Radiation Chemistry of Alcohols. Part XXI.† Ultraviolet Photolysis (λ 185 nm) of Methoxyethanol in the Liquid Phase

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The main products of the photolysis (λ 185 nm) of neat liquid methoxyethanol (quantum yields in parentheses) are H_2 (0.27), CH_2O (0.19), CH_4 (0.15), methoxyacetaldehyde (0.10), ethylene glycol (0.10), ethanol (0.09), and methanol (0.05). The quantum yields of 34 products altogether have been measured. It is concluded that there are two major reactions (i) and (ii), involving homolytic splitting of the O–H and O–CH_3 bonds. Molecular

$$HOCH_2CH_2OCH_3 \longrightarrow H\cdot + \cdot OCH_2CH_2OCH_3 \qquad (i)$$

$$\longrightarrow HOCH_2CH_2O\cdot + \cdot CH_3 \qquad (ii)$$

fragmentation reactions and the homolytic scission of other bonds play a minor role. In the presence of N_2O (saturated solution) $\phi(H_2)$ is decreased by *ca.* 10% while $\phi(N_2)$ is 0.08 indicating that photoionisation processes are only moderately important. In dilute aqueous solution $\phi(H_2)$ and $\phi(CH_4)$ are strongly decreased.

In the context of the photolysis of alcohols[1-5] and ethers[6-8] at 185 nm the study of methoxyethanol introduces a new aspect. It is the simplest molecule which unites both functions.

It has been shown that the main process in the photolysis of primary and secondary alcohols[1-5] is O–H scission. Ethers mainly suffer C–O cleavage.[6-8] The lowest photoexcited state in these compounds is an $n \longrightarrow \sigma^*$ state. Bond breakage in methoxyethanol is therefore expected also to involve mainly the oxygen atoms.

The chemistry of the energized methoxyethanol molecule has received little general attention. The γ-radiolysis of methoxyethanol glass at 77 K was undertaken to study the behaviour of the trapped electron.[9] Products were not determined. The photolysis of $FeCl_3$–methoxyethanol solutions[10] led to formaldehyde, acetaldehyde, methanol, and gaseous products after >10% conversion. The product pattern of methoxyethanol photolysis at 185 nm is expected to be complex. Some of the radicals in this system are structural analogues of

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† Part XX, H.-P. Schuchmann, C. von Sonntag, and D. Schulte-Frohlinde, *J. Photochem.*, 1975, **4**, 63.

[1] C. von Sonntag, *Tetrahedron*, 1969, **25**, 5853.

[2] C. von Sonntag, *Z. phys. Chem.* (*Frankfurt*), 1970, **69**, 292.

[3] C. von Sonntag, *Z. Naturforsch.*, 1972, **27b**, 42.

[4] D. Sänger and C. von Sonntag, *Tetrahedron*, 1970, **26**, 5489.

[5] H. J. van der Linde and C. von Sonntag, *Photochem. Photobiol.*, 1971, **13**, 147.

[6] C. von Sonntag, H.-P. Schuchmann, and G. Schomburg, *Tetrahedron*, 1972, **28**, 4333.

[7] H.-P. Schuchmann and C. von Sonntag, *Tetrahedron*, 1973, **29**, 1811.

[8] H.-P. Schuchmann and C. von Sonntag, *Tetrahedron*, 1973, **29**, 3351.

[9] L. Kosa-Somogyi, M. Gécs, and M. Vizesi, 2nd Tihany Symposium Radiation Chem., 1966, p. 275.

[10] H. Inoue, K. Tamaki, N. Komakine, and E. Imoto, *Bull. Chem. Soc. Japan*, 1966, **39**, 1577.

radicals found in ethylene glycol photolysis [5] and radiolysis [11,12] which undergo fragmentation reactions.

Methoxyethanol can be considered as a simple model for carbohydrates, which, in their cyclic forms, carry hydroxy-groups and an ether function in the hemiacetal bridge. Of particular interest in this respect could be the photolytic behaviour of methoxyethanol in aqueous solution.

