Autoxidation of Allyl Ether Compounds. Part 1. Reactivity of Allyl Ether Alcohols.

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Cobalt catalyzed liquid phase autoxidations of some primary and secondary allyl ether alcohols were studied at 30 and 40 °C. An optimum concentration for the catalyst was found, above which cobalt behaved like an inhibitor. Autoxidations of secondary allyl ether alcohols started immediately after adding the catalyst but the reactions of the allyl ethers of primary diols were preceded by induction periods. Induction periods depended on the carbon chain length of the diol and were not observed after methylating the hydroxyl group of the allyl ether alcohol. The phenomena are explained as resulting from inter- and intramolecular hydrogen bonding, which controls the autoxidation by decreasing the electron density on the etheral oxygen.

In spite of the numerous papers describing the air-drying resins prepared by using allyl ether compounds as an autoxidisable monomer,[1–4] only a few papers dealing with the correlation of structural properties to the autoxidation behaviour of allyl ether compounds have been published. Mleziva et al.[5] have studied glycerol allyl ether esters as additives for noninhibited polyester laquers. Salistyi et al.[6] have reported the oxidation of oligomeric allyl ethers being affected by the weight and mol fraction of unsaturation in the compound. Valentine et al.[7] found the relative autoxidation rate of a polyfunctional allyl ester slower than that of an allyl ether compound of the same functionality. The oxidation rates of polyfunctional allyl ethers of some polyols and their esters have been measured in cyclohexane in the presence of azobisisobutyronitrile.[8] No structural effects, however, on the mechanism or the oxidation rate of these compounds were found. Sharp and Patrick[9] investigated the formation of hydroperoxides of butyl and 2-ethylhexyl allyl ethers. Unfortunately the rates of the oxidations were not reported. Mlerziva et al.[10] measured autoxidation rates for a number of allyl ethers. The studies were accomplished by monitoring the decrease of the gas pressure in the reaction vessel during oxidation. The allyl ethers of glycerol and butanol were the most reactive compounds, while the oxygen uptake of allyl butyrate was found almost negligible. Generally, the lower the electron density on the α-position in the allyl ether group, the higher was the autoxidation rate of the compound.

In the present study some structural effects of diols on the autoxidation behaviour of their monoallyl ethers have been investigated. The oxidation rates were determined at a constant pressure by monitoring the decrease of the relative oxygen concentration in the reaction vessel by gas chromatography. As compared to volumetric or gravimetric methods, the possible errors because of the formation of volatile reaction products could thus be avoided.

RESULTS AND DISCUSSION

In the autoxidation of hydrocarbons[11–13] and polyoxyalkylenediols[14] the cobalt compounds used as catalysts have also been found to act as inhibitors when present in higher concentrations. A similar phenomenon was also observed in the oxidation of monoallyl ether of ethylene glycol (1) in the presence of cobalt naphtenate (Fig. 1). The cobalt concentration of 0.0323 mol%, a little

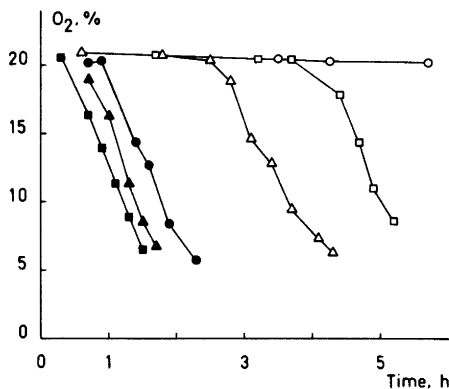*Fig. 1.* Effect of catalyst concentration on the autoxidation of 2-(2-propenyloxy)-ethanol (*1*) at 40 °C. Cobalt concentration (mol %, by mol of allyl ether): ▲ 0.00645, ■ 0.0161, ● 0.0323, △ 0.0806, □ 0.161, ○ 0.323.
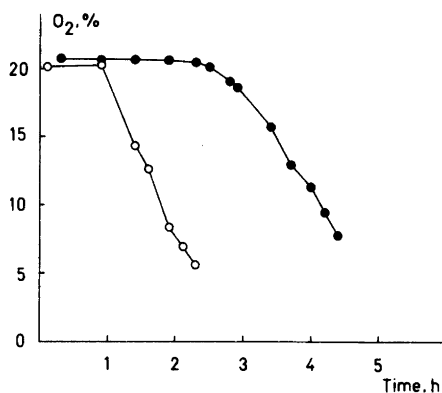

