

## Catalytic Transformations of Cyclohexanol on Group VIII Metal Catalysts

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Transformations of cyclohexanol and cyclohexanone have been studied over various Group VIII metals as catalysts. For each metal the predominant reaction of cyclohexanol was dehydrogenation to cyclohexanone. Two main groups of metals can be distinguished. Selectively *dehydrogenating metals* are those where dehydrogenation stops at the stage of cyclohexanone (Os, Co, Fe, Re, Ru). *Aromatizing metals* catalyze also the further dehydrogenation of cyclohexanone to aromatics (Pd, Pt, Ni). Rh and Ir occupy an intermediate position: they dehydrogenate in nitrogen and aromatize in hydrogen. Radiotracer methods show that cyclohexanone is the intermediate of phenol formation, except for Pt and Pd where there is a "direct" route of phenol formation from cyclohexanol. Benzene is the product of the hydrogenolytic splitting of the phenolic OH group. Dehydration of cyclohexanol to cyclohexene is not important, although it occurs over some dehydrogenating metals. Ru is the only metal where there is considerable additional formation of benzene *via* cyclohexene. Hydrogenolysis of the alcoholic OH group was not observed. Hydrogenolysis of the C-C bond of the ring is favoured by hydrogen carrier gas; it is considerable over dehydrogenating metals as well as Rh and Ir. The enhanced reactivity of cyclohexanol as compared with cyclohexane is due to the presence of the OH group facilitating the interaction of the molecule with the surface. Knor's model of localized/free-electron interplay as well as the number of unpaired *d* electrons could be used to interpret the different activity of various metals.

### INTRODUCTION

Cyclohexanol undergoes mainly dehydrogenation on reaction over metal catalysts. Its primary product is cyclohexanone; a deeper dehydrogenation may also give phenol (1-3). The hydrogenolytic splitting of the OH group from phenol to give benzene has been observed over Pt (3, 4). The analogous reaction has been claimed with the OH group of cyclohexanol (5) but our previous results disproved this process over nickel (1) and platinum (6).

Radiotracer studies demonstrated a stepwise cyclohexanol  $\rightarrow$  cyclohexanone  $\rightarrow$  phenol dehydrogenation over copper and nickel (1, 2), whereas also a direct cyclohexanol  $\rightarrow$  phenol route was observed over platinum (2, 6). Dehydration to cyclohexene was negligible over these metals but considerable under the effect of alumina (5) or even carbon (6) support.

Our studies in the field of catalytic trans-

formations of cyclic and aliphatic hydrocarbons (7, 8) over several Group VIII metals stimulated us to extend the study to cyclohexanol transformations over these metals. The catalytic reactions of cyclohexane seem to represent some analogy. As far as activity of various metals is concerned, maximum dehydrogenation activity was observed with fcc metals of atomic diameters between 0.268 and 0.277 nm (Rh, Ir, Pd, Pt). A similar maximum appeared with cph metals in the same diameter range (Ru, Re) with absolute values of about 1-1.5 orders of magnitude lower. The dehydrogenation activity of bcc metals was lowest (9). As far as the reaction pathway is concerned, Pt and Pd gave benzene practically without any cyclohexene intermediate; intermediate cyclohexene formation was considerable over Ni and Co, whereas Rh and Ir had an intermediate position (7). This represents another regularity: the selectivity of metals in cyclohexene formation is

correlated with their position in the Periodic Table (consequently with their electron structure). It is a matter of great interest how the introduction of an oxygen atom into the molecule affects its reactivity. One would expect that the molecule reacts with participation of its polar oxygen atom which results in an enhanced total reactivity together with the increase of selectivity of products formed via interaction of the oxygen atom and the catalyst surface.

This paper attempts to sum up the main results of an extended work carried out in the field of catalytic transformations of cyclohexanol. Because of the usually high rate of its dehydrogenation, the reaction mixture contained in several cases high amounts of cyclohexanone. This justified the study of the reactions of cyclohexanone, too. Several experimental details have been or are being reported elsewhere (1, 4, 6, 10, 11); here some activity and selectivity data as well as radiotracer measurements and spectroscopic evidence (12–14) will be used to evaluate the correlations between the nature of a metal and its catalytic properties.

#### EXPERIMENTAL

**Apparatus.** The pulse-microcatalytic apparatus, suitable also for carrying out radiotracer experiments, was described in Ref. (3), together with the analytical procedure.

**Reagents.** Cyclohexanol, cyclohexanone, cyclohexane, and cyclohexene were of 100% purity as shown by gas chromatographic analysis (sensitivity:  $10^{-3}$  mol%). [ $1-^{14}\text{C}$ ]Cyclohexanol was synthesized in our Institute<sup>1</sup> and contained no detectable impurities. It was used as a component of mixtures with inactive cyclohexanone, cyclohexane, and cyclohexene. The specific activity of the mixtures was about 4 MBq/cm<sup>3</sup>.

**Catalysts.** Unsupported metals were used.

<sup>1</sup> The authors express their gratitude to Mrs. E. Bursics-Szekeres for kindly performing this synthesis.

Specific surfaces and crystallite sizes of the catalysts are shown in Table 1. Details of preparation, regeneration, etc., are reported in Refs. (10, 11).

