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Dehydrogenation and Amination of Cyclohexanol by Pt Catalysts

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The reaction paths for dehydrogenation and amination of cyclohexanol over Pt/C catalysts have been studied in a continuous-flow microreactor. Dehydrogenation in the absence of adsorbed hydrogen results in parallel path formation of cyclohexanone and phenol. With adsorbed hydrogen, products are limited to cyclohexane, benzene, and cyclohexanediol. Amination proceeds via a strongly adsorbed cyclohexylamine intermediate produced from reaction of vapor-phase cyclohexanol with adsorbed NH species. Deactivation is due to surface fouling by strongly held polymeric material.

INTRODUCTION

Aniline is manufactured commercially by the catalytic hydrogenation of nitrobenzene and the amination of chlorobenzene. Multistage processes are required with feed stocks such as cyclohexanol. A more attractive single stage process based on the dehydrogenative amination of cyclohexanol has been described by Barker (*1*) and by Carrubba and Golden (*2*), but very little has been published on the mechanism or kinetics. The purpose of this research was to study the reaction paths for cyclohexanol amination over supported Pt catalysts and to describe the deactivation of these catalysts.

Possible reaction paths are shown in Fig. 1. Thermodynamic standard free energy changes for each step at 300°C were calculated from the data of Stull *et al.* (*3*). Path (1a) is hydrogenolysis of the C–OH bond, followed by (1b), dehydrogenation to benzene. All other paths involve dehydrogenation and dehydroxylation followed by amination or vice versa.

According to Swift and Bozik (*4*) vapor-phase dehydrogenation of both cyclohexanol and cyclohexanone results in phenol over Ni/SiO_2 catalysts. This agrees with earlier work by Orzechowski (*5*) who found cyclohexanone to be the intermediate. Takagi *et al.* (*6*) demonstrated with deuterium exchange of cyclohexanol over noble metal catalysts that only the hydroxyl hydrogen was replaced. This implies a mono-adsorbed species involving OH dissociation in the presence of hydrogen. For Pt catalysts, these authors also showed that cyclohexanone hydrogenation, and presumably cyclohexanol dehydrogenation, proceeds via an intermediate di-adsorbed at the hydroxyl and C-1 positions. Paál *et al.* (*7*) used radiotracer measurements to confirm that Pt provides a direct pathway for the dehydrogenation of cyclohexanol to phenol whereas Cu and Ni give phenol exclusively via cyclohexanone.

Except for the patent literature, the only published results on cyclohexanol amination are those of Kozlov and Akhmetshina (*8*) and Kliger (*9*). Kozlov and Akhmetshina used Al_2O_3 as the catalyst and found that path (1a) occurred at pressures of 5–10 atm. Kliger used a sintered iron catalyst and reported 85% conversion to aniline at 250°C, 50 atm, $NH_3:H_2$ ratio of

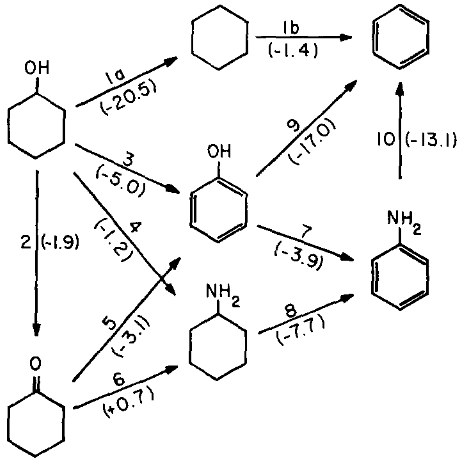


FIG. 1. Possible reaction paths for cyclohexanol dehydrogenation and amination. Values in parentheses are the standard Gibbs free energies kilocalories per mole at 300°C.

0.7, and a space velocity of 250 g l^{-1} hr^{-1}. These authors showed the presence of cyclohexylamine, presumably as an intermediate.

Process conditions and product distributions claimed in the relevant patents are given in Tables 1 and 2. It is significant that none of these authors reported the formation of cyclohexanone, neither was any large amount of benzene or cyclohexane found. No deactivation studies were made and no kinetic data given.

