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Effect of Cyclic Polyether on the Base Catalyzed Disproportionation of 1,3-Cyclohexadiene

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The base catalyzed disproportionation of 1,3-cyclohexadiene to benzene and cyclohexene was studied in 1,4-dioxane at 50 °C with potassium *tert*-butylate as catalyst in the presence of varying amounts of 18-crown-6-cyclic polyether. The reaction kinetics showed a second order dependence on the cyclohexadiene concentration. At constant concentration of potassium *tert*-butylate the reaction rate increased moderately when the molar ratio of cyclic polyether to potassium *tert*-butylate was increased up to about one, at higher ratio the rate was almost constant. The increase in rate produced by the cyclic polyether may be explained as a result of complexation of the potassium ion with cyclic polyether, thus, increasing the catalytic activity of potassium *tert*-butylate. The cyclic ether seems to have only a small effect on the hydride transfer reaction step.

Cyclohexadiene and some of its derivatives are known to disproportionate thermally [1,2] and catalytically over metals,[3,4] cationic metal complexes [5,6] and strong bases.[7,8] The homogeneous base catalyzed disproportionation of 1,3-cyclohexadiene to benzene and cyclohexene was shown to take place quantitatively when the diene was treated with potassium *tert*-butylate in dimethyl sulfoxide.[8] The isomerization between 1,3- and 1,4-cyclohexadiene was so rapid that either isomer would lead to the same result. In *tert*-butyl alcohol solution only isomerization was observed with no disproportionation. Substituents in the cyclohexadiene ring may decrease [9] or increase [10] the rate of disproportionation.

The aim of the present work was to study the effect of 18-crown-6-cyclic polyether on the catalytic activity of potassium *tert*-butylate on the disproportionation of 1,3-cyclohexadiene in the low polar solvent, 1,4-dioxane.

The overall reaction is

EXPERIMENTAL

Reagents. 1,4-Dioxane "Zur Analyse" from E. Merck AG. The contaminating peroxides were removed by reduction with sodium metal and small amounts of water. The dioxane was refluxed with sodium metal for 48 h, then distilled under an atmosphere of nitrogen, b.p. 100 – 101 °C. tert-*Butyl alcohol* "für Chromatographie" from E. Merck AG. *1,3-Cyclohexadiene* "pure" from Koch-Light Laboratories. The purity was checked by mass spectrometry and gas chromatography. The gas chromatographic analysis showed that the diene contained about 0.1 % of both benzene and cyclohexene. *Potassium metal* from Riedel de Haën AG. *18-Crown-6-cyclic polyether* from A/S Borregaard, melting point 39 – 41 °C. The purity was checked by gas chromatography where only one peak was observed. *Methanol* "zur Analyse" from E. Merck AG. *Nitrogen* "highly purified" from Norsk Hydro a.s. Nitrogen (including argon) contents higher than 99.99 %, water content less than 0.001 %.

Preparation of catalyst solution. The potassium *tert*-butylate was prepared by reacting a solution of *tert*-butyl alcohol (about 1.0 mol/l) in 1,4-dioxane with an excess of potassium metal. The reaction mixture was then refluxed for 48 h. Traces of hydroxide were allowed to settle, and the solution was kept under nitrogen

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atmosphere. The concentration of the stock solution was determined by titration with standardized hydrochloric acid solution. The catalyst solutions for the kinetic runs were prepared by diluting the stock solution with purified 1,4-dioxane to the required concentration. The preparations were carried out in an atmosphere of nitrogen.

Procedure. The disproportionation reaction was carried out in septum bottles with teflon "Mininert" valves (from Precision Sampling Corporation). The required amount of cyclic ether was weighed into the bottle, then 10 ml of potassium *tert*-butylate solution was added. The mixture was kept in a thermostat until it attained the required temperature. The reaction was started by adding 1 ml of 1,3-cyclohexadiene to the mixture and the bottle was vigorously shaken. The entire procedure was performed under nitrogen atmosphere. At different time intervals (using 1 ml syringe) 0.5 ml samples were withdrawn. The samples were quenched by dilution with methanol to the appropriate concentration for spectrophotometric analysis.

The reaction was followed by measuring the UV absorption maximum at 259 nm characteristic for 1,3-cyclohexadiene. These measurements were carried out on a Hilger & Watts H 999 Ultrascan spectrophotometer.

Some samples were also analyzed by gas chromatography. A Perkin Elmer F 33 gas chromatograph was used, equipped with flame ionization detector and a 3 mm column, 4 m long, filled with 13½ % bis-2-methoxyethyl adipate and 6½ % di(2-ethyl hexyl)sebacate on Chromosorb P, 80–100 mesh.

RESULTS AND DISCUSSION

The disproportionation of 1,3-cyclohexadiene catalyzed by potassium *tert*-butylate in 1,4-dioxane in the presence of 18-crown-6-cyclic polyether was shown by gas chromatographic analysis to give benzene and cyclohexene in a 1:1 molar ratio as the only reaction products even at high conversion. Conversions measured by UV absorption were found to agree well with gas chromatographic analysis. Thus, at high conversion the UV spectrum showed the characteristic absorption for benzene.

