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NOTES

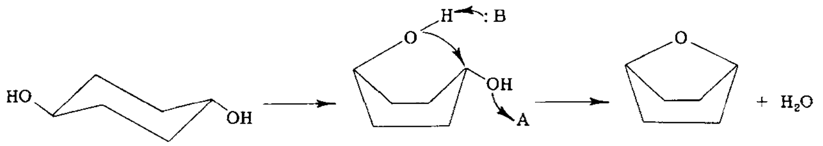
Hydrogenolysis of Alcohols*

IV. Dehydration of *cis*- and *trans*-1,4-Cyclohexanediol over Nickel-Kieselguhr Catalyst: Contribution to the Mechanism of Ether Formation

In previous papers of these series it was reported that reduced nickel oxide as such or deposited on supports can convert alcohols to ethers (*1–3*). The reaction was carried out in a pulse reactor at 160–190° in the presence of hydrogen and at atmospheric pressure. When the experiments were made with primary and secondary alkanols, reductive dehydroxylation accompanied ether formation. These two reactions were associated with the intrinsic acidic sites of the catalyst. Alkanediols, such as 1,4-butanediol and 1,5-pentanediol, also produced good yields of the corresponding cyclic ethers (*3*).

The reactions over reduced nickel oxide catalysts, although occurring in the presence of hydrogen were similar in many respects to the dehydration of alcohols over aluminas (*4*). The reductive dehydroxylation occurred probably through an intermediate olefin formation, followed by hydrogenation. It has been demonstrated that over aluminas the dehydration proceeded via a trans-elimination reaction and it was concluded that intrinsic acidic and basic sites of the aluminas participated in the reaction (*4, 5*). This was recently confirmed by Trambouze and co-workers (*6*).

In order to test the stereochemistry of the elimination reaction over reduced nickel–kieselguhr catalyst, it was decided to study the dehydration of *cis*- and *trans*-1,4-cyclohexanediol. Mannassen and Pines (*7*) showed that *trans*-1,4-cyclohexanediol produced exclusively 1,4-epoxycyclohexane when passed over alumina, while the *cis*-diol formed 4-hydroxycyclohexene. The formation of the epoxide was explained by a *trans*-elimination reaction:



(B: = basic sites; A = acid sites)

A mixture of *cis*- and *trans*-1,4-cyclohexanediol was prepared by hydrogenation of hydroquinone (*8*). The separation of the two stereoisomers was accomplished by acetylation of the mixture with acetic anhydride (*8, 9*). The diacetates were purified by fractional crystallization from acetone, hexane, and followed by vacuum distillation.

The experiments were made in a micropulse reactor (*10*) using the procedure described previously (*1, 3*). The catalyst consisted of nickel–kieselguhr containing 6%

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TABLE 1

REACTION OF *cis*- AND *trans*-1,4-CYCLOHEXANEDIOL OVER NICKEL-KIESELGUHR CATALYST[a]

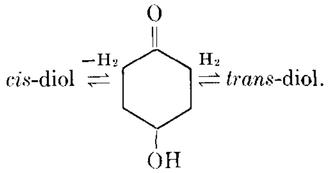
Pressure (atm)	1		1		1		8		15	
Temp (°C)	129		136		142		142		142	
1,4-diol	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*
Conversion	28.4	14.1	64.8	37.7	85.1	58.8	—[b]	—[b]	—[b]	—[b]
Composition of reacted product (mole %)										
Cyclohexane	21	15	37	40	50	52	16	9	15	16
Cyclohexanol	48	69	43	44	32	34	60	78	65	79
1,4-Epoxycyclohexane	31	16	20	15	17	14	24	13	20	5
R[c]	1.9		1.3		1.2		1.9		4.0	

[a] Experimental conditions: catalyst 200 mg, ~150–200 mesh size; hydrogen flow, 100 ml/min; injection 10 μl.

[b] Unreacted diol was not completely recovered, and thus the exact estimation of conversion could not be given. From quantitative observation it seems that the conversion decreases with pressure.

