

Selective Bromination of Halobenzenes Using Zeolite Catalysts

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The substitution of halobenzenes by bromine at 25°C is catalyzed by Y-type zeolites, partially exchanged with di- and trivalent cations. Catalyst activity and *para/ortho* ratio depend upon the type of cation, the extent of cation exchange, the activation temperature, the solvent, and the amount of catalyst used. In all cases the *para/ortho* ratio was substantially higher than with conventional procedures. Catalyst deactivation by hydrogen bromide, liberated during the reaction, was suppressed by adding sodium hydrogen carbonate and zeolite KA. The highest *para/ortho* ratios were obtained in a solvent-free procedure. The acidic Brønsted sites of the zeolite are considered to be the catalytically active sites.

INTRODUCTION

In the field of electrophilic aromatic substitution many papers have been published (1, 2) on the use of synthetic zeolites as catalysts for aromatic alkylation. However, the deactivation characteristics (2) are a major obstacle for the commercial application in these processes. Relatively little attention has been paid to the use of zeolites in the field of aromatic halogenation. Levina *et al.* (3-5) showed that bromination of benzene is catalyzed by Fe-containing zeolites, without mentioning the quantitative composition of the reaction products. Recently, Van Dijk *et al.* (6) reported on the liquid phase bromination of aromatic compounds using NaCaX and NaCaFeX zeolites. When applying these catalysts in large enough quantities to allow complete adsorption of the re-

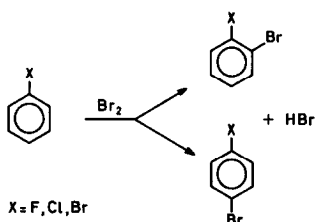
actants high *para/ortho* ratios were observed. However, when using these zeolites in catalytic quantities much lower conversions and *para/ortho* ratios (6) have been found.

Rosen and Gandler (7) studied the bromination of 4-nitrobiphenyl adsorbed on silica. The *para/ortho* ratio observed on silica was similar to that obtained upon FeCl₃-catalyzed bromination in solution. Yaroslavsky (8) used silica as the catalyst in the liquid phase bromination and chlorination of alkylbenzenes; *para/ortho* ratios observed seemed to be slightly higher than with halogenation catalyzed by FeBr₃ or FeCl₃, respectively. Generally, data on the use of zeolite catalysts (1, 2) show that the main factors determining activity are the structure of the lattice, the Si/Al ratio, the nature of the cation, and the degree of cation exchange. Selectivity in parallel reactions is governed by the electrostatic forces within the zeolites and/or the restricted orientation of the adsorbed

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molecules and their transition states in the pores of the crystal. The electrostatic forces within the zeolite crystal are enhanced by a high Si/Al ratio and by the presence of multivalent cations. Therefore, we investigated the use of various cation-exchanged forms of Y-type zeolites, for catalyzing the bromination reaction. Halobenzenes have been selected as test reactants. Here bromination results first in *para*- and *ortho*-substituted products followed by a slow consecutive reaction to 2,4-dibromohalobenzenes.



The selectivity for the parallel reactions is expressed as the *para/ortho* ratio (*p/o*). The influence of several variables such as the type of cation, the extent of cation exchange, and the activation conditions of the zeolite on catalyst activity and *para/ortho* selectivity was investigated. Also the effect of several additives was studied. Most experiments were carried out using a slurry technique in a halogenated solvent; in addition, some solvent-free experiments are reported.

EXPERIMENTAL

Reagents. Pure grade reagents and solvents were used. The halobenzenes were obtained from Aldrich. Bromine, methylene chloride, and chloroform were obtained from Baker and carbon tetrachloride from Merck. Methylene chloride and chloroform were purified according to Ref. (9). Liquids were dried using zeolite KA (3A). The zeolite powders KA, NaY (SK-40), NaX (13X), CaX (10X), and SK-500 (extrudates of a commercial rare earth exchanged NaY zeolite, which were ground) were obtained from the Union Carbide Corpora-

tion. NH₄Y, MgY, CaY, and CeY were obtained from NaY by ion exchange with 0.1- to 0.5-N aqueous solutions of the corresponding metal chlorides. CaY-82 means that 82% of the Na ions were replaced by Ca ions. Amorphous silica-alumina with the trade name Ketjenat HA-LPV was obtained from Akzo Chemie B.V. The zeolites were activated as described earlier (10).

