# Kinetics of Peroxyradical Attack at Cyclic Hydrocarbons: Ring-Strain Effects on H-Abstraction

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Dedicated to Prof. Dr. Christoph Rüchardt on the Occasion of his 65th Birthday

**Abstract.** Relative autoxidation rates were determined for the cycloalkanes  $C_7$  to  $C_{12}$ , the methyl cycloalkanes  $C_6$  to  $C_9$  and the ethyl cycloalkanes  $C_5$  to  $C_9$  (ring size in each case) by competitive oxidation of the cycloparaffins with cumene. In the case of the methyl and ethyl cycloalkanes the reactivities of the tertiary C-H bonds could be calculated from the amounts

of tertiary alcohols formed after  $LiAlH_4$  reduction of the oxidates. As expected, the C-H reactivities are especially low in six-membered cycloparaffins and especially high in five-, seven- and eight-membered cycloparaffins. The C-H reactivity of cyclododecane lies in the same order of magnitude as the reactivities of secondary C-H bonds of normal paraffins.

It has been known since the early 50s that the change in ring strain of carbocyclic compounds, which must be expected if one carbon atom changes its hybridization from sp<sup>3</sup> to sp<sup>2</sup>, depends on the ring size. This leads not only to different  $S_N1/E1$  reaction rates of cycloalkyl tosylates [1, 2] and 1-methyl cycloalkylchlorides [3, 4] but also to different cyanohydrin formation equilibria of cycloketones [5, 6] depending on ring size. H. C. Brown proposed the term I-strain for such dependence of reaction rates or equilibria on ring size [7, 8]. From experimental data it is clear that in carbocylic four- and six-membered rings the transformation of one sp<sup>3</sup> ring atom to sp<sup>2</sup> is especially difficult but that this transformation proceeds particularly easily in five-, seven- and eight-membered rings.

Corresponding ring size effects must be expected for radical-forming reactions of carbocyclic compounds. Actually, in the decomposition of 1,1'-dicyano azocycloalkanes [9], 1,1'-diphenyl azocycloalkanes [10] and 1,1'-dimethyl azocycloalkanes [11] the four- and six-ring compounds reacted with especially low rates whereas the five- and the seven-membered compounds reacted much faster. In the decomposition of cycloalkyl peroxycarboxylic tert-butylesters [12] corresponding ring size effects on the reaction rates were found. Particularly high effects in the expected direction were observed in the thermal decomposition of 1,1'-diphenyl-1,1'-bicycloalkyls [13, 14].

In all references given above the radical-forming reactions were unimolecular. Only two publications deal with radical-forming C-H abstraction reactions from carbocyclic compounds. Bunce and Hadley studied the photochlorination and the photobromination of cycloalkanes [15]. They did not find a significant ring strain effect in the photochlorination, but in the photobromination the expected differences of reaction rates depending on the ring size were observed. In our group the autoxidation of phenyl cycloalkanes was investigated, and the expected differences of the reaction rates were found [16].

In this publication we deal with the determination of relative rates of autoxidation of unsubstituted cycloalkanes by their cooxidation with cumene. Because this cooxidation was possible only at temperatures of at least 100 °C we could not include cyclopentane (b.p. 49.5 °C) and cyclohexane (b.p. 80.8 °C). Therefore we also studied the cooxidation of the methyl cycloalkanes (from methyl cyclohexane to methyl cyclononane) and the ethyl cycloalkanes (from ethyl cyclopentane to ethyl cyclononane) with cumene at 85 °C. The oxygen absorption was limited in all cases to 10 mmol per 100 mmol hydrocarbon. The oxidates were reduced with lithium aluminum hydride, and the alcohols formed were determined by gaschromatography. From the molar proportion of the alcohols formed from the cyclic paraffins and of 2-phenyl propan-2-ol (formed from cumene) the relative rates of oxidation of the cycloparaffins and of individual C-H bonds could be calculated [16-18] (Table 1). These relative rates correspond to the attack of peroxy radicals at the C-H bonds of the cycloparaffins on the one hand and of cumene on the other. In the case of the methyl and ethyl cycloalkanes gross reactivities are not given because of the great number of secondary alcohols formed and the uncertainty of their determina-

