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The Nature of the Hydrolysis of Chlorobenzene over Calcium Phosphate Apatite

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In the second stage of the Raschig phenol process chlorobenzene is hydrolyzed at 375–450° to phenol over what has now been found to be a calcium hydroxyapatite catalyst:

$$2C_6H_5Cl + Ca_{10}(OH)_2(PO_4)_6 \rightarrow 2C_6H_5OH + Ca_{10}Cl_2(PO_4)_6.$$

Steam, admitted simultaneously with the chlorobenzene, regenerates the hydroxyapatite:

$$2H_2O + Ca_{10}Cl_2(PO_4)_6 \rightarrow 2HCl + Ca_{10}(OH)_2(PO_4)_6.$$

The best catalytic performance is obtained from a high surface area (50–100 m^2/g), partially amorphous calcium phosphate apatite prepared by an aqueous precipitation procedure. The calcium ions can be isomorphously replaced with strontium, barium and the phosphate ions by arsenate ion, etc., to also yield active catalysts. Similar apatites prepared by high temperature techniques and the other calcium phosphates are not catalytically active. Copper (II) is a highly effective cocatalyst, while other transition metal ions are inactive.

The mechanism of the chlorobenzene hydrolysis reaction seems to be a nucleophilic displacement of the aryl-chloride by hydroxide with substantially complete retention of substituent position on the benzene ring. Any benzyne component of this reaction is less than 5%.

INTRODUCTION

The Raschig phenol synthesis (*1*) involves two basic steps. In the first one, excess benzene, air and hydrogen chloride are passed over a copper chloride-on-alumina catalyst at 225–275° (*2*) to yield chlorobenzene:

$$C_6H_6 + \tfrac{1}{2}O_2 + HCl \rightarrow C_6H_5Cl + H_2O. \qquad (1)$$

The chlorobenzene is then hydrolyzed at 375–450° over a "calcium phosphate" catalyst, often promoted by copper ion (*3, 4, 5*):

$$C_6H_5Cl + H_2O \rightarrow C_6H_5OH + HCl. \qquad (2)$$

The hydrochloric acid is recycled into the first stage. The net reaction is the indirect oxidation of benzene to phenol:

$$C_6H_6 + \tfrac{1}{2}O_2 \rightarrow C_6H_5OH. \qquad (3)$$

Several hundred million pounds of phenol are made by this process annually.

As will be shown later, the "calcium phosphate" employed as catalyst for the second step (Eq. 2), is a calcium hydroxyapatite, $Ca_{10}(OH)_2(PO_4)_6$. This is one member of a widely distributed group of minerals (*6, 7*) which have in common the formula:

$$M_{10}^{+2}(A^{-1})_2(BO_4^{-3})_6.$$

M^{+2} is a cation whose radius is >0.9 Å (*8*).
A^{-1} is OH, F, Cl, sometimes Br.
B is P, As, or S, Si, Cr, V, Mn, etc., with charges suitably balanced (*8, 9*).

These apatites are widely distributed in nature; many phosphate deposits are calcium fluoride phosphate apatite; bone, teeth mineral (*10*) and some shells are apatitic in character. Numerous calcium, lead, arsenic, etc., minerals are basically apatites (*6*).

The structure of the calcium hydroxy, fluoro, or chlorophosphate apatites has been examined in great detail (*11*). It has a hexagonal unit cell ($P6_3/m$) and a characteristic c/a of 0.70–0.74 (*6*). Most calcium ions occur as triangles stacked on a screw axis (c-axis, Fig. 1). Each triangle is rotated 60° about this c-axis with respect to the triangles above or below it. Between these triangles and on the c-axis are located the hydroxide (or chloride, fluoride) ions. The remaining calcium ions form a column about this screw axis and the phosphate tetrahedra are dispersed through the structure in a complex manner. The crystal allows no preferential cleavage.

