Photolysis ($\lambda = 185$ nm) of Liquid Acetaldehyde Dimethyl Acetal*

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Deaerated liquid acetaldehyde dimethyl acetal has been photolyzed at $\lambda = 185$ nm, and 28 products have been determined. The major ones with their quantum yields are: methanol (0.59), methane (0.26), ethyl methyl ether (0.17), methyl vinyl ether (0.16), methyl formate (0.14), ketene dimethyl acetal (0.1), ethane (0.06), hydrogen (0.06), and acetaldehyde (0.06).

The major primary processes are suggested to be the scission of the $C-OCH_3$ bonds (homolytic and molecular) and of the $O-CH_3$ bonds (homolytic). Minor processes are hydrogen elimination reactions and the scission of the $C-CH_3$ bond.

Introduction

The photolysis of saturated acetals has found little attention in the past, and only 1,3-dioxolan[1] and formaldehyde dimethyl acetal[2] have been studied so far. The present study on acetaldehyde dimethyl acetal and the following paper on pivalaldehyde dimethyl acetal[3] are directed towards a better understanding of substituent effects both on the primary photolytic events and the subsequent free radical reactions in the open chain acetals.

Experimental

The starting material (Merck) was fractionated to a purity (GC) $> 99.98\%$. Irradiations, actinometry, separations and quantitative determinations by GC were done as described previously[2]. Glass capillary columns were used in the temperature-programmed mode, with liquid phases Marlophen 814, optimal for the more volatile products, and Carbowax 20 M, more suitable for the less volatile ones. For most of the products authentic material was available. The rest was assigned by GC–MS (cf. Table I). GC-response factors for these compounds were calculated on an increment basis[4]. Formaldehyde was measured photometrically[5]. The molar extinction coefficient was determined as described earlier[2] using vapour pressure data[6].

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Results and Discussion

The molar extinction coefficient of acetaldehyde dimethyl acetal near $\lambda = 185$ is given in Fig. 1. For the exciting wavelength 185 nm it extrapolates (Fig. 1) to ca. 50 l mol^{-1} cm^{-1}. The other major line
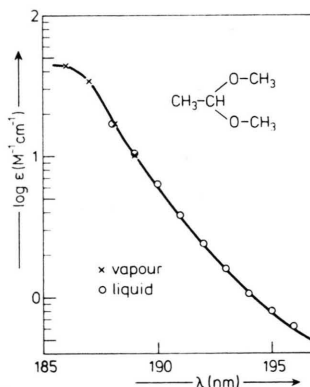

Fig. 1. The molar extinction coefficient of acetaldehyde dimethyl acetal between 186 and 196 nm.

at λ 254 nm emitted by the Hg low pressure arc used is not absorbed significantly and does not contribute to the photolysis of the acetal. Table I gives the products and their quantum yields. The latter are based on $\varphi(H_2) = 0.4$ for the Farkas actinometer[7]. The relative quantum yields are thought to be accurate within $\pm 10\%$ except for methyl formate, acetaldehyde, and ketene dimethyl acetal, these three being probably too low, and the

Table I. 185 nm Photolysis products of liquid deaerated acetaldehyde dimethyl acetal, and quantum yields. Conversion 0.03 to 0.3%, 10°.

