Short Communication

Photolysis at 185 nm of liquid oxepane*

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There is evidence that the mechanism of the UV photolysis of cyclic ethers depends on ring size. On excitation in the first absorption band (below 200 nm), cyclic ethers of small ring size usually undergo extensive fragmentation even in the condensed state [1 - 6]. Ethylene is formed in a relatively high yield from oxetane [1] and 1,4-dioxane [3, 4], and cyclo-propanes are formed from tetrahydrofurans [2]. However, this is not the case for tetrahydropyran [7] where hydrocarbon formation is negligible; the main products are pent-4-en-1-ol and valeraldehyde which are isomeric with the starting material. There is an analogy here with the behaviour of open-chain ethers, *e.g.* diethyl ether [8] where cleavage of the C—O bond leads to the formation of ethanol and ethylene on the one hand and acetaldehyde and ethane on the other. In order to substantiate further our impression that the photolysis mechanism of oxacyclanes of larger ring size generally resembles that of tetrahydropyran and unbranched open-chain ethers, we studied the photolysis of oxepane.

Oxepane (Aldrich) was fractionated to a purity of better than 99.8%, as determined by gas chromatography. Deaerated samples were irradiated at 15 °C with a low pressure mercury lamp (only the 185 nm line is photoactive, see Fig. 1) and analysed using gas chromatography and gas chromatography-mass spectrometry. The experimental conditions were very similar to those previously employed [7], with conversions kept to below 0.1%. The quantum yields of the identified products are given in Table 1. The unidentified products observed in the gas chromatogram amount to less than 5% of the oxepane destroyed. Oxacycloheptenes could have been formed with small quantum yields (see later), but their gas chromatographic peaks would be overlain by that of the starting material.

The results summarized in Table 1 indicate that the main features of the photolysis mechanism must be those shown in Scheme 1. The main products, hex-5-en-1-ol (VI) and hexanal (V), might be formed directly in true molecular processes (reactions (1) and (3)) and/or by an intramolecular

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*Part XI of the series Strahlenchemie von Ethern; for Part X see ref. 3.
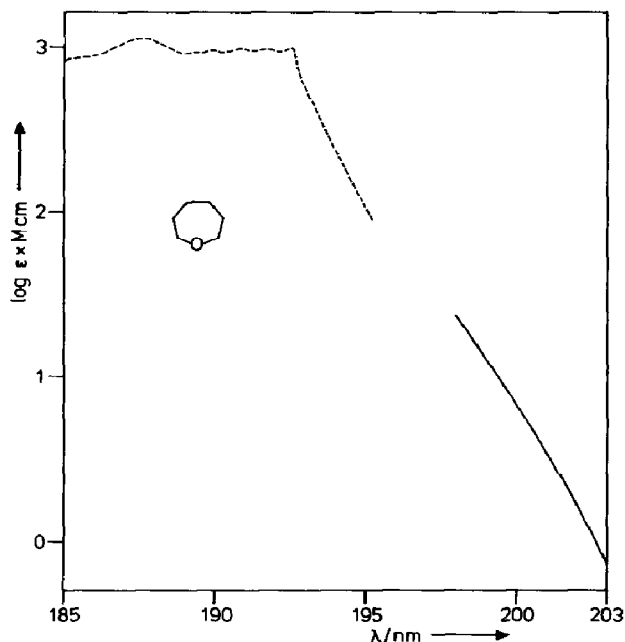
Fig. 1. The molar extinction coefficient of oxepane between 185 and 203 nm: ———, liquid; - - -, vapour.

disproportionation of an intermediate biradical (reaction (2) followed by reactions (4) and (5)). Indeed the most important, but in the present system unobservable, process might be ring closure of the biradical to the starting material (reaction (−2)). Evidence for such a ring closure exists in the cis- and trans-2,5-dimethyltetrahydrofuran system where a photoisomerization with high quantum yields has been observed [2]. In the present system the formation of the product 3'-hydroxypropylcyclopropane (VII) is considered to be further evidence for the intermediacy of the biradical. Although both primary alkyl and oxyl radicals readily abstract secondary hydrogen atoms, at room temperature oxyl radicals react several orders of magnitude faster than primary alkyl radicals (cf. methyl and methoxyl radicals) [9, 10]. An intramolecular hydrogen abstraction reaction by the oxyl end of the bi-radical (reaction (6)) can result in a new biradical which ring closes to the cyclopropane derivative (reaction (7)). Similar ring closures of biradicals occur, following the Norrish type II reaction of ketones [11]. Although reaction (6) is at a disadvantage energetically compared with reactions (4) and (5), this could be largely compensated for by its ability to proceed through a six-membered transition state. In any case, all three processes must be very fast because none of $\phi(V)$, $\phi(VI)$ and $\phi(VII)$ are significantly diminished in samples saturated with oxygen ($[O_2] \approx 10^{-2}$ M) or ethylene ($[C_2H_4] \approx 10^{-1}$ M) at atmospheric pressure. In contrast, the products which are formed from monoradicals are quenched strongly by oxygen and partially by ethylene. Among the products detected in the presence of ethylene are α-, β- and

TABLE 1

Quantum yields of primary products identified in the 185 nm
photolysis of deaerated liquid oxepane