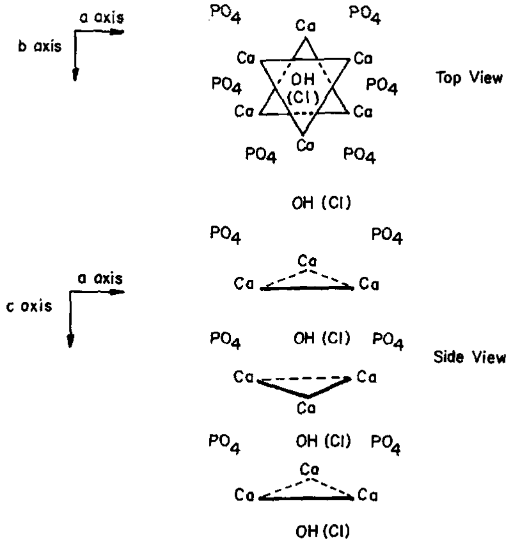

FIG. 1. Partial crystal structure of calcium hydroxy apatite (*11*).

Synthetic apatites, prepared by an aqueous precipitation-hydrolysis technique, are frequently non-stoichiometric (Ca/P from about 1.40 to the theoretical 1.67) (*12*). There are a variety of theories which claim to account for this behavior (*13*). The facts are, that the X-ray diffraction patterns of these non-stoichiometric materials are apatitic (c/a about 0.73) and they can be indexed to fit an apatite lattice (*14*). The precipitation prepared calcium phosphate-apatites are initially amorphous but then gradually crystallize into the apatite lattice. This process has been studied in detail (*15*). Such freshly prepared apatites have large surface areas (10–120 m^2/g) (*12, 16*). It was found that calcium, in the apatite lattice, exchanges rapidly with aqueous cupric ion up to a limit of about 3 copper ions per unit cell ($Ca_{10}(OH)_2(PO_4)_6$) without changing the apatite lattice (*8*). Calcium chlorophosphate-apatite can be hydrolyzed with steam (at 1300° for 2 weeks) to yield the hydroxyapatite and hydrogen chloride (*16*).

The present study concerns itself with a general examination of this Raschig second stage chlorobenzene hydrolysis catalyst, its nature, function, possible mechanism of the hydrolysis reaction, and the copper promotional effect. Non-stoichiometric apatites have recently been used to study butanol dehydration and similar reactions (*13, 17*).

EXPERIMENTAL

Chemicals

All inorganic chemicals were reagent grade or of similarly high quality. The water used was distilled and sparged with nitrogen (to expell carbon dioxide) prior to use. The organic reference chemicals were from Eastman Kodak or Aldrich Chemical Company. The *p*-fluorochlorobenzene was purchased from Chemical Procurement Laboratories and used as received.

Analytical Methods

The X-ray powder patterns were run on a North American Philips X-ray Diffractometer using Cu-Kα radiation (Ni-filtered) and recorded on film or a strip chart counter arrangement. The electron paramagnetic resonance data were obtained with a Varian 4000 spectrometer using a 6-in. magnet. The gross vapor phase chromatographic (vpc) analyses were carried out on an F & M-500 instrument using a 2 m — 10% OV-1 (on Gas Chrom-Q) column. The fluorophenol isomers (as the *o*-trimethylsilyl derivatives) and the fluorochlorobenzene isomer analyses were carried out on a Perkin-Elmer capillary chromatograph using a DC-550, 0.025 cm i.d. capillary tube, 100 m in length (80°, 2 atm He, 100:1 splitter ratio, flame detector). The *o*- and *m*-$F\text{-}C_6H_4OSi(CH_3)_3$ isomers could not be resolved from each other, but the paraisomer was well resolved from *o*-*m* peak. No *p*-$ClC_6H_4OSi(CH_3)_3$ was observed. The various ClC_6H_4F isomers were very well resolved.

Rapid catalyst testing was carried out with a modified F & M-609 flame ionization gas chromatograph.[1] In place of the usual column was a 6.3 mm (i.d.) × 45 cm stainless steel tube. The entrance side contained 1.0 g-20–50 mesh catalyst, the exit side 1.0 g kaolin.[2] Water saturated nitrogen (95°, 2 atm) was used as carrier gas (15 ml/min) while pulses of chlorobenzene (0.5 μl) were injected through the instrument's injection port. The exit gases passed through an oxygen-hydrogen flame detector (retention times: benzene-chlorobenzene 2–5 sec (sharp peaks); phenol 30–60 sec as a broad peak with maximum at about 45 sec.[3] This catalyst testing technique yields dynamic data (due to continuous separation of reagents and products) and not equilibrium data; e.g., an 85% conversion per pass does not mean that the equilibrium

$$C_6H_5Cl + H_2O \rightleftharpoons C_6H_5OH + HCl \tag{4}$$

is far on the product side. Furthermore, this technique allows the examination of only the very initial activity of the catalyst; usually only an active or inactive reading can be obtained. Nevertheless, the testing was very rapid, reproducible and qualitatively reliable.