EXPERIMENTAL

Methoxyethanol (Merck) was distilled and fractionated until g.l.c. pure ($>99.9\%$). Its absorption spectrum between 185 and 200 nm (Figure 1) was measured using a Cary 17 spectrophotometer, the cell compartment of which had been purged with nitrogen. The extinction coefficients of methoxyethanol in the vapour phase and in aqueous solution were measured at 185 nm in 1 cm Suprasil cells (Hellma, Mullheim). The cell was filled with vapour after evacuation. The vapour was admitted into the cell from a bulb where methoxyethanol was kept at 17°, and allowed to equilibrate at 20°. Under these conditions the vapour pressure was 7.5 mmHg, from which the concentration of vapour in the cell could be calculated. The absorption spectrum of liquid methoxyethanol was measured at longer wavelengths using a 0.01 cm Suprasil cell. This thickness was realized by inserting a 0.09 cm Suprasil platelet into a 0.10 cm cell.

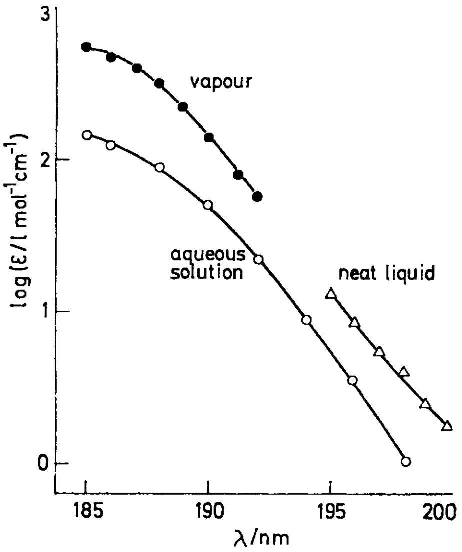

FIGURE 1 Extinction coefficient of neat methoxyethanol and of its dilute ($<10^{-1}$M) aqueous solutions as a function of wavelength in the range λ 185—200 nm

After deaerating with argon, aliquot portions (4.0 ml) were photolysed at 15° in a 1 cm Suprasil cell using a low pressure Hg arc as previously described.[13] The quantum flux of the lamp at 185 nm was determined using 5M-ethanol in water as an actinometer solution, and measuring the hydrogen liberated during photolysis. The hydrogen quantum yield of 0.4 can be derived [2] using Dainton and Fowles' value of 1.0 for the nitrogen formation in the 185 nm photolysis of N_2O [14] in an aqueous medium. During the course of the work the flux absorbed per cell volume changed from 2.25×10^{18} to 2.00×10^{18} quanta min^{-1}. Irradiation times did not exceed 50 min in quantitative experiments.

Details of the columns and conditions used in the gas chromatographic analysis of the photolysis products are shown in Supplementary Publication No. SUP 21455 (8 pp.).* Hydrogen was carried directly onto the column by a stream of argon as previously described.[13] Methane and ethane were displaced from the liquid by a stream of argon and collected in an evacuated glass bulb before injection. The other products except formaldehyde and glycolaldehyde were analysed by liquid injection. The instruments used for analysis were Perkin-Elmer 900 and F20 chromatographs and a Varian 1400 chromatograph. All were equipped with flame ionisation detectors. Sources of the reference compounds used in the analysis are listed in SUP 21455.*

Some problems were encountered in the analysis of the higher molecular weight products. These represent polyols methylated to varying extents. A 2 m 2% polyethylene glycol on Chromosorb W glass column was found to give an acceptable resolution of these products (SUP 21455).* Some of the peaks could not be assigned. Attempts to identify such peaks through mass spectrometry failed because of uncharacteristic fragmentation patterns and the absence of the parent masses in the spectrum. The identification of most of the other peaks was confirmed using a 2 m Marlophen 87 on Chromosorb G glass column. Formaldehyde and glycolaldehyde were determined colorimetrically using the methods of Nash [15] and Ahmed *et al.*,[16] respectively. Methoxyacetaldehyde was found to interfere quantitatively with the glycolaldehyde test and it was necessary first to determine the quantum yield of methoxyacetaldehyde by g.l.c. and then to use this result to correct the apparent glycolaldehyde yield obtained using the colorimetric method. Some experiments were done on samples which prior to irradiation had been saturated with nitrous oxide by bubbling for 20 min. Nitrogen was determined in the same way as hydrogen (see above) except that helium was used as the carrier gas.

