# PHOTOLYSIS AT 185 NM OF DIMETHYL ETHER IN AQUEOUS SOLUTION: INVOLVEMENT OF THE HYDROXYMETHYL RADICAL
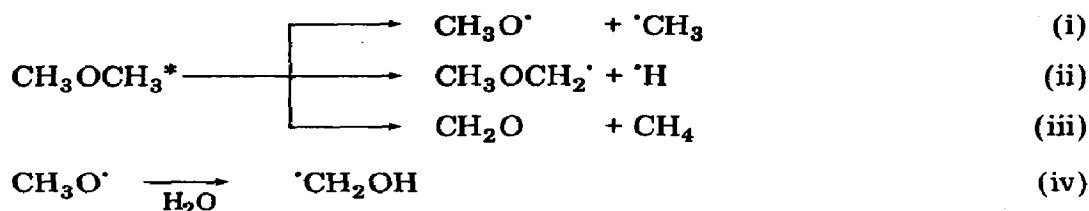
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## Summary

In the 185 nm photolysis of aqueous solutions of dimethyl ether (saturated at atmospheric pressure; 1.1 M) the following products are formed (quantum yields in parentheses): methane (0.06); hydrogen (0.03); methanol (0.02); 1,2-dimethoxyethane (0.014); formaldehyde (0.012); 2-methoxyethanol (0.012); ethylene glycol (0.009); ethanol (0.005); methyl ethyl ether (0.001). These products are explained by three primary processes (reactions (i) - (iii)), the rearrangement process (reaction (iv)) known to be undergone by alkoxyl radicals in aqueous solution and subsequent free-radical reactions.

$$CH_3OCH_3^* \longrightarrow \begin{cases} CH_3O^{\cdot} + {}^{\cdot}CH_3 & \text{(i)} \\ CH_3OCH_2^{\cdot} + {}^{\cdot}H & \text{(ii)} \\ CH_2O + CH_4 & \text{(iii)} \end{cases}$$

$$CH_3O^{\cdot} \xrightarrow[H_2O]{} {}^{\cdot}CH_2OH \qquad \text{(iv)}$$

In aqueous solutions the quantum yield of primary processes leading to products is smaller by about an order of magnitude than those in cyclohexane solutions or those previously found with similar ethers as pure liquids. This apparently means that water as a solvent has a quenching effect. In aqueous solutions there is an excited species which is reactive towards nitrous oxide and a proton, leading to the formation of nitrogen and hydrogen respectively. Free hydrated electrons generated by photoionization do not appear to be involved in these reactions.

## 1. Introduction

Saturated ethers start to absorb radiation in the UV near wavelengths of 200 nm with a maximum near 185 nm [1]. This first absorption band is considered to be due to an n → Rydberg transition [2]. In pure liquid open-

chain ethers, excitation at 185 nm leads mainly to the scission of a C—O bond. Results obtained in the photolysis of dimethyl ether in the gas phase [3, 4] can also be interpreted in these terms [5]. Thus, for dimethyl ether, methoxyl and methyl radicals should be the predominant primary radicals:

$$CH_3OCH_3 \xrightarrow{h\nu} CH_3O^{\cdot} + {}^{\cdot}CH_3 \tag{1}$$
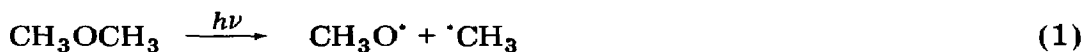
In the pure liquid ethers and in the gas phase the methoxyl radicals will react readily with the starting material:

$$CH_3O^{\cdot} + CH_3OCH_3 \longrightarrow CH_3OH + {}^{\cdot}CH_2OCH_3 \tag{2}$$

The rate constant for this reaction is probably not much different from that determined [6] for the reaction of the methoxyl radical with methanol ($k(CH_3O^{\cdot} + CH_3OH) = 2.6 \times 10^5 \ M^{-1} \ s^{-1}$).

It has been reported [7] that primary and secondary alkoxyl radicals in aqueous solution are transformed into the corresponding α-hydroxyalkyl radicals, e.g.

$$CH_3O^{\cdot} \xrightarrow{H_2O} {}^{\cdot}CH_2OH \tag{3}$$

Thus it is expected that the photolysis of open-chain ethers in aqueous solution will give a set of products which is different from that observed in the absence of water.