The *p*-FC_6H_4Cl hydrolysis and similar long term chlorobenzene hydrolyses were carried out in an electrically heated catalyst chamber (2.5 × 30 cm) into which both water and organics were continuously metered and the products withdrawn as condensate.

Catalyst, Etc., Preparation

The various calcium phosphates (Table 3) were prepared by known procedures. The Ca-P analyses and d-spacings were comparable with authentic compounds: $CaHPO_4 \cdot 2H_2O$ (*18*); $CaHPO_4$ (*19*); $Ca_2P_2O_7$ (*19*); $Ca(H_2PO_4)_2 \cdot H_2O$ (*20*); $CaCl_2 \cdot Ca(H_2PO_4)_2 \cdot 2H_2O$ (*21*); $Ca_4H(PO_4)_3 \cdot xH_2O$ (*22*); $\beta\text{-}Ca_3(PO_4)_2$ (*23*). The calcium, strontium, and barium hydroxyapatites were prepared from metal nitrates and ammonium phosphate at 25° in carbon dioxide-free water (*24*). The calcium hydroxy arsenate-apatite was prepared similarly. The X-ray powder patterns of these substances were somewhat diffuse but they all contained the principal diffractions characteristic of the apatite lattice.

Copper doping was carried out by adding a dilute aqueous cupric chloride solution slowly to a well stirred slurry of the apatites so that a 1% copper (by wt) solid resulted. The apatites immediately exchanged calcium for copper, leaving a colorless liquid and a light blue solid. Doping with the other transition metal salts was carried out similarly.

RESULTS AND DISCUSSION

The patent literature (*3, 4, 5*) does not appear to recognize the fact that the "calcium phosphates," which are claimed as the chlorobenzene hydrolysis catalyst, are in fact, calcium hydroxyapatite. The identification of this particular calcium phosphate as the effective chlorobenzene hydrolysis catalyst rests on four pieces of evidence: elemental analyses, X-ray powder patterns, synthesis of an authentic calcium hydroxyapatite which proved to be a highly effective catalyst, and the inability

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[1] Flame ionization detects carbon containing compounds, e.g., chlorobenzene, phenol, etc., while the carrier gases (water, nitrogen) and other volatiles (hydrochloric acid) are passed undetected.

[2] The kaolin is inactive under the experimental conditions (350–500°) but it serves to separate the chlorobenzene-benzene from the phenol very adequately.

[3] Usually it was found necessary to activate a catalyst with chlorobenzene or phenol (2–4 × 0.5 μl) before reproducible results could be obtained. Phenol is strongly adsorbed on both catalyst and kaolin.

TABLE 1

Elemental Analyses of Various Chlorobenzene Hydrolysis Catalysts

	% Ca	% P	Ca/P (atomic ratio)	% Cl	% Cu	Surface Area (m^2/g) (BET-N_2)
Unused commercial catalyst	35.3	18.4	1.48	0.1	0.73	—
Used commercial catalyst	37.2	18.5	1.56	1.3	0.08	7
Synthetic calcium hydroxy apatite[a]	38.7	18.7	1.61	—	—	120
Calcd. for $Ca_{10}(OH)_2(PO_4)_6$	39.9	18.5	1.67	—	—	—
Calcd. for $Ca_{10}Cl_2(PO_4)_6$	37.45	17.9	1.67	6.73	—	—

[a] Prepared by aqueous precipitation-hydrolysis procedure (see Experimental section).

of a variety of similar calcium phosphates to act as catalysts.