ring size	substituent	temperature °C	gross reactivity (mean deviation)	sec-C-H bonds (mean deviation)	tert-C-H bond (mean deviation)
7	Н	100	0.446 (0.016)	0.032 (0.001)	
8	Н	110	0.716 (0.012)	0.045 (0.001)	_
9	Н	110	0.678 (0.035)	0.038 (0.002)	_
10	Н	110	0.578 (0.026)	0.029 (0.001)	- Million
11	Н	110	0.606 (0.018)	0.028 (0.001)	_
12	Н	110	0.268 (0.011)	0.011 (0.001)	_
6	Me	85			0.102 (0.004)
7	Me	85	_	- -	0.261 (0.008)
8	Me	85		_	0.258 (0.013)
9	Me	85	-	-	0.115 (0.005)
5	Et	85	-	-	0.128 (0.009)
6	Et	85	_	-	0.072(0.005)
7	Et	85	_	_	0.122(0.005)
8	Et	85	_	_	0.148 (0.010)
9	Et	85	_	— .	0.128 (0.005)

Table 1 Relative rates of peroxyradical attack at cycloparaffins (with respect to cumene) determined by cooxidation of the cycloparaffins with cumene

tion. The reactivities of the secondary C-H bonds in the unsubstituted cycloparaffins correspond to expectation. They are especially high in cyclooctane and decrease with increasing ring size. The value for cyclododecane is about the same as the reactivity of secondary C-H bonds in normal paraffins [19]. In the cases of the methyl and the ethyl cycloalkanes the cyclohexane derivatives expectedly have lower tert-C-H reactivities than the cyclopentane and cycloheptane derivatives. The ring size dependence corresponds to that in the photobromination of cycloalkanes [15]. Both bromine atoms [20] and peroxy radicals [17, 19] have higher selectivities than chlorine atoms [20] in H abstraction from aliphatic C-H bonds and therefore it is understandable that ring size effects are found in photobromination and autoxidation but not in photochlorination.

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## Experimental

#### **Starting Hydrocarbons**

Most of the nonbranched cycloalkanes were commercially available. We got cyclodecane from Prof. Dr. G. Wilke (Max-Planck Institute for Coal Research, Mülheim). Cyclononane was prepared from cyclooctanone via ring enlargement with diazomethane; cycloundecane was prepared from cyclododecanone via Favorskij ring reduction and subsequent oxidative decarboxylation of the cycloundecane carboxylic acid obtained.

## Cyclononane from Cyclooctanone

The method of Kohler (ring enlargement with N-nitroso-N-methyl urethane and potassium carbonate in methanol) [21] gave mixtures of cycloketones with only about 20 % cyclononanone. We varied the conditions of ring enlargement and obtained the best results (about 40% of cyclononanone in the ketone mixture) with N-nitroso-N-methyl p-toluene sulphonamide and sodium hydroxide in methanol.

In a 2 l-flask equipped with stirrer and dropping funnel 100 g cyclooctanone (0.79 mol) were dissolved in 500 ml methanol. The mixture was cooled to -5 to 0 °C. Then during 6 h 338 g (1.6 mol) N-nitroso-N-methyl p-toluenesulphonamide and a NaOH solution prepared from 80 g (2.0 mol) NaOH, 100 ml water and 300 ml methanol were cautiously added under continuous stirring in small portions at -5 to 0°C. After additional 2 h stirring at -5 to 0°C the reaction mixture was poured into 11 water. The organic phase was separated and the aqueous phase extracted three times with 250 ml ether each time. The combined organic phases were washed with water and dried over Na<sub>2</sub>SO<sub>4</sub>. After removal of the ether a mixture of 46 % cyclooctanone, 42 % cyclononanone and 12 % cyclodecanone was obtained by vacuum distillation. The mixture was separated by distillation at 4.0 kPa over a packed column of 120 cm height with a reflux ratio of 4 : 1. So we obtained about 15 % of the mixture as cyclononanone with b.p. 120-130 °C/ 4.0 kPa and a purity >98 %. The cyclononanone was reduced with LiAlH<sub>4</sub> to cyclononanol. The cyclononanol was dehydrated with KHSO4 to cyclononene which was then hydrogenated at 80 °C/10 MPa with diethyl ether as the solvent and Raney-Ni as the catalyst.

#### Cycloundecane from Cyclododecanone

The bromination of cyclododecanone and the Favorskij rearrangement of  $\alpha$ -bromo cyclododecanone were accomplished according to [22]. The cycloundecane carboxylic acid was oxidized with lead tetraacetate in dimethyl acetamide as the solvent [23] and gave cycloundecene in moderate yields.

