Journal für praktische Chemie Chemiker-Zeitung © Johann Ambrosius Barth 1995

Kinetics and Regioselectivity of the Autoxidation of Monocyclic Olefins and of Bicyclo[2.2.1]heptene

Gerlinde Lauterbach and Wilhelm Pritzkow

Merseburg, Institute of Technical and Macromolecular Chemistry of the Martin Luther University Halle-Wittenberg

Received October 4th, 1994

It was found both in the working group of F.R. Mayo [1] and in our own group [2] that the proportion of epoxide and allyl hydroperoxide formation from cyclic olefins during their oxidation with molecular oxygen depends dramatically on the ring size. From cyclopentene and cyclohexene only about 10 % epoxide is obtained whereas from cycloheptene about 30 % and from cyclooctene about 60 % epoxide is formed. Bicyclo[2.2.1]heptene [3,4] and bicyclo[2.2.2]octene [5] give only epoxides, their allylic C-H bonds are unreactive because they are bridgehead C-H bonds in bicyclic ring systems, and the corresponding carbon radicals cannot be stabilized by mesomerism with the C=C bond (Bredt's rule).

The results on the autoxidation of cyclic olefins can either be explained by differences of the reactivities of the allylic C-H bonds or by differences of the reactivities of the C=C double bonds with the chain-propagating peroxy radicals. The decision between these possibilities can be made by determining the relative reaction rates of the allylic C-H bonds and of the C=C double bonds with reference to one and the same standard compound.

We have studied the competitive oxidation of the monocyclic C_5 to C_8 olefins and of bicyclo[2.2.1]heptene with cumene and determined the reactivities of both the allylic C-H bonds (formation of allylic hydroperoxides, after reduction with LiAlH₄ only cycloalkenols) and the C=C bonds (formation of epoxides, after reduction with LiAlH₄ cycloalka-

 Table 1 Kinetics and regioselectivity of the autoxidation of cyclic nd bicyclic olefins

olefin	temper- ature °C	gross reactivity k _{rel} ^{a)}	C=C ^{a)}	allylic C-H ^{a)}
cyclopentene	35	8.2±0.8	0.24 ± 0.04	1.98±0.19
cyclohexene	65	6.6 ± 0.3	$0.56 {\pm} 0.02$	$1.62 {\pm} 0.06$
cycloheptene cyclooctene	65	4.9 ± 0.1	$1.02 {\pm} 0.11$	$0.97{\pm}0.03$
	65	$1.6 {\pm} 0.1$	$1.16 {\pm} 0.04$	$0.10{\pm}0.01$
bicyclo[2.2.1]- heptene	65	6.5±0.5	6.5±0.5	-

^{a)} mean value of five independent experiments in each case; determined by competitive oxidation with cumene; related to the tertiary C-H bond of cumene nols) with reference to the tertiary C-H bond of cumene (Table 1).

The results show that both the allylic C-H reactivity and the reactivity of the C=C double bond depend on the ring size. The oxidizabilities of the olefins studied were determined in [6]. They change in the same manner as the gross reactivities shown in Table 1 (which may be considered as relative chain propagation constants). Therefore one can conclude that the chain termination constants of all the olefins studied lie in the same order of magnitude.

We thank the Fonds der Chemischen Industrie for financial support.

Experimental

The oxidations and the LiAlH₄ reductions were accomplished as described in [7]. At first the pure olefins were oxidized and reduced in order to seek for good conditions for the gaschromatographic analysis. The epoxides with the exception of bicyclo[2.2.1]heptene-oxide were reduced by LiAlH₄ to the corresponding cycloalkanols. In the case of cycloocteneoxide this reduction was always incomplete. Following epoxide yields (related to the sum of gaschromatographically detectable compounds) were obtained from the pure olefins: cyclopentene, 13.4 %; cyclohexene, 6,7 %, cycloheptene, 18.3 %; cyclooctene, 78.8 %; bicyclo[2.2.1]heptene, 100 %.

Five competitive oxidations with different mole ratios in each case were accomplished with all olefins studied. The gross reactivities and the relative reactivities of the C-H and the C=C groups collated in Table 1 are mean values calculated from the analysis of the reduction products from the competitive oxidations.

References

- D.E. Van Sickle, F.R. Mayo, R.M. Arluck, J. Am. Chem. Soc. 87 (1965) 4824
- [2] K. Blau, U. Müller, W. Pritzkow, W. Schmidt-Renner, Z. Sedshaw, J. Prakt. Chem. 322 (1980) 915
- [3] D.E. Van Sickle, F.R. Mayo, R.M. Arluck, J. Org. Chem. 32 (1967) 3680

- [4] Ch. Duschek, W. Grimm, M. Hampel, R. Jauch, W. Pritzkow, H. Rosner, J. Prakt. Chem. 317 (1975) 1027
- [5] R.G. Naick, W. Pritzkow, J. Rasche, J. Prakt. Chem. 319 (1977) 785
- [6] M. Futu-Tangu, E. Lawson, W. Pritzkow, V. Voerkel, J. Prakt. Chem. 325 (1983) 545
- [7] G. Lauterbach, W. Pritzkow, J. Prakt. Chem. 336 (1994) 83
- Address for correspondence:
- Prof. Dr. W. Pritzkow
- Institut für Technische und Makromolekulare Chemie
- Martin-Luther-Universität
- D-06217 Merseburg, Germany