Standard procedure for zeolite-catalyzed aromatic bromination. Halobenzene (30 mmole), catalyst (1 g), and solvent (15 ml) were stirred at 25°C for 15 min. After adding a solution of bromine (30 to 45 mmole) in the same solvent (10 ml) bromination was followed by taking samples of the reaction mixture at suitable intervals. 4-N KOH was added to the samples in order to quench the reaction and to desorb reactants and products from the zeolite. The organic layer was dried, centrifuged, and subjected to GC analysis using SP 2250 (3% on Chromosorb GHP) as the stationary phase. In separate experiments it was shown that the desorption procedure resulted in a recovery greater than 99%.

Excess catalyst bromination. Halobenzene (4 mmole), catalyst (4 g), and carbon tetrachloride (20 ml) were stirred at 25°C for 15 min. A solution of bromine (4 mmole) in carbon tetrachloride (5 ml) was added. After 2 hr the reaction was quenched with 4-N KOH (25 ml). The organic layer was separated, dried, centrifuged, and subjected to GC analysis.

Solvent-free bromination. The halobenzene was adsorbed by the zeolite (1.5 to 2.0 g) from the gas phase in a desiccator. The actual amount of adsorbed benzene (1 to 5 mmole) was determined by weighing. The loaded zeolite was then exposed to the required amount of bromine (1.5 to 7.0 mmole). After complete (visible) adsorption of the bromine (1 to 2 hr), 4-N KOH (15 ml) was added to the zeolite and the slurry was extracted with carbon tetra-

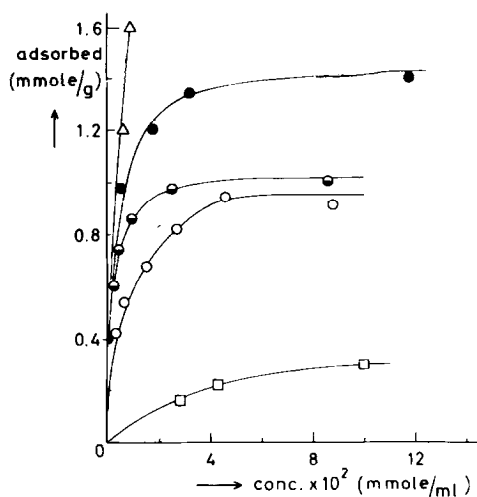


FIG. 1. Adsorption isotherms for hydrogen bromide (Δ); *o*-dibromobenzene (\bullet); bromobenzene (\ominus); *p*-dibromobenzene (\circ); and bromine (\square) on zeolite CaY-82 at 25°C from carbon tetrachloride.

chloride (4×5 ml). After drying and centrifuging the organic solution was subjected to GC analysis.

Adsorption. The concentration of the bromobenzenes before and after adsorption was determined with a Perkin Elmer 521 Grating Infrared Spectrophotometer in the region 2800 to 3200 cm^{-1} . The adsorption of bromine was followed by adding excess of aqueous 5% KI solution to the samples and titrating iodine formed with sodium thiosulfate (0.1 *N*). Hydrogen bromide was determined by titration with sodium hydroxide (0.1 *N*) using methyl red as indicator. In the competitive adsorption experiments of equimolar amounts of two aromatic compounds, the concentrations during adsorption were followed by GC analysis, using 1,3,5-tri-*t*-butylbenzene, assumed *not* to be adsorbed, as an internal standard. In the competitive adsorption of hydrogen bromide and aromatic compounds the concentration of hydrogen bromide was determined by titration and the concentration of the aromatic compound by GC analysis.

RESULTS AND DISCUSSION

Several zeolites were examined using the bromination of bromobenzene as a test reaction. Only dibromobenzenes were observed as the products. Without zeolite no conversion of bromobenzene was obtained. Compared to FeCl_3 catalysis (*p/o* 3 to 4), zeolites showed a higher selectivity in these experiments and a lower activity (on a weight basis). The order of activity found was

$\text{CaA, KY} < \text{NaY} \ll \text{CaX} < \text{SK-500,}$

$\text{CeY} < \text{NH}_4\text{Y, MgY, CaY.}$

Zeolites which are known to have high acidities such as $\text{NH}_4\text{Y, CaY, MgY, CeY,}$ and SK-500, showed high activities. The low activity of CaA is explained by the inaccessibility of its inner surface for benzene derivatives. The zeolites SK-500, CeY, $\text{NH}_4\text{Y, MgY,}$ and CaY were chosen for a more thorough examination.

