The 185 nm Photolysis of 1,4-Dioxane in the Liquid Phase*

Heinz-Peter Schuchmann, Heinz Bandmann, and Clemens von Sonntag

Institut für Strahlenchemie im Max-Planck-Institut für Kohlenforschung, Mülheim a. d. Ruhr

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The main products in the 185 nm photolysis of neat 1,4-dioxane are formaldehyde ($\Phi = 0.25$), glycol monovinyl ether (0.17), and ethylene (0.15). Some hydrogen (0.04), carbon monoxide (0.01), acetaldehyde (0.03), oxetane (0.04), and bidioxanyl (0.01) are also formed. On $N_2O$-saturation, the quantum yields of these products are diminished by about 30%, and $N_2O$ (0.59) and hydroxydioxane (0.4) become the main products. They are thought to be formed in the reaction sequence:

\[
\text{dioxane} \xrightarrow{h\nu} \text{dioxane*} \\
\text{dioxane*} + N_2O \rightarrow \text{dioxane} + N_2 + O \\
O + \text{dioxane} \rightarrow \text{hydroxydioxane}
\]

In aqueous dioxane, photoionisation is possible due to a greater lowering of the ionisation threshold. In dioxane/water 20:80 the main products are $H_2$ (0.50) and bidioxanyl (0.45), most likely formed in consequence of:

\[
\begin{align*}
(\text{dioxane})_{aq} \xrightarrow{h\nu} (\text{dioxane})_{aq}^- + e_{aq}^- \\
(\text{dioxane})_{aq}^- \rightarrow (\text{dioxane}^-H) + H^+ \\
\text{H}^+ + \text{dioxane} \rightarrow H_2 + (\text{dioxane}^-H) \\
2(\text{dioxane}^-H) \rightarrow \text{bidioxanyl}
\end{align*}
\]

Introduction

The UV photolysis of 1,4-dioxane in the condensed [1–6] and gas phase [7] has found some attention, including an ESR study [6] at 77 K. There is also a report [8] on the ruby laser-induced decomposition in the gas phase.

Carbonyl compounds, especially formaldehyde, are formed in high quantum yields as primary products. Thus it is not surprising that the liquid phase photolyses of dioxane carried out to only moderate conversions already lead to a variety of products [2, 3]. In the gas phase at 147 nm, the quantum yield of primary dioxane disappearance is close to unity, with formaldehyde and ethylene as the main products formed in a ratio of about 2:1 [7].

UV-irradiated dioxane has been shown to fluoresce from the liquid [4, 5, 9, 10] but not from the vapour state [9]. This fluorescence is suppressed by $N_2O$ [4, 5] and other quenchers. It has been shown [4] that in aqueous $N_2O$-saturated dioxane the hydrogen quantum yield falls while the nitrogen quantum yield rises in a complementary fashion over a pH range from zero to five, indicating that photoionisation occurs in the photolysis of aqueous dioxane.

The present study has been undertaken to obtain an insight into the complete fragmentation pattern of excited dioxane. Furthermore, $N_2O$ has been used as a probe to help answer the question whether at 185 nm photoionisation occurs also in neat dioxane, since it had been found in its aqueous solution [4]. As will be shown, photoionisation does not occur in neat dioxane, but in the presence of $N_2O$ energy is transferred to $N_2O$ leading to its decomposition into $N_2$ and an O-atom.

Experimental

Analytical grade 1,4-dioxane was distilled twice from sodium under argon on a 3 m fractionating column filled with glass helices, at a reflux ratio of 30:1. Gas chromatography of the purified material with flame ionization detection indicated that impurities were less than 10 ppm.

The photolyses were carried out at 185 nm as previously described (cf. [11]). Liquid samples were put in a suprasil QS cell and deaerated by purging with high-purity argon for 20 min, and irradiated at 15 °C with a low pressure mercury lamp. $N_2O$-saturated samples were prepared by bubbling with $N_2O$ instead of argon. Saturation at atmospheric pressure corresponds to an $N_2O$ concentration of ~0.12 M [12]. Dosimetry was performed with the ethanol actinometer [13]. Typical dose rates were $8.3 \times 10^{15}$ quanta $\cdot s^{-1}$ with 2 ml samples and $24.2 \times 10^{15}$ with 4 ml samples.
Product yields were linear with dose up to irradiation times of 30 min. Excepting formaldehyde and hydroxydioxane the products were analyzed directly by GC (stationary phases used were P 4000 and polypropylene glycol). They were identified by GC and GC–MS using reference material. Glycol monovinyl ether [14], bidioxanyl [1], 1,4-dioxene [15], and hydroxydioxane [16] were synthesized. Formaldehyde was determined photometrically by the acetylacetone-ammonium acetate method [17].