#### RESULTS

##### (a) Activity and Selectivity

Typical conversion values (per unit catalyst surface) of cyclohexanol are shown in Table 2. Similar values for its important dehydrogenation product, cyclohexanone, have been collected in Table 3. Due to the marked effect of hydrogen on platinum-catalyzed reactions (e.g., (3)), results obtained in nitrogen and hydrogen atmospheres are compared in both tables.

Data in Tables 2 and 3 correspond mostly to medium 20–40% conversion of the pulse

TABLE 1  
Specific Surfaces and Crystallite Sizes of the Catalysts<sup>a</sup>

Metal	Specific surface (m <sup>2</sup> g <sup>-1</sup> )	Crystallite size (nm)	Remarks
Fe	8.0	—	Reduced from (COO) <sub>2</sub> Fe
Co-powder	2.5	60	Pure fcc
Co-black	10.8	22	1:1 fcc and cph
Ni	4.6	45	Reduced from Ni(OH) <sub>2</sub>
Ru	30.0	90	Precipitated
Rh	1.8	30	by HCHO in aqueous medium
Pd	3.7	34	
Re	7.0	22	Reduced from NH <sub>4</sub> ReO <sub>4</sub>
Os	1.5	50	Commercial powder
Ir(I)	3.7	32	Precipitated by HCHO
Ir(II)	7.3	—	Catalyst No. 2 from Ref. (15)
Pt	2.9	55	Precipitated by HCHO

<sup>a</sup> The authors are indebted to Drs. L. Kertész and I. Manninger for X-ray diffraction measurements as well as to Mr. L. Tóth for specific surface (N<sub>2</sub>/BET) determinations.

TABLE 2  
 Activity of Various Metals in Cyclohexanol Transformations<sup>a</sup>

Metal	Gas	10 <sup>16</sup> molecules/m <sup>2</sup> catalyst						
		Overall activity	<C <sub>6</sub>	C <sub>6</sub> H <sub>12</sub> + C <sub>6</sub> H <sub>10</sub>	C <sub>6</sub> H <sub>10</sub> O	C <sub>6</sub> H <sub>5</sub> OH	C <sub>6</sub> H <sub>6</sub>	Others <sup>b</sup>
Os	N <sub>2</sub>	640	5	1	611	20	3	—
	H <sub>2</sub>	1129	538	8	574	4	5	0.5
Co(p)	N <sub>2</sub>	3427	8	10	3275	117	6	10
	H <sub>2</sub>	2573	25	24	2434	84	3	4
Co(b)	N <sub>2</sub>	998	36	33	789	91	19	30
	H <sub>2</sub>	1046 (1500 <sup>c</sup> )	769	28	71	34	56	89
Fe	H <sub>2</sub>	387	10	157	200	11	3	6
	N <sub>2</sub>	1879	5	314	1442	46	65	6
Re	H <sub>2</sub>	1711 (2050 <sup>c</sup> )	306	544	800	24	32	7
	N <sub>2</sub>	277	—	71	187	7	13	—
Ru	H <sub>2</sub>	333	103	12	169	17	32	—
	N <sub>2</sub>	558	9	0.2	442	99	5	3
Rh	H <sub>2</sub>	2600	1932	—	99	95	462	11
	N <sub>2</sub>	688	136	0.5	452	70	27	3
Ir(I)	H <sub>2</sub>	1167	540	3	270	232	117	6
	N <sub>2</sub>	1852	38	3	800	868	53	90
Ni	H <sub>2</sub>	1343	60	—	843	376	49	15
	N <sub>2</sub>	1205	9	—	17	960	218	1
Pd	H <sub>2</sub>	814	—	2	243	495	74	—
	N <sub>2</sub>	1762	11	0.5	193	921	636	—
Pt	H <sub>2</sub>	1655	20	19	440	777	400	—

<sup>a</sup>  $T = 573$  K, pulse system, pulses of 1  $\mu$ l each; conversion calculated per standard pulse.

<sup>b</sup> Mainly C<sub>6</sub>-oxygenated products (*n*-hexanal and hexanones).

<sup>c</sup> Extrapolated on the basis of temperature dependence because of too high conversion at the given temperature.

of feed. The overall conversion of cyclohexanone is almost always lower than that of cyclohexanol, except for three cases (Rh in H<sub>2</sub> and Pd in both H<sub>2</sub> and N<sub>2</sub>).

Hydrogen generally accelerates overall conversion. This effect is more obvious for cyclohexanone. Ni, Pd, and Pt (with cyclohexanol, also Co-powder) are the metals where lower conversions are obtained in hydrogen atmosphere than in inert gas (Table 4).

In addition to overall conversions, the activity for individual products has also been calculated and shown in Tables 2 and 3, as the amount of molecules formed per

unit surface. This way was preferred in this work to the "product ratio" proposed by some workers (16).

Dehydrogenation to cyclohexanone is the main reaction of cyclohexanol in nitrogen. More or less phenol and benzene are also observed, especially with Ni, Pd, and Pt. These are the metals where aromatization of cyclohexanone is also remarkable. Hydrogen accelerates cracking reactions; dehydrogenation and aromatization are influenced to a much lesser extent. Hydrogenation of cyclohexanone is promoted by hydrogen although Co powder is the only metal where this reaction is considerable.

