The UV Photolysis ($\lambda = 185$ nm) of Liquid Methyl n-Propyl Ether

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Methyl n-Propyl Ether, UV Photolysis, Quantum Yields, Radicals, Molecular Elimination Processes

The main products of the 185 nm photolysis of liquid methyl n-propyl ether (quantum yields in parentheses) are n-propanol (0.70), methane (0.29), sec-butyl methyl ether (0.20), methanol (0.16), propionaldehyde (0.13), 3,4-dimethoxyhexane (0.09), ethane (0.08), and ethyl n-propyl ether (0.08). The quantum yields of further 24 minor products have been measured. The quantum yield of the sum of primary photochemical processes, the main ones of which are the homolytic scissions of the C-O bonds (reactions i and ii), is close to unity.

\[
\begin{align*}
(i) \quad \text{hv} \quad & \quad \text{CH}_3\text{-O-CH}_2\text{-CH}_3 \rightarrow \text{CH}_3\cdot + \cdot\text{O-CH}_2\text{-CH}_3 \quad (\Phi \approx 0.70) \\
(ii) \quad \text{hv} \quad & \quad \rightarrow \text{CH}_3\text{-O.} + \cdot\text{CH}_2\text{-CH}_3 \quad (\Phi \approx 0.15) \\
(iii) \quad \text{hv} \quad & \quad \rightarrow \text{CH}_4 + \cdot\text{CHO-CH}_2\text{-CH}_3 \quad (\Phi \approx 0.13)
\end{align*}
\]

Reaction (i) is favoured over reaction (ii) by nearly a factor of five. The elimination of molecular methane (iii) is the only other process of importance. C-H and C-C bond splitting is marginal.

Introduction

The photolysis, radiolysis or pyrolysis of methyl n-propyl ether (MPE) does not seem to have hitherto received attention. The 185 nm photolysis of some open-chain saturated ethers\textsuperscript{1-3}, which begin to show strong absorption below 200 nm, has indicated that strong absorption should occur in n-propyl ethers, which is an indication of the primary processes. The C-O bond homolysis (a) and/or molecular fragmentation (including cage disproportionation reactions) leading to alcohol and olefin (b), and aldehyde and alkane (c).

\[
\begin{align*}
\text{hv} \quad & \quad \text{R-O-R} \rightarrow \text{R-O} + \text{R'} \quad (a) \\
\text{hv} \quad & \quad \rightarrow \text{R'CH}_2\text{OH} + \text{Olefin} \quad (b) \\
\text{hv} \quad & \quad \rightarrow \text{R'CH=O} + \text{Alkane} \quad (c)
\end{align*}
\]

Part VII of the series: Strahlenchemie von Äthern.

Process (a) is reminiscent of the photochemical $\alpha$-cleavage of ketones, since in both classes of compounds photochemical cleavage mainly occurs $\alpha$ to the excited functional group. In the ketones this is by way of an $n-\pi^*$ excitation. In ethers, the excited state is $n-\sigma^*$. It is tempting to compare the asymmetrical ethers with the linear asymmetrical ketones as regards $\alpha$-cleavage. Such ketones when excited in their first UV absorption band favour the loss of that alkyl radical which is more stabilized\textsuperscript{5}. Ethyl loss exceeds methyl loss in the case of ethyl methyl ketone\textsuperscript{6}. Analogous conclusions can be drawn from data\textsuperscript{7} on the photolysis of methyl $n$-propyl, methyl sec-propyl, $n$-amyl methyl, $n$-butyl methyl and sec-butyl methyl ketones.

In the case of the ethers the picture seems to be less clear. tert-Butyl methyl ether preferentially

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loses tert-butyl\(^3\) but, as will be shown below, MPE cleaves mostly the CH\(_3\)–O bond while the formation of propyl radicals is of secondary importance.

**Experimental**

MPE was synthesized from sodium \(n\)-propanolate and dimethyl sulfate (cf. \(^4\)) distilled over sodium and fractionated on a 500 mm slit tube column at a reflux ratio of 100:1. The ether was gas-chromatographically pure except for an impurity of isopropyl methyl ether, about 10 ppm. This did not show a measurable decrease on photolysis and thus proved harmless.

The molar extinction coefficient of deoxygenated methyl \(n\)-propyl ether was determined on a Cary model 17 spectrophotograph. At wavelengths near 185 nm, absorption is intense; \(\varepsilon\) (185 nm) \(\approx 2300\) 1 mol\(^{-1}\) cm\(^{-1}\).