2 g (10 mmol) Cu(OAc)<sub>2</sub>·H<sub>2</sub>O, 0.8 g (10 mmol) pyridine and 300 ml dimethyl acetamide were given into a threenecked flask equipped with stirrer, dropping funnel and reflux condenser. The mixture was cooled to 0 °C, then 44.3 g (100 mmol) Pb(OAc)<sub>4</sub> were added slowly. In order to eliminate oxygen, the cooled apparatus (0 °C) was evacuated to <3 kPa and then filled with argon. The mixture was heated to 50 °C in a water bath. At this temperature 39.6 g (200 mmol) cycloundecane carboxylic acid were added dropwise. After 3 h stirring at 50 °C the mixture was heated for 1 h to 90 °C. The reaction mixture was poured into 1 l water. The aqueous mixture was extracted four times with 100 ml pentane each time. The combined organic phases were washed with water and dried over Na<sub>2</sub>SO<sub>4</sub>. After removal of the pentane the product was distilled in vacuo.

5 to 10 g with b.p. 95-130 °C/2.0 kPa were obtained. This fraction contained mainly cycloundecene. From the residue excess cycloundecane carboxylic acid (b.p. 150-160 °C/0.15 kPa) was isolated. The cycloundecene fractions of 10 preparations were combined and redistilled over a 30 cm-Vigreux column (reflux ratio 3:1). 45 g of a fraction boiling at 95-105 °C/2.0 kPa were obtained. The capillary gaschromatogram showed one peak corresponding to more than 95 % and a second peak with a slightly higher retention time corresponding to about 2%. Some other peaks with higher retention times were also detected. In the <sup>13</sup>C-nmr spectrum four intensive signals (131.2 ppm; 34.1 ppm; 26.9 ppm; 25.8 ppm) typical for cycloolefins [24] appeared. The relatively high value for the  $sp^2$  carbon is an argument for the trans-configuration of the cycloundecene. A small signal at 130.8 ppm may be assigned to the cis-olefin. A signal at 26.0 ppm probably must be assigned to cycloundecane [24]. In the <sup>1</sup>H-nmr spectrum three groups of signals appeared (5.4-5.5 ppm; 2.0-2.2 ppm; 1.1-1.6 ppm) which can be assigned to the olefinic protons, the allylic protons and the protons of the other CH<sub>2</sub> groups. The relative intensities correspond to this assignment. The formation of both olefins and paraffins is typical for the oxidative decarboxylation of carboxylic acids with lead tetraacetate [23]. The cycloundecene was hydrogenated at 80°C/10 MPa using diethyl ether as the solvent and Raney-Ni as the catalyst. The cycloundecane obtained (b.p. 98-100 °C/2.4 kPa) showed only one peak in the capillary gaschromatogram. In the <sup>13</sup>C-nmr spectrum (26.3 ppm) and in the <sup>1</sup>H-nmr spectrum (1.44 ppm) one signal appeared in each case.

## Methyl- and Ethyl Cycloalkanes

Methyl cyclohexane was commercially available. All other methyl cycloalkanes were prepared from the corresponding cycloalkanones via the 1-methyl cycloalkanols, and the 1-methyl cyloalkenes. The dehydration of the 1-methyl cycloalkanols was accomplished by distillation over KHSO<sub>4</sub>. The hydrogenation of the 1-methyl cycloalkenes took place at 80 °C/10 MPa in diethyl ether as the solvent and with Raney-Ni as the catalyst. The ethyl cycloalkanes were prepared analogously.

## **Competitive Oxidations**

The competitive oxidations and the LiAlH<sub>4</sub> reductions were accomplished according to [18] at the temperatures given in Table 1. In most cases the alcohols formed were analyzed by isothermal gaschromatography (katharometer as detector) using packed columns of 5 m length (15 % Carbowax or 15 % Apiezone + 3 % KOH on Inertone). Only the products of the ethyl cycloalkanes were analyzed by temperature-programmed capillary gas chromotography (25 m column CP-SIL-43; nitrogen as the carrier gas; flame ionization detector). From the relative peak areas the relative molar amounts of the alcohols were calculated assuming that the relative peak

areas correspond to relative masses. The correctness of this assumption was proved experimentally. The relative rates of formation of the individual alcohols (with respect to the rate of formation of 2-phenyl propan-2-ol) were obtained using the equation:

$$k_{rel} = \frac{[cumene] \cdot [alcohol from the cycloparaffin]}{[cycloparaffin] \cdot [2-phenyl propan-2-ol]}$$

The relative rates of peroxyradical attack at individual C-H bonds were calculated from the relative rates of formation of the different alcohols taking into account the number of equivalent C-H bonds.

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