[c] Ratio of epoxyclyclohexane from *trans* to *cis*-diol.

nickel (*2*). The experimental results which are given in Table 1 show that the *trans*-diol reacts more readily and produces higher yields of 1,4-epoxycyclohexane than the *cis*-diol. It is uncertain whether the *cis*-diol actually produces the epoxide or whether it epimerizes first to the *trans*-diol, and the latter forms the epoxide. At 126°, 20% and at 148°, 31% of the recovered cyclohexanediol was epimerized from *cis*- to *trans*-diol. The epimerization most probably occurred via a dehydrogenation–hydrogenation step:



In agreement with this postulate the ratio of 1,4-epoxycyclohexane produced from *trans*- over *cis*-diol greatly increases when the reaction is made under pressure; at 142° the ratio is 1.2, 1.9, and 4.0 at pressures of 1, 8, and 15 atm.

Cyclohexane was most probably produced, in major part, as a consequence of the hydrogenolysis of epoxycyclohexane. An experiment made with 1,4-epoxycyclohexane over the nickel-kieselguhr catalyst at 137° showed that 30% of the 1,4-epoxycyclohexane reacted to 95% cyclohexane and 5% cyclohexanol.

The preferential formation of 1,4-epoxycyclohexane from *trans*-1,4-cyclohexanediol is an indication that the elimination of water from alcohols in the presence of nickel–kieselguhr proceeds via a trans-elimination reaction requiring the participation of intrinsic acidic and basis sites of the nickel catalyst. In this respect the reaction is very similar to the dehydration reactions over aluminas.

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The Activities of Lead Oxide-Silica Gel Catalyst for Acrylonitrile Synthesis from Propylene and Nitric Oxide

A catalytic process was patented for acrylonitrile synthesis from propylene and nitric oxide that employs lead titanate catalyst (*1*). We have reported that the activity of this kind of catalyst depends on the valence change of lead (*2*). A new type catalyst, lead oxide supported on silica gel, is investigated in this paper which showed high activity for the reaction. It seems reasonable to conclude that lead ion (II) plays a role of the active center in this catalyst from the result of correlation between the X-ray diffraction and activity for acrylonitrile formation (*2*). The effects of lead oxide concentration on the conversions of propylene and nitric oxide and on the selectivities of the products are also examined to elucidate the working state of the catalysis. The products of this reaction are acrylonitrile, acetonitrile, carbon dioxide, and higher boiling materials.

Experimental

The experiments were carried out with a conventional fixed-bed flow reactor heated in a cylindrical furnace. The purity of propylene was 99.8%, and the impurities were propane and ethane. Nitric oxide was produced by adding ferrous sulfate powder into aqueous solution of sodium nitrate (*3*). A small amount of higher oxides of nitrogen was removed by 10% aqueous sodium hydroxide solution. The purity of nitric oxide was 97% and nitrogen was detected as a sole impurity. Nitrogen was also fed to reactor as a diluent gas. The catalyst was prepared in the following way. Aqueous solution of lead nitrate was added dropwisely over a period of several hours to the rapidly stirred aqueous slurry of silica gel (60–80 mesh, having a BET surface area of 530 m^2/g) heated in an oil bath maintained at 120–130°C. The quantity of lead nitrate was dosed to give the desired concentration of lead ion in the finished catalyst. The aqueous slurry of the silica gel was subjected to heat in an oil bath for additional 3 hr followed by evaporation to dryness in an oven at 100°C, and formed into tablets of 3 mm dia. × 2 mm. Prior to use, the tablets were calcined in air at 500°C for 6 hr. The liquid products were analyzed by packed column gas chromatography (10% of di-nonyl phthalate on Chromosorb-W). Analyses of propylene and nitric oxide at the inlet and outlet of the reactor were made by gas chromatography by use of the columns packed with alumina and molecular sieve 5A, respectively. The temperature of the reaction zone was controlled within ±1°C.

Results and Discussion

Lead oxide carried on the catalyst were from 0.6 to 35.1 wt %. Lead atoms were proved to be well dispersed on the surface of silica gel by X-ray diffraction and electronic microscope as well (*2*). Fig. 1 shows the marked linear increase in catalytic activity with the increase in lead ion concen-