EXPERIMENTAL

The continuous-flow microreactor used in this study is shown in Fig. 2. Purified hydrogen was mixed with ammonia in the desired ratio and passed through a feed saturator containing liquid cyclohexanol at 95°C, so that a partial pressure of 0.066 atm of cyclohexanol vapor was established. The maximum flow rate of the mixed hydrogen and ammonia was 100 ml/min. For most of the measurements reported here, the mole ratio of NH_3 to H_2 was maintained at 2 while the flow rate was varied to change the residence time. This change in flow rate had little effect on the partial pressure of cyclohexanol. All lines beyond the saturator were heated in order to keep the temperature above 95°C and thus prevent condensation.

TABLE 1

Process Conditions: R. S. Baker (*1*)

Catalyst	Pt/C
Feed	$NH_3:H_2:C_6H_{12}O = 16:1:1$
Temperature	315°C
Pressure	12 psig
LHSV	0.5
Conversion	100%
Product	89% aniline 5% cyclohexylamine 5% benzene 1% higher-boiling material

TABLE 2

Process Conditions: R. V. Carrubba and R. L. Golden (*2*)

Catalyst	Pt/SiO_2
Feed	$NH_3:H_2:C_6H_{12}O = 8:4:1$
Temperature	315°C
Pressure	50 psig
LHSV	0.5
Conversion	87.3%
Product	89% aniline 11% cyclohexylamine

The feed passed downflow through the reactor, a $\frac{1}{4}$-in.-i.d. stainless-steel tube with a 2-cm bed. Catalyst loadings of from 0.05

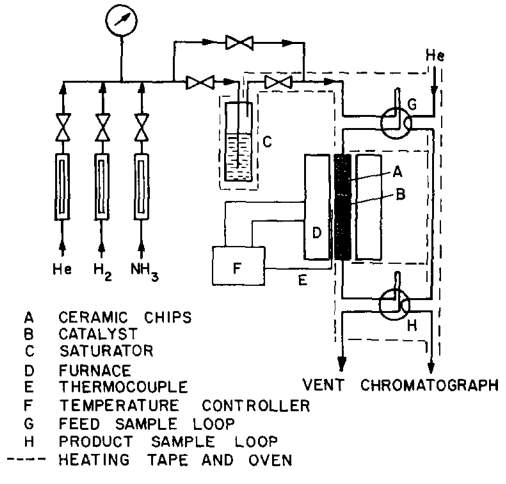


FIG. 2. Experimental reactor system.

to 0.2 g were crushed to a mesh size of 80–90 and mixed with inert particles of the same size.

Gas sampling valves were located on both sides of the reactor to allow pulses of either the feed or the product to be injected into the chromatograph. This was an F & M 700 gas chromatograph with a flame ionization detector. The analytical system included two 10-ft × $\frac{1}{8}$-in. columns of 70/80 mesh GP 29 Carbowax on Anakrom ABD, programmed to operate at 20°C/min from 100 to 250°C. Calibration and retention times were compiled for all possible compounds.

The catalysts were 0.5% Pt/C and 0.5% Pt/Al_2O_3 manufactured by Englehard Industries. Each catalyst was reduced at 300°C in hydrogen for 16 hr. A series of dehydrogenation runs was first made at 300°C, initially with helium and then with hydrogen as the feed carrier. After reloading with a fresh catalyst, the feed carrier was changed to the ammonia–hydrogen mixture for the amination measurements. This took 12 hr to complete. The flow rate was then maintained at a fixed value and the deactivation data taken over a period of about 400 hr.