Reactions such as reaction (3) may also play a role in auto-oxidation. It is postulated that in auto-oxidation reactions, among other processes, there is formation of alkoxyl radicals:

$$2\,H-\overset{|}{\underset{|}{C}}-O-O^{\cdot} \longrightarrow 2\,H-\overset{|}{\underset{|}{C}}-O^{\cdot} + O_2 \tag{4}$$
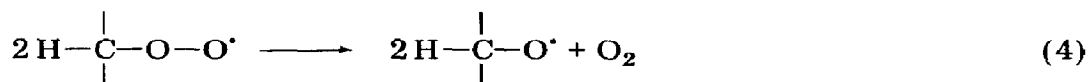
In aqueous solutions these alkoxyl radicals may then be transformed into the corresponding hydroxyalkyl radicals [8]. The subsequent chemistry is governed by the fate of the peroxy and peroxyl radicals formed by the addition of oxygen to the α-hydroxyalkyl radical, the chemistry of which has recently had some attention (for a review see ref. 9).

The transformation of alkoxyl radicals into hydroxyalkyl radicals has previously been demonstrated using the electron spin resonance technique [7]. In the present paper further evidence with respect to this reaction is given from a study of the products. Some results pertinent to the primary photolysis processes of dimethyl ether in aqueous solutions are also discussed.

## 2. Experimental procedure

Aqueous solutions of 1.1 ± 0.1 M dimethyl ether were prepared by saturating triply distilled water at 15 °C with dimethyl ether at atmospheric

pressure. The concentration was determined by gas chromatography (GC). Solutions of a mixture of dimethyl ether and nitrous oxide (2:1 by volume) of various acidities (sulphuric acid) were irradiated and the concentrations of hydrogen, nitrogen and methane were measured as functions of pH (down to pH 2.5; at higher acid concentrations photolysis of the acid will interfere). In these cases the concentration of the ether is $0.74 \pm 0.1$ M; that of nitrous oxide is $8 \times 10^{-3}$ M. A few experiments were performed with solutions of dimethyl ether in cyclohexane that were nearly saturated at 15 °C. Under these conditions the volume of the solution is about 15% larger than the volume of the ether-free solvent, *i.e.* a mole fraction of roughly 0.3 for the ether is estimated.

At 185 nm the molar extinction coefficient of dimethyl ether in aqueous solution was determined to be about 240 $M^{-1}$ $cm^{-1}$, measured on a Cary model 17 spectrometer. The molar extinction coefficient $\epsilon_{H_2O}$ is considerably less ($\epsilon_{H_2O}(185) = 0.025$ $M^{-1}$ $cm^{-1}$ [10]) and was determined to be 0.022 $M^{-1}$ $cm^{-1}$ in the present case. At the concentrations used here, all the 185 nm light is absorbed by the dimethyl ether (in aqueous solution $\epsilon_{N_2O}(185) = 60 \pm 8$ $M^{-1}$ $cm^{-1}$ [11] and $\epsilon_{SO_4^{2-}}(185) \approx 200$ $M^{-1}$ $cm^{-1}$ [12]). The solutions were photolysed with the full light of a low pressure mercury lamp (Graentzel, Karlsruhe). Only the 185 nm light is photoactive in this system. Its quantum flux was determined with an ethanol actinometer (5 M $C_2H_5OH$ in $H_2O$; $\Phi(H_2) = 0.4$ [1]) and was found to be $4.5 \times 10^{17}$ quanta $min^{-1}$ (at 185 nm) for a 2 ml sample. Products except formaldehyde were identified with the use of reference material and quantitatively determined by using GC [13, 14]. This necessitated the GC analysis of trace quantities of organic solutes in water [14]. A double-column system, consisting of a precolumn 3 m long of 10% P4000 on Teflon and a column 8 m long of 15% P4000 on Celite (potassium hydroxide treated; 60 - 100 mesh (main)) was found to be most useful. Forward flow was maintained for sufficiently long that the products which migrate faster than water could enter the main column, after which the flow through the precolumn would be reversed in order to flush out the water. Another column combination sometimes used consisted of the same precolumn plus a column 5 m long of 15% CW400 on Embacel (60 - 100 mesh). 2-Methoxyethanol was determined using the precolumn only, without any back flush. Ethylene glycol was analysed on a CW-20M-coated glass capillary from samples that had been concentrated by evaporation and taken up in methanol. Formaldehyde was determined photometrically with the acetylacetone–ammonium acetate method [15]. Yield–dose curves were linear in the dose range studied, which was between $2.5 \times 10^{18}$ and $3 \times 10^{19}$ quanta for a 2 ml sample.

