

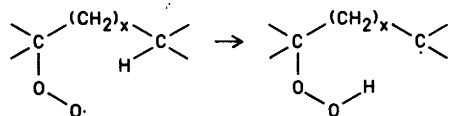
Autoxidation of Allyl Ether Compounds. Part II. Reactivity of Alkyl Allyl Ethers

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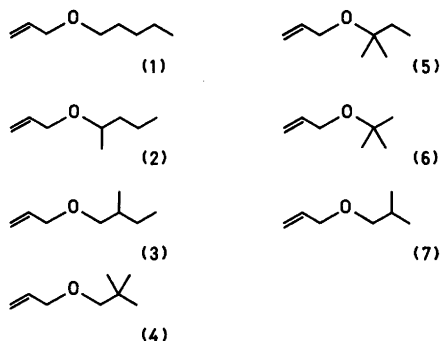
The effect of the structure of alkyl allyl ethers on their autoxidation behaviour was investigated by measuring oxygen consumption rates in cobalt catalyzed liquid phase oxidations at 30 °C. The oxidation rates were found to vary considerably depending on the structure of the alkyl group. The rate determining step is intramolecular. The structural effects on the oxidation rates were interpreted as differences in the isomerization rates of peroxy radicals *via* intramolecular hydrogen transfers. The ease of the hydrogen abstractions were found to decrease in the order of $\beta > \gamma > \alpha$ depending on the position of the hydrogen in the alkyl group relative to the ethereal oxygen. The contribution of a hydrogen to the autoxidation rate was also found to depend on the nature of the broken C-H bond, decreasing in the order of *tert* > *sec* > *prim*.

Autoxidations of hydrocarbons have been described exclusively in the literature.¹ One of the essential mechanisms in the chain branching process of oxidations is the isomerization of alkylperoxy radicals *via* intramolecular hydrogen transfer² (Scheme 1). These intramolecular hydrogen abstractions have been reported to be especially favoured when the reactive hydrogen is attached to the carbon atom α , β or γ to the peroxy radical leading to 5-, 6- or 7-membered rings in the transition state.³ Fish⁴ has calculated theoretical rate constants for the gas phase reaction in Scheme 1 and found the process most



Scheme 1.

rapid when the abstracted hydrogen is located on the β -carbon to the peroxy radical. α - and γ -carbons were clearly in more unfavourable positions and the hydrogen at the δ -carbons were the least reactive. Generally the ease of the hydrogen abstraction was found to depend on the nature of the C-H bond broken, the reactivity decreasing in the order of *tert* > *sec* > *prim*. Not only in gas phase oxidations when the low concentrations favour intramolecular reactions have these cyclic isomerizations of peroxy radicals been observed, but also in the liquid phase autoxidations of hydrocarbons.⁵ In Rust's, study⁵ oxidations were investigated by analyzing the reaction products. The intramolecular peroxy radical attack was found highly efficient at the β -position and somewhat less so at the γ -carbon. α - and δ -positions were quite unreactive. In the present study structural effects of alkyl allyl ethers on their autoxidation behaviour were investigated by measuring rates of oxygen uptakes in cobalt catalyzed liquid phase oxidations at ambient temperature.



Scheme 2.

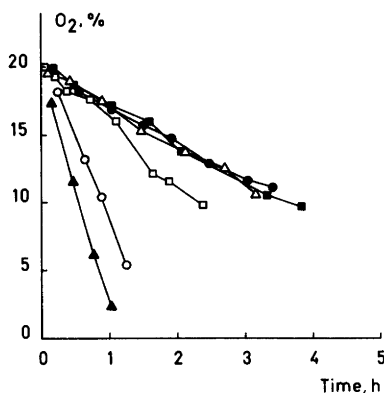


Fig. 1. Autoxidations of alkyl allyl ethers at 30 °C. Compounds: ● (1), □ (2), △ (3), ▲ (4), ○ (5), ■ (6), ■ (7).

RESULTS AND DISCUSSION

The autoxidation rates of alkyl allyl ethers (1–7, Scheme 2) varied significantly depending on the structure of the alkyl group (Fig. 1).