Table I. Retention times of products. Sources of reference compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Relative retention time</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>2.5(^a)</td>
<td>l’Air liquide</td>
</tr>
<tr>
<td>Methane</td>
<td>1.4(^b)</td>
<td></td>
</tr>
<tr>
<td>Ethylenle</td>
<td>2.5(^b)</td>
<td></td>
</tr>
<tr>
<td>Ethene</td>
<td>3.0(^b)</td>
<td></td>
</tr>
<tr>
<td>Propylene</td>
<td>6.4(^b)</td>
<td>Matheson</td>
</tr>
<tr>
<td>Propane</td>
<td>6.9(^b)</td>
<td>l’Air liquide</td>
</tr>
<tr>
<td>Cyclopropane</td>
<td>8.0(^b)</td>
<td>Matheson</td>
</tr>
<tr>
<td>(n)-Butane</td>
<td>19.3(^b)</td>
<td>0.11(^d)</td>
</tr>
<tr>
<td>(n)-Pentane</td>
<td></td>
<td>14.8(^e)</td>
</tr>
<tr>
<td>(n)-Hexane</td>
<td></td>
<td>23.8(^f)</td>
</tr>
<tr>
<td>Dimethyl ether</td>
<td>0.23(^g)</td>
<td>Matheson</td>
</tr>
<tr>
<td>Ethyl methyl ether</td>
<td>0.36(^h)</td>
<td>g</td>
</tr>
<tr>
<td>Methyl vinyl ether</td>
<td>0.46(^i)</td>
<td></td>
</tr>
<tr>
<td>(Methyl propyl ether)</td>
<td>0.64(^j)</td>
<td></td>
</tr>
<tr>
<td>(i)-Butyl methyl ether</td>
<td>0.86(^k)</td>
<td></td>
</tr>
<tr>
<td>Ethyl (n)-propyl ether</td>
<td>0.95(^l)</td>
<td></td>
</tr>
<tr>
<td>sec-Butyl methyl ether</td>
<td>1.00(^m)</td>
<td></td>
</tr>
<tr>
<td>Allyl methyl ether</td>
<td>1.10(^n)</td>
<td></td>
</tr>
<tr>
<td>Methyl (n)-propenyl ether ((\text{trans}))</td>
<td>1.23(^o)</td>
<td></td>
</tr>
<tr>
<td>Methyl (n)-propenyl ether ((\text{cis}))</td>
<td>1.39(^p)</td>
<td></td>
</tr>
<tr>
<td>3-Methoxypentane</td>
<td>1.74(^q)</td>
<td></td>
</tr>
<tr>
<td>Propionaldehyde</td>
<td>1.86(^r)</td>
<td></td>
</tr>
<tr>
<td>(n)-Butyl (n)-propyl ether</td>
<td>2.56(^s)</td>
<td></td>
</tr>
<tr>
<td>3-Methoxycyclohexane</td>
<td>2.63(^t)</td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td>2.80(^u)</td>
<td></td>
</tr>
<tr>
<td>(n)-Propanol</td>
<td>3.91(^v)</td>
<td>1.00(^w)</td>
</tr>
<tr>
<td>3,4-Dimethoxycyclohexane(^f)</td>
<td>4.34(^x)</td>
<td>n</td>
</tr>
<tr>
<td>1-Methoxy-3-(n)-propoxypropane</td>
<td>4.48(^y)</td>
<td>o</td>
</tr>
<tr>
<td>1-(n)-Propoxy-2-methoxybutane</td>
<td>4.54(^z)</td>
<td>p</td>
</tr>
<tr>
<td>1,2-Di-(n)-propoxyethane</td>
<td>4.86(^{aq})</td>
<td>q</td>
</tr>
</tbody>
</table>