Hydroxydioxane (tautomeric with (2-hydroxyethoxy)acetaldehyde) formed as a major product in the presence of N2O, was not amenable to direct quantitative GC analysis. Its mass spectrum, however, could be obtained by GC–MS; m/e (%): 45(100), 28(85), 29(42), 43(35), 31(25), 42(23), 75(23), 58(22), 86(3), 87(3), 104 (M⁺; 3). For its quantitation, the photolyzed sample was taken up in water, reduced with NaBH₄ and 1,4-butanediol added as an internal standard. The hydroxydioxane is thereby transformed to diethylene glycol, similar to other cyclic hemiacetals [18]. The reduced sample was neutralized with acid cation exchanger, filtered, and the boric acid removed by evaporating several times to dryness with methanol. The residue containing the diols was trimethylsilylated and gas chromatographed (stationary phase OV 101). The experimental error in the determination of hydroxydioxane in probably not less than 30% while for the other products it is thought not to exceed 10%.

Some photolyses were carried out with dioxane dried over LiAlH₄. In an experiment to test the stability of dioxane toward LiAlH₄, a mixture of both was kept in a photolytic cell at room temperature, and the hydrogen that evolved on standing in the dark was periodically measured in the usual way [19].

The fluorescence was excited with light from a hydrogen lamp H 30 DS (suprasil window) and registered in the front face illumination mode, using a Carl Zeiss spectrophotometer PMQ II, equipped with two monochromators and the complementary device Carl Zeiss ZF M 4.

The molar extinction coefficient of oxygen-free dioxane liquid and vapour was determined employing a procedure described previously [11], with a Cary model 17 spectrophotometer. In Fig. 1, the maxima and minima of the gas phase extinction coefficient curve are indicated as measured.

Results

1,4-Dioxane absorbs strongly at 185 nm. We have found a molar extinction coefficient of about \(2 \times 10^3\) mol\(^{-1}\) cm\(^{-1}\) for the vapour, the spectrum showing considerable structure [20] between 185 and 200 nm. It is remarkable that the extinction coefficients of the vapour and the degassed liquid near 200 nm fail to match by about one order of magnitude (Fig. 1) which probably means that aggregates exist in the liquid (cf. however [9]), and it is expected that at 185 nm the liquid absorbs with similar or even higher strength than the gas phase. N₂O saturation did not have any apparent effect on the absorption spectrum of liquid dioxane. Dioxane decomposition was immeasurably small with a vycor quartz plate interposed between lamp and cell, i.e. there is no photolysis at 254 nm.

The quantum yields of the products from the photolysis of dry dioxane (neat and N₂O-saturated) are given in Table I. Several minor unidentified products were observed, with a total quantum yield obtained at about 0.02. Ethane [6] is absent. Ethylene oxide, 1,4-dioxene and ethoxyacetaldehyde have not been found. Preliminary results [13] had indicated the formation of 2-methyl-1,3-dioxolane.

<table>
<thead>
<tr>
<th>Product</th>
<th>Neat</th>
<th>N₂O-saturated</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>0.04</td>
<td>0.01</td>
</tr>
<tr>
<td>CO</td>
<td>0.01</td>
<td>not determined</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>0.15</td>
<td>0.10</td>
</tr>
<tr>
<td>CH₃O</td>
<td>0.25</td>
<td>0.14</td>
</tr>
<tr>
<td>CH₃CHO</td>
<td>0.03</td>
<td>0.02</td>
</tr>
<tr>
<td>oxetane</td>
<td>0.04</td>
<td>0.03</td>
</tr>
<tr>
<td>CH₂=CH–OCH₂CH₂OH</td>
<td>0.17</td>
<td>0.10</td>
</tr>
<tr>
<td>bidioxanyl (meso + dl)</td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>N₂</td>
<td>absent</td>
<td>0.59</td>
</tr>
<tr>
<td>hydroxydioxane</td>
<td>absent</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Table I. Quantum yields of products from the 185 nm photolysis of dry liquid 1,4-dioxane in the absence and presence of N₂O (N₂O at atmospheric pressure).
at a quantum yield near 0.01. We now conclude that this is not a photolysis product. At conversions higher than those employed in the kinetic runs which were attained in the samples intended for mass spectrometry, traces of hydroxymethylidioxane were detected as assigned in MS: m/e (\%): 87 (100), 31 (70), 43 (30), 29 (18), 45 (16), 57 (15), 86 (15), 74 (10), 118 (M+; 3).

