Changes in the hydrogenative ring-opening mechanism of cyclohexene oxide over Cu/SiO_2 resulting from the addition of cyclohexene, a major product

András Fási [a] and István Pálinkó [b,*]

[a] *Chemical Research Center of the Hungarian Academy of Sciences, PO Box 17, H-1525 Budapest, Hungary*
[b] *Department of Organic Chemistry, József Attila University, Dóm tér 8, H-6720 Szeged, Hungary*
E-mail: palinko@chem.u-szeged.hu

Received 6 October 1998; accepted 12 February 1999

The ring-opening mechanism influencing effect of a major product in the cyclohexene oxide–D_2 system was investigated over a Cu/SiO_2 catalyst. This product is cyclohexene, thus, the hydrogenative ring opening of a 1 : 1 cyclohexene oxide–cyclohexene mixture was studied in the presence of D_2 at 403 K in a closed circulation reactor. It was found that the mechanism of single C–O scission was not affected, but that of the double C–O scission was changed. Simultaneous bond cleavage was the major route of ring opening in the additive-free system and it became consecutive on cyclohexene addition. Added cyclohexene was hydrogenated with a very low rate, but it transformed the surface of the catalyst and, thus, facilitated the change in the mechanism. An explanation concerning the seemingly anomalous lack of deuterium in a product (cyclohexane) not seen in the additive-free system is also suggested.

Keywords: hydrogenative ring opening, cyclohexene oxide, cyclohexene additive, Cu/SiO_2, deuterium

1. Introduction

Recently, it was found that cyclohexene oxide reacts over Cu/SiO_2 with appreciable velocity in a circulation reactor in the presence of hydrogen/deuterium even at moderate temperature [1]. Various products were detected (scheme 1) and their thorough examination made clear that they were formed in two ways: via single or double C–O bond scission.

The lack of deuterium in cyclohexene epoxide proves that its adsorption is irreversible, i.e., when it touches down the surface the ring opens in one way or another. Hydrogen (or deuterium) is also needed either as a reactant or for promoting product desorption. Ring opening stops without it; fast self-poisoning occurs. These observations coincide with previous experiences with various epoxides [2–4]. It was also observed that the two routes of ring opening were comparable initially, and that of double C–O scission became more important as the reaction advanced. The major deoxygenation product was cyclohexene. On the one hand, it was established previously that for the transformations of cyclohexene over Cu/SiO_2 a metal surface decorated with hydrogen-rich carbonaceous residues was advantageous [5]. On the other hand, it is known that upon adsorption, since it starts at the ring oxygen, epoxides make the surface ionic [6]. These two effects may not support each other; they may pose different requirements for the two types of ring scission. A way of collecting more information on it, is attempting to enhance one of the effects. In an earlier work the surface oxidation effect was enlarged by preoxidation of the surface of various silica-supported metal catalysts [6] (among them Cu/SiO_2). This contribution communicates the observations when the other surface transformation pathway is enlarged. Now, characteristics of the hydrogenative transformations of a 1 : 1 cyclohexene oxide–cyclohexene mixture over Cu/SiO_2 are examined. In order to obtain more information on the reaction mechanism and the catalytic surface, D_2 is used instead of H_2, and deuterium distribution is also determined in the products as well as in molecules hydrogenated off the used catalyst.