Adsorption

The adsorption (at 25°C) on CaY of reactants and products in the bromination of bromobenzene was investigated in carbon tetrachloride. Figure 1 shows the adsorption isotherms. Bromine is only weakly adsorbed from carbon tetrachloride.

Competitive adsorption experiments showed the strength of adsorption to be

$\text{HBr, 1,2,3-tribromo-} > \textit{o}\text{-dibromo-}$
 $> \text{bromo-} > \text{1,2,4-tribromo-}$
 $> \textit{p}\text{-dibromobenzene.}$

This sequence resembles the order of the dipole moments. In view of the strong adsorption of hydrogen bromide and the adsorption of the dibromobenzenes a decrease in the reaction rate is expected as the reaction proceeds. Similar adsorption selectivities are expected for chloro- and fluorobenzene and their brominated products.

Effect of the Activation Temperature

The effect of the activation temperature of the zeolite on the conversion of bromobenzene and the *p/o* selectivity was examined using NH_4Y , CaY , and SK-500 as the catalyst. The results are shown in Fig. 2. The activation was carried out in air. Similar results were obtained when activating in nitrogen. For SK-500 a maximum activity was obtained at an activation temperature of about 300°C. With CaY a similar result was obtained. For NH_4Y and CaY higher temperatures, of 450 and 520°C, respectively, are required. These optimum temperatures correspond with those where the zeolites possess maximum total Brønsted acidity. Thus when plotting the acidity of NH_4Y (11) and CaY (12) against the activities (defined as $10/t_{50\%}$) we noted a linear correlation. For comparison the activity of an amorphous silica-alumina cracking catalyst was investigated. Again we noted that the optimum activation temperature (400°C)

is the temperature where maximum Brønsted acidity exists on the silica-alumina surface (13). Probably the low activity of NaY is explained by the small amount of Brønsted acidity (14), and the low stability against hydrogen bromide.

Influence of the Extent of Cation Exchange

NaNH_4Y , NaMgY , NaCaY , and NaCeY zeolites with a varying degree of Na exchange were obtained by a conventional cation exchange procedure. As shown in Fig. 3 there is a strong influence of the degree of cation exchange on the activity and the *p/o* ratio of the catalyst. The high *p/o* ratio in the bromination of chloro- and fluorobenzene is noteworthy and is distinctly higher than with FeCl_3 catalysis (*p/o* 4 and 12, respectively). The influence of the extent of cation exchange may be connected with the following phenomena:

(i) the coordination of the reactants to the cations,

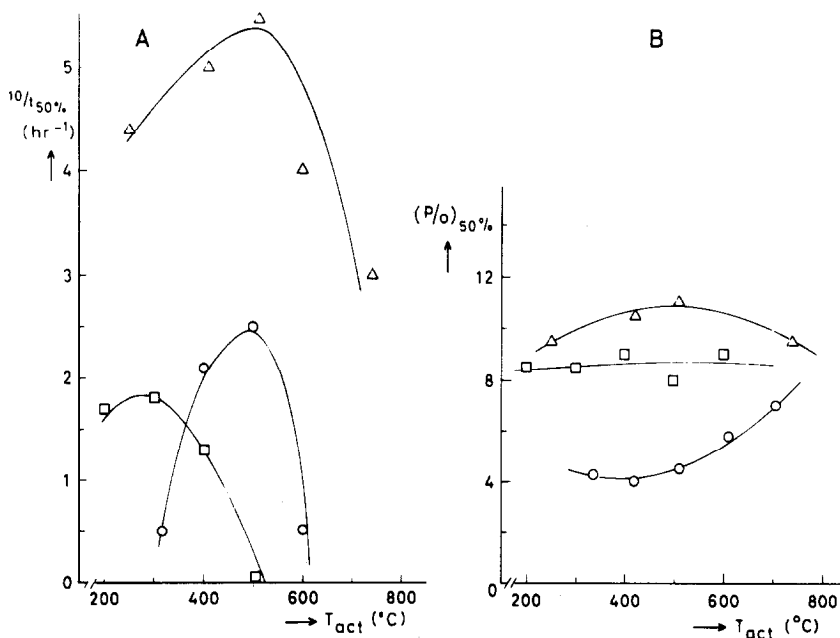


FIG. 2. Influence of the activation temperature of the zeolite in the bromination of bromobenzene (CCl_4 , 25°C) on (A) activity $10/t_{50\%}$; (B) *p/o* selectivity at 50% conversion. (Δ) CaY-75 ; (\circ) $\text{NH}_4\text{Y-67}$; (\square) SK-500.

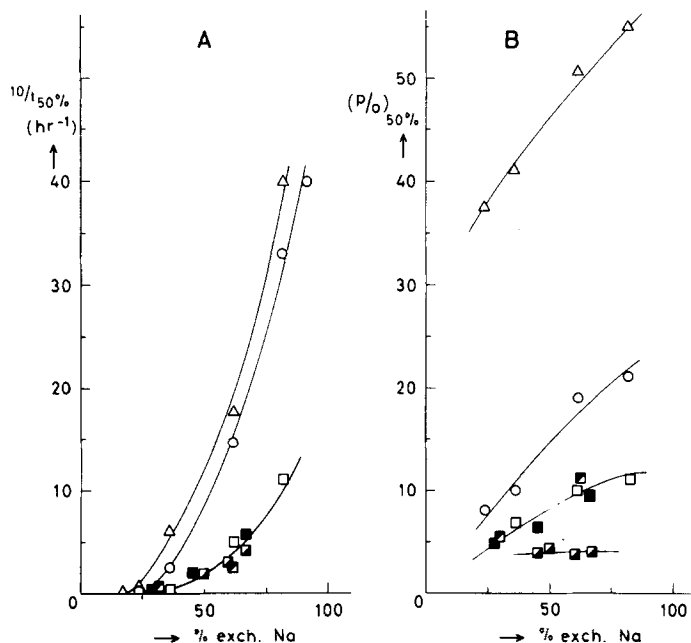


FIG. 3. Influence of the degree of cation exchange of NaY on the activity (A) and *p/o* selectivity at 50% conversion (B) in the bromination of the halobenzenes. (Δ) NaCaY, fluorobenzene; (\circ) NaCaY, chlorobenzene; (\square) NaCaY, bromobenzene; (\blacksquare) NaMgY, bromobenzene; (\blacksquare) NaCeY, bromobenzene; (\blacksquare) NaNH_4Y , bromobenzene. All zeolites were activated at 400°C.

(ii) the acidic centers which may be Brønsted or Lewis type (the concentra-

tion of these centers increases with increasing cation exchange),

(iii) the change in the electrostatic field.

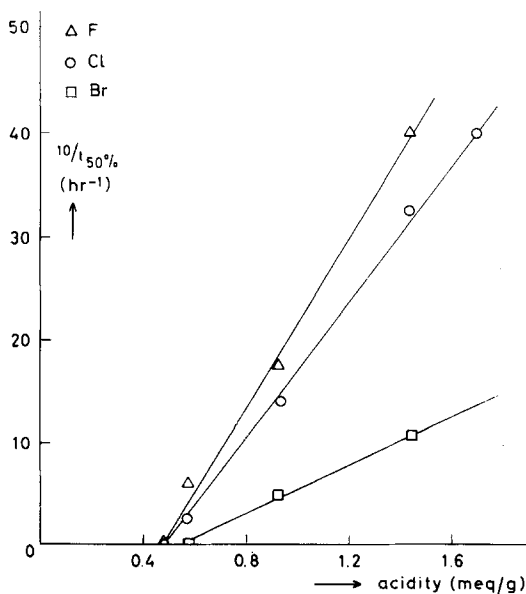
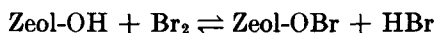


FIG. 4. Activity versus acidity ($H_0 < 6.8$) in the bromination of the halobenzenes over NaCaY (CCl_4 , 25°C).