In aqueous solution, the quantum yields of some products have been determined as a function of dioxane concentration (Figs. 2 and 3). In a mixture containing 20\% dioxane \(\Phi(H_2)\) (Fig. 2) and \(\Phi(bidioxanyl) = 0.55\) match. In the presence of \(N_2O\), the quantum yield of hydroxydioxane falls with decreasing dioxane concentration. A 20:80 dioxane/water mixture gives a value of about 0.04 whereas in neat dioxane this is an order of magnitude larger (Table I). No \(H_2O_2\) was detected.

Cyclohexene oxide is formed with a quantum yield of 0.02 in the photolysis of an \(N_2O\)-saturated mixture of dioxane and cyclohexene (10:1).

In order to see if traces of moisture make a difference as far as the photolysis is concerned, dioxane kept over LiAlH\(_4\) for three days was transferred on a vacuum line into the photolysis cell by recondensation, and photolyzed. The ethylene and hydrogen quantum yields were measured and found the same as those from dioxane not so treated with LiAlH\(_4\). Further, a sample of dioxane in which some LiAlH\(_4\) had been suspended gave the same ethylene quantum yield. The apparent hydrogen quantum yield from the latter sample, however, was about a hundred times higher. On standing, a deaerated suspension of LiAlH\(_4\) in dioxane slowly decomposed, giving off hydrogen. Thus, 2 ml of suspension, four days after preparation, yielded \(6.8 \times 10^{-6}\) mol \(H_2\), and went on to yield about \(2.5 \times 10^{-5}\) mol \(H_2\) per week for several weeks, after which \(H_2\) monitoring was discontinued.

In agreement with other work [5] it has been found that \(N_2O\) quenches the fluorescence (at 246 nm) of dioxane. Saturation at atmospheric pressure, \([N_2O] = 0.12\) M [12], leads to a reduction of the fluorescence quantum yield by 85%.

Discussion

Our results show that the photolysis of neat liquid 1,4-dioxane differs from that reported for the vapour mainly in that fragmentation processes are partly arrested through more efficient thermalization in the liquid. It is of moderate complexity if photolysis of products [2, 3] is avoided. The primary processes that we think can explain our findings are given in Scheme 1 and are discussed below.

![Scheme 1. Primary processes in the 185 nm photolysis of neat liquid dioxane. \(\Phi\) (primary processes) \(\approx 0.4\) in the absence of \(N_2O\).]
There is a discrepancy between some of our results and those of another study [5] of the liquid dioxane photolysis. In the absence of N₂O, the ethylene and hydrogen quantum yields were found as follows: C₂H₄, 0.15 (this work) vs. 0.55 [5]; H₂, 0.04 (this work) vs. 0.26 [5]. Fig. 2 indicates that \( \Phi(H₂) \) from completely dry dioxane should not be larger than the value we have measured. In accordance with this, the photolysis of dioxane which had been stored over LiAlH₄ and which was condensed into the photolysis cell in vacuo gave \( \Phi(H₂) = 0.03 \).

Since we have observed that the presence of traces of LiAlH₄ in the photolyzed sample leads to an extraordinarily high \( \Phi(H₂) \), we believe that not only dioxane photolysis products such as monovinyl glycol ether act as hydrogen sources, but also, that the photolysis at 254 nm of a LiAlH₄-dioxane adduct might lead to hydroxyl compounds [21] and thus give rise to further hydrogen. In this context it is also of interest that dioxane in contact with LiAlH₄ is slowly decomposed under the formation of hydrogen. Small amounts of moisture might conceivably make a difference as far as \( \Phi(C₂H₄) \) is concerned (cf. Fig. 3). However, the ethylene quantum yield from samples of neat dioxane and of dioxane with LiAlH₄ suspended therein is the same, from which we conclude that any residual moisture in our starting material is sufficiently small so as not to modify the course of the photolysis.

We have no explanation for these differences but point out that our ethylene and hydrogen values have been reproduced several times in several series of runs many weeks or months apart, using different batches of purified dioxane. In any case, the values in [5] seem too high. Beside ethylene we have found glycol monovinyl ether with a quantum yield of 0.17 (Table I) which in the frame of reference of [5] corresponds to 0.62 if one applies our yield ratios for these products to [5]. In [5], this would lead to a quantum yield for the primary processes which would be higher than unity. The values of reference [5] seem, therefore, to be unacceptable.