2. Experimental

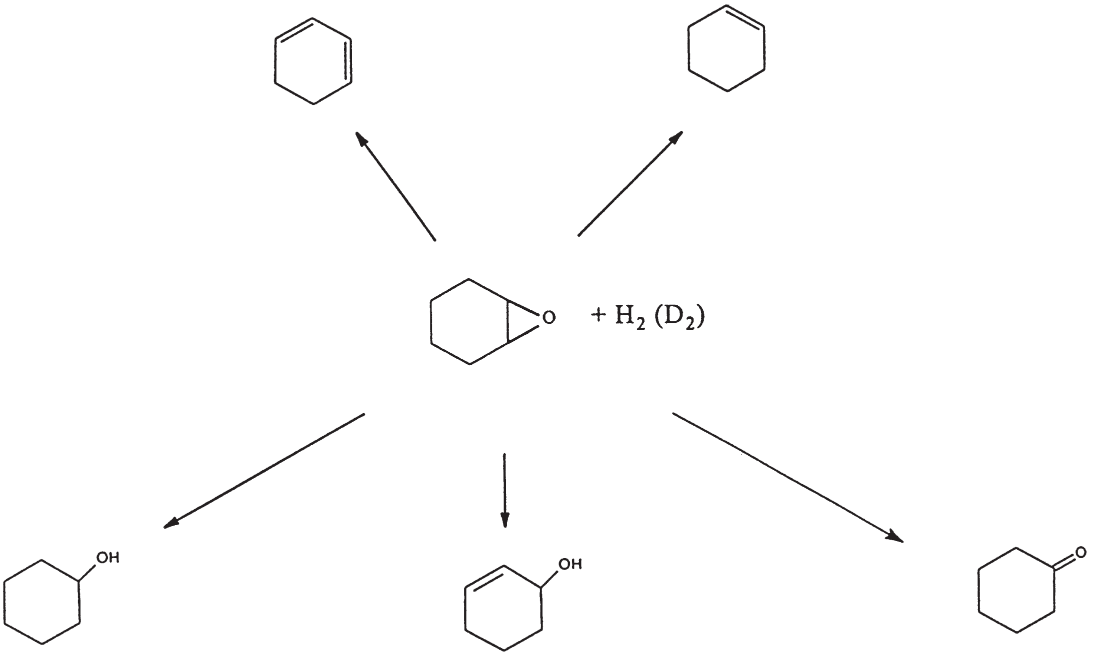
Cyclohexene oxide was a Fluka product with the purity of 99.9+% by the GC-MS method. Cyclohexene was obtained via the dehydration of cyclohexanol. After distillation its purity was checked by the GC-MS method. It was found 99.9+% pure. In order to destroy possibly formed peroxides, it was passed through a column filled with freshly activated basic alumina (Camag) under inert (Ar) atmosphere before filling it into a closed evacuated vial for further use in the static circulation reactor.

Deuterium (D_2 gas) was obtained through the electrolysis of D_2O (purity was 99.8%) in a General Electric 15EHG generator. The gas was deoxygenated with a MODEL 1000 Oxygen Trap (CRS, USA) before use.

The Cu/SiO_2 catalyst was prepared by the ion-exchange method. Support was Strem large pore (120–230 mesh) silica gel. It was immersed in a tetramminecopper(II) so-

---

[*] To whom correspondence should be addressed.



Scheme 1. Transformation pathways of cyclohexene oxide in the presence of H_2/D_2 over Cu/SiO_2 at 403 K.

lution at pH 11. After 24 h the blue product was washed thoroughly with doubly distilled water and dried at 393 K (24 h). After calcination (773 K, 3 h in air) the catalyst was reduced in a hydrogen stream (673 K, 2 h) and kept in a vacuum desiccator until use. Metal loading was 6.36%. The percentage of surface copper atoms was 14.6 by N_2O titration at 363 K. After reduction 7% of the copper atoms remained ionic, possibly as Cu^+ ions [7].

The reactions were carried out in a conventional closed circulation reactor. The volume of the reactor was 69 cm^3, and total volume of the system was 169.4 cm^3. The reactor was heated with an air thermostat. The volume of the sampling capillary was 0.05 cm^3 and the total sampling volume was 0.15 cm^3. A Hewlett–Packard (HP) model 5890 gas chromatograph equipped with a flame ionization detector (FID) was attached to the system. Data analysis was performed on an HP 3396A integrator. A 50 m long HP-1 capillary column was used for separating the reactants and the products. The column was operated in the isothermal mode (oven temperature 323 K) with helium as the carrier gas (flow rate 1.3 cm^3/min).