Fig. 3. Effect of temperature on the autoxidation of 2-(2-propenyloxy)-ethanol (*1*). Cobalt concentration 0.0323 mol % by mol of allyl ether. ○ (40 °C), ● (30 °C).

more than the optimum, was used in further studies for reproducibility reasons.

The autoxidation of primary allyl ether alcohols [Compounds (*1*)–(*5*), Figs. 2 and 5] was preceded by induction periods ranging from a few hours to tens of hours. An increase in the temperature shortened the induction period but essentially did not affect the measured rate of the oxygen uptake (Fig. 3). The secondary allyl ether alcohols behaved quite differently. The oxidation of the compounds (*6*) and (*7*) started immediately after adding the catalyst. Allyl lactate (*8*), also a
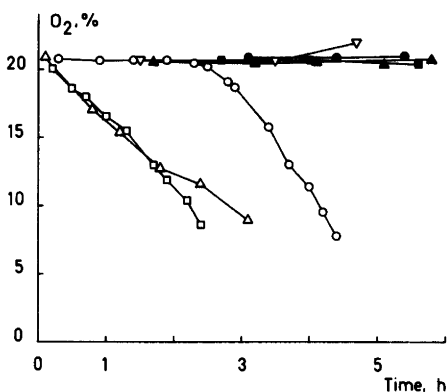

Fig. 2. Autoxidations of primary and secondary allyl ether alcohols at 30 °C. Co-concentration 0.0323 mol % by mol of allyl ether. Compounds: ○ (1), ● (2), ■ (3), ▲ (5), □ (6), △ (7), ▽ (8).

secondary alcohol with allylic unsaturation, was an exception, however.

In the general mechanism of autoxidation (Scheme 1) the initiation and the formation of hydroperoxides are the rate determining steps.[15] In the case of allyl ethers, formation of the radical R· *via* scission of the C–H bond at the allylic methylene group is particularly favoured by the resonance stabilization due to the double bond and also to the unshared electron pair of the etheral oxygen[16] leading to a very low bond energy.

$$R-H \longrightarrow R· + H·$$
$$R· + O_2 \longrightarrow ROO·$$
$$ROO· + R-H \longrightarrow ROOH + R·$$
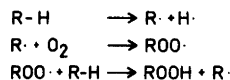
In case of allyl lactate (*8*), the inhibition of the autoxidation can be explained as the result of a decrease in the electron density on the ethereal oxygen due to the resonance of the electron pair with the adjacent carbonyl, leading to the lowered stability of the allylic radical.

The inhibiting effect of alcohols or the retardation of the autoxidation of hydroxyl group containing compounds have been explained by the effect of alcohols upon the efficiency of metal salt catalysts[17] or, as suggested in more recent papers, because of the deactivation of peroxy radicals *via* hydrogen bonding.[18,19]