TABLE 3  
Activity of Various Metals in Cyclohexanone Transformations<sup>a</sup>

Metal	Gas	10 <sup>16</sup> molecules/m <sup>2</sup> catalyst							
		Overall activity	<C <sub>6</sub>	C <sub>6</sub> H <sub>12</sub> + C <sub>6</sub> H <sub>10</sub>	C <sub>6</sub> H <sub>11</sub> OH	C <sub>6</sub> H <sub>5</sub> OH	C <sub>6</sub> H <sub>6</sub>	C <sub>6</sub> H <sub>6</sub> O	Others <sup>b</sup>
Os	N <sub>2</sub>	18	1.8	0.2	—	3.6	0.8	11.6	—
	H <sub>2</sub>	627	485	7	125	5	4	—	1
Co(p)	N <sub>2</sub>	133	2	0.4	—	36.3	1.1	91	2
	H <sub>2</sub>	740	50	27	543	103	9	—	8
Co(b)	N <sub>2</sub>	100	14	9	13	40	13	7	4
	H <sub>2</sub>	920	689	32	37	37	41	—	84
Fe	H <sub>2</sub>	215	13	121	58	14	2.5	—	6.5
Re	N <sub>2</sub>	268	3	90	14	59	63	30	10
	H <sub>2</sub>	1150	413	478	161	34	53	—	11
Ru	N <sub>2</sub>	8	—	1.5	4	2.5	—	—	—
	H <sub>2</sub>	150	109	4	22	8	7	—	—
Rh	N <sub>2</sub>	125	3	—	—	114	4	2	2
	H <sub>2</sub>	3444	1803	—	42	876	697	—	25
Ir(I)	N <sub>2</sub>	136	51	—	—	69	11	4	1
	H <sub>2</sub>	948	490	2	86	233	131	—	6
Ni	N <sub>2</sub>	691	19	—	21	574	21	9	46
	H <sub>2</sub>	617	40	—	271	268	28	—	10
Pd	N <sub>2</sub>	2200 <sup>c</sup>	10	—	1	1980	200	—	1
	H <sub>2</sub>	951	—	3	59	808	81	—	—
Pt	N <sub>2</sub>	1607	15	—	14	1028	552	—	—
	H <sub>2</sub>	1410	16	17	210	833	333	—	1

<sup>a</sup>  $T = 573$  K, pulse system, pulses of  $1 \mu\text{l}$  each; conversion calculated per standard pulse.

<sup>b</sup> Mainly oxygenated C<sub>6</sub> products (*n*-hexanal and hexanones).

<sup>c</sup> Extrapolated on the basis of the temperature dependence because of too high conversion at the given temperature. Selectivity values actually measured were used to calculate the yields of individual compounds.

TABLE 4  
The Ratio of Reactivities over Various Metals

Metal	Os	Co(p)	Co(b)	Fe	Re	Ru	Rh	Ir(I)	Ni	Pd	Pt
$X_{\text{H}}/X_{\text{N}}$ (-ol)	1.8	0.75	1.5 <sup>a</sup>	—	1.1 <sup>a</sup>	1.2	4.7	1.7	0.73	0.68	0.9
$X_{\text{H}}/X_{\text{N}}$ (-one)	35	5.6	9.2	—	4.3	19	27	7.0	0.90	0.62	0.88
$r_{\text{ol}}/r_{\text{one}}$ N <sub>2</sub>	36	26	10	—	7.0	35	4.5	5.0	2.7	0.8	1.1
$r_{\text{ol}}/r_{\text{one}}$ H <sub>2</sub>	2.3	3.5	1.1	1.8	1.5	2.2	0.75	1.2	2.2	0.6 <sup>a</sup>	1.2

Note.  $T = 573$  K.  $X_{\text{H}}/X_{\text{N}}$ : the ratio of conversions measured in hydrogen and nitrogen for cyclohexanol (-ol) and cyclohexanone (-one), respectively.  $r_{\text{ol}}/r_{\text{one}}$ : the ratio of conversions of cyclohexanol and cyclohexanone, in nitrogen and hydrogen, respectively.

<sup>a</sup> Extrapolated values (cf. footnote *c* of Tables 2 and 3).

Various metals promote individual reaction steps to various extents, and therefore various products predominate. The compositions seen in the tables are produced by consecutive and parallel reactions (they are not initial compositions). It was necessary, however, to select such high conversions to obtain information on slower processes, too. Considering the data shown in Tables 2 and 3, the following classification of metals can be given:

1. Group A consists of Os, Co, Re, Ru, and Fe. They promote cyclohexanone formation, and therefore they are called *dehydrogenating metals*. Cyclohexane and cyclohexene always appear but their amount is considerable over Re only. Both cyclohexanol and cyclohexanone give phenol with rather low yields. Its intermediate, cyclohexenone appears with cyclohexanone (and in rare cases, also with cyclohexanol) feed.

2. Group B consists of Ni, Pd, and Pt. They form rather high amounts of phenol and also benzene and are called *aromatizing metals*.

