212 (1983).
- [33] N_2O -saturated solutions of *tert*-butanol (10^{-2} M) yielded $G(\text{H}_2\text{O}_2) = 0.85$.
- [34] F. S. Dainton and S. R. Logan, *Trans. Faraday Soc.* **61**, 715 (1965).
- [35] H. Luther, D. Boenisch, and G. Baumgarten, *Brennstoff-Chemie* **47**, 375 (1966).
- [36] H. Aron, S. Nagoi, K. Matsuda, and M. Hatada, *Z. Phys. Chem. N.F.* **131**, 57 (1982).
- [37] B. Kakać and Z. J. Vejdelek, *Handbuch der photometrischen Analyse organischer Verbindungen*, Verlag Chemie, Weinheim 1974, p. 257.
- [38] A. O. Allen, C. J. Hochenadel, J. A. Ghormley, and T. W. Davis, *J. Phys. Chem.* **56**, 575 (1952).
- [39] A. Rieche and W. Brumshagen, *Ber. Dtsch. Chem. Ges.* **61**, 951 (1928).
- [40] V. V. Sarayeva, in N. M. Emanuel' (ed.): *The Oxidation of Hydrocarbons in the Liquid Phase*, Pergamon Press, Oxford 1965, p. 288.