From the studies concerning the intramolecular hydrogen bonding in the monomethyl ethers of ethane, propane and butane diols,[20] it

can be concluded that also the monoallyl ethers of these diols can exist in the cyclic conformations (Scheme 2).
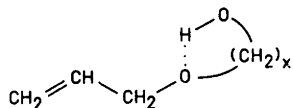
Hexamethylene glycol has no intramolecular H-bond,[21] which can be interpreted to mean that also the monoallyl ether of this diol can be only intermolecularly hydrogen bonded. The strength of the intramolecular H-bond in the methyl ether of a diol increases strongly in going from 2-methoxyethanol to 4-methoxybutanol.[20] On the other hand, the compound with the strongest hydrogen bond has the lowest equilibrium constant for the equilibrium between nonbonded and bonded conformations. The strengths of the intramolecular bonds in the methyl ethers of ethane and propane diols are essentially weaker than external hydrogen bonds, being only 22 % and 63 %, respectively, from the strength measured for the intermolecular bond between butanol and dibutyl ether.[20]

The slow initiation in the oxidation of primary allyl ether alcohols ($1-5$) can be accounted for by hydrogen bonding in these compounds. When the existence of hydrogen bonds was made impossible by methylating the hydroxyl groups, the induction periods were not observed and the autoxidation rates were controlled merely by the polarity of the compound: the more polar the
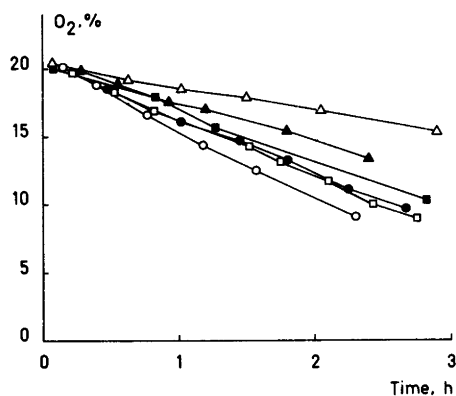

Fig. 4. Autoxidations of methylated allyl ether alcohols at 30 °C. Co-concentration 0.0323 mol % by mol of allyl ether. Compounds: ▲ (*9*), ■ (*10*), □ (*11*), △ (*12*), ● (*13*), ○ (*14*).
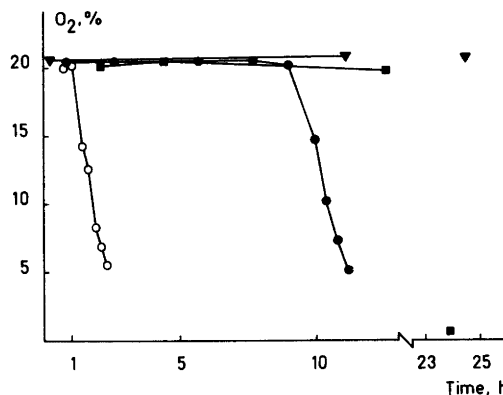
Fig. 5. Effect of the carbon chain length on the autoxidation of its monoallyl ether at 40 °C. Co-concentration 0.0323 mol % by mol of allyl ether. Compounds: ○ (*1*), ● (*2*), ■ (*3*), ▼ (*4*).

ether the faster was the rate of oxidation (Fig. 4), possibly due to the better solubility of oxygen into the liquid phase. The weaker hydrogen bond in the case of secondary hydroxyl groups in compounds *6* and *7* causes less disturbance in the mechanism of the autoxidation and the induction periods are thus not observed (Fig. 2). The effect of the hydrogen bonding on the autoxidation *via* deactivating the catalyst or by the solvation of the peroxy radicals cannot be considered a very likely mechanism in the oxidations studied. The catalyst concentration used and also the concentration of the possible peroxy radicals during the induction periods, before any oxygen consumption could be observed, were on such a low level that a sufficient number of hydroxyl groups capable of participating in the inhibiting process can be regarded to be available similarly in all of the cases of the primary allyl ether alcohols. Still, the autoxidation behaviour of these compounds varied quite considerably depending on their carbon chain length (Fig. 5). The inhibition arising from hydrogen bonding can be explained better by the interaction between the hydroxyl groups and the ethereal oxygen in the primary allyl ether alcohols, which leads to the decrease in the electron density of the oxygen, deactivating the ether towards the initiation reaction. In ethane- and propanediol allyl ethers part of the molecules are in the cyclic conformations that contain a weaker hydrogen bond than is the case with the rest of the molecules being externally hydrogen bonded. The weakly bonded molecules