3. Group C includes Rh and Ir and represents a transition between the above two groups.

These groups also differ from each other as far as the effect of *hydrogen* is concerned. Hydrogen enhances *cracking*, especially of cyclohexanone, with Group A metals (Tables 2 and 3). At the same time, it suppresses dehydrogenation and aromatization processes; Co-black is the only metal where this reaction of cyclohexanol is strongly hindered. No cyclohexenone is observed in hydrogen: dehydrogenation may be slowed down but goes to aromatics. Co powder and nickel produce most cyclohexanol (Table 3). Another common feature of Ni and Co is their close  $X_H/X_N(-ol)$  values (Table 4).

Cracking over Group B metals is hardly affected by hydrogen. The extent of dehydrogenation increases, that of aromatization decreases. The overall activity (Table 4) somewhat decreases in hydrogen. Hy-

drogen is favorable for dehydration over Re.

Most interesting hydrogen effects are observed with Group C metals. In nitrogen they belong undoubtedly to the class of "dehydrogenating" metals. In hydrogen, however, their pattern of activity changes. Although cracking activity (as in Group A) increases very markedly, at the same time aromatization activity also increases and, unlike Group B, the product composition is shifted towards phenol and benzene (Tables 2 and 3).

The aromatizing activity of the metals is compared in Fig. 1. For cyclohexanol and cyclohexanone, nearly identical ranks are obtained. The "promotion" of Ir and especially Rh to the group of good aromatizing metals in hydrogen is obvious.

A detailed study of *temperature effects* is reported elsewhere (10). This confirms that the 573 K value selected for comparison is a typical temperature where dehydrogenation reactions can be well studied. At lower temperature, the cyclohexanol  $\rightleftharpoons$  cyclohexanone reversible sequence is shifted towards the left-hand side. At higher temperatures cracking reactions become predominant with Group A and C metals, whereas extensive formation of phenol and its transformation to benzene prevail with Group B metals.

#### (b) Radiotracer Studies of Reaction Pathways

Application of reacting mixtures of labelled and unlabelled components has been proved to be useful in detecting reaction pathways (2, 4, 6). The tracer method is useful in solving two problems:

(i) the pathway of phenol formation from cyclohexanol (*via* cyclohexanone or directly) (2);

(ii) the route of hydrocarbon formation (5, 6) (benzene formation from phenol or cyclohexane formation from cyclohexanol *via* hydrogenolytic splitting of the OH group or cyclohexene formation from cyclohexanol *via* dehydration).

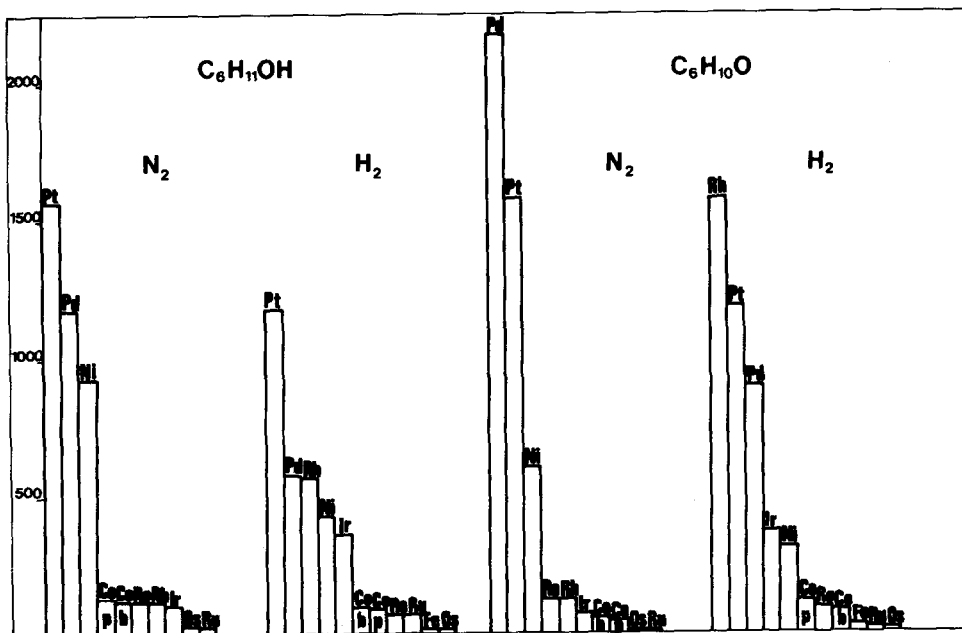


FIG. 1. Aromatizing activities ( $10^{16}$  molecules/m<sup>2</sup> catalyst per standard pulse) of cyclohexanol and cyclohexanone in hydrogen and nitrogen.

The mixture of [1-<sup>14</sup>C]cyclohexanol plus inactive cyclohexanone was reacted in order to solve Problem (i). At the same time,

it gave also useful information as far as Problem (ii) is concerned but this problem required also the application of mixtures of