## 3. Results and discussion

The major products in the 185 nm photolysis of aqueous deoxygenated solutions of dimethyl ether are hydrogen, methane, formaldehyde and 1,2-
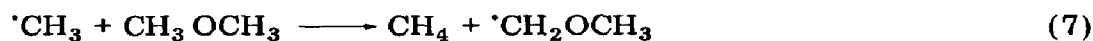
**TABLE 1**

Products and their quantum yields in the 185 nm photolysis of dimethyl ether in saturated aqueous solution at 15 °C in the absence of oxygen

| Product | Quantum yield |
|---|---|
| $H_2$ | 0.03 |
| $CH_4$ | 0.06 |
| $CH_3CH_3$ | $< 0.001$ |
| $CH_2O$ | 0.012 |
| $CH_3OH$ | 0.02 |
| $CH_3CH_2OH$ | 0.005 |
| $HOCH_2CH_2OH$ | 0.009 |
| $CH_3OCH_2CH_3$ | 0.001 |
| $CH_3OCH_2CH_2OH$ | 0.012 |
| $CH_3OCH_2CH_2OCH_3$ | 0.014 |

$[CH_3OCH_3] = 1.1 \pm 0.1$ M. Errors are estimated to be $\pm 25\%$.

dimethoxyethane, but products containing the structural element $-CH_2OH$ such as 2-methoxyethanol, ethanol and ethylene glycol are also found (Table 1). The first set of products is readily explained by the photolytical processes (1), (5) and (6) and by the subsequent hydrogen abstraction reactions (2), (7) and (8) together with the combination reaction (9).

$$CH_3OCH_3 \xrightarrow{h\nu} CH_2O + CH_4 \tag{5}$$

$$CH_3OCH_3 \xrightarrow{h\nu} CH_3OCH_2^{\cdot} + H^{\cdot} \tag{6}$$

$$^{\cdot}CH_3 + CH_3OCH_3 \longrightarrow CH_4 + {}^{\cdot}CH_2OCH_3 \tag{7}$$

$$H^{\cdot} + CH_3OCH_3 \longrightarrow H_2 + {}^{\cdot}CH_2OCH_3 \tag{8}$$

$$2\,{}^{\cdot}CH_2OCH_3 \longrightarrow CH_3OCH_2CH_2OCH_3 \tag{9}$$

Hydrogen and 1,2-dimethoxyethane would also arise if $H_2$ and methoxy-carbene were formed in the primary photochemical act, the methoxycarbene inserting into the starting material. Formation of $H_2$ and carbenes is not uncommon in vacuum UV photolysis (cf. ref. 16). The present experiments do not enable a distinction to be made between such a process and a reaction sequence as depicted by reaction (6) followed by the reactions (8) and (9).

As mentioned, it is expected [7] that in aqueous solution the methoxyl radical, besides giving methanol in reaction (2), is also transformed into the hydroxymethyl radical (reaction (3)). The combination of the methoxyl radical with the other radicals gives the observed products ethanol and 2-methoxyethanol:

$$^{\cdot}CH_2OH + {}^{\cdot}CH_3 \longrightarrow CH_3CH_2OH \tag{10}$$

$$^{\cdot}CH_2OH + CH_3OCH_2^{\cdot} \longrightarrow CH_3OCH_2CH_2OH \tag{11}$$

Its self-termination gives ethylene glycol:

$$2 \, ^{\cdot}CH_2OH \longrightarrow HOCH_2CH_2OH \qquad (12)$$

The material balance is less than satisfactory compared with non-aqueous samples [17 - 20], owing to difficulties inherent in the gas chromatography of aqueous samples. Even so, some further mechanistic conclusions can be drawn. $\Phi(CH_2O)$ is quite high. The free-radical contribution to formaldehyde by

$$2 \, ^{\cdot}CH_2OH \longrightarrow CH_2O + CH_3OH \qquad (13)$$

can be neglected because of the low disproportionation/combination ratio of the hydroxymethyl radicals ($k_{13}/k_{12} \approx 0.1$ [21]) and the low value of $\Phi(HOCH_2CH_2OH)$. Another conceivable source is

$$^{\cdot}CH_2OH + \, ^{\cdot}CH_2OCH_3 \longrightarrow CH_2O + CH_3OCH_3 \qquad (14)$$
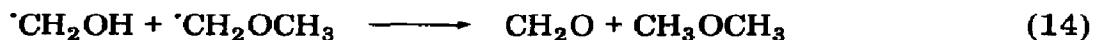
In order to make reaction (5) unnecessary for the mechanism, $k_{14}/k_{11}$ would have to approach unity. No value for this ratio seems to exist in the literature; however, we expect it to be similar to $k_{13}/k_{12}$ (approximately 0.1) and we think that the major part of the formaldehyde produced stems from the molecular process (5).