are more reactive towards initiation and thus shorter induction periods are observed in the oxidation of these ethers. The intra- and inter-molecular bonds in butanediol monoallyl ether and the intermolecular bonds in hexamethylene-diol monoallyl ether are considerably stronger leading to a lower electron density on the ethereal oxygen in these compounds and thus also to longer induction periods than in the former cases.
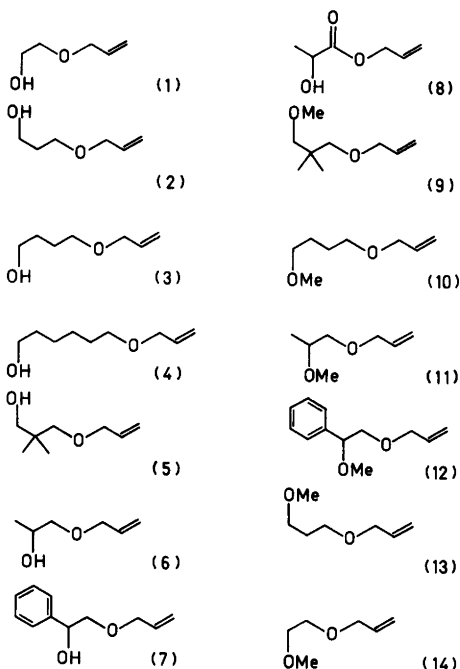
EXPERIMENTAL

Purities of the allyl ethers were checked by a Hewlett-Packard 5710A GC using both Apiezon L and Carbowax 20M (10 % on Chromosorb W/AW−DMCS, 80−100 mesh, 0.3×210 cm) columns. Structures were verified by a Jeol FX60 Fourier transform spectrometer using CDCl$_3$ as solvent. Spectra are presented in decoupled form with off-resonance results in parentheses. Refractive indices were determined on an Abbe re-fractometer (Bellingham & Stanley Ltd) Cobalt naphthenate (8 w % Co in mineral spirits), Servo bv-delden, The Netherlands, was used as a catalyst.

Autoxidations were carried out in a 155 ml glass hypovial with a magnetic stirrer, using air as oxidant. The compound under study (40 mmol)

and the Co-catalyst were sealed in the vial and immersed in a thermostated water bath. The pressure in the vial was kept constant during the experiments by replacing the oxygen consumed in the oxidation by helium. Helium was led into the reaction vessel through a thin syringe needle corresponding to the pressure of 11 cm height of dibutyl phthalate.

Monitoring the progress of the autoxidations was done by analysing samples of 0.2 ml taken from gas phases of reaction mixtures by Varian Aerograph Series 1800 GC. A 0.3×400 cm stainless steel column packed with 5A molecular sieves (45/60 mesh, Ohio Valley Specialty Chem-ical Inc., Ohio, U.S.A.) was used to separate nitrogen and oxygen at 100 °C. Helium was used as carrier gas (40 ml/min), detection by TC-detector. Argon eluted at the same retention time with oxygen. The area percentage of the oxygen-argon peak as calculated from the total area of the peaks was used as a measure for the relative oxygen concentration. Integration of the peaks was performed by a Hewlett-Packard 3352 Data System.

2-(2-Propenyloxy)-ethanol (1) was prepared from allyl alcohol and ethylene oxide.[22] Purifica-tion by repeated distillation yielded the product: b.p. 160.5 °C/101.7 kPa, n^{30} 1.4316. ^{13}C NMR: δ 135.0 (d), 117.0 (t), 72.2 (t), 71.7 (t), 61.4 (t).