No.	Product	φ
1	H_2	0.06
2	CH_4	0.26
3	C_2H_4	0.004
4	C_2H_6	0.058
5	CO	$< 10^{-4}$
6	CO_2	$< 10^{-4}$
7	CH_2O	0.01
8	CH_3OH	0.59
9	CH_3CHO	0.06
10	CH_3OCH_3	0.006
11	$HCOOCH_3$	0.14
12	$CH_3OCH=CH_2$	0.16
13	$CH_3OC_2H_5$	0.17
14	C_2H_5CHO	0.01
15	$CH_3OCH(CH_3)_2$	0.042
16	$CH_2(OCH_3)_2$	0.005
17	$CH_2=C(OCH_3)_2$ [a]	0.1
18	$CH_3CH(OCH_3)(OC_2H_5)$	0.047
19	$(CH_3)_2C(OCH_3)_2$	0.030
20	$CH(OCH_3)_3$	0.003
21	$CH_3C(OCH_3)_3$	$< 10^{-3}$
22	$CH_3CH-OCH_3$ $\vert$ *meso + dl* $CH_3CH-OCH_3$	0.01
23	$CH_3C(OCH_3)_2$ [b] $\vert$ $CH_3CH-OCH_3$	0.02
24	$O-CH(CH_3)(OCH_3)$ [b] $\vert$ $CH_2-CH(CH_3)(OCH_3)$	0.05
25	$HC(OCH_3)_2$ [b] $\vert$ $CH_3C(OCH_3)_2$	0.002
26	$CH_2-CH(OCH_3)_2$ [b] $\vert$ $O-CH(CH_3)(OCH_3)$	0.002
27	$CH_2-C(CH_3)(OCH_3)_2$ [b] $\vert$ $O-CH(CH_3)(OCH_3)$	0.01
28	$CH_2O-CH(CH_3)(OCH_3)$ [b] $\vert$ $CH_2O-CH(CH_3)(OCH_3)$	0.01

[a] Reference material [13] kindly supplied by Dr. RITTER-THOMAS of this Institute.
[b] Identified by GC–MS only.

latter poorly reproducible. Several minor products remain unidentified. Some appeared with GC retention times beyond those of the dehydro dimers. However, their combined estimated quantum yield probably does not exceed 0.05.

In our previous studies on saturated ethers [8–11] it has often been possible to estimate the importance of primary processes on the basis of known disproportionation/dimerisation ratios of radical pairs. This, however, is not possible here because no such data are available for the radicals formed in the present system. Nevertheless, the quantum yield
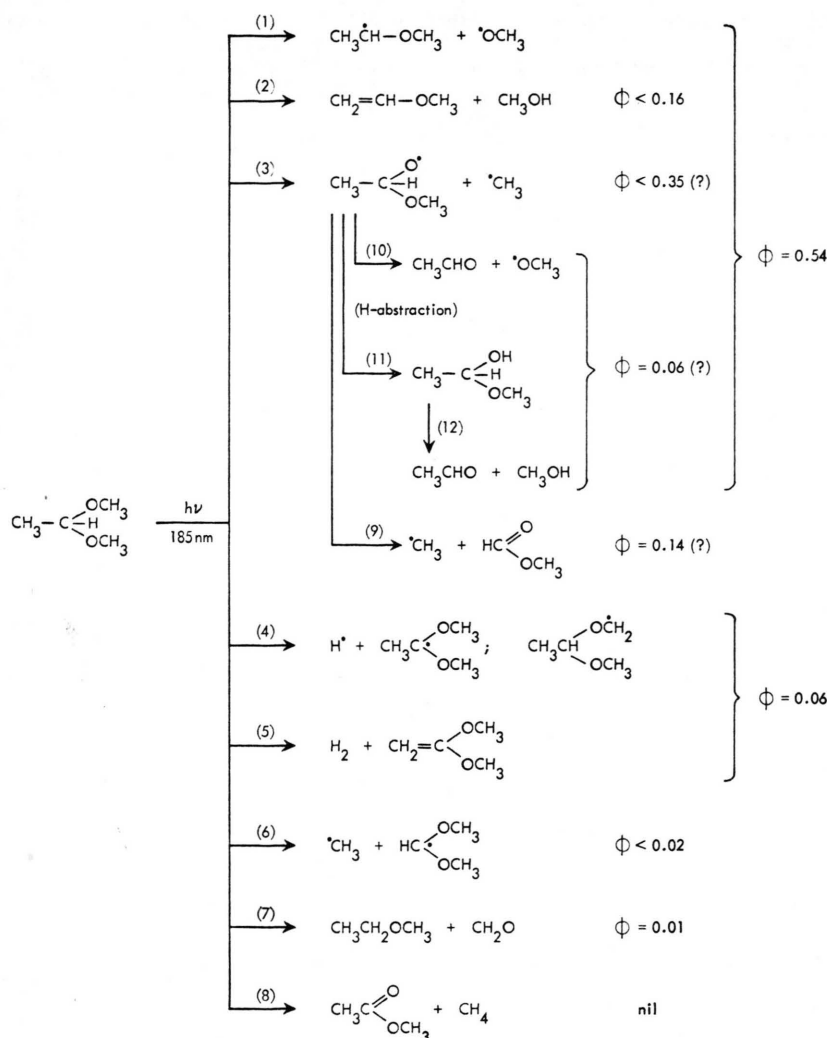
data (Table I) do permit conclusions to be drawn regarding the importance of several primary processes. Upper limits for some processes can be deduced from the quantum yields of key products where a sharp separation of routes of product formation is not possible.