The most common mechanism in the propagation of autoxidations involves the rapid reaction between oxygen and a free radical, followed by the slower inter- or intramolecular process leading to the regeneration of a radical via the abstraction of a hydrogen atom by a peroxy radical.⁶ The distinct difference observed in the oxidation rates of the same functional groups containing isomeric *t*-amyl and neopentyl ethers (compounds 5 and 4, Fig. 2) reveals that the autoxidations studied are controlled by an intramolecular mechanism. The result can be ex-

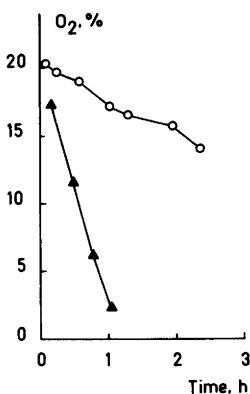
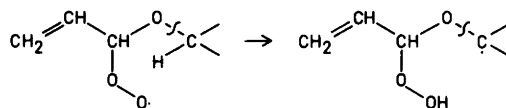


Fig. 2. Autoxidation of *t*-amyl (5) (▲) and neopentyl (4) (○) allyl ether at 30 °C.



Scheme 3.

plained by suggesting the intramolecular isomerization of peroxy radicals (Scheme 3) as the rate determining step in the autoxidations. The rates of these hydrogen transfer processes in the oxidation of hydrocarbons are generally known to depend both on the nature of the C–H bond to be cleaved and the position of this carbon atom relative to the peroxy radical.⁴ The quantitative effects of these variables on the autoxidation rates of alkyl allyl ethers were found difficult to determine by experimental methods, because the variables cannot be varied independently from each other: changing the number of hydrogens on any of the carbons in the alkyl group of an ether by alkyl substitution also changes the number of hydrogens on other positions in the molecule.

The oxidation results were interpreted by defining the measured rate of oxygen absorption of a compound (r) as a linear combination of terms $k_{j,l} \cdot n_{j,l}$, where $n_{j,l}$ is the number of the equivalent hydrogens and $k_{j,l}$ describes the reactivity of these hydrogens [eqn. (1)].

$$r = \sum_j \sum_l k_{j,l} \cdot n_{j,l} \quad (1)$$

The index j denotes the nature of the hydrogen and l the position of the carbon atom bearing this hydrogen as presented in Table 1. Only the α -, β - and γ -carbons were taken into account. The absolute values of the slopes of the lines fitted by the method of least sum of squares to the data presented in Figs. 1 and 2 were taken as the

Table 1. Constants $k_{j,l}$ for the hydrogen transferred.

Nature of C–H bond broken	Position of the carbon atom to the etheral oxygen		
	α	β	γ
Primary	$k_{1,1}$	$k_{1,2}$	$k_{1,3}$
Secondary	$k_{2,1}$	$k_{2,2}$	$k_{2,3}$
Tertiary	$k_{3,1}$	$k_{3,2}$	$k_{3,3}$

Table 2. Oxidation rates of alkyl allyl ethers.

Compound	Absolute value of the slope of the oxidation curve
1	2.54
2	4.55
3	2.95
4	2.56
5	16.1
6	12.9
7	2.75

oxidation rates of the ethers. Only the straight parts of these relative oxygen concentration *versus* time correlations were treated by leaving out the observations <0.2 h. Solving the linear set of eqns. (2)–(8) obtained by writing eqn. (1) for all of the seven ethers (compounds 1–7) studied gave values for $k_{j,l}$ as presented in Table 3.

$$2k_{2,1} + 2k_{2,2} + 2k_{2,3} = 2.54 \quad (2)$$

$$k_{3,1} + 3k_{1,2} + 2k_{2,2} + 2k_{2,3} = 4.55 \quad (3)$$

$$2k_{2,1} + k_{3,2} + 3k_{1,3} + 2k_{2,3} = 2.95 \quad (4)$$

$$2k_{2,1} + 9k_{1,3} = 2.56 \quad (5)$$

$$6k_{1,2} + 2k_{2,2} + 3k_{1,3} = 16.1 \quad (6)$$

$$9k_{1,2} = 12.9 \quad (7)$$

$$2k_{2,1} + k_{3,2} + 6k_{1,3} = 2.75 \quad (8)$$

The constants $k_{j,l}$ cannot be regarded as reaction rate constants for the intramolecular hydrogen transfers but they describe the relative importance of hydrogens of different nature and

Table 3. Values of $k_{j,b}$ the solution of the set of equations.