Number	Product	ϕ
I	Hydrogen	0.05
II	Methane	$<10^{-4}$
III	Ethylene	0.003
IV	Propene + propane	0.001
V	Hexanal	0.09
VI	Hex-5-en-1-ol	0.20
VII	3-Hydroxypropylcyclopropane[a,b]	0.015
VIII	n-Hexanol	0.015
IX	α,α'-Dehydrodimers[a]	0.018
X	Other dehydrodimers[a]	0.006
XI	2(6'-Hydroxyhexyl)-oxepane[a,c]	0.04
XII	1,12-Dodecanediol	$<10^{-3}$

[a]Structure assigned on the basis of the mass spectral and gas chromatographic properties.
[b]The mass spectral and gas chromatographic properties of product VII are those of a C_6 alcohol with a molecular weight of 100. It is neither of the straight-chain hexen-1-ols. Although the mass spectrum is very similar to that of 5-hexen-1-ol, its gas chromatography is different. Main m/e values (%): 67 (100), 54 (90), 41 (65), 42 (64), 31 (50), 57 (38), 39 (35), 55 (30), 27 (23), 29 (21), 82 (20).
[c]Product XI (non-derivatized, base peak m/e 99) yields a trimethylsilyl derivative whose mass spectrum is indicative of 2-(6'-trimethylsilyloxyhexyl)-oxepane (base peak m/e 99; parent peak m/e 272, 2%).
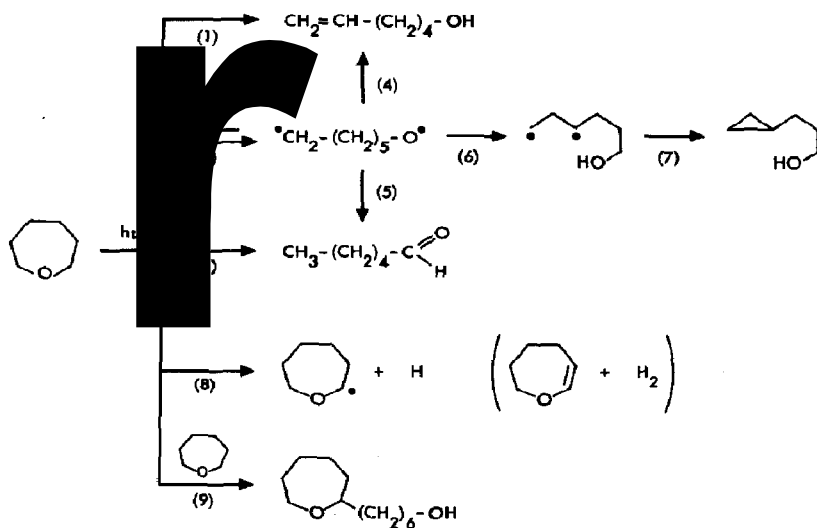
Scheme 1. The proposed photolysis mechanism.

γ-ethyloxepane, the α-substituted product being formed preferentially. Some hydrogen is found and, as with other ethers, its source could be either a homolytic cleavage of the α hydrogen or the elimination of molecular hydrogen (reaction (8)) or both.

At first glance, products VIII and XI seem to indicate an involvement of $\cdot CH_2$—$(CH_2)_5OH$ radicals. In liquid ether systems alkyl radicals are known to undergo combination reactions as well as hydrogen abstraction reactions. We recall that alkyl radicals are formed in the photolysis of open-chain ethers such as diethyl ether [8] and methyl propyl ether [12]. It has been established that these radicals react to a large extent by recombination, partly leading to hydrocarbons such as ethane ($\phi = 0.08$ [12]) and n-butane ($\phi = 0.07$ [8], $\phi = 0.03$ [12]). This suggests that ω-hydroxyalkyl radicals should be sufficiently unreactive with respect to hydrogen abstraction to be able to undergo diol formation with or without prior rearrangement [13, 14]. The absence of detectable amounts of 1,12-dodecanediol (XII) (or branched dodecanediols) and the further fact that ϕ(XI) and ϕ(VIII) are not measurably reduced by oxygen and ethylene indicate that the free $\cdot CH_2$-$(-CH_2)_5OH$ radical must be excluded. This leaves for examination the supposition that a caged radical pair, formed through hydrogen abstraction by the biradical from the substrate, accounts for VIII and XI. It is difficult to see how the cage could be so impermeable that escape of the participating monoradicals is entirely prevented. The same applies *a fortiori* to the tetrahydropyran system [7] where the ratio of the product homologous to XI to the corresponding diol is larger than 200. For systems of comparable viscosity of the solvents (among them cyclohexane) and comparable size of the molecules from which the radical pair is generated, cage effects of between 0.2 and 0.6 have been quoted [15]. At 20 °C the viscosities of tetrahydropyran and cyclohexane are 0.88 and 0.98 cP respectively [16]. A cage effect of roughly 0.5 in the tetrahydropyran system is therefore expected. This is far from the case which would require a cage effect of almost unity. Therefore a radical combination reaction as the source of XI is ruled out and we postulate the photodimerization reaction (9) as the most likely mechanism. It could be suggested that n-hexanol (VIII) is formed through "disproportionation" occurring in the excited state (Scheme 2) despite the fact that no oxacycloheptenes were detected (see earlier). It should be noted that, in the photolysis of tetrahydrofuran [2] and in the photolysis of tetrahydropyran [7], n-butanol and n-pentanol respectively have been found.
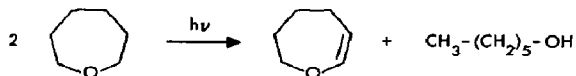
Scheme 2. "Disproportionation" of oxepane.

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