\(^a\) Elution time, minutes. Column: active coal, 4 m, 5 mm i.d., 23\(^\circ\), 28 ml Ar/min.
\(^b\) Elution time, minutes. Column: Porapak Q 100–120 mesh, 2.3 m, 2.2 mm i.d., 110\(^\circ\), 13 ml Ar/min.
\(^c\) Elution time, minutes. Column combination: P 4000 (15\% on Celite KOH treated, 60–100 mesh) 3 m, 2.2 mm i.d.; plus Uncon – 50 LB 550 X (20\% on Chromosorb P, 60–80 mesh), 7 m, 2.2 mm i.d.; 60\(^\circ\), 9 ml Ar/min.
\(^d\) Column: P 4000 (15\% on Celite, KOH treated, 60–100 mesh), 10 m, 2.2 mm i.d., 60\(^\circ\) for 16 min, temperature programmed 60\(^\circ\)–170\(^\circ\) (3\(^\circ\)/min), 10 ml Ar/min.
\(^e\) Column as d, operated isothermally at 170 \(^\circ\)C.
\(^f\) Peak broadened because the diastereomers are slightly resolved.
\(^g\) From the sodium alcoholate and methyl iodide.
\(^h\) From sodium \(n\)-propanolate and dimethyl sulfate.
\(^i\) From sodium \(n\)-propanolate and ethyl bromide.
\(^j\) From sodium methanolate and allyl bromide.
\(^k\) Obtained from propionaldehyde diethyl acetal through the action of NaHSO\(_4\), \(^1\(^i\).
\(^l\) From sodium \(n\)-butanolate and \(n\)-propyl bromide.
\(^m\) Deoxygenated \(n\)-propanol was \(\gamma\)-irradiated for 100 hours, then distilled off. The small liquid residue consisted mainly of hexanediol (3,4). This was methylated in the usual way via the sodium alcoholate and methyl iodide.
\(^n\) Propanediol (1,3) was reacted with two equivalents of sodium. One equivalent of propyl iodide was then added, and when this had reacted, one equivalent of methyl iodide.
\(^o\) Butene oxide (1,2) was hydrolyzed into the butanediol. The dried diol was reacted with two equivalents of sodium. One equivalent of propyl iodide was then added, followed by one equivalent of methyl iodide.
\(^p\) See Lichteneberger and Martin\(^10\).
Fig. 1. (The plateau-like aspect of the spectrum near 185 nm is probably due to lack of resolution; the spectrum of diethyl ether is known² to be structured in the region of the first maximum). In this wavelength region the extinction of the vapour, contained in a 1 cm suprasil QS cell, was measured. The evacuated cell was connected to a bulb with the ether kept at —57 °C and left to equilibrate. The pressure is then 3.8 Torr, and the ether concentration in the cell at 20 °C is 2.08 × 10⁻⁴ mol/l. At wavelengths above 193 nm the extinction coefficient of the liquid could be determined using a 0.01 cm layer realized by means of a 0.090 cm suprasil spacer in a 0.100 cm cell.

![Graph](image-url)

Fig. 1. The molar extinction coefficient of methyl n-propyl ether between 185 and 200 nm.

The photolyses were carried out at 185 nm as previously described¹⁻³ in a suprasil QS cell (Hellma, Müllheim) using a low pressure Hg arc (Graentzel, Karlsruhe). The 254 nm line of the arc was found to be photochemically inactive. The yield-dose dependence of all products was linear. Conversions did not exceed 0.1%. Photolysis times were up to 15 minutes. Dosimetry was performed with the ethanol actinometer⁹⁻¹¹ using an H₂ quantum yield of 0.4¹². Dose rates ranged from 0.48 to 0.66 × 10⁻⁴ quanta/min. Samples were prepared, deaerated and analyzed mainly as previously described¹⁻². All products except formaldehyde were analyzed by gas chromatography using liquid or vapour injection. All major products except three were calibrated by measuring the GC response of a known amount of pure authentic reference material. Methyl n-propenyl ether was calibrated using ethyl vinyl ether; 3,4-dimethoxyhexane and 2-methoxy-1-n-propoxybutane, using 1,3-dipropoxyethane.

The gaseous products hydrogen, methane, ethylene, and ethane were also analyzed by scrubbing the irradiated sample¹³. Formaldehyde was determined photometrically by means of the acetylacetone/ammonium acetate method¹⁴. Gas-chromatographical details and sources of the reference compounds are given in Table I. All GC peaks were assigned with the help of authentic reference material, and GC-MS combination analysis. Reference compounds were purified by fractionation or preparative gas-chromatography as required.