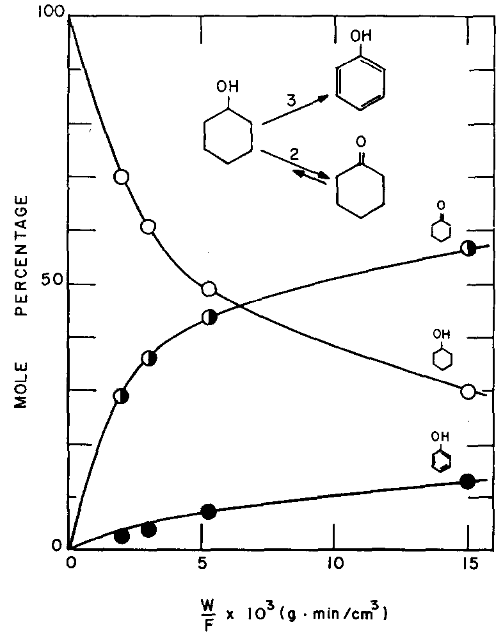


FIG. 3. Dehydrogenation of cyclohexanol with helium carrier gas.

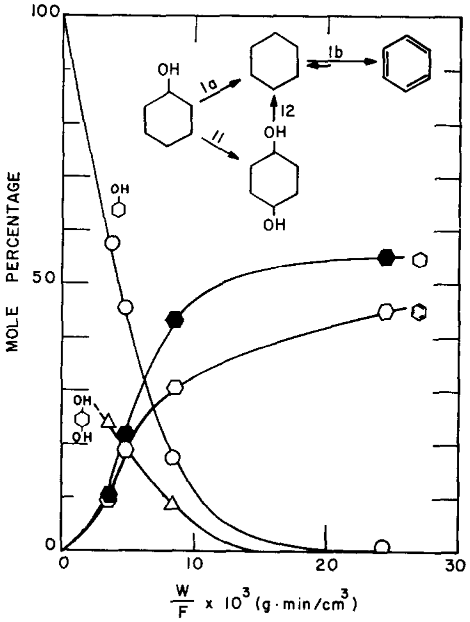


FIG. 4. Dehydrogenation of cyclohexanol with hydrogen carrier gas.

RESULTS

1. *Dehydrogenation*

Dehydrogenation of cyclohexanol gives very different results depending on whether helium or hydrogen is used as the carrier gas for the reaction stream. Product distributions with helium are shown in Fig. 3. The only reactions are the parallel paths (3) and (2), resulting in dehydrogenation of either the ring or the hydroxyl group to form phenol and cyclohexanone, respectively. Equilibrium is not achieved and the disappearance of the cyclohexanol is not simple order but follows a complex product-inhibition pattern.

Product distributions in the presence of hydrogen are given in Fig. 4. In this case the main products are cyclohexane, benzene, and small amounts of cyclohexanediol.

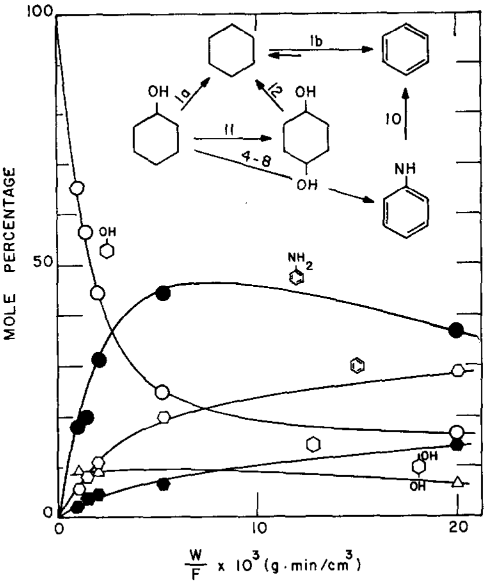


Fig. 5. Amination of cyclohexanol.

Cyclohexane is present in excess of equilibrium so that the sequence of reaction steps is (1a), hydrogenolysis of the C–OH bond, followed by (1b), dehydrogenation to benzene. No cyclohexanone or phenol was found. Chromatographic identification indicated that the 1,4-form of cyclohexanediol predominated. The initial large amount of this compound suggests the series path (11) and (12).

The disappearance of cyclohexanol does not follow a product-inhibited behavior but appears to be close to zero order.