Table 1 gives the analyses of commercial fresh and used catalyst and laboratory synthetic hydroxyapatite. The important Ca/P ratio of the commercial catalyst (1.48–1.56) shows a divergence from the synthetic (1.61) and theoretical value (1.67). The possible reasons for these differences are discussed elsewhere (*13*). X-ray powder patterns of fresh, commercial catalysts have only diffuse lines which are not readily indexed; nevertheless, they are superimposable on the most intense diffraction lines in the synthetic apatite or the used commercial catalyst. The latter, as well as the synthetic apatite, can be indexed readily and the diffraction patterns are identical with the ASTM apatite (*14*) (Table 2). The used commercial catalyst also exhibits weak β-tricalcium phosphate diffraction lines. A number of other calcium phosphates have been synthesized and all shown to be totally inactive (Table 3) in the chlorobenzene hydrolysis reaction under conditions where the synthetic apatite and fresh commercial material were both highly active. This evidence leaves little doubt that the effective catalyst in this reaction is the calcium hydroxyapatite.

This hydrolysis reaction can be broken down into two consecutive steps:

$$C_6H_5Cl + \text{apatite-OH} \rightarrow C_6H_5OH + \text{apatite-Cl} \quad (5)$$

and

$$\text{apatite-Cl} + H_2O \rightarrow \text{apatite-OH} + HCl. \quad (6)$$

First, gaseous chlorobenzene reacts with the hydroxyapatite to yield phenol and chloroapatite. The latter, under the same reaction conditions is hydrolyzed to hydroxyapatite by the steam which is fed simultaneously

TABLE 2

d-Spacings for Chlorobenzene Hydrolysis Catalysts

Known $Ca_{10}(OH)_2(PO_4)_6$ (*14*)	Synthetic Apatite (Heated 350°, 60 hr)	Used Commercial Catalyst
8.17 vw	8.1 mw	8.4 w
5.26 vvw[a]	5.25 vw	5.25 w
4.72 vw[b]	4.70 vw	
		4.45 w*
		4.13 vw*
4.07 vw	4.08 w	
3.88 vw	3.88 w	3.91 vw
3.51 vvw		3.55 w
3.44 m[c]	3.42 ms	3.40 ms
		3.31 m
		3.25 vw*
3.17 mw[d]	3.17 w	3.15 vw
3.08 mw	3.09 mw	3.09 ms
		3.04 ms
		2.91 ms*
2.81 vs	2.81 vs	2.85 s
2.78 ms[e]	2.77 ms	2.77 vs
2.72 ms	2.71 s	2.68 w
2.63 mw	2.63 m	2.63 mw

[a] vvw = very, very weak.

[b] vw = very weak.

[c] m = medium.

[d] mw = medium weak.

[e] ms = medium strong, etc.

* Diffraction lines in β-$Ca_3(PO_4)_2$.

TABLE 3

CATALYTIC EFFECTIVENESS OF VARIOUS CALCIUM PHOSPHATES

Material	Catalytic Effectiveness[a]
Fresh Plant Catalyst	very active
Synthetic $Ca_{10}(OH)_2(PO_4)_6$[b]	very active
$CaHPO_4 \cdot 2H_2O$	inactive
$CaHPO_4$	"
$Ca_2P_2O_7$	"
$Ca(H_2PO_4)_2 \cdot H_2O$	"
$CaCl_2 \cdot Ca(H_2PO_4)_2 \cdot 2H_2O$	"
$Ca_4H(PO_4)_3 \cdot xH_2O$	"
β-$Ca_3(PO_4)_2$	"

[a] All Cu^{+2} doped; catalytic testing carried out in the modified F & M-609 unit.

[b] Only apatite prepared via the aqueous precipitation procedure was active. Apatite prepared via high temperature sintering methods, etc., were totally inactive. Armour and Co. Anorganic Bone—"OSSAR"—was also found to be inactive. (Ethylenediamine extracted bovin femur shaft.)

TABLE 4

EFFECT OF TRANSITION METAL DOPING ON CALCIUM APATITE CATALYTIC EFFECTIVENESS

Salt[a]	Catalyst?[b]
$AgNO_3$	no
$Ni(NO_3)_2 \cdot 6H_2O$	"
$Co(NO_3)_2 \cdot 6H_2O$	"
$MnCl_2 \cdot 4H_2O$	"
$NiCl_2 \cdot 3H_2O$	"
$CoCl_2 \cdot 3H_2O$	"
$Cu(NO_3)_2 \cdot 6H_2O$	yes
$CuCl_2$	yes
$PdCl_2$ + 0.1N HCl	no
$FeCl_3$	"
$PdCl_2 + CuCl_2$	slight
$VOSO_4 \cdot 2H_2O$	no
$KPtCl_3$	v. slight (?)
AgCl Conc. NH_4OH	" "
$HfCl_4$	no
Ag[illegible]O_4	"

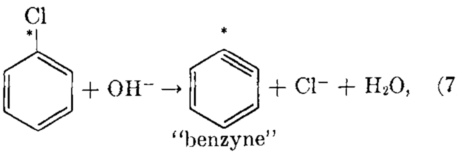
[a] About 1% by weight.