### Results and Discussion

Similar to other aliphatic ethers¹⁻³, methyl n-propyl ether absorbs strongly below 200 nm, as shown in Fig. 1. The 185 nm photolysis products of the deaerated liquid are listed in Table II with

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Quantum Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃OCH₂CHCH₃</td>
<td>0.015</td>
</tr>
<tr>
<td>CH₃</td>
<td></td>
</tr>
<tr>
<td>CH₂OCH₃H₄</td>
<td>0.002</td>
</tr>
<tr>
<td>C₂H₅OCH₂H₇</td>
<td>0.002</td>
</tr>
<tr>
<td>CH₂OCH₂CH₃</td>
<td>0.003</td>
</tr>
<tr>
<td>C₂H₅OC₃H₇</td>
<td>0.029</td>
</tr>
<tr>
<td>C₂H₅CHCH₃</td>
<td>0.046</td>
</tr>
<tr>
<td>C₂H₅CH₂OH</td>
<td>0.046</td>
</tr>
<tr>
<td>C₂H₅CHCH₂OCH₃</td>
<td>0.093</td>
</tr>
<tr>
<td>C₂H₅CH₂OCH₃</td>
<td>0.003</td>
</tr>
<tr>
<td>CH₂OCH₂H₇</td>
<td>0.077</td>
</tr>
<tr>
<td>C₂H₅CH₂OC₂H₅</td>
<td>0.014</td>
</tr>
<tr>
<td>C₂H₅OCH₂H₇</td>
<td>0.014</td>
</tr>
<tr>
<td>C₂H₅OC₂H₅</td>
<td>0.014</td>
</tr>
<tr>
<td>C₂H₅OC₂H₅</td>
<td>0.014</td>
</tr>
</tbody>
</table>

The photolysis products are listed in Table II with quantum yields.
their quantum yields giving an overall material balance of C\textsubscript{4.00}H\textsubscript{10.10}O\textsubscript{1.00}. The relative quantum yields of most products are considered accurate to within 10\%, errors arising in the product determination and calibration procedures. The major products methyl propenyl ether, 3,4-dimethoxyhexane and 1-n-propoxy-2-methoxybutane were measured with less certainty since sufficiently pure authentic reference material was not available for calibration. There is the possibility of a further error inherent in the actinometry; this might affect the absolute quantum yield values.

Cleavage of the excited (\( \lambda = 185 \text{ nm} \pm 154 \text{ kcal mol}^{-1} \)) ether molecule leads to radicals (reactions (1)-(5)) and molecular fragments (reactions (6)-(13)). Primary step quantum yields can be estimated (see below) from the product quantum yields so that a mechanism can be formulated (primary step quantum yields, in parentheses; 
\[ R = \text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_3, \text{CH}_3\text{OCH}_2\text{CH}_3, \text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3; \text{r, any radical).} \]

\[
\begin{align*}
(1) \text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_3 & \xrightarrow{h\nu} \text{CH}_3 + \cdot\text{OCH}_2\text{CH}_2\text{CH}_3 & (0.70) \\
(2) \xrightarrow{h\nu} & \text{CH}_3\text{O} + \cdot\text{CH}_2\text{CH}_2\text{CH}_3 & (0.14 \text{ to } 0.16) \\
(3) \xrightarrow{h\nu} & \text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_3 + \cdot\text{CH}_3 & (< 10^{-2}) \\
(4) \xrightarrow{h\nu} & \text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_3 + \cdot\text{CH}_3 & (< 10^{-2}) \\
(5) \xrightarrow{h\nu} & \text{H} + \text{R}^\cdot \\
(6) \xrightarrow{h\nu} & \text{H}_2 + \text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_3 & (~ 0.02) \\
(7) \xrightarrow{h\nu} & \text{H}_2 + \text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_3 - \text{CH}_3 & (< 10^{-2}) \\
(8) \xrightarrow{h\nu} & \text{CH}_4 + \text{OCHCH}_3\text{CH}_3 & (0.13) \\
(9) \xrightarrow{h\nu} & \text{CH}_4 + \text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_3 & (< 10^{-2}) \\
(10) \xrightarrow{h\nu} & \text{CH}_3\text{O} + \text{CH}_3\text{CH}_2\text{CH}_3 & (< 10^{-1}) \\
(11) \xrightarrow{h\nu} & \text{CH}_3\text{OH} + \text{CH}_2\text{CH} = \text{CHCH}_3 & (< 0.02) \\
(12) \xrightarrow{h\nu} & \text{CH}_3\text{OH} + \text{cyclo-C}_3\text{H}_6 & (< 10^{-3}) \\
(13) \xrightarrow{h\nu} & \text{CH}_3\text{OCH}_3 + \text{C}_2\text{H}_4 & (< 10^{-3}) \\
\end{align*}
\]

A striking fact is that only reactions (1, 2, 8) are of any material importance.