2. Amination

Ammonia–hydrogen mixtures yield the product distribution shown in Fig. 5. Cyclohexane, benzene, and cyclohexanediol originate by steps (1a), (1b), and (11). Aniline concentration passes through a maximum indicating a series reaction (*4–8*) and (*10*). No phenol or cyclohexylamine was detected over the fresh catalyst. However, with deactivation a measurable amount of cyclohexylamine was found. This implies that a strongly adsorbed cyclohexylamine intermediate precedes the desorption of aniline so that steps (4) and (8) are followed. Steps (6) and (8) are also possibilities if the hydrogen partial pressure is small enough so that the formation of cyclohexanone is not inhibited. Since Fig. 5 shows no cyclohexanone, even at low conversions, it appears that these steps are absent for these conditions. Desorption of cyclohexylamine does not occur until a sufficiently large surface concentration is achieved as the process time increases. Cyclohexanol disappearance is not first order but shows very pronounced inhibition by adsorbed products or the intermediate cyclohexylamine species. Cyclohexanol conversions are much less than equilibrium values so that the back reaction is not responsible for the decrease in rate. In all of these measurements, the integral reactor results are not precise enough to allow evaluation of the complex rate equations.

3. Deactivation of the Catalyst

Product distributions for runs up to 400 hr are shown in Fig. 6 and indicate a very pronounced deactivation of the cata-

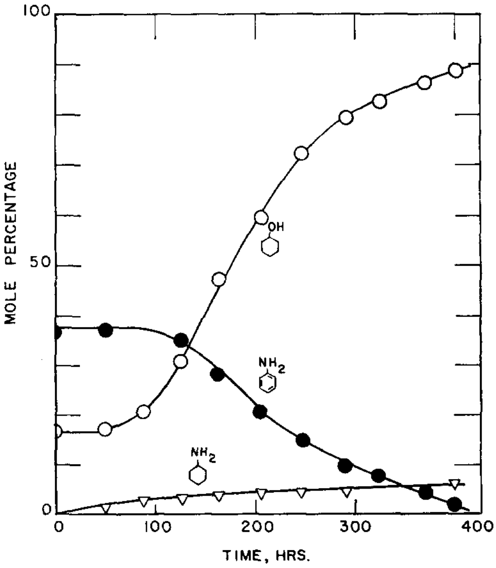


Fig. 6. Deactivation of cyclohexanol amination reaction (W/F constant at 2.0 × 10^{-3} g·min/cm^3).

TABLE 3

Hydrogenative Regeneration of Deactivated Catalysts

Product	Mole percentage of product		
	Before regeneration	First regeneration (16 hr)	Second regeneration (16 hr)
Cyclohexanol	90.0	82.5	81.9
Cyclohexane	0.7	1.5	1.9
Benzene	0.6	4.2	3.7
Aniline	3.9	11.8	12.5

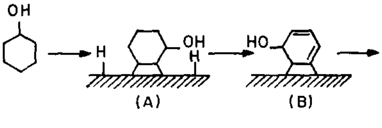
lyst. Conversion and aniline production drops steadily but selectivity to benzene and cyclohexane also decreases with deactivation. Small amounts of cyclohexylamine appear as the deactivation increases. Regeneration in pure hydrogen was only partially successful in restoring the original activity, as demonstrated in Table 3.

The experiments outlined above were repeated with Pt/Al_2O_3 catalysts. Results were almost identical, so that the nature of the support plays no role in establishing the reaction path.

DISCUSSION

Under these conditions, dehydrogenation is not equilibrium limited, either with or without external hydrogen. The effect of excess hydrogen is to change the mechanistic path. Low cyclohexanol partial pressures in helium carrier gas result in dehydrogenation to cyclohexanone and phenol, with the former predominating. With an excess of hydrogen, however, these products are excluded and dehydrogenation proceeds to cyclohexane and benzene. A parallel reaction, the formation of cyclohexanediol, also occurs.