RESULTS

The spectra of methoxyethanol in the vapour phase, liquid phase, and in dilute aqueous solution are shown in Figure 1. The extinction coefficient of methoxyethanol at 185 nm is *ca.* 150 l mol^{-1} cm^{-1} in aqueous solution over a concentration range 10^{-1}—10^{-2} M, but is much higher, 550 l mol^{-1} cm^{-1}, in the vapour. It was not possible to obtain the spectrum of the neat liquid at the shorter wavelengths owing to the high absorbance of layers even as thin as 0.01 cm but it appears from the diagram that the liquid and the vapour must have very similar spectra in this wavelength region.

Methoxyethanol neat and dissolved in water has been photolysed at 185 nm with a low pressure Hg arc whose 254 nm light is inactive in this system as shown by the absence of products when a vycor filter was placed before

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1974, Index issue. Items less than 10 pp. are supplied as full-size copies.

[11] F. Seidler and C. von Sonntag, *Z. Naturforsch.*, 1969, **24b**, 780.

[12] P. J. Venter, H. J. van der Linde, and R. A. Basson, *J.C.S. Chem. Comm.*, 1972, 187.

[13] D. Sänger and C. von Sonntag, *Tetrahedron*, 1970, **26**, 5489.

[14] F. S. Dainton and P. Fowles, *Proc. Roy. Soc.*, 1965, **287A**, 295.

[15] T. Nash, *Biochem. J.*, 1953, **55**, 416.

[16] M. Ahmed, M. Awan, and D. Mohammed, *J. Chem. Soc.* (*B*), 1968, 946.

the cell. Photolysis products of neat methoxyethanol and their quantum yields are listed in the Table.

185 nm photolysis quantum yields of liquid methoxyethanol (O_2-free, 15°)

No.	Product	Source reaction *	Quantum yield
1	H_2		0.27
2	CH_4		0.15
3	C_2H_6	$\dot{C}H_3 + \dot{C}H_3$	0.002
4	CH_3OH		0.05
5	CH_3CH_2OH		0.09
6	C_3H_7OH	$\dot{C}H_3$ + (V)	0.001
7	CH_3OCH_3		0.024
8	$CH_3OCH{=}CH_2$		0.004
9	$CH_3OC_2H_5$		0.004
10	$CH_3OC_3H_7$	$\dot{C}H_3$ + (VI)	0.0005
11	CH_2O		0.19
12	CH_3CHO		0.023
13	CH_3OCH_2CHO		0.10
14	$HOCH_2CHO$		<0.01
15	$HOCH_2CH_2OH$		0.10
16	$CH_3OCH_2CH_2OCH_3$	(IV) + (IV)	0.001
17	$HOCH_2CH_2CH_2OH$	(III) + (V)	<0.001
18	$HOCH_2CH_2CH_2CH_2OH$	(V) + (V)	0.0005
19	$HOCH_2CH_2OCH_2CH_2OH$	(III) + (VII)	0.02_3
20	$CH_3OCH_2CH_2OCH_2CH_2OH$	(IV) + (VII)	0.01_3
21	$CH_3OCH_2CHOHCH_2OH$	(III) + (IX)	0.02_3
22	$CH_2OHCH(OCH_3)CH_2OH$	(III) + (VIII)	0.02_3
23	$CH_3OCH_2CH(OCH_3)CH_2OH$	(IV) + (VIII)	0.01_5
24	$CH_3OCH_2CHOHCH_2OCH_3$	(IV) + (IX)	0.01_4
25	$CH_3OCH_2CHOHCH_2CH_2OH$	(V) + (IX)	<0.003
26	$CH_2OHCH(OCH_3)CH_2CH_2OH$	(V) + (VIII)	<0.003
27	$CH_2OHCH(OCH_3)CH_2CH_2OCH_3$	(VI) + (VIII)	<0.002
28	$CH_3OCH_2CHOHCH_2CH_2OCH_3$	(VI) + (IX)	<0.002
29	$HOCH_2CH_2OCH_2CH_2OCH_2CH_2OH$	(VII) + (VII)	0.01_6
30	$CH_2OHCH(OCH_3)CH_2OCH_2CH_2OH$	(VII) + (VIII)	0.03_0
31	$CH_3OCH_2CHOHCH_2OCH_2CH_2OH$	(VII) + (IX)	0.03_1
32	$CH_2OHCH(OCH_3)CH(OCH_3)CH_2OH$	(VIII) + (VIII)	0.01_4
33	$CH_3OCH_2CHOHCHOHCH_2OCH_3$	(IX) + (IX)	0.01_6
34	$CH_2OHCH(OCH_3)CHOHCH_2OCH_3$	(VIII) + (IX)	0.01_4