The disproportionation of 1,3-cyclohexadiene was found to follow second order kinetics. This is in accordance with the result of Hofman *et al.*[8] for the base catalyzed reaction in dimethyl sulfoxide at 55 °C. The integrated form of the second order rate equation may be written as

$$(c_0-c)/c=c_0kt$$

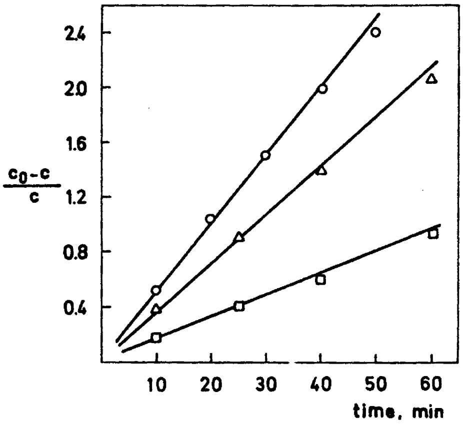


Fig. 1. Second order plots for the base catalyzed disproportionation of 1,3-cyclohexadiene in 1,4-dioxane solution. Temperature 50 °C. Concentration of potassium *tert*-butylate 0.38 mol/l. Concentration of cyclohexadiene at start $c_0=0.95$ mol/l. Concentration of 18-crown-6-cyclic polyether: 0.46 mol/l (○), 0.27 mol/l (△), 0.09 mol/l (□).

where c_0 is the initial concentration of 1,3-cyclohexadiene, c is the concentration at time t, and k is the second order rate constant.

Fig. 1 shows examples of the second order plot of the kinetic runs. The second order rate constant was evaluated from the slope of the straight line.

Fig. 2 shows the effect of the cyclic ether concentration on the experimental second order

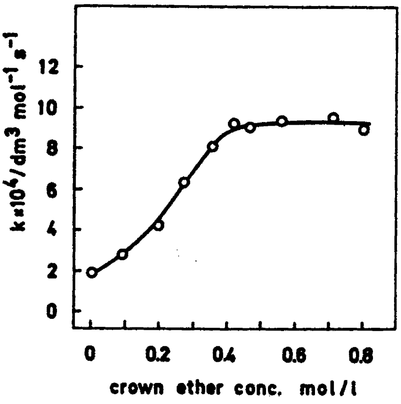


Fig. 2. Effect of the crown ether concentration on the second order rate constant at constant concentration of potassium *tert*-butylate, 0.38 mol/l. Temperature 50 °C.

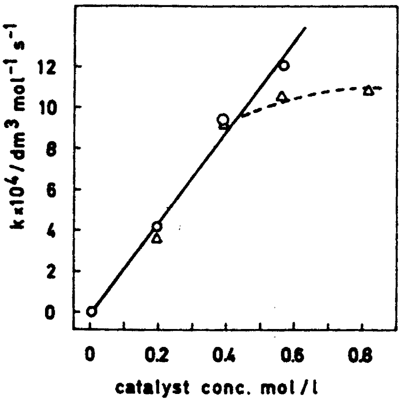
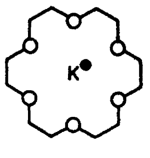


Fig. 3. Effect of the concentration of potassium *tert*-butylate on the second order rate constant at two different concentrations of cyclic polyether: 0.41 mol/l (△), 0.55 mol/l (○). Temperature 50 °C.

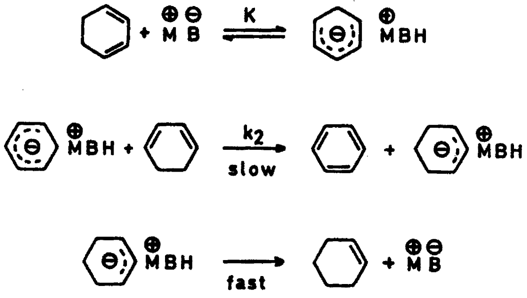
rate constant at constant concentration of potassium *tert*-butylate of 0.38 mol/l at 50 °C. The rate constant increased with increasing ratio cyclic ether/potassium *tert*-butylate up to a molar ratio close to 1. At higher ratios the rate constant remained almost constant.

Such a result may be explained by complexation of the alkali metal ion with the macrocyclic polyether,[11] leading to an increased activity of the catalyst. The crown ethers are known to fill effectively the coordination sites of alkali metal cations and to convert contact ion pairs into separated ions or separated ion pairs.[12,13] The upper limit of the reaction rate reached at a molar ratio of cyclic ether/potassium *tert*-butylate of about 1:1 is in accordance with a 1:1 complex between 18-crown-6-cyclic polyether and potassium ions.[14,15]



In Fig. 3 the experimental second order rate constant is plotted as a function of the concentration of *tert*-butylate at two given concentrations of cyclic ether. There seems to be a linear relationship between the rate constant and the concentration of potassium *tert*-butylate when the amount of cyclic ether is sufficient to complex all the potassium ions present. The observed increase in rate is less when the concentration of potassium *tert*-butylate was increased above the concentration of cyclic ether. This smaller increase might be due to the smaller catalytic activity of the non-separated ion pairs.