3-(2-Propenyloxy)-1-propanol (2). 1,3-Pro-panediol (228 g, 3 mol) and KOH (168 g, 3 mol) were dissolved in THF (150 ml). Allyl bromide (260 ml, 3 mol) was added slowly to the refluxing mixture. Refluxing was continued 30 min after the reaction ceased. After filtering and evapora-tion of THF a crude product consisting of unreacted diol and its allyl ethers was obtained. The reaction product was mixed with water (450 ml) and diallyl ether was distilled off as an azeotrope. Monoallyl ether was extracted from the remaining mixture with ether and purified by distillation under reduced pressure. B.p. 106.3−106.9 °C/6.27 kPa, n^{30} 1.4354. ^{13}C NMR: δ 134.9 (d), 116.7 (t), 71.9 (t), 67.9 (t), 59.8 (t), 32.6 (t).

4-(2-Propenyloxy)-1-butanol (3). Synthesis and purification was analogous to (2). B.p. 120.5−121.0 °C/5.20 kPa, n^{30} 1.4399. ^{13}C NMR: δ 134.7 (d), 117.0 (t), 71.8 (t), 70.2 (t), 62.3 (t), 29.9 (t), 26.5 (t).

6-(2-Propenyloxy)-1-hexanol (4). The synthesis was analogous to (2). The purification was done as described for (5). B.p. 130.8 °C/2.20 kPa, n^{30} 1.4453. ^{13}C NMR: δ 135.0 (d), 116.4 (t), 71.6 (t), 70.3 (t) 61.9 (t), 32.6 (t), 29.7 (t), 26.1 (t), 25.8 (t).

2,2-Dimethyl-3-(-propenyloxy)-1-propanol (5). Neopentyl glycol (104 g, 1 mol) was dissolved in

THF (500 ml). 50 % NaH-dispersion in oil (40.2 g, 0.84 mol) was added carefully at the refluxing temperature. When the evolution of hydrogen ceased, allyl bromide (96 ml, 1.1 mol) was added during 20 min to the viscous reaction mixture at 63 °C. After additional stirring for 10 min, the mixture was filtered and distilled under reduced pressure. The fraction 74−76.5 °C/1.33 kPa consisting of unreacted diol and allyl ethers was at first washed with water to remove the diol and then further purified chemically. The crude product (54 g) and maleic anhydride (69 g, 0.7 mol) was dissolved in THF (100 ml). 1 ml of conc. sulfuric acid was added and the mixture refluxed for 45 min. THF was evaporated and 250 ml H_2O added together with a sufficient amount of 48 % NaOH solution to neutralize the mixture. After filtering and washing off the unreacted diallyl ether with ether, NaOH solution (46 g) was added and the mixture refluxed for 25 min to hydrolyze the ester of monoallyl ether. Monoallyl ether of neopentylglycol was recovered from the reaction mixture by extraction with ether. After washing with water, drying and evaporating the solvent, the residue was purified by distillation giving the final product: B.p. 103.0−103.6 °C/5.47–kPa, n^{30} 1.4342. ^{13}C NMR: δ 135.0 (d), 116.3 (t), 77.7 (t), 72.3 (t), 69.8 (t), 36.6 (s), 21.8 (q).

1-(2-Propenyloxy)-2-propanol (6). Preparation was carried out according to Swern *et al.*[23] The product was purified by vacuum distillation and then redistilled twice through a bubble cup column of 15 plates at atmospheric pressure using a reflux ratio of 1:10. B.p. 156.8 °C/100.6 kPa, n^{30} 1.426. ^{13}C NMR: δ 135.0 (d), 116.9 (t), 76.0 (t), 72.2 (t), 66.2 (d), 19.3 (q).

1-Phenyl-2-(2-propenyloxy)-1-ethanol (7). The procedure of Swern *et al.*[23] was used. B.p. 131.7 °C/1.33 kPa, n^{30} 1.5173. ^{13}C NMR: δ 138.6 (s), 134.5 (d), 128.5 (d), 128.0 (d), 126.9 (d), 117.0 (t), 82.2 (d), 69.8 (t), 67.3 (t).