Nature of C–H bond broken	Position of the carbon atom to the ethereal oxygen		
	α	β	γ
Primary	—	1.43	0.858
Secondary	–2.58	2.46	1.39
Tertiary	–7.45	2.76	—

spatial location in the autoxidation mechanism of alkyl allyl ethers. The contribution of the hydrogens on different carbons with respect to the ethereal oxygen in the allyl group to the rate of oxygen uptake of an alkyl allyl ether can be seen to decrease in the order of $\beta > \gamma > \alpha$. The result means that the most favourable transition state in the rate-determining step of the autoxidations of alkyl allyl ethers involves rather a 7- than a 6-membered ring, as has been reported to be the case in oxidations of hydrocarbons according to theoretical calculations.⁴ At β - and γ -positions the relative significance of the hydrogens of different nature is increased from primary to tertiary. Only one compound having a tertiary α -hydrogen was included in the alkyl allyl ethers studied, which means that the information available might not be sufficient for the interpretation of the different result obtained for the α -hydrogens.

EXPERIMENTAL

Methods. The identification and analysis of the alkyl allyl ethers and the oxidation experiments by using air as oxidant were carried out as described in the preceding paper.⁷ Cobalt naphthenate (8 w% Co in mineral spirits, Servo bv-delden Netherlands) was used as a catalyst, corresponding to the cobalt concentration of 0.0323 mol % by moles of alkyl allyl ether. Monitoring the progress of the oxidations was done by gas chromatography as explained in Part I. The area percentage of the oxygen-argon peak from the total area of oxygen, argon and nitrogen peaks was used as a measure for the relative oxygen concentration.

Preparation of allyl ethers. Alcohol (1 mol) was dissolved in tetrahydrofuran (300 ml) and 50 % NaH-dispersion in oil (57.6 g, 1.2 mol) was added carefully to the mixture. When the evolution of hydrogen was ended, allyl bromide (95 ml, 1.1 mol) was introduced during 20 min to the stirred refluxing mixture. After additional stirring for 10 min the reaction mixture was filtered and the product purified by repeated distillations through a 30 cm Vigreux column.

1-(2-Propenyloxy)-pentane (1). B.p. 143.0–143.5 °C/99.6 kPa, n_D^{30} 1.408. ¹³C NMR: 135.5 (d), 116.2 (t), 71.9 (t), 70.6 (t), 29.9 (t), 28.7 (t), 22.9 (t), 14.2 (q).

1-Methyl-1-(2-propenyloxy)-butane (2). B.p. 131.2–131.5 °C/101.4 kPa, n_D^{30} 1.405. ¹³C NMR: δ 136.0 (d), 115.9 (t), 74.8 (d), 69.5 (t), 39.3 (t), 19.8 (q), 19.0 (t), 14.3 (q).

2-Methyl-1-(2-propenyloxy)-butane (3). B.p. 134.3–134.4 °C/102.2 kPa, n^{30} 1.4065. ^{13}C NMR: δ 135.5 (d), 116.1 (t), 75.7 (t), 72.1 (t), 35.3 (d), 26.5 (t), 16.7 (q), 11.4 (q).

2,2-Dimethyl-1-(2-propenyloxy)-propane (4). B.p. 116.2 °C/98.8 kPa, n^{30} 1.3974. ^{13}C NMR: δ 135.5 (d), 115.8 (t), 80.9 (t), 72.3 (t), 32.2 (d), 26.9 (q).

1,1-Dimethyl-1-(2-propenyloxy)-propane (5). B.p. 128.0–128.2 °C/102.6 kPa, n^{30} 1.4080. ^{13}C NMR: δ 136.6 (d), 114.8 (t), 74.8 (s), 62.6 (t), 33.1 (t), 25.2 (q), 8.2 (q).

1,1-Dimethyl-1-(2-propenyloxy)-ethane (6). B.p. 100.9–101.0 °C/101.7 kPa, n^{30} 1.3963. ^{13}C NMR δ 136.7 (d), 115.0 (t), 72.9 (s), 63.1 (t), 27.7 (q).

2-Methyl-1-(2-propenyloxy)-propane (7). B.p. 106.0–106.5 °C/102.9 kPa, n^{30} 1.3957. ^{13}C NMR: δ 135.5 (d), 116.1 (t), 77.4 (t), 72.1 (t), 28.8 (d), 19.6 (q).

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