[b] Catalytic testing carried out in modified F & M-609 unit.

with the chlorobenzene into the reactor. The analyses show that the used commercial catalyst (Table 1) is partially in the chloroapatite form (1.3% Cl found, 6.73% theory for $Ca_{10}Cl_2(PO_4)_6$). The surface area of the used catalyst is also quite low (7 m^2/g vs. about 120 m^2/g for synthetic material).

The commercial catalyst contains 0.5–1% of copper (II) as promoter. The effect of this adjuvant is pronounced. Given a certain set of experimental conditions, 1% copper promoted catalyst will yield about the same conversion to phenol (per pass) as the copper-less catalyst will at a 80–110° higher reaction temperature. Other transition metals tested (in the 1% concentration range) did not show any significant effects beyond that of the unpromoted catalyst (Table 4). Both used and unused copper promoted catalysts have a clear Cu (II) electron paramagnetic resonance signal (Cu (I) is diamagnetic); the signal of the used catalyst is about two and one-half times as strong as that of the fresh catalyst (at the same copper concentration). This implies that there is no net reduction of copper (II) in the hydrolysis cycle, although it does not exclude a transient reduction and reoxidation during the reaction cycle.[4] The precise role of the copper ion is not known. This metal is a specific catalyst for nucleophilic aromatic (not aliphatic) substitution reactions (*25, 26, 27*) but generally only in the cuprous oxidation state (*25*). Copper (I), but not copper (II) ion,[5] is known to form aromatic π-complexes (*28*).

These nucleophilic aromatic displacement reactions proceed by different reaction paths. One route is via a benzyne intermediate (*29*),



(7)

and

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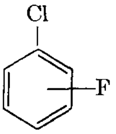
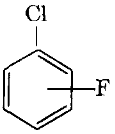
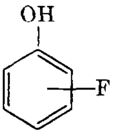
[4] In commercial practice, a good deal of carbon and tars are formed in the chlorobenzene hydrolysis. This carbon could function as a reductant for copper (II). Copper (II) is also known to be reduced to copper (I) or even the metal by phenol or phenoxide ion at room temperature (*25*).

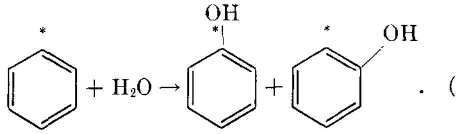
[5] At room temperature; obviously the situation may be entirely different in the 350–450° range.

TABLE 5

RESULTS OF THE HYDROLYSIS OF *p*-FLUOROCHLOROBENZENE OVER APATITE CATALYST[a]

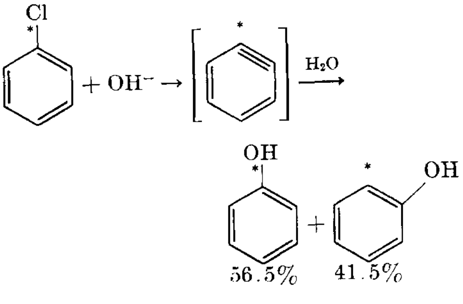
Isomer	Feed 	Product 	Product 
p	89.1	88.9	95.4
m	0.4	0.3	4.6
o	10.5	10.8	

[a] About 5–7% conversion per pass at 450° in the 2.5 × 30 cm reactor; 0.52 g mole ClC_6H_4F/1-cat/hr plus 20 mole steam/mole ClC_6H_4F. About 1% benzene was formed.