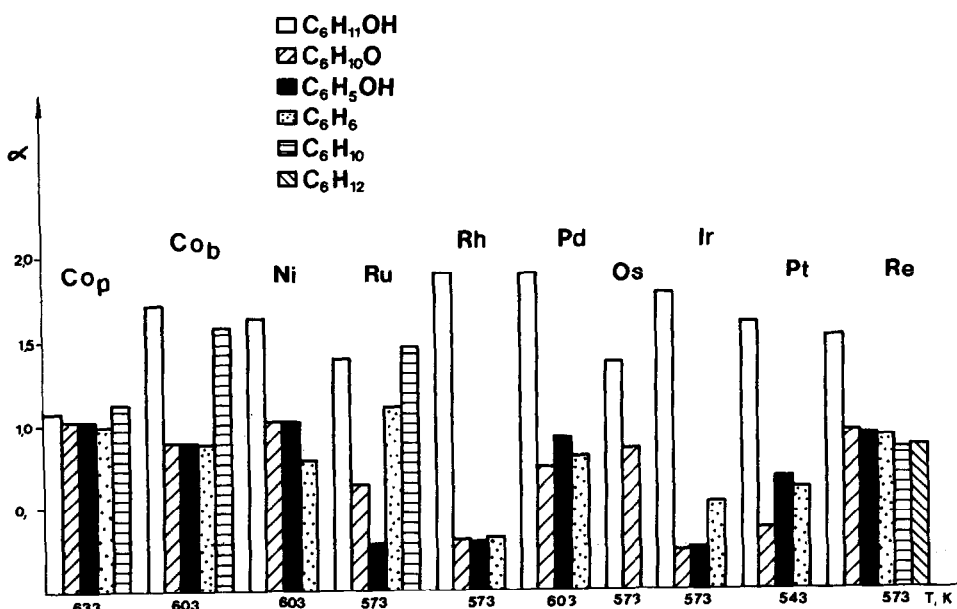


FIG. 2. Relative molar radioactivity values obtained from the reaction of [<sup>14</sup>C]cyclohexanol + inactive cyclohexanone measured in  $N_2$ .

inactive cyclohexane and cyclohexene with labelled cyclohexanol.

Results are shown in Fig. 2 and Tables 5 and 6. No detectable radioactivity was found in the products over osmium. The evaluation is done on the basis of "relative molar activity" ( $\alpha$ ) expressed in terms of " $r\%/m\%$ " (radioactivity percentage over mole percentage) as defined in Ref. (7).

To obtain this value, the composition in mole percentage is calculated ( $m\%$ ) and then a similar procedure is carried out for the radioactivities: the activities of individual components (expressed in counts measured on the detector unit) are summarized and the radioactivity percentage of individual components is calculated ( $r\%$ ). If the radioactivity were evenly distributed in each component, the result ( $r\%/m\%$ ) should give unity for each of them. This,

TABLE 5

Specific Radioactivity ( $\alpha$ ) of Products Formed in the Reaction of a Mixture of [ $1-^{14}\text{C}$ ]Cyclohexanol plus Inactive Cyclohexene

Metal	$T$ (K)	Specific radioactivity, $r\%/m\%$			
		Oxygenated compounds	$\text{C}_6\text{H}_{12}$	$\text{C}_6\text{H}_{10}$	$\text{C}_6\text{H}_6$
Feed	—	2.25	—	—	—
Os	573	2.16	—	—	—
Co(p)	573	2.15	—	0.007	0.69
Co(b)	633	2.17	—	0.16	1.53
Re	603	2.25	0.68	0.14	0.64
Ru	633	2.20	—	0.23	0.12
Rh	603	2.27	—	—	0.17
Ir(II)	603	2.16	—	0.065	0.053
Ni	603	2.22	—	—	0.05
Pd	573	3.53 <sup>a</sup>	—	—	0.12
Pt	543	2.67 <sup>b</sup>	—	—	0.25
	543	2.84 <sup>b</sup>	—	—	0.11
	543	2.99 <sup>b</sup>	—	—	0.05

<sup>a</sup> Feed,  $\alpha$ : 3.73.

<sup>b</sup> According to (4), feed:  $\alpha_{\text{C}_6\text{H}_{10}\text{O}} = 11.4$ ;  $\alpha_{\text{C}_6\text{H}_{11}\text{OH}} = 3.7$ .

TABLE 6

Specific Radioactivity ( $\alpha$ ) of Products Formed in the Reaction of a Mixture of [ $1-^{14}\text{C}$ ]Cyclohexanol plus Inactive Cyclohexane

Metal	$T$ (K)	Specific radioactivity, $r\%/m\%$			
		Oxygenated compounds	$\text{C}_6\text{H}_{12}$	$\text{C}_6\text{H}_{10}$	$\text{C}_6\text{H}_6$
Feed	—	2.16	—	—	—
Os	573	2.16	—	—	—
Co(p)	633	2.08	—	2.12	2.13
Co(b)	573	2.12	—	2.09	2.16
Re	603	2.18	0.051	1.84	1.75
Ru	603	2.04 <sup>a</sup>	—	1.83	1.69
Rh	603	2.19	—	—	1.30
Ir(II)	573	2.06	—	—	1.10
Ni	603	2.11	—	—	1.45
Pd	513	2.12	—	—	0.72
Pt	513	1.23 <sup>b</sup>	—	—	1.41
	543	1.04 <sup>b</sup>	—	—	1.11
	573	1.20 <sup>b</sup>	—	—	0.87

<sup>a</sup> Feed:  $\alpha$ : 2.07.

<sup>b</sup> According to (4), feed:  $\alpha_{\text{C}_6\text{H}_{10}\text{O}} = 0.12$ ;  $\alpha_{\text{C}_6\text{H}_{11}\text{OH}} = 1.38$ .

however, is not the case since we introduce one radioactive and one inactive component. The change of the initial  $r\%/m\%$  value after reaction means material transport between radioactive and inactive components (7). Thus the comparison of initial and final  $\alpha$  values gives us the necessary information without knowing the "molar radioactivity" expressed in activity per mole units.