* (III) $\cdot CH_2OH$; (IV) $\cdot CH_2OCH_3$; (V) $\cdot CH_2CH_2OH$; (VI) $\cdot CH_2CH_2OCH_3$; (VII) $\cdot CH_2OCH_2CH_2OH$; (VIII) $CH_2O\dot{C}HCH_2OH$; (IX) $CH_3OCH_2\dot{C}HOH$. The source reaction represents the major mode of formation of the product.

Quantum yield–dose plots are given in Figure 2. After 50 min. irradiation (*ca.* 10^{20} quanta absorbed in 4 ml) the H_2 quantum yield is still constant. This dose corresponds to a conversion of *ca.* 0.3%. The relative quantum yields of the major products are considered accurate within a margin of 10%. Those of the higher products which are partially methylated polyols are probably not accurate to better than 20%, owing to their high polarity and poor g.l.c. peak shape.

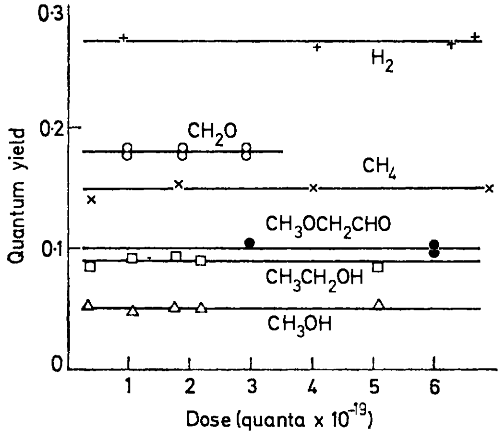

FIGURE 2 Liquid methoxyethanol 185 nm photolysis quantum yields of major products as a function of absorbed dose. Sample volume 4 ml, temperature 15°, O_2-free

The possibility of a further error inherent in the actinometry exists and could affect absolute quantum yield values. The product list is incomplete; some peaks which show linearity with dose could not be identified; the g.l.c. peaks of the methyl-substituted methoxyethanol compounds could not be separated from the methoxyethanol itself which shows severe tailing.

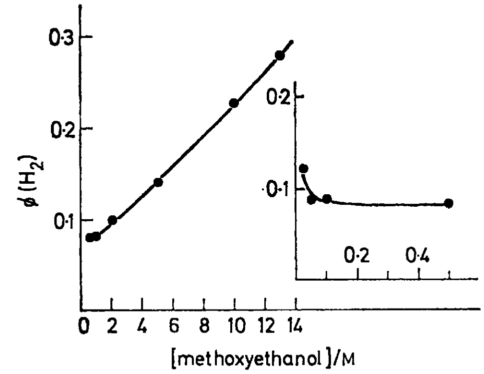

FIGURE 3 H_2 quantum yield from the 185 nm photolysis of aqueous methoxyethanol solutions as a function of concentration. The insert shows the behaviour at low substrate concentrations

Some photolytic runs were done with methoxyethanol–water mixtures. The quantum yield–concentration dependence of the two major volatile (and thus easily analysable) products hydrogen and methane is shown in Figures 3 and 4. Both the hydrogen and methane quantum yields are found to decrease strongly with increasing water content. Saturating with N_2O reduces $\phi(H_2)$ by 10% whereas $\phi(CH_4)$ is unaffected. $\phi(N_2)$ has been found to be 0.08.