As to (i), cations such as Mg(II), Ca(II), and Ce(III) prefer locations at site I in the zeolite (15) which might be accessible for bromine but certainly not for the halobenzenes. Up to an exchange level of 55% the catalytic activity should be roughly the same as for the NaY catalyst. Experimentally this has not been observed, suggesting (i) is not a major factor. As illustrated in Fig. 4 the activities of the different NaCaY zeolites can be correlated with their acidities (16) (which are mainly of the Brønsted type). Perhaps the structural hydroxyl groups, which remain on the surface after a thermal activation, can act as the catalytic sites by activating bromine according to



as has been suggested by Rosen and Gandler (7) for the activation of bromine by silica.

As shown by the data in Fig. 3 the selectivity of the catalyst generally increases with an increase in the degree of cation exchange. The reverse is observed when the zeolites were applied in quantities (6) large enough to allow the complete adsorption of the reactants (Fig. 5) (excess catalyst method). The high selectivities observed in this procedure appear to be independent of the type of cation. These *p/o* ratios, which are considered initial selectivities in the catalytic procedure, induced us to study the effect of the hydrogen bromide liberated in the reaction in more detail.

p/o Selectivity and the Action of HBr

In Table 1 the effect of the amount of CaY on the selectivity in aromatic bromination is shown. When more catalyst is

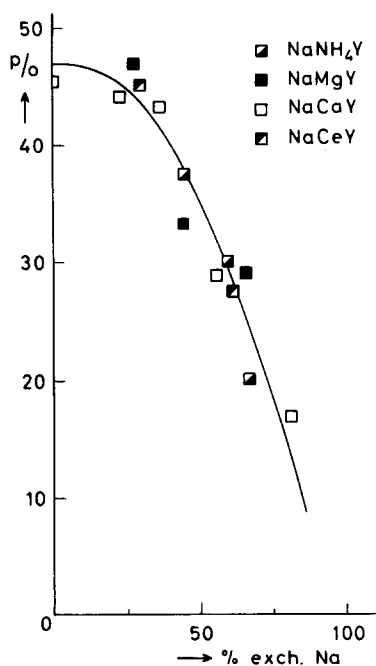


Fig. 5. Initial *p/o* selectivity in the bromination of bromobenzene (excess catalyst method) over zeolites activated at 400°C.

TABLE 1
The Effect of the Amount of CaY on *p/o* in the Bromination of Halobenzenes

X	C ₆ H ₅ X/CaY (mmole/g)	<i>p/o</i>
Br ^a	60	12 ^c
Br ^a	30	14 ^c
Br ^a	15	17 ^c
Br ^b	1	20 ^d
Cl ^b	1	40 ^d
F ^b	1	79 ^d

^a Bromobenzene (30 mmole), bromine (45 mmole), and CaY-82 were stirred in carbon tetrachloride (25 ml) at 25°C.

^b As *a*, but with halobenzene (4 mmole) and bromine (4 mmole).

^c *p/o* at 50% conversion.

^d *p/o* at 99% conversion.

used the *p/o* selectivity increases. When brominating fluoro-, chloro-, and bromobenzene over amorphous silica-alumina a constant *p/o* of 50, 10, and 9 is observed, respectively. In accordance with these data, a continuously decreasing *p/o* ratio was observed during zeolite-catalyzed bromination. Additional experiments showed that the decrease of the *p/o* ratio was not caused by isomerization of *para* into *ortho*-dibromobenzene.

The decrease in selectivity observed during reaction when using zeolites was accompanied by a deactivation of the catalyst. Figure 6 shows the results of some experiments where CaY after several hours in the bromination reaction was filtered, washed with carbon tetrachloride, and reused in a subsequent bromination experiment. The decrease in activity and selectivity observed was found to depend on the time under reaction conditions. Treatment of a suspension of CaY in carbon tetrachloride with excess gaseous HBr had a pronounced effect on the selectivity of the zeolite when subsequently used in the bromination reaction (Table 2). Also a decrease in activity was observed when the zeolite was activated at 520°C

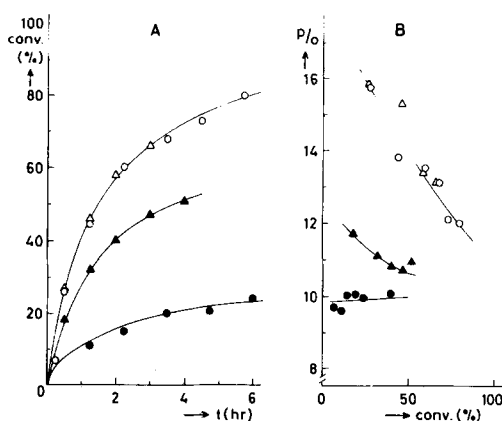
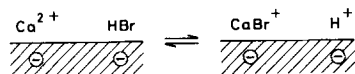