Methanol (**8**) is the major product. It originates from the process (1) (see Scheme) followed by hydrogen abstraction from the substrate by the reactive $CH_3O\cdot$ radical, and perhaps also from the molecular route (2). An upper limit for the latter process is $\varphi(\mathbf{12}) = 0.16$. A third route to methanol (**8**) is *via* the reactions (10) or (11) subsequent to the primary process (3) which eventually give rise to acetaldehyde (**9**). Competing with processes (10) and (11) is the fragmentation reaction (9) giving rise to methyl formate (**11**). Fragmentation [*e.g.* (9) and (10)] as well as hydrogen abstraction [*e.g.* (11)] are reactions typical for alkoxy radicals. The exact contribution of reactions (3), (9), (10), and (11) is not clear. Inserting the quantum yield values of the products containing the methyl fragment, **2**, **4**, **15**, **18**, and **19**, of methyl formate (**11**), and of acetaldehyde (**9**), there is a disbalance between reaction (3) and the subsequent reactions (9), (10), and (11). We think that the methyl formate yield value, and perhaps the acetaldehyde value, might have been found too low. The value of $\varphi = 0.35$ for reaction (3) as given in the Scheme is based on the quantum yields of the methyl-containing products, subtracting $\varphi(\cdot CH_3) = 0.14$ for reaction (9). An increased importance of reaction (9) means that the importance of reaction (3) is simultaneously decreased.

Processes (4) and (5) might be distinguished if the disproportionation/dimerisation ratios of all radicals present in this system were known. Their sum is given by $\varphi(H_2) = 0.06$.

Processes (6) and (7) are of little importance, as is suggested by the quantum yields of products with the $\cdot CH(OCH_3)_2$ unit, such as **16**, **25**, and **26**, and formaldehyde (**7**).

Methyl acetate which might be formed *via* reaction (8) has been specifically sought and shown to be absent ($\varphi < 10^{-3}$). This is surprising because both formaldehyde dimethyl acetal [2] and pivalaldehyde dimethyl acetal [3] have analogous processes as important routes. However, it has been shown in the case of the two stereoisomers of 2,5-dimethyltetrahydrofuran [12] that mere configurational differences between the *cis* and the *trans* isomers may have a

Scheme. Primary processes in the 185 nm photolysis of liquid deaerated acetaldehyde dimethyl acetal.

substantial influence on the photochemistry, at least as far as product ratios are concerned. Furthermore, process (7) is negligible whereas the corresponding processes in the other acetals [2,3] are quite important. This is thought to be due to the availability of hydrogen atoms β to the methoxy groups which can give rise to methanol elimination (process 2). In the photolysis of straight chain ethers [9,11], it has been observed that methanol elimination competes favourably with formaldehyde elimination. Processes (6), (9) and (10) will be discussed in the following paper in the light of the results obtained with pivalaldehyde dimethyl acetal.

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