Allyl lactate (8). A mixture of ethyl lactate (226 ml, 2 mol), allylalcohol (408 ml, 6 mol) and sodium methoxide (6 g) was refluxed and the liberated ethanol distilled off until no ethyl lactate could be detected in the solution. The product was further purified by distillation. B.p. 96.8−97.5 °C/6.80 kPa, n^{30} 1.432. ^{13}C NMR: δ 175.4 (s), 132.1 (d), 118.5 (t), 66.9 (d), 65.8 (t), 20.2 (q).

2,2-Dimethyl-1-methoxy-3-(2-propenyloxy)-propane (9). Neopentyl glycol (313 g, 3 mol) and KOH (237 g, 4.2 mol) were dissolved in THF (400 ml). Dimethyl sulfate (280 ml, 3 mol) was added during 30 min to the refluxing mixture. The solids were filtered off, THF evaporated and the monomethyl ether of the diol separated by

distillation, b.p. 154.9−157.5 °C. Monomethyl ether (142 g, 1.2 mol) was treated with NaH (50 % in oil, 56 g, 1.2 mol) in THF (100 ml) and finally alkylated with allyl bromide (122 ml, 1.4 mol) at reflux temperature. After filtration the product was distilled through a 30 cm Vigreux-column. B.p. 161.3−161.9 °C/100.8 kPa, n^{30} 1.413. ^{13}C NMR: δ 135.5 (d), 115.8 (t), 79.2 (t), 76.4 (t), 72.2 (t), 59.0 (q), 36.4 (s), 22.3 (q).

1-Methoxy-4-(2-propenyloxy)-butane (10). The synthesis was analogous to (7). B.p. 87.0−87.5 °C/5.27 kPa, n^{30} 1.4180. ^{13}C NMR: δ 135.3 (d), 116.1 (t), 72.5 (t), 71.7 (t), 70.1 (t), 58.3 (q), 26.5 (t).

2-Methoxy-1-(2-propenyloxy)-propane (11). 70 g (0.6 mol) of (5) was treated with NaH (50 % in oil, 34.8 g, 0.73 mol) and alkylated with methyl iodide (53 ml, 0.84 mol). After filtration and distillation the product boiling at 138.8−139 °C/98.8 kPa was obtained. $n^{30}=1.408$, ^{13}C NMR: δ 135.5 (d), 116.2 (t), 76.2 (d), 74.2 (t), 72.3 (t), 56.7 (q), 16.9 (q).

1-Methoxy-1-phenyl-2-(2-propenyloxy)-ethane (12). The preparation was carried out analogously to (9) using (6) (13 g, 0.32 mol) as starting material. THF (80 ml) was now added to decrease the viscosity of the reaction mixture. B.p. 141.6−141.8 °C/4.20 kPa, n^{30} 1.4957, ^{13}C NMR: δ 139.8 (s), 135.1 (d), 128.3 (d), 127.8 (d), 127.0 (d), 116.2 (t), 80.5 (d), 77.4 (t), 69.7 (t), 58.9 (q).

1-Methoxy-3-(2-propenyloxy)-propane (13). A similar procedure as in the preparation of (7) was used to prepare the monomethylether of 1,3-propane diol. Allylation was carried out according to the synthesis of (2). B.p. 150.0−150.4 °C/100.4 kPa, n^{30} 1.412. ^{13}C NMR: δ 135.5 (d), 116.0 (t), 71.8 (t), 69.8 (t), 67.3 (t), 58.5 (q), 30.4 (t).

1-Methoxy-2-(2-propenyloxy)ethane (14). The preparation was carried out analogously to (2) using monomethyl ether of ethylene glycol as starting material. B.p. 131.7−132.0 °C/103.3 kPa, n^{30} 1.408. ^{13}C NMR: δ 135.4 (d), 116.3 (t), 72.2 (t), 69.7 (t), 58.8 (q).

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