(8)

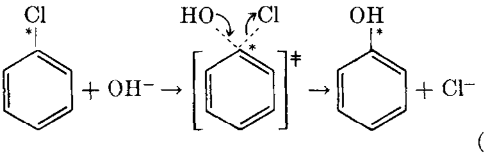
The strongly basic hydroxide ion abstracts a proton from the carbon adjacent to the chloride ion and, probably simultaneously with loss of the chloride ion, a highly reactive transient makes its appearance (benzyne). This reacts at once with available proton donors, here water, to form phenol. If the original chloride bearing carbon had had a C^{14} label, then the resulting phenol should be 50% phenol-1-C^{14} and 50% phenol-2-C^{14} (neglecting a very small C^{14} isotope effect and possible readdition of hydrogen chloride to the benzyne intermediate, etc.). Other investigators who have carried out the aqueous sodium hydroxide hydrolysis of chlorobenzene-1-C^{14} at 340° and 395° (*30, 31*) (in the absence of copper), found that about half of the resulting phenol was phenol-1-C^{14} and the remainder mostly phenol-2-C^{14}. This is clear evidence of a benzyne intermediate under those particular reaction conditions:



(9)

In this work it was found that when *p*-fluorochlorobenzene[6] was hydrolyzed (Table 5) at 450° over a copper promoted calcium phosphate apatite, the resulting product contained 95.4% *p*-fluorophenol and 4.6% *o* + *m*-fluorophenol. The low percentage of *o* + *m* isomers indicated that the benzyne component of this hydrolysis reaction must have been very low. It may well be that the *o* + *m* fluorophenol was mostly the ortho isomer since the *p*-chlorofluorobenzene feed contained 10.5% of the ortho isomer. Presumably, the *o*-fluorochlorobenzene hydrolyzes much more slowly than the para isomer, probably for steric reasons.

There is another reaction path by way of which such nucleophilic aromatic substitution can proceed. This is straight-forward nucleophilic substitution on the chloride bearing carbon,



(10)

In certain aryl halides (e.g., 2,4,6-trinitrochlorobenzene) the transition state appears

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[6] It would have been theoretically sounder to use C^{14} labeled chlorobenzene but experimentally this is far more cumbersome. The results which were obtained serve to discriminate between the various reaction mechanisms quite adequately. Both the *p*-fluorochlorobenzene and the *p*-fluorophenol are stable under the reaction conditions. An attempt to use *p*-chlorotoluene results in very extensive decomposition.

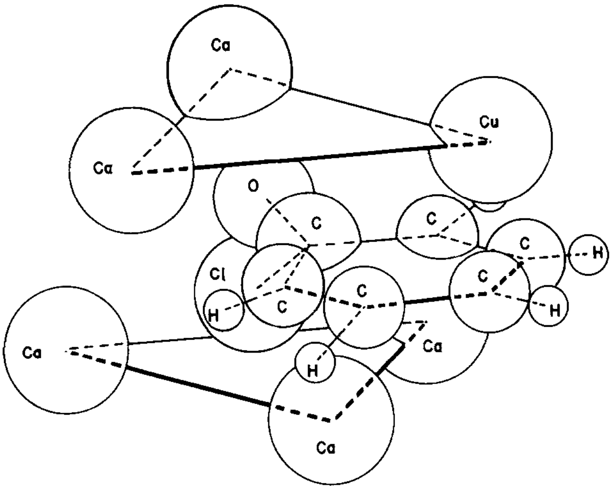
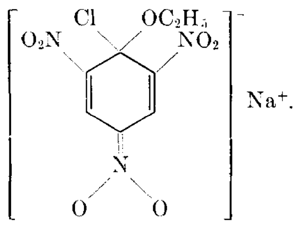


FIG. 2. Perspective of proposed transition state of chlorobenzene-hydroxy apatite reaction.

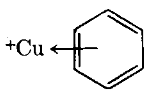
to become a stable, isolable intermediate. In such an intermediate (generally called Meisenheimer complex) the ring has lost its aromaticity and has become a cyclohexadiene derivative,



Many such complexes have actually been isolated and variously characterized (*32*, *33*, *34*). Experimentally it has also been found that in many of these activated molecules, fluoride is more readily displaced than chloride (F ≫ Cl) (*32*).