The reactants (0.8 kPa of cyclohexene oxide alone or its mixture with 0.8 kPa of cyclohexene and 20.0 kPa D_2) were premixed in the circulation part of the system before the reaction. (Cyclohexene oxide and cyclohexene were subjected to several freeze–evacuate–thaw cycles before preparing the mixture.) The reaction temperature was 403 K. Basically two types of reactions were performed. The first measurement was run over a fresh sample of catalyst, while restart reaction was done over the used catalyst subjected to evacuation (30 min, 1 Pa, 403 K) before the reaction. To obtain information about weakly held residues, they were hydrogenated off the surface by 53.2 kPa of D_2 at 673 K for 1 h.

Product composition as well as deuterium distribution were determined. The latter was calculated on the basis and vicinity of the parent peaks. In the calculations the natural abundance for ^{13}C and D, the C–H and C–D fragmentation reactions were taken into account.

3. Results and discussion

As has been mentioned above, single and double ring openings are comparable transformation pathways for cyclohexene epoxide free of hydrocarbon additive. It is certainly so at 20.0 kPa D_2 pressure as data in table 1 (table 1(a)) attest.

Cyclohexene formation even becomes faster than that of the oxygen-containing compounds combined. The major oxygen-containing product is cyclohexanone initially, and remains so later on as well. Its quantity increases as the reaction advances. The initially unimportant cyclohexanol becomes significant as the reaction proceeds.

When the 1 : 1 mixture of cyclohexene and cyclohexene oxide was allowed to react on a fresh sample of catalyst, an overall activity enhancement in cyclohexene oxide transformations was observed (table 1(b)). Initially (after the 5 min sampling), product distribution of compounds with one oxygen atom (single C–O scission) resembled to that of the system free of added cyclohexene (except that 2-cyclohexene-1-ol was not found at all). As the reaction proceeds this situation changes significantly. Cyclohexanone disappears, i.e., it is further transformed and cyclohexanol becomes the sole single C–O scission product. Its quantity increases as the reaction advances, similarly to the additive-free system. The majority of cyclohexene oxide is accumulated in cyclohexene. Certain amount of cyclohexene is hydrogenated to

Table 1
Product distribution in the transformations of cyclohexene oxide over Cu/SiO_2 (20 mg) at 403 K.[a]

	t (min)	Cyclohexane	Cyclohexadiene	Cyclohexene	Cyclohexene oxide	Cyclohexanol	Cyclohexanone	2-cyclohexene-1-ol
(a)	0	–	–	–	100	–	–	–
	5	–	0.2	3.1	91.7	0.6	3.9	0.5
	20	–	0.2	21.7	58.0	4.7	15.1	0.3
	35	–	0.1	39.0	34.0	10.0	16.8	0.1
(b)	0	–	–	50	50	–	–	–
	5	0.2	–	61.4	33.8	0.1	4.5	–
	15	1.5	–	76.1	10.2	6.5	5.8	–
	25	4.0	–	78.3	2.7	13.0	2.1	–
	35	7.3	–	77.8	0.8	14.2	0	–
(c)	0	–	–	50	50	–	–	–
	5	0.1	–	53.0	46.9	0	0	0
	15	0.6	–	60.0	30.4	4.1	4.5	0.3
	25	1.2	–	68.0	16.1	7.2	7.0	0.5
	35	1.6	–	73.5	7.3	9.8	7.5	0.4

[a] (a) 0.8 kPa cyclohexene oxide + 20.0 kPa D_2, fresh catalyst; (b) 0.8 kPa cyclohexene oxide + 0.8 kPa cyclohexene + 20.0 kPa D_2, fresh catalyst; (c) 0.8 kPa cyclohexene oxide + 0.8 kPa cyclohexene + 20.0 kPa D_2, restart reaction (30 min evacuation at 403 K after the previous reaction).