Fig. 6. Reuse of CaY-82 in the bromination of bromobenzene (CCl_4 , 25°C), (O, Δ) 1st reaction; (\blacktriangle) reuse after 3-hr reaction conditions; (\bullet) reuse after 24-hr reaction conditions.

before the HBr treatment. This deactivation is connected with a decreased crystallinity of the zeolites. X-Ray analysis showed that with CaY-520 $^\circ\text{C}$ roughly 20% reduction of the crystallinity had occurred whereas with CaY-400 $^\circ\text{C}$ hardly any decay was observed after the HBr treatment. In a modification of the procedure where the zeolite in carbon tetrachloride first was contacted with bromine for 1 hr and then with bromobenzene no effect was observed. We suggest that the deactivation of the zeolite by HBr is also connected with an ion exchange process which transforms the zeolite gradually into a low-activity HY-type zeolite.



Realizing the high initial p/o ratio we tried to reduce the deactivation of the zeolite. Two approaches were investigated.

(A) Use of zeolites with high HBr stability. Use of dealuminated (17) NaCaY zeolites in bromination experiments showed no improvement. The acid stable zeolites H-mordenite (Zeolon 100), H-ZSM-5 (18), HL, and CaL showed a very low activity in the bromination reaction even at 75°C . Of these only H-mordenite is unable to

adsorb bromobenzene from the carbon tetrachloride solution.

(B) Removal of HBr from the reaction medium. Several alkaline and alkaline-earth carbonates, hydrogen carbonates, sodium phosphates, and also sodium acetate were tested as additives in a zeolite-catalyzed liquid phase bromination. Best results were obtained with sodium hydrogen carbonate. However, in the reaction of HBr and hydrogen carbonate, carbon dioxide and water are formed. The latter deactivates the catalyst by adsorption and by accelerating deactivation by HBr. By adding sodium hydrogen carbonate and zeolite KA, which selectively adsorbs the water formed, these results were further improved (see Table 3). It was also possible to increase the activity and the selectivity of zeolites with very low catalytic activities such as NaY, NaX, and CaX. In conclusion HBr capture reduces decay and coadsorption and forms a substantial improvement of the bromination procedure.

Effect of Partial Poisoning of the Zeolite Surface

The high p/o ratios observed are assumed to be due to reaction inside the crystalline zeolite cavities. As a loss in

TABLE 2

Influence of HBr and Br_2 Pretreatment of CaY on Activity and p/o -ratio^a

T_{act} ($^\circ\text{C}$)	Pretreatment	$t_{50\%}$ (min)	$p/o-50\%$ ^b
520	—	66	12.5
520	1 hr Br_2	66	12.5
520	1 hr HBr	150	7.5
400	—	60	12.5
400	1 hr Br_2	70	12.5
400	1 hr HBr	70	9.8

^a Bromobenzene (30 mmole), bromine (45 mmole), and CaY-82 (1 g) were stirred in carbon tetrachloride (25 ml) at 25°C .

^b p/o at 50% conversion.

crystallinity results in lower *p/o* ratios (Fig. 6), the reaction on the amorphous part of the surface of the catalyst is considered to proceed with a lower selectivity. Selective poisoning of the outer surface of a fresh catalyst with bulky compounds (19) such as tri-*o*-cresyl phosphate did not influence the *p/o*. This is not surprising in view of the low contribution of the outer surface to the total catalytically active surface. In order to find out whether sites with different *p/o* selectivity are operative at the inner surface, the zeolite was partially poisoned with strongly adsorbing compounds. Several amines and methanol were added in amounts of 1 molecule/cavity. Roughly the same *p/o*

selectivities were observed as without the adsorption of poisoning compounds. The results in Fig. 7 show that the activity decreased in the order of increasing basicity and molecular volume of the poison. Pyridine which is supposed to react with Brønsted and Lewis sites causes a smaller decrease than 2,6-dimethylpyridine which selectively reacts with Brønsted sites (20). This supports the idea that hydroxyl groups (Brønsted acid sites) are the catalytic active sites.