In the case of the non-activated aromatic displacements (here chlorofluorobenzene) the reactivity of the halides is generally reversed (Cl ≫ F) (*32*) and there is no Meisenheimer intermediate of demonstratable stability (e.g., the intermediate becomes a transition state). Experimentally, it was found that the apatite catalyzed hydrolysis of *p*-fluorochlorobenzene lead exclusively to the *p*-fluorophenol. For this reason, it is most likely that the copper promoted, apatite hydrolysis of chlorobenzene proceeds via a synchronous reaction, illustrated in Eq. (10).

It is of interest to speculate how this reaction could proceed on the apatite surface. For such a reaction to occur, the chlorobenzene molecule, the copper ion, and the hydroxide ion must simultaneously be in close geometric proximity. Such a situation is illustrated in Fig. 2. Here, one calcium ion, in the calcium column, is replaced by copper ion. Between the two Ca_2Cu-Ca_3 triangles lies the activated complex composed of the hydroxide ion and the chlorobenzene molecule. This assembly fits well between these two triangles as long as the ring is parallel to the triangles; the ring is too large for a perpendicular entry (distance between triangles is 3.44 Å (*35*)).[7] It can be seen that one of the carbon-carbon double bonds of the ring fits neatly immediately below the copper ion (1.72 Å distance). This distance is about 0.4 Å shorter than the copper-ring



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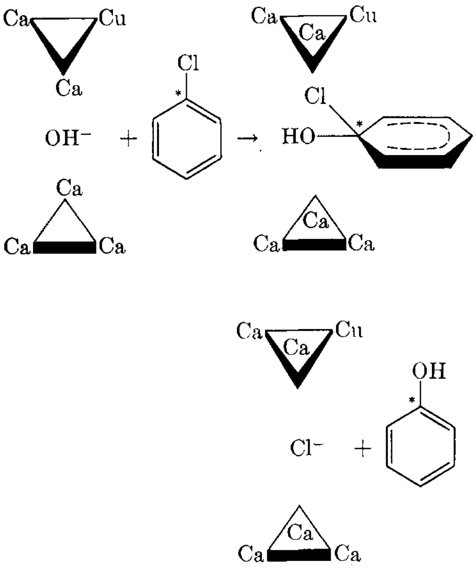
[7] The ring dimensions were taken from a crystal structure of a similar complex (2,4,6-trinitro-1,1-dimethoxy-cyclohexadiene potassium salt (*34*)). The C-O (1.43 Å) and C-Cl (1.76 Å) distances are taken as covalent tetrahedral carbon-X bonds. The O-C-Cl angle had to be compressed from the normal 110° (*34*) to 75° in order to avoid steric interference. The assumption is made that the activated complex is geometrically similar to that of the Meisenheimer salt.

distance found (2.13 Å) in the crystal structure of $C_6H_6Cu^+ AlCl_4^-$ (*28*).

The displacement of chloride by hydroxide ion would, therefore, appear to proceed as follows: a chlorobenzene molecule inserts itself between the Ca_2Cu-Ca_3 triangles in such a way that the chloride ion faces inward. The molecule is held in place and polarized ("activated") by the nearby copper ion and this complex exchanges ligands. The phenol molecule then desorbs, leaving the chloroapatite behind. This in turn, steam-hydrolyzes to hydrogen chloride and hydroxyapatite.



(11)

This scheme is in accord with the experimental facts; strong promotion by copper ion, retention of the substituent position on the ring, and a transition state geometry which is reasonable in view of the known structures of the apatite (*35*), a Meisenheimer complex (*34*), and a copper ion-benzene complex (*28*).

Since the ions in the apatite lattice can be isomorphously replaced by ones of similar size (*8, 9*), it appeared to be of interest to see whether such substitution products would produce active catalysts. The data (Table 6) show that the strontium and barium apatites are poor to very good and differ in their response to copper doping. The replacement of phosphate by arsenate yielded catalysts of high activity. From this it may be concluded that apatites in general are catalysts for the hydrolysis of chlorobenzene to phenol.

TABLE 6
CATALYTIC ACTIVITY OF VARIOUS APATITES

$M_{10}(OH)_2(RO_4)_6$		Relative Catalytic Effectiveness[a]	
M =	R =	with copper, 400°	without copper, 500°
Ca (II)	P	very good	good
Sr (II)	P	very good	poor
Ba (II)	P	poor	very good
Ca (II)	As	very good	—

[a] Catalyst testing carried out in modified F & M-609 unit.

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