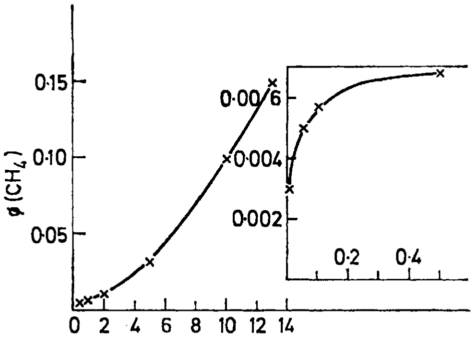

FIGURE 4 CH_4 quantum yield from the photolysis of aqueous methoxyethanol solutions as a function of concentration. The insert shows the behaviour at low substrate concentrations

DISCUSSION

The energy of the 185 nm quantum (equivalent to 154 kcal mol^{-1}) is sufficient to cleave any of the bonds in the methoxyethanol molecule. This leads to radical formation or molecular fragmentation [reactions (1)—(12)]. Cage disproportionations cannot be distinguished here from genuine molecular fragmentation processes. Multiple fragmentation is considered unlikely. Reactions (1)—(12) and subsequent radical reactions (estimated quantum yields in parentheses) are sufficient to explain the products (Table). Owing to the dissymmetry of the methoxyethanol molecule there are 13 different radicals in this system, and the number of conceivable radical reactions including hydrogen abstraction from methoxyethanol, disproportionations, combinations, and fragmentations, is over 100, too many to list.

However, most of the conceivable primary processes (1)—(12) are of little importance, and the major processes can be evaluated. Values for the quantum yields, or at least their upper limits, can immediately be given for six of the 12 primary processes [(3), (5), (7), (9), (11), and (12)] on the basis of the quantum yields of methoxyacetaldehyde, methyl vinyl ether, glycolaldehyde, ethanol, dimethyl ether, and acetaldehyde, respectively. The hydrogen atom is a highly reactive radical abstracting a hydrogen atom from the substrate [reaction (13)] rather than reacting with other radicals. Thus $\phi(H_2)$ represents the sum of the primary processes (1)—(3). In the photolysis of other alcohols [1-5] it has been shown that the homolytic scission of the O–H bond and elimination of H_2 is very much (>80%) favoured over the homolytic scission of a C–H bond (<20%). By analogy we believe that process (2) will contribute only little to the hydrogen yield which is largely represented by processes (1) and (3). The methoxyl radical behaves similar to the hydrogen atom [reaction (15)]. Thus $\phi(CH_3OH)$ is an upper limit to the sum of the reactions (8) and (12).

$$CH_3OCH_2CH_2OH \xrightarrow{h\nu} CH_3OCH_2CH_2O\cdot + H\cdot \qquad (1)$$

$$\xrightarrow{h\nu} R\cdot + H\cdot \qquad 0{\cdot}27 \qquad (2)$$

$$\xrightarrow{h\nu} CH_3OCH_2CH{=}O + H_2 \qquad <0.10 \qquad 0{\cdot}29 \qquad (3)$$

$$\xrightarrow{h\nu} CH_3OCH_2CH_2\cdot + \cdot OH \qquad \sim 0.01 \qquad (4)$$

$$\xrightarrow{h\nu} CH_3OCH{=}CH_2 + H_2O \qquad <0.01 \qquad (5)$$

$$\xrightarrow{h\nu} CH_3\cdot + \cdot OCH_2CH_2OH \qquad 0.14—0.29\ (\sim 0.18) \qquad (6)$$

$$\xrightarrow{h\nu} CH_4 + O{=}CHCH_2OH \qquad 0.01 \qquad 0.27—0.44\ (\textit{ca.}\ 0.31) \qquad (7)$$