At this point we may only speculate on the nature of the adsorbed intermediates consistent with these observations. Since absorbed hydrogen prevents the formation of cyclohexanone and phenol, these compounds may result from a multi-point adsorbed complex. Initial adsorption could occur at either a C–C or a C–OH pair. These would both require four adjacent metals atoms to accommodate the hydrocarbon and hydrogen atoms. Thus, possible reaction paths are



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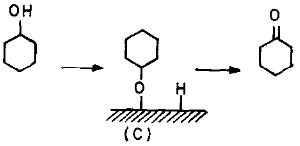


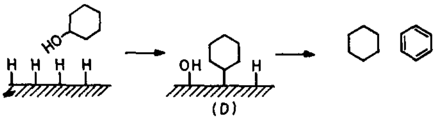
II

In path (I), intermediate (A) is formed and followed by stepwise dehydrogenation to (B) which then desorbs as phenol. Path (II) originates with (C), which desorbs as cyclohexanone. The absence of cyclohexane in the product implies that the rupture of the C–O bond in (C) does not take place. Path (II) is about four times faster than path (I). Support for intermediate (C) was found by Takagi *et al.* (*6*) using deuterium exchange. These authors found no ring exchange, but neither was phenol formed under their conditions. The existence of (A), however, is very likely in view of the well-known ability of Pt to dehydrogenate cyclohexane. The question of path (5), the formation of phenol via cyclohexanone, is not resolved by the data of Fig. 3. Paál *et al.* (*7*) indicate both paths (3) and (2–5) with Pt, although the former predominates. In this case a possibility is the adsorption of cyclohexanone as (C) followed by conversion to (A) and then to phenol via (B). These mechanisms imply a rate equation of the form

$$\text{rate} = \frac{kb_A P_A}{(1 + b_A P_A + b_K P_K + b_P P_P)}$$

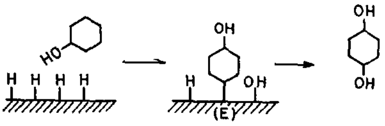
where the subscripts A, K, and P refer to cyclohexanol, cyclohexanone, and phenol respectively. The results in Fig. 3 qualitatively follow this type of expression, although exact evaluation of the constants was not attempted.

With excess hydrogen, the surface is saturated with adsorbed hydrogen atoms. Species (A) and (B) are less likely to form since the required spacing of vacant sites is more difficult. However, the hydroxylic hydrogen of the cyclohexanol may hydrogen bond with adsorbed hydrogen leading to the path



III

The C–O bond of the cyclohexanol is weakened by the polarization of the adsorbed hydrogen atoms, resulting in rupture with adsorption of species (D), which desorbs as cyclohexane or undergoes stepwise dehydrogenation to benzene. This last process must be a fairly slow step since adjacent pairs of surface atoms are required. An alternate intermediate involving single-point dissociative adsorption at the oxygen atom, as in (C), must be ruled out, since this would also yield cyclohexanone. The presence of 1,4-cyclohexanediol is indeed puzzling. It is produced very rapidly in the initial phase of the reaction and is quickly converted to cyclohexane and benzene. It does not occur in the absence of hydrogen since no benzene or cyclohexane results. It would appear that adsorbed hydrogen again forces a single-point absorption, thus

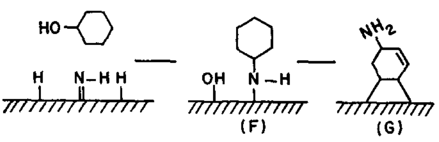


IV

Takagi *et al.* (*6*) found no deuterium exchange with the ring hydrogen of cyclohexanol, thus disputing the existence of (E). Possibly the presence of the OH surface species modifies the sites sufficiently to allow (E) or the reaction may be directly between molecular cyclohexanol and adsorbed OH. It is anticipated that a transition from path (III) to paths (II) and (I) would occur as the partial pressure of hydrogen is lowered below that necessary to sustain a mono-layer coverage.

If the rate equation is indeed zero order, as implied in Fig. 4, then the formation of species (D) and (E) is very rapid and all possible sites are saturated with strongly absorbed molecules.