Table 2
Deuterium distribution in the most important ring-opening products of cyclohexene oxide over Cu/SiO_2 (20 mg) at 403 K.[a]

	t (min)	Conv.[b] (%)	Deuterium distribution (%)											
			Cyclohexane			Cyclohexene			Cyclohexanol		Cyclohexanone			
			d_0	d_1	d_2	d_0	d_1	d_2	d_2	d_3	d_0	d_1	d_2	d_3
(a)	5	8.3	–	–	–	100	0	0	66.2	22.1	11.2	56.5	31.0	1.3
	20	42.0	–	–	–	98.0	2.0	0	46.4	33.3	3.4	43.3	40.6	12.7
	35	66.0	–	–	–	93.2	5.1	1.7	31.9	40.3	1.7	31.6	41.1	22.4
(b)	5	16.2	0	100	0	93.2	6.5	0.3	76.2	23.8	8.3	36.1	38.7	16.9
	15	39.9	3.1	72.8	21.7	89.7	9.0	1.1	21.9	34.7	1.3	32.4	43.0	20.6
	25	47.3	9.5	57.2	24.2	84.8	11.9	2.3	16.4	33.9	0	26.8	52.9	20.3
	35	49.2	10.1	51.1	21.3	78.4	15.4	4.3	14.0	32.2	–	–	–	–

[a] (a) 0.8 kPa cyclohexene oxide + 20.0 kPa D_2; (b) 0.8 kPa cyclohexene oxide + 0.8 kPa cyclohexene + 20.0 kPa D_2.
[b] Conversion of cyclohexene oxide.

cyclohexane. On the basis of our previous experiences [8] this was expected and now, its rate is found to be slow. At this point, we may assume that cyclohexane is formed via the hydrogenation of the added cyclohexene. This assumption is strengthened by the fact that cyclohexane is not formed from the hydrogenative ring opening of cyclohexene oxide without the cyclohexene additive.

Deuterium distributions in single and double scission products are given in table 2. Table 2(a) contains data relevant to the transformation without added cyclohexene and table 2(b) displays those, relevant to the reactions of the cyclohexene oxide–cyclohexene–D_2 mixture.

Two ways of comparison will be given. First, initial distributions will be analyzed, then the overall picture in both types of ring-opening pathways is discussed. Mechanistically, the initial distributions are more important, because at the start multiple H–D exchange is limited.

Initially, the deuterium distribution in cyclohexanol is very similar in the cyclohexene oxide–D_2 and the cyclohexene oxide–cyclohexene–D_2 systems. Direct deuterium addition is the major route, however, hydrogenative ring opening through π-allyl adsorbed species is also significant as indicated by the appreciable proportion of cyclohexanol-d_3. There is deuterium in cyclohexanone as well, with maximuma in d_1 and d_2 in both systems. This means that adding cyclohexene to the cyclohexene oxide–D_2 mixture does not change the mechanism of single C–O cleavage.

At first sight the deuterium distribution in the double C–O scission product, in cyclohexene, is very similar in both systems, however, a non-negligible amount of cyclohexene-d_1 is also found in the cyclohexene oxide–cyclohexene–D_2 reacting mixture. The proportion of cyclohexene-d_1 is smaller in the additive-free system even at the 35 min sampling than in the cyclohexene oxide–cyclohexene–D_2 mixture initially (5 min sampling). This should mean that another pathway than simple deoxygenation (simultaneous double C–O scission) with cyclohexene-d_0 formation must also be operational. Since there is a significant amount of cyclohexanone-d_1, the amount of cyclohexanone decreases (and the compound disappears) as

Table 3
Quantities and deuterium content of products hydrogenated off the surface of Cu/SiO_2 (conditions: 53.2 kPa D_2, 673 K, 1 h) used in the reaction of the 0.8 kPa cyclohexene oxide + 0.8 kPa cyclohexene + 20.0 kPa D_2 mixture at 403 K.

Product	Product distribution (mol%)	Deuterium content
Unidentified	4.2	0
Cyclohexane	6.4	d_2, but significant d_{12} too
Cyclohexene	5.7	d_4
Benzene	83.7	d_6