$$\xrightarrow{h\nu} CH_3O\cdot + \cdot CH_2CH_2OH \qquad 0.03—0.05 \qquad (8)$$

$$\xrightarrow{h\nu} CH_2O + CH_3CH_2OH \qquad <0.09 \qquad (9)$$

$$\xrightarrow{h\nu} CH_3OCH_2\cdot + \cdot CH_2OH \qquad <0.07 \qquad (10)$$

$$\xrightarrow{h\nu} CH_3OCH_3 + CH_2O \qquad <0.02 \qquad <0.09 \qquad (11)$$

$$\xrightarrow{h\nu} CH_3CHO + CH_3OH \qquad \leqslant 0.02 \qquad (12)$$

$$H\cdot + M \longrightarrow R\cdot + H_2 \qquad (13)$$

$$\cdot CH_3 + M \longrightarrow R\cdot + CH_4 \qquad (14)$$

$$CH_3O\cdot + M \longrightarrow R\cdot + CH_3OH \qquad (15)$$

$$\cdot OH + M \longrightarrow R\cdot + H_2O \qquad (16)$$

$$CH_3OCH_2CH_2O\cdot + M \longrightarrow R\cdot + M \qquad (17)$$

$$HOCH_2CH_2O\cdot + M \longrightarrow R\cdot + HOCH_2CH_2OH \qquad (18)$$

$$CH_3OCH_2CH_2O\cdot \longrightarrow CH_2O + CH_3OCH_2\cdot \qquad (19)$$

$$HOCH_2CH_2O\cdot \longrightarrow CH_2O + \cdot CH_2OH \qquad (20)$$

$M = CH_3OCH_2CH_2OH$ $R = \cdot CH_2OCH_2CH_2OH$, $CH_3O\dot{C}HCH_2OH$, or $CH_3OCH_2\dot{C}HOH$

We are now left with the quantum yields of the primary processes (4), (6), and (10). These can only be assessed less accurately, but on the basis of the products 9, 27, and 28 it appears that $\phi(4)$ is *ca.* 0.01 or less. On the basis of the disproportionation and combination products of the $CH_3OCH_2\cdot$ radical (IV) (7, 9, 20, 23, and 24), the quantum yield of the primary process (10) is <0.07. The quantum yield of the homolytic scission of the ether linkage according to reaction (6) is very difficult to assess. The methyl radical has less power to abstract than the hydrogen atom or the methoxyl radical and will undergo hydrogen abstraction [reaction (14)] as well as addition reactions. Hence $\phi(CH_4)$ is only a lower limit to $\phi(6)$. A better lower limit cannot be given since the combination products of $CH_3\cdot$ radicals with the most abundant radicals (VII)—(IX) could not be measured. An estimate of the extreme upper limit for $\phi(6)$ is based on the conceivable products from the other radical, $HOCH_2CH_2O\cdot$. It is highly abstractive as well as prone to fragmentation.[5] In the hydrogen abstraction process ethylene glycol is formed [reaction (18)] and fragmentation gives formaldehyde and $\cdot CH_2OH$ [reaction (20)]. The combined quantum yield of ethylene glycol and formaldehyde is 0.29. Since process (9), (11), and (19) also yield formaldehyde, and $\cdot CH_2OH$ radicals formed in processes (10) and (20) can dimerize and give some ethylene glycol, $\phi(6)$ is probably much overestimated at 0.29, and a value of *ca.* 0.18 is considered more likely.

Despite the fact that the estimates are not precise the results show the following. The ether and the hydroxy functions are about equally strongly affected in the photolysis. There appears to be no significant energy transfer from one chromophore to the other, and a preferential fragmentation at either the ether or the alcohol function is thus not induced. Another feature is that the ether function is mainly cleaved such that methyl is lost rather than methoxy. Methyl n-propyl ether[17] resembles methoxyethanol in this respect. There is fragmentation of the $\cdot OCH_2CH_2OH$ and possibly the $\cdot OCH_2CH_2OCH_3$ radical [reactions (20) and (19)]. The former process had been found in the ethylene glycol work.[5] It seems that another fragmentation process, $CH_3OCH_2\cdot CHOH \longrightarrow \cdot CH_2CHO + CH_3OH$, analogous to the H_2O elimination step which is characteristic of vicinal diol radicals[5,11,12,18] is probably a minor one [ϕ(acetaldehyde) *ca.* 0.02].