It is recalled that pure liquid ethers such as diethyl ether [17], $t$-butyl methyl ether [18], di-$t$-butyl ether [19] and methyl-$n$-propyl ether [20] all decompose with the sum of the quantum yields of product-forming processes approaching unity. Similarly, photolysis of solutions of dimethyl ether in cyclohexane saturated at room temperature produces methane and ethane with quantum yields of 0.39 and 0.04 respectively, which gives a lower limit of about 0.5 for the quantum yield for C—O bond cleavage of this ether in a non-hydroxylic medium. In aqueous solutions of dimethyl ether this value is about an order of magnitude smaller. Here the solvent water appears to quench the excited ether efficiently (as it does with alcohols [1]). It is not clear whether this happens because of exciplex formation. In the ground state there is evidence [22] for the existence of clusters of the form [ether·$(H_2O)_n$].

In Fig. 1 it is shown that neutral solutions which contain $8 \times 10^{-3}$ M $N_2O$ yield $\Phi(N_2) = 0.04$. Nitrogen formation can be quenched by the addition of protons whereby hydrogen is generated. Methane formation appears to be independent of pH. The hydrogen and nitrogen quantum yield curves (Fig. 1) suggest that nitrous oxide and protons compete for the same species. In the aqueous 1,4-dioxane system, in which a very similar phenomenon has been observed [23], two possible precursors have been discussed: (1) photo-ionization such that a 1,4-dioxane radical cation and a free hydrated electron result; (2) production of an excited molecule (excited complex of molecules) which transfers an electron to $N_2O$ or $H^+$ (*cf.* reactions (15) and (17)). There are now indications that the lifetime of the intermediate formed on photolysis is shorter than that of the solvated electron generated in the same system by ionizing radiation [24]. In the present system we also favour a mechanism that does not involve the participation of free solvated electrons,
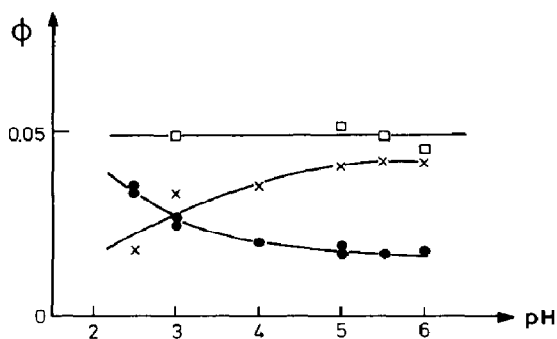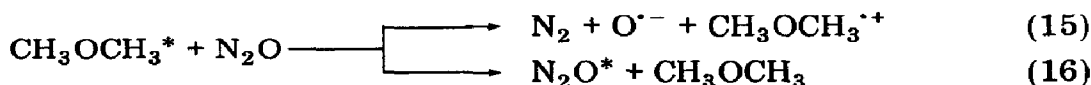
Fig. 1. The UV photolysis of oxygen-free acidic aqueous solutions of dimethyl ether ($[CH_3OCH_3] = 0.74 \pm 0.07$ M; $[N_2O] = 0.010$ M): ●, $\Phi(H_2)$; ×, $\Phi(N_2)$; □, $\Phi(CH_4)$.

particularly because the gas phase ionization potential of dimethyl ether (10.0 eV) is considerably higher than that of 1,4-dioxane (9.13 eV) [25]. For 1,4-dioxane, photoionization might just be energetically possible at 185 nm (6.7 eV), considering that the ionization potential of a given compound is lowered by about 3 eV from the gas phase to aqueous solutions [26, 27]. For nitrous oxide, an energy transfer process (reaction (16)) (*cf.* ref. 28) must be considered as an alternative to electron transfer (reaction (15)). Such a process would also liberate nitrogen (reaction (18)).

$$CH_3OCH_3{}^* + N_2O \longrightarrow \begin{cases} N_2 + O^{\cdot -} + CH_3OCH_3{}^{\cdot +} \quad (15) \\ N_2O^* + CH_3OCH_3 \quad\quad\quad\quad (16) \end{cases}$$

$$CH_3OCH_3{}^* + H^+ \longrightarrow H^{\cdot} + CH_3OCH_3{}^{\cdot +} \quad (17)$$

$$N_2O^* \longrightarrow N_2 + O \quad (18)$$

In the aqueous 1,4-dioxane–nitrous oxide system $\Phi(N_2)$ approached unity on saturation at atmospheric pressure ($[N_2O] = 2.4 \times 10^{-2}$ M). In the present system the nitrous oxide concentration is only $8 \times 10^{-3}$ M, whilst $\Phi(N_2) = 0.04$. Two reasons for the low value of $\Phi(N_2)$ can be given.

(1) The lifetime of the intermediate may be considerably shorter than that of the 1,4-dioxane system [24].

(2) The intermediate may be long lived (longer than 25 ns) but may be formed with only a low probability.

It might be possible to distinguish between these alternatives by studying the system at pressures of nitrous oxide that exceed those that could be applied in the present study.

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