the reaction proceeds and cyclohexene-d_1 increases with increasing contact time, one may conclude that cyclohexanone is the source of cyclohexene-d_1. Furthermore, the significance of cyclohexane-d_1 in the cyclohexene oxide–cyclohexene–D_2 system indicates that the source of these molecules is also in cyclohexanone. A small proportion of deuterium-containing cyclohexane, that is cyclohexane-d_2, comes from the hydrogenation of added cyclohexene. Let us point out that the deuterogenation of cyclohexene over the same Cu/SiO_2 under similar conditions provided with cyclohexane-d_2 as the major deuterium-containing product, while cyclohexane-d_1 was not found at all [8]. Consequently, the source of cyclohexane-d_1 in the cyclohexene oxide–cyclohexene–D_2 system is not the deuterogenation of the added cyclohexene. Another small portion of cyclohexane, that is cyclohexane-d_0, may be originated from cyclohexene. Certain cyclohexenes molecules when adsorbed, may dispropotionate over the surface, resulting in dissociatively adsorbed benzene and adsorbed hydrogen, which may add to the surface bound precursor of desorbed cyclohexane. Thus, the possible source of hydrogen should be hydrogen-rich surface residues. They can be derived from the adsorbed (added) cyclohexene accumulating and transforming over the surface of the catalyst as the reaction proceeds. However, since deuterium is abundant in our system, the route leading to cyclohexane-d_0 has minor importance.

Analysis of the working surface through hydrogenating residues off with D_2 (for quantitative and qualitative findings, see table 3) revealed that the adsorbed form of highly deuterated benzene is the most abundant carbonaceous residue. (Actually, only perdeuterated benzene was detected, but H–D exchange may have occurred during the procedure.) Cyclohexene and cyclohexane were also found among the products, indicating the presence of relatively loosely held hydrogen-rich species over the working surface. Even though they are not so strongly adsorbed as the benzene precursor, their residence time is not negligible, as the presence of multiply exchanged species indicates.

In a restart experiment (evacuation of the reactant–product mixture and introducing a new reactant mixture onto the used catalyst, see data in table 1(c)) the reactions of cyclohexene oxide slow down, approximately to the level experienced in the cyclohexene oxide–D_2 system over a fresh sample of catalyst (compare data to those of table 1(a)). After an induction period the product distribution, thus, the active surface resembles that of the fresh catalyst with cyclohexene oxide plus D_2 only. 2-cyclohexene-1-ol can be observed again, cyclohexanone does not disappear, but grows with increasing reaction time just like cyclohexanol. The relative importance of this compound is higher now than it was over the fresh catalyst without cyclohexene additive. To continue listing the similarities, the main reaction is still the double C–O scission resulting in cyclohexene formation. Over the used catalyst cyclohexene hydrogenates slower than over the fresh sample, in accordance with what was experienced earlier [5].

4. Conclusions

Observing and comparing deuterium distribution results in the ring-opening reactions of cyclohexene oxide and cyclohexene oxide in the presence of one major product – the cyclohexene – revealed that the mechanism of a major way of bond scission, the single C–O cleavage route, is not influenced significantly, especially not at the initial stages. However, the mechanism of the other route – the double C–O scission – has changed considerably. It was the simultaneous scission of adsorbed cyclohexene oxide in the additive-free system, and it became consecutive in the cyclohexene oxide–cyclohexene–D_2 mixture.

Evidence for the presence and participation of adsorbed hydrogen-containing carbonaceous residues in the reaction was found from the analysis of the working surface.

During the reaction in the cyclohexene oxide–cyclohexene–D_2 system the fresh catalyst transforms gradually, and finally, as results of the restart reaction attest, it ends up as a surface that closely resembles to that evolved in the system free of added cyclohexene.

References

[1] A. Fási and I. Pálinkó, J. Catal. 181 (1999) 28.

[2] G. Sénéchal and D. Cornet, Bull. Soc. Chim. Fr. (1971) 773, 783.

[3] J.C. Duchet and D. Cornet, Bull. Soc. Chim. Fr. (1975) 1135, 1141.

[4] G.C. Accrombessi, P. Geneste, J.-L. Olivé and A.A. Pavia, J. Org. Chem. 45 (1980) 4139.

[5] A. Fási, I. Pálinkó and M. Bartók, Appl. Catal. A 166 (1998) 185.

[6] I. Pálinkó, J. Mol. Catal. A 140 (1999) 195.

[7] I. Pálinkó, Á. Molnár, J.T. Kiss and M. Bartók, J. Catal. 121 (1990) 396.

[8] A. Fási, I. Pálinkó, T. Katona and M. Bartók, J. Catal. 167 (1997) 215.