The relative molar radioactivity ( $\alpha$ ) of phenol exceeds that of cyclohexanone with platinum and palladium only (Fig. 2). These are the metals where "direct" phenol formation (i.e., at least partly without desorption of cyclohexanone intermediate) is observed.

The radioactivity of benzene was equal to that of phenol with most of the metals. Its main route of formation must therefore

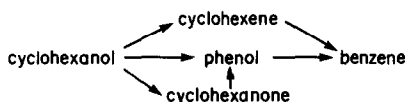
be the hydrogenolytic splitting of the phenolic OH group. The somewhat lower radioactivity of benzene (as compared with phenol) with Ni, Pd, and Pt indicates that inactive cyclohexanone contributed considerably to benzene formation. These are the metals where the relative reactivity of cyclohexanone is rather high ( $r_{ol}/r_{one}$  in Table 4).

With ruthenium, the  $\alpha$  value of benzene is higher than that of phenol; at the same time, much radioactive cyclohexene appears. This means that *dehydration* must be the predominant route of  $C_6$ -cyclic hydrocarbon formation.

The specific radioactivity of cyclohexene exceeded that of the benzene fraction with both Co catalysts, too. The existence of the dehydration reaction was confirmed by the appearance of radioactivity in cyclohexene when  $[^{14}C]$ cyclohexanol plus inactive cyclohexene was reacted (Table 5). Re is most active in dehydration.

The possibility of hydrogenolytic splitting of the alcoholic OH group was studied by reacting the mixture of  $[^{14}C]$  cyclohexanol and inactive cyclohexane (Table 6). Rhenium is the only metal where radioactivity is found in the cyclohexane fraction. This, however, can be attributed to the fact that Re hydrogenates cyclohexene exceptionally readily as shown by direct experiments (11). Thus, the splitting of the alcoholic OH group has been disproved over each metal catalyst.

The above data show that the following reaction sequence is valid for the metals studied:



Direct phenol formation occurs with Pd and Pt; dehydration over Co, Re, Ru, and Fe may represent a parallel (or eventually the main) route for benzene formation.

## DISCUSSION

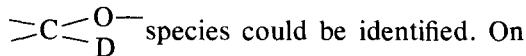
As formulated in the Introduction, one of the tasks of the present paper was to determine how the introduction of an oxygen atom into the six-membered ring alters its reactivity. Metal-catalyzed reactions of *cyclohexanol* and *cyclohexane* show both similarities and differences. The best aromatizing metals are the same for both reactants (Pt, Pd, Rh, and Ir—cf. Fig. 1 and Ref. (9)). Here, however, the similarities end. The differences begin with the behaviour of Rh and Ir which do not fragment cyclohexane ring appreciably (7), but show a very high cracking activity for the oxygenated ring. This is true for other metals, too (Pt and Pd being exceptional). Another difference is that metals of low cyclohexane dehydrogenating activity (e.g., Co, Fe, Os, Ru) produce low amounts of cyclohexene and benzene; with cyclohexanol, however, dehydrogenation to cyclohexanone may be a very pronounced transformation over them. This dehydrogenation reaction is specific for the oxygenated  $C_6$  ring, and therefore the cyclohexane  $\rightarrow$  cyclohexene process cannot be regarded as an analogous process.

The reactivity differences between the cyclohexane and cyclohexanol pair must be attributed to the presence of an oxygen atom in the latter compound. It is logical to assume that the latter reactant interacts with the catalyst surface via its oxygen atom. Infrared spectroscopic evidence may help us to elucidate the nature of surface intermediates, even if we realize that infrared spectroscopy is unable to detect surface intermediates if they are short living (i.e., just the most reactive ones). Experimental evidence collected by Szilágyi *et al.* in our laboratory (12–14) is summarized briefly in the following paragraph.

The obvious first step is the interaction of the OH group with the catalyst; this results in an adsorbed O–M species. This could be detected by indirect evidence over Ni/SiO<sub>2</sub> catalyst (14). The O–M band cannot be



observed in the spectral range studied (12–14) but if deuterated cyclohexanol with a  $\geq\text{CDOD}$  group was adsorbed, the C–D frequency belonging to a surface



Rh (13) and Pt (12) catalysts a rapid accumulation of surface carbonyls (cyclohexanone) was reported. This is held by the metal either by its  $\pi$  bond or through one of the lone electron pairs of oxygen (12).

With platinum, the dissociation of the hydrogen atoms on the carbon atoms neighbouring to the alcohol group commences at about 353 K, as shown by experiments with deuterated cyclohexanol. Above 393 K the shift of frequencies of bands assigned to the carbon–oxygen bond indicates the formation of  $\pi$ -allylic species which may have a transitional structure between ketone and enol. Above 500 K, a surface phenolate is observed. The same appears when cyclohexanone is adsorbed (13).

With rhodium, heating to 483 K results in the appearance of bands characteristic of adsorbed CO and large amounts of gas-phase methane (13). Essentially the same picture is valid for nickel but formation of benzene is also observed (14).