**Possible routes to products**

It has been shown with open-chain aliphatic ethers that the major primary processes involve the scission of a C–O bond [13]. In 1,4-dioxane such a process would lead to the 1,4-dioxo-hexamethylene diradical (reaction 2 in Scheme 1). Owing to the possible intermediacy of this diradical the quantum yields of the main products do not permit a breakdown into the exact contributions of processes 1, 2, and 3 (Scheme 1). Similar problems are encountered in the establishment of the photolysis mechanisms for other cyclic compounds, such as 1,3-dioxolanes [22], tetrahydropryan [23], and tetrahydrofurans [24]. The homolytic C–O bond cleavage is assumed to occur in all these cases just as with aliphatic open-chain ethers. The low quantum yields of acetaldelyde and hydrogen (Table I) suggest that processes 3, 4, and 5 in Scheme 1 play a minor role.

The overall quantum yield of product formation is only around 0.4. Although fluorescence is observed its quantum yield of ~0.03 [9] is far from making up the difference to unity. In fact, part of this may be due to reclosure of the biradical formed in reaction 2 of Scheme 1. In the 185 nm photolysis of cis- and of trans-2,5-dimethyltetrahydrofuran [24] such a process has been shown to be of importance. However, there will be other deactivating processes. The quantum yield of the sum of the primary processes leading to the products (Table I) is ca. 0.42. The rest (\( \Phi = 0.58 \)) is deactivated to the ground state whereby a small proportion of the energy is emitted as fluorescence (\( \varphi(\text{fluorescence}) = 0.03 \) [10]). On N₂O-saturation the quantum yield of the sum of the primary processes leading to products is reduced by about 1/3. Assuming the same proportion acting on the excited states which do not lead to products in the absence of N₂O, one obtains a maximum estimate of 0.35 for \( \Phi(N₂) \) if this portion of energy has been transferred to N₂O (see below). However, the measured \( \Phi(N₂) \) is 0.59.

Therefore there must be a state which transfers energy to N₂O more efficiently than the product-forming state. This state might be the fluorescent state which is, in fact, suppressed on N₂O saturation more strongly (by 85%) than the product-forming state (by 35%). The fluorescent species has been thought to be an excimer [9, 5]. The excitation of a ground state aggregate has to be considered, as the extinction coefficient of the liquid is markedly different from that of the gas phase. Such an effect has not been observed so far with other ethers [cf. 13, p. 66], nor do other ethers show marked fluorescence. An argument against the presence of ground-state aggregates has been put forward [9] on the basis of the fact that the extinction coefficient of dioxane was found to be independent of concentration in a fluorocarbon solvent. However, it is
not clear whether the monomer predominates in such a poorly solvating medium, even at the low concentrations investigated [9].

The lifetime of the product-forming state can be estimated from the lifetime of the fluorescent state, and the effect of N2O on the quantum yield of fluorescence and products, if equal energy transfer rates to N2O from the fluorescing and the product-forming state are assumed. As the fluorescence lifetime is 2 ns [10] and the fluorescence is about eight times as efficiently quenched than the product formation the lifetime of the product-forming state would be around 0.3 ns.

**Energy transfer to N2O.**

**The question of solvated electrons**

The observations [4] that the fluorescence of neat dioxane is quenched by N2O, and that dioxane N2O-saturated at atmospheric pressure shows a remarkably high nitrogen quantum yield of 0.59 led to the hypothesis that solvated electrons might be playing an important part in the dioxane photolysis. Evidence for this has been given for aqueous dioxane [4].