In attempting to speculate on the surface mechanism for cyclohexanol dehydrogenation in the presence of ammonia, it is necessary to explain the absence of cyclohexylamine as a vapor-phase intermediate and the fact that cyclohexane (or benzene) does not react with ammonia. If the mechanism involved species (D), then reaction between cyclohexane and ammonia would be possible. The surface intermediate may be a complex involving cyclohexanol and adsorbed ammonia. Furthermore, this complex must undergo ring dehydrogenation before desorption takes place. Transition from (F) to (G) proceeds via a stepwise (or multiple) desorption–adsorption path. Thus,



V

may occur with subsequent desorption of aniline. The surface is covered with adsorbed hydrogen atoms and ammonia species in various degrees of dehydrogenation. Formation of species (F) requires that the presence of the hydroxyl group sufficiently perturbs the ring energy so that adsorption on the nitrogen may occur. Cyclohexane is presumably unable to do this. The aminated species must be strongly adsorbed since strong product inhibition is present. Cyclohexanol and the dehydrogenated products are weakly held by comparison. Reaction paths (4–8) occur in competition with (1a) and (1b). Cyclohexanone has not been considered as an intermediate in the formation of cyclohexylamine since cyclohexanone was not detected in the presence of hydrogen alone nor in the products shown in Fig. 5. With lower hydrogen concentration, however, path (2–6–8) may be a possibility. It is not possible at this time to demonstrate the slow step in the mechanism but rate equations of the type

$$\text{rate} = kb_AP_A/(1 + \sum b_iP_i)$$

are to be expected.

Deactivation may be caused by sintering, oxidation of the platinum by the hydroxyl groups formed, or fouling of the surface by carbonaceous residues resulting from slow but extensive dehydrogenation of the many adsorbed species or the products of their polymerization, etc.

Sintering is unlikely to be a significant factor under these conditions. Oxidation is possible but improbable with the excess hydrogen used in these experiments. However, under process conditions involving low hydrogen partial pressures, surface oxidation may become extensive.

Deactivation is obviously due to some type of surface fouling. This manifests itself in the steady decline of overall activity and the appearance of cyclohexylamine with loss of available sites for ring dehydrogenation.

Since hydrogenation does not regenerate the catalyst, the residue must involve considerable polymerization and dehydrogenation and can only be removed by oxidation. It is impossible to deduce the exact nature of the polymer. It could originate from either cyclohexanediol or from secondary amines. In view of the demonstrated reactivity of cyclohexanediol to cyclohexane and benzene, secondary amines are more likely. Further work will be necessary to elucidate this point.

Improved selectivity to aniline would be achieved by operation at lower hydrogen pressures, but this might also result in shorter catalyst life. Low conversions with recycle or cyclic operation of several reactors with frequent oxidative regeneration may offer improved process performance.

Since both ammonia dissociation and dehydrogenation activity are necessary for cyclohexanol amination to aniline, successful catalyst systems will be found, like platinum, among the Group VIII metals. In particular, the Group VIII_3 metals, with strong dehydrogenation activity but weakly held nitrogen intermediates offer the best candidates. There is no evidence for dual site involvement or for active support effects.

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REFERENCES

1. Baker, R. S., U. S. Patent 3,442,950 (1969).
2. Carrubba, R. V., and Golden, R. L., U. S. Patent 3,347,921 (1967).
3. Stull, D. R., Westrum, E. F., Jr., and Sinke, G. C., "The Chemical Thermodynamics of Organic Compounds." John Wiley, New York, 1969.
4. Swift, H. E., and Bozik, J. E., *J. Catal.* **12**, 5 (1968).
5. Orzechowski, A., *Mem. Soc. Roy. Sci. Liege* **12**, 11 (1952).
6. Takagi, Y., Teratani, S., and Tanaka, K., *J. Catal.* **27**, 79 (1972).
7. Paál, Z., Peter, A., and Tetenyl, P., *React. Kinet. Catal. Lett.* **1**, 121 (1974).
8. Kozlov, W. S., and Akhmetshina, L., *Dokl.Akad. Nauk SSSR* **85**, 91 (1952).
9. Kliger, G. A., *Neftkhimiya* **5**, 569 (1965).