The ir spectrum observed on Pt corresponds to the adsorbed species I–IV shown

in Fig. 3. The reaction pathways deduced from product distribution (Tables 2 and 3) and ir studies are in good agreement. The  $\pi$ -allylic species proposed largely on an intuitive basis in Refs. (3, 6) have obtained additional independent supporting evidence. The analogous catalytic activity of palladium points to the fact that similar surface species may predominate on its surface, too. Recent results obtained with hydrocarbons reacting over palladium confirm the enhanced ability of this metal to form  $\pi$ -complex-like adsorbed species (17).

Species II in Fig. 3 is a  $\pi$ -adsorbed cyclohexanone. If such species were the only active ones in dehydrogenation, then cyclohexanone should give the same or rather higher conversions of dehydrogenated products than cyclohexanol. The overall conversion of cyclohexanol is, however, in most cases higher than that of cyclohexanone (Table 4) and this is true also for individual reaction types, e.g., for cracking (Tables 2 and 3). Thus, species like II in Fig. 3 cannot be responsible alone for the catalytic conversions observed.

Here we have arrived at the problem of reactivity differences between cyclohexanone and cyclohexanol. This may be due to a different degree of dissociation of the adsorbed species or to a different degree of coke formation from the two reactants. To

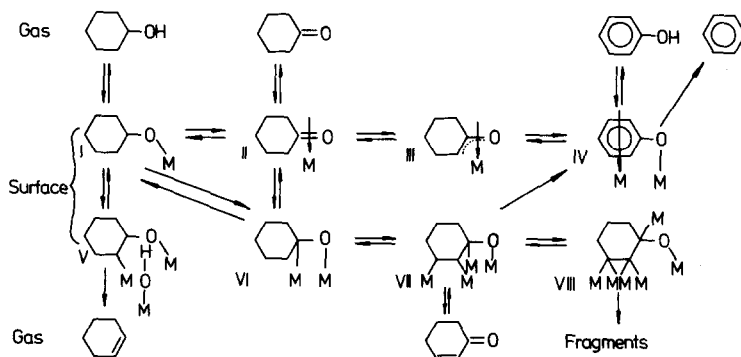


FIG. 3. Reaction scheme of cyclohexanol (and cyclohexanone) transformations over metals. Surface species I–IV are highly probable and partly proven by ir studies. Species V is assumed to be responsible for dehydration and VI–VIII represent typical ones of several possible similar species which must be responsible for  $\sigma$ -type reactions.

this end, one important fact should be underlined. If species II is formed from cyclohexanol, hydrogen is liberated (and, presumably, mostly retained by the catalyst) whereas no hydrogen evolution occurs with cyclohexanone. We have to refer to other studies carried out with hydrocarbons (18, 19) showing that hydrogen prevents deactivation of metal catalysts by deeply dissociated species. Thus, deactivation should be more significant with cyclohexanone feed. Species II is more reactive if hydrogen is simultaneously present on the surface. This is valid, first of all, for Group B metals where aromatization activity (and, also, overall reactivity) is not suppressed by hydrogen atmosphere (Table 4). These metals are able to use hydrogen released during dehydrogenation for hydrogenative splitting of the phenolic OH group (3).

There is another possibility, namely, that there are other types of active species participating in the reaction. This alternative is illustrated by species VI–VIII in Fig. 3. The appearance of cyclohexenone points to the reality of species VII. This might dissociate further (species VIII is just an example of this process). It is well known that C–C bond rupture involves such deeply dissociated intermediates (18). In nitrogen, these remain on the surface whereas hydrogen facilitates their removal: cracking activity increases in the latter case.

Dehydration should be mentioned separately. It is observed with Fe, Co, Re, and Ru, i.e., with metals whose oxides are most stable. A correlation was found earlier between the oxidation enthalpy of metals and their dehydration activity (22). Although the catalysts were pretreated by hydrogen, some strongly bonded oxygen may have remained causing dehydration. This is especially true for Re. Hydrogen–oxygen titration of this metal showed that only 10% of the surface oxygen could be removed by hydrogen. It is not excluded, therefore, that dehydration occurred over combined metal–oxygen active centres stable in hydrogen, too. This is supported by the fact

that the activity and selectivity of iron catalyst were affected only to a small extent by oxygen pulses.

The main reactions observed can be summarized as follows.

Cyclohexanol arriving at the surface suffers a dissociation of its O–H bond. This step cannot be confirmed by ir spectroscopy and it is concluded largely on the basis of differences of the reactivity of cyclohexane and cyclohexanol. The short-living alcoholate transforms to a  $\pi$ -bonded adsorbed ketone which can be formed directly from gas-phase cyclohexanone. This species is supported by ir evidence. Its further fate depends (i) on the nature of the metal and (ii) on the amount of hydrogen available.

(i) The most probable reaction route over Group B metals is that  $\pi$ -allylic adsorbed intermediates are formed which lead to aromatics. This is concluded mainly on the basis of analogous experiments carried out with hydrocarbons (7, 17–19) as well as ir spectroscopy (12). During aromatization, cyclohexanone may or may not desorb from the surface; this latter probability is, however, significant over Pd and Pt only. This puts forward the possibility of the dehydrogenation of the ring without the interaction of the OH group with the surface. The enhanced reactivity, however, as well as ir spectroscopy, shows that this is a less probable pathway.