The observed kinetics may be explained by the following mechanism.



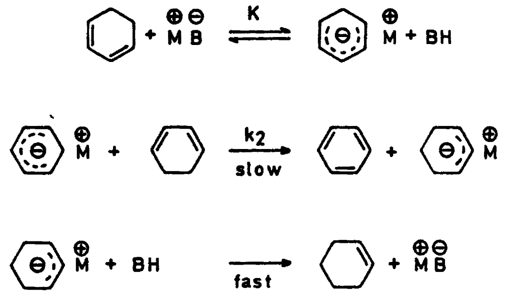
which involves carbon-carbon hydride ion transfer as the rate determining step. The proton transfer reaction is supposed to be fast compared to the hydride transfer, and the first step would then be an equilibrium. It is assumed that the carbanion is not free but form an ion pair complex with the cation and the alcohol formed in the first step. The cation may at the same time be strongly complexed to a cyclic polyether molecule as mentioned above.

From the proposed mechanism the following theoretical rate expression is derived

$$r = k_2K[A]^2[\overset{\oplus}{M}\,\overset{\ominus}{B}]$$

where k_2 is the rate constant for the second step and K is the equilibrium constant for the first step. [A] is the concentration of cyclohexadiene and $[\overset{\oplus}{M}\,\overset{\ominus}{B}]$ is the concentration of catalyst. The reaction is second order with respect to cyclohexadiene and first order with respect to catalyst as observed.

With potassium *tert*-butylate in dioxane solution the concentration of carbanion is expected to be very small and so also the concentration of *tert*-butyl alcohol formed in the first step. If the solvent or the reactants have not been completely dry, then the water present would react with the *tert*-butylate forming *tert*-butyl alcohol. In such a case a previously suggested mechanism [8,10] may explain the observed kinetics for the disproportionation reaction



This mechanism gives the following rate expression

$$r = k_2K[A]^2[\overset{\oplus}{M}\,\overset{\ominus}{B}]/[B\,H]$$

If the amount of *tert*-butyl alcohol (BH) formed from moisture present is much higher than the amount formed in the first step, then the concentration of the alcohol [BH] in the denominator may be considered constant, and the rate would be second order with respect to cyclohexadiene and first order with respect to catalyst. In this case the amount of moisture is supposed to be independent of $[\overset{\oplus}{M}\,\overset{\ominus}{B}]$ and $[\overset{\oplus}{M}\,\overset{\ominus}{B}] \gg [B\,H]$.

A similar mechanism was suggested for the reaction in the presence of sodium amide in liquid ammonia.[7]

The role of the cation in hydride transfer reactions in liquid phase is not well understood. The effect of cyclic ether on the hydride transfer step is probably small. The addition of cyclic ether is expected to shift the equilibrium (first step) to the right (K increases) because the *tert*-butylate anion has a more concentrated negative charge than the cyclohexadienyl anion. The effective ionic radius of the latter may therefore be considered larger than that of the former anion. Complexation of the cation with the cyclic ether increases the effective radius of the cation. The effect of increasing the size of the cation on the basisity of the ion pair, and on the cation-anion bond strength is higher with a small than with a large anion.

In base catalyzed isomerization reactions where a proton transfer is rate determining, the effect of cyclic ether on the rate is expected to be very large.[16] In proton abstraction reactions there is a great difference in reactivity between separated ion pairs and contact ion pairs of the base. In this work on the disproportionation of cyclohexadiene, involving a rate determining hydride transfer step, we find only a moderate increase in rate by adding cyclic ether. At a constant base concentration of 0.38 mol/l the rate constant increased only 5 times when the cyclic ether concentration was increased from zero to 0.41 mol/l.

The use of dimethyl sulfoxide as a solvent would be expected to have about the same effect on catalyst activity as addition of crown ether to the dioxane solution. In both cases the catalyst ion pairs are transferred into the separated forms. Interpolation of the data of Hofmann *et al.*[8] really shows that the rate constant for the disproportionation reaction in dimethyl sulfoxide at 50 °C is about the same as found in dioxane with cyclic polyether added. The small difference (about 25 % higher rate constant in dimethyl sulfoxide) may be attributed to the ability of the sulfoxide to bind strongly alcohols by hydrogen bonding. It is known that cyclohexadiene does not disproportionate in *tert*-butyl alcohol as solvent,[8] and some *tert*-butyl alcohol is reversibly formed in the first step of the reaction. The failure of 1,3-cyclohexadiene to undergo disproportionation in *tert*-butyl alcohol as a solvent [8] may be explained by the two effects: (1) Deactivation of the base by hydrogen bonds, and (2) strong solvation of the carbanion with rapid transfer of a proton from the alcohol solvent to the cyclohexadienyl anion.

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