As found for methanol[1] and ethanol[2] C–OH bond cleavage seems to be of small importance ($<3\%$). C–C Bond cleavage is somewhat more frequent here (*ca.* 10%) than with ethanol[2] (1.5%), as well as, per individual C–C bond, diethyl ether[6] ($<0.5\%$), methyl t-butyl ether[7] (1.5%), and di-t-butyl ether[8] (1%). It is less than in aqueous ethylene glycol[5] (25%).

A recent study[19] indicates that ionic processes may take part in the 185 nm photolysis of 1,4-dioxan. In an attempt to clarify whether photoionization occurs in the present system some photolyses of N_2O-saturated methoxyethanol were performed. It was found that in the presence of N_2O nitrogen is formed, $\phi(H_2)$ is decreased, and $\phi(CH_4)$ remains unchanged. These results suggest that the sequence (21)—(23) plays only a minor role. About 10% of the hydrogen production is quenched in the N_2O-saturated methoxyethanol. $\phi(N_2)$, 0.08, is higher than the difference between the hydrogen quantum yields, 0.03, in the absence and presence of N_2O. It is not clear what causes this nonequivalence. A similar, though smaller, discrepancy was found in the radiolysis of propan-2-ol[20] and ascribed to a chain reaction of the overall nature $N_2O^- \longrightarrow N_2 + O^-$; $O^- + R_2CHOH + N_2O \longrightarrow H_2O + R_2CO + N_2O^-$.

$$CH_3OCH_2CH_2OH \xrightarrow{h\nu} CH_3OCH_2CH_2OH^{\cdot+} + e^- \qquad (21)$$

$$CH_3OCH_2CH_2OH^{\cdot+} + CH_3OCH_2CH_2OH \longrightarrow CH_3OCH_2CH_2OH_2^+ + CH_4OCH_2CH_2O\cdot \qquad (22)$$

$$CH_3OCH_2CH_2OH_2^+ + e^- \longrightarrow CH_3OCH_2CH_2OH + H \qquad (23)$$

Photolysis in Aqueous Solution.—The presence of water was found to have a strong effect on the photolysis of methoxyethanol as shown in Figures 3 and 4. The quantum yields of two of the major products, hydrogen and methane, were found to decrease from 0.27 and 0.15 respectively in the neat liquid, to 0.085 and 0.004 at 10^{-1}M. At this concentration 90% of the light is still absorbed by methoxyethanol. Below this concentration the quantum yields are no longer linear with dose suggesting that at these relatively high conversions of the starting material product photolysis is becoming important. These results are analogous to what has been found in the photolysis of ethanol[2] and propan-2-ol.[3,21] At present it is not known why this effect occurs. As shown in Figure 1 water greatly decreases the extinction coefficient of methoxyethanol at 185 nm from 550 in the vapour phase to 150 l mol^{-1} cm^{-1} in 10^{-2}M aqueous solution. It is possible that the polar effect of the solvent causes the $n \longrightarrow \sigma^*$ transition to undergo a ' blue shift '. Obviously water has a marked effect on both the photolysis and spectral properties of methoxyethanol.

The foregoing results indicate that in the photolysis of carbohydrates cleavage of the O–H and the ring C–O bonds might be major processes. The latter is strongly quenched in aqueous solutions of methoxyethanol. It is therefore not surprising that $\phi(H_2)$ from 2-deoxyribose [ε(185 nm) *ca.* 200 l mol^{-1} cm^{-1}] is <0.1 in the photolysis of its dilute (<0.5M) aqueous solutions.[22]

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[17] H.-P. Schuchmann and C. von Sonntag, *Z. Naturforsch.*, 1975, **306**, 399.

[18] R. E. Florin, F. Sicilio, and L. A. Wall, *J. Res. Nat. Bur. Standards*, 1968, **A72**, 49.

[19] C. von Sonntag and H. Bandmann, *J. Phys. Chem.*, 1974, **78**, 2181.

[20] J. C. Russell and G. R. Freeman, *J. Phys. Chem.*, 1968, **72**, 808.

[21] U. Sokolov and G. Stein, *J. Chem. Phys.*, 1966, **44**, 3329.

[22] R. Ford and C. von Sonntag, unpublished results.