Another route prevails over Group A metals. Here dehydrogenation results mainly in cyclohexanone; aromatization occurs to a limited extent. These metals (Fe, Co, Ru, Os, Re) tend to form multiple carbon–metal bonds with hydrocarbons as shown also by exchange (20) and hydrogenolysis (18, 19) experiments. Therefore multiply  $\sigma$ -bonded surface intermediates, which tend to block the active sites, are more probable over them than in the first group. Clearly, Group C Rh and Ir behave in an analogous way in nitrogen.

(ii) Hydrogen given off during dehydrogenation or added as a carrier gas may sup-

press somewhat aromatization over Group A metals as shown by Table 4. This effect, however, is not significant. With Group B metals, hydrogen removes deeply dissociated species blocking the surface. This is manifested in the enormous growth of the overall conversion, due, however, almost entirely to the increase of the cracking yields (Tables 2 and 3). Thus, the alternative explanation that the difference between the aromatizing abilities of Groups A and B could be attributed to the stronger blocking of the former by carbonaceous deposits (leaving the dehydrogenating activity almost intact) does not fit well with these facts: Group A metals *are* active in hydrogen, but due to the different character of the surface species their activity is manifested in cracking reactions, not in aromatization. On the other hand, the intrinsic aromatization activity of Group C metals (Rh and Ir), which is suppressed by extensive coke formation in  $N_2$ , also appears in hydrogen. Introduction of cyclohexane, benzene (21), or even cyclohexanol (3) does not cause considerable deactivation of Pt; since Pd behaves very similarly (17) we think that deactivation may not play a considerable role in determining the activity and selectivity of Group B metals.

An attempt to correlate the differences enumerated with the electron structure of the metals will be put forward in the Appendix. Of course, it would be illusory to look for a straightforward correlation; the parallelism between the electron structure and catalytic properties shows, however, at least a remarkable related trend. Further, very careful studies are necessary to elucidate the underlying principles.

#### APPENDIX

Catalytic properties of metals have often been correlated with their electronic properties without arriving, however, at direct correlations of universal validity. One of the electronic properties often used by chemists originates from the Resonating

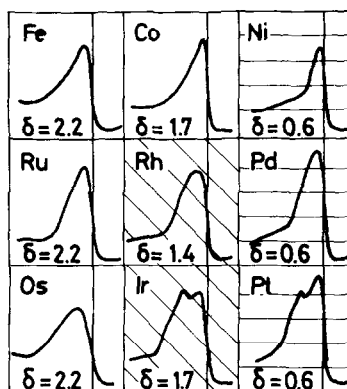


FIG. 4. Photoelectron spectra of Group VIII metals. After Baer *et al.* (25). The number of unpaired electrons ( $\delta$ ) is also shown. White squares denote Group A, horizontal shading Group B, and oblique shading Group C metals.

Valence Bond Theory of Pauling (23) and has been summarized by Baker and Jenkins (24).

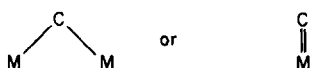
An actual metal surface consists of resonating configurations with various numbers of electrons in the "atomic," "valence," and "metallic" orbitals. The number of electrons in the unpaired, nonbonding state (denoted henceforth by  $\delta$ ) can be calculated for various metals. The value of  $\delta$  decreases from left to right in the rows of the Periodic Table. To a first, rough approximation, the higher the value of  $\delta$  the more electron density is available for localized  $\sigma$ -type bonding.

With more atomic orbitals (i.e., in lower rows of the Periodic Table) the mutual overlap of the electrons is more perfect. This is reflected by the photoelectron spectra of the corresponding metals (25). Figure 4 depicts these spectra together with the  $\delta$  values taken from Ref. (20). These broad bands tend to split by spin-orbit coupling and probably some crystal field effect which separates the  $t_{2g}$  and  $e_g$  levels.<sup>2</sup>

Knor (26) describes the formation of chemisorptive bonds as follows. First the approaching molecule repels the deloca-

<sup>2</sup> The authors wish to thank one of the referees for drawing their attention to this particular point.

lized metallic ( $t_{2g}$ ) electrons and its own electron structure becomes deformed. Upon formation of localized chemical bonds with "atomic" ( $e_p$ )-type orbitals, the delocalized electron can interact simultaneously with the electron orbitals of the adsorbate. Group A metals (and Ni) are those where multiple exchange and hydrogenolysis are extensive (18–20). This was attributed to the formation of multiple metal-carbon bonds which may possess either  $\sigma$  or a certain  $\pi$  character:



Pt and Pd are those metals (17, 18, 27) which tend to form  $\pi$  or  $\pi$ -allylic complexes on the surface:



Figure 4 demonstrates that, if such a correlation exists, the  $\delta$  value and the shape of the electron band are both important for determining the character of the metal. The comparison of Os and Ni, for example, indicates that the  $\delta$  value is the more important of the two.

The position of Rh and Ir justifies their intermediate character. Here the electronic interaction of hydrogen with the metal can be pointed out: it can transfer some electrons into the metallic state so that the population becomes favorable for aromatization. At the same time, their cracking activity remains high, similar to their behaviour in hydrocarbon reactions (28). Such a modification of catalytic properties by electronic promoters is far from being unknown and this effect of hydrogen deserves more attention.

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