The following considerations lead to an estimate of the primary process quantum yields. The alkoxy radicals and the H atom, being strong H acceptors, undergo practically only\textsuperscript{17,1} abstraction reactions (14, 15, and 16). Radicals such as methoxymethyl and methoxethyl are weakly abstractive and mostly participate in radical termination reactions. Methyl and n-propyl are of an intermediate character.

\[
\begin{align*}
(14) \text{H}^\cdot + \text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_3 & \rightarrow \text{H}_2 + \text{R}^\cdot \\
(15) \text{CH}_3\text{O} + \text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_3 & \rightarrow \text{CH}_2\text{OH} + \text{R}^\cdot \\
(16) \text{CH}_3\text{CH}_2\text{CH}_2\text{O} + \text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_3 & \rightarrow \text{C}_3\text{H}_8\text{OH} + \text{R}^\cdot \\
(17) \text{CH}_3 + \text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_3 & \rightarrow \text{CH}_4 + \text{R}^\cdot \\
(18) \text{CH}_3\text{CH}_2\text{CH}_2\text{O} + \text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_3 & \rightarrow \text{C}_3\text{H}_8 + \text{R}^\cdot \\
(19) \text{r} + \text{r} & \rightarrow \text{products}
\end{align*}
\]
A consideration of the radicals present in the light of thermochemical and kinetic data\textsuperscript{1,2} indicates that with none of them can fragmentation\textsuperscript{3} compete against the above reactions. Many of the products found are formed from radical combination. Since all the major and most of the minor products have been measured, limits can be placed on the primary quantum yields with considerable confidence. Thus, propionaldehyde could arise only in reaction (8) so that $\Phi$ (propionaldehyde) = $\Phi$ (8). Similar considerations apply to reactions (9) to (13). The sum of reactions (5), (6), and (7) cannot exceed 0.02 because $\Phi$ is strongly abstractive and therefore is not removed in recombination reactions. Moreover, $\Phi$ (7) = $\Phi$ (allyl methyl ether). The contributions of (5) and (6) cannot be separated, for the complementary product to H\textsubscript{2} in (6), methyl propenyl ether, is formed also through disproportionation reactions of the radicals CH\textsubscript{3}OCH\textsubscript{2}CH\textsubscript{2} and CH\textsubscript{3}OCH\textsubscript{2}CH\textsubscript{2}. $\Phi$ (1) must equal $\Phi$ (propionaldehyde) - $\Phi$ (methanol) - $\Phi$ (11) - $\Phi$ (12). Estimates for the latter two have already been discussed.

No such straightforward arguments can be applied to reactions (4) and (5) but the very low yield of dimethyl and ethyl methyl ethers would seem to indicate that the quantum yields for the formation of the corresponding radicals are no larger than about 10\textsuperscript{-4}.

It is apparent that as in the cases of the previously studied ethers\textsuperscript{1,2}, the cleavage of the C–O bond is by far the most important process. The Me–O bond is about five times more likely to break (reaction (1)) than the Pr–O bond (reaction (2)). The aldehyde-forming molecular elimination reactions (8) and (10) show this tendency in favour of Me–O cleavage to an even more extreme degree ($\Phi$ (8)/$\Phi$ (10) > 13). C–C bond cleavage is minimal, as also is $\Phi$ atom and H\textsubscript{2} molecule loss. It is remarkable that the sum of primary process quantum yields closely approaches unity. This would seem to preclude the occurrence of cage back reactions and may indicate that in the 185 nm photolysis of saturated ethers only a minor part of the molecular product owes its existence to cage disproportionation reactions even in such cases where the sum of primary process quantum yields is considerably less than unity (diethyl\textsuperscript{1} and tert-butyl methyl ethers\textsuperscript{5}).

Except for (12), the types of primary processes resemble those found previously\textsuperscript{1,2}, as expected. Process (12) yields methanol and cyclo-propane. The formation of the latter suggests that the oxygen of the excited ether molecule is able to abstract the $\gamma$-hydrogen. Similar reactions have been studied previously\textsuperscript{20} in the photolysis of n-butyl ethyl and methyl n-pentyl ethers where small amounts of cyclo-butane and methyl-cyclo-butane were found.

Reaction (11) is rather ineffective as shown by the low quantum yield of propene. Most of the propene is probably due to disproportionation reactions of the n-propyl radicals. In any case, $\Phi$ (propene) (0.02) represents the upper limit of $\Phi$ (11).

We would like to thank Dr. G. Schomburg for his cooperation in the gas-chromatographic analysis which was carried out by Ms. E. Bastian.

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