The present study of neat dioxane reveals that on N2O saturation all products except bidioxanyl are diminished. Bidioxanyl is about doubled and hydroxydioxane is found with a quantum yield near that of N2 (Table I). For neat dioxane, the lowering of its ionization potential with respect to the gas phase value is less than for its aqueous solution. Photoionization energy thresholds for solutes in various solvents [26] suggest that in neat liquid dioxane the ionization energy is lowered relative to the gas phase value by between 2.1 and 2.4 eV (1,4-dioxane was not measured but compare: for liquid 2-methyltetrahydrofuran, the difference is 2.1 eV, for diethyl ether, 2.3 eV, and for t-butanol, 2.4 eV [25, 26]). In water, the ionization threshold energy is lowered by about 3 eV [25, 26]. For the dioxane vapour ionisation potential differing values have been published, ranging from 9.13 [27] through 9.52 [28] to 9.8 eV [29]. 185 nm light yields 6.7 eV per quantum, so that photionization of neat liquid dioxane might just be possible energetically. However, the quantum yield of N2 is quite large. Moreover, the fact that bidioxanyl is only weakly enhanced suggests that processes comprising hydrogen abstraction steps are not brought about to a significant extent by N2O. Therefore, sequences implying the reaction $e^- + N_2O \rightarrow N_2 + O^-$ seem of small importance ($O^-$ acts as a strong hydrogen atom abstractor). Besides, the large yield of hydroxydioxane suggests that oxygen insertion takes place. Such reactions are undergone by O($^1D$) generated, for example, in the direct photolysis of N2O [30]. O($^1D$) also adds to olefins giving the epoxide [31]. Indeed, we have found that cyclohexene oxide is formed when an N2O-saturated 10:1 mixture of dioxane and cyclohexene is photolyzed. The direct photolysis of N2O in the present system cannot contribute, on account of the low extinction coefficient of N2O ($\varepsilon$ (185 nm) = 36 M$^{-1}$ cm$^{-1}$ [32]) and the high extinction coefficient of the dioxane. We therefore conclude, in accordance with [5], that in the photolysis of non-aqueous dioxane N2O is destroyed mostly through energy transfer from singlet excited dioxane, and to a small extent at most through solvated electrons. Such energy transfer has been postulated before though the chemical consequence of this process was not explored [5]. The essential feature of the nonaqueous dioxane photolysis in the presence of N2O is therefore summarized as follows:

$$
\begin{align*}
\text{dioxane} & \rightarrow \text{dioxane*} \\
\text{dioxane*} & \rightarrow \text{products} \\
\text{dioxane*} + \text{N2O} & \rightarrow \text{dioxane + N2 + O} \\
\text{dioxane + O} & \rightarrow \text{hydroxydioxane}
\end{align*}
$$

Another example with similar behaviour is known: photoexcited (163 nm) cyclohexane transfers energy to N2O and the formation of cyclohexanol is observed [33].

The results obtained with aqueous solutions, especially the dependence of $\Phi$(H2) on water concentration (Fig. 2) indicate that the mechanism does not change abruptly but that the importance of solvated electrons increases gradually so that when dioxane concentrations near 7 mol% (30% v:v) are reached, they mediate most of the photochemistry. Here it is of interest to note that in water-dioxane mixtures, the absorption spectrum of the solvated electron, down to a mole fraction of 53% water, is the same as in pure water [34].

The presence of solvated electrons in aqueous solutions of dioxane had been inferred from the particular form of the pH dependence of $\Phi$(H2) and $\Phi$(N2) from N2O-saturated solutions [4]. There is now some further supporting evidence. In neat dioxane energy transfer to N2O leads to an O-atom
Photolysis of Dioxane

which inserts into dioxane to give hydroxydioxane. In aqueous solution, the quantum yield of this product is very much reduced while hydrogen peroxide, a product conceivably formed from water by insertion of the O-atom, is also not found. Instead, bidioxanyl is the major product, and it is formed most likely according to the reaction sequence:

\[
\begin{align*}
\text{dioxane} & \xrightarrow{h\nu} (\text{dioxane})^+ + e_{aq}^- \\
(d\text{ioxane})^+ & \xrightarrow{} (\text{dioxane-H})^- + H^+ \\
e_{aq}^- + H^+ & \xrightarrow{} H^2 \\
e_{aq}^- + N_2O & \xrightarrow{} \cdot OH + OH^- + N_2 \\
H^+ + \text{dioxane} & \xrightarrow{} H_2 + (d\text{ioxane-H})^- \\
\cdot OH + \text{dioxane} & \xrightarrow{} H_2O + (d\text{ioxane-H})^- \\
2(d\text{ioxane-H})^- & \xrightarrow{} \text{bidioxanyl}
\end{align*}
\]

There are probably other solvent influences as well. Drastic changes in the photolytic behaviour of alcohols depending on the kind of solvent and the alcohol concentration have been found in previous work [35-37]. However, these effects are at present not understood.

Recently, a chain reaction of the type

\[
R^\cdot + N_2O \rightarrow N_2 + RO^\cdot \\
RO^\cdot + RH \rightarrow ROH + R^\cdot
\]

has been uncovered in the \(\gamma\)-radiolysis of aqueous solutions of isopropanol (RH) at elevated temperatures [38]. Extrapolating their data, one estimates that this chain would cease (G < 5 molecules N_{2} per 100 eV \(\gamma\)-energy absorbed) below 130 °C. The low temperature at which the present experiments were carried out and the virtual absence of hydroxydioxane in the photolysis of the aqueous dioxane solutions all but rules out a similar chain in the present system.