Solvent Effect

The influence of the polarity of the solvent on the reaction rate and *p/o* selec-

TABLE 3
Effect of the Addition of NaHCO₃ and KA^a

X ^b	Catalyst	Additives	<i>t</i> _{50%} (hr)	<i>p/o</i> —50%	Conversion after 5 hr (%)
Br	CaY-82	—	1.25	12.4	78
Br	CaY-82	KA	1.25	12.5	77
Br	CaY-82	NaHCO ₃	1	15.6	60
Br	CaY-82	NaHCO ₃ , KA	0.50	16.5	77
Br	NH ₄ Y-57	—	3.25	3.9	60
Br	NH ₄ Y-57	NaHCO ₃ , KA	2.50	7.0	63
Br	MgY-68	—	1.75	8.2	60
Br	MgY-68	NaHCO ₃ , KA	1.25	15.0	70
Br	CeY-89	—	4	16.0	50
Br	CeY-89	NaHCO ₃ , KA	1	26.0	91
Br	NaY ^d	—	—	14.0 ^e	12
Br	NaY ^e	NaHCO ₃ , KA	—	19.9 ^e	37
Br	NaX	—	—	21.7 ^e	<2
Br	NaX	NaHCO ₃ , KA	—	15.9 ^e	4
Br	CaX	—	—	9.5 ^e	13
Br	CaX	NaHCO ₃ , KA	—	13.2 ^e	38
Cl ^f	CaY-82	—	0.7	24	86
Cl ^f	CaY-82	NaHCO ₃ , KA	0.25	34	89
F ^f	CaY-82	—	0.35	73	90
F ^f	CaY-82	NaHCO ₃ , KA	0.20	85	93

^a Halobenzene (30 mmole), bromine (45 mmole), and catalyst (1 g), were stirred in carbon tetrachloride (25 ml) at 25°C. All zeolites were activated at 400°C except CaY (520°C). Additives were used in quantities of 3 g of NaHCO₃ and 2.5 g of KA.

^b Halobenzene C₆H₅X.

^c *p/o* after 5-hr reaction.

^d After 90-hr reaction, 17% conversion, *p/o* 9.9.

^e After 90-hr reaction, 84% conversion, *p/o* 18.

^f Bromine 35 mmole.

tivity was studied by brominating bromobenzene over CaY in carbon tetrachloride, chloroform, and methylene chloride. As shown in Table 4 an increase in polarity of the solvent is accompanied by a decrease in reaction rate and an increase in *p/o* selectivity. The former is explained by a decrease in the concentration of bromobenzene in the zeolite. Thus 2 g of CaY adsorbed 85, 17, and <1% of the bromobenzene in a solution of 2 mmole of bromobenzene in 15 ml of CCl₄, CHCl₃, and CH₂Cl₂, respectively at 25°C. More satisfactory reaction rates were obtained by raising the reaction temperature, which has no effect on the *p/o* selectivity. Selectivity and reaction rate were further increased by adding NaHCO₃ and KA. In view of these results we investigated a solvent-free bromination at room temperature by consecutively adsorbing aromatic reactant and bromine. As shown in Table 5 very high *p/o* selectivities were obtained.

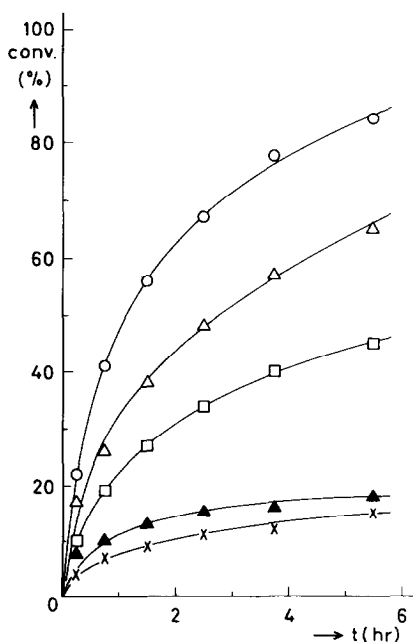


FIG. 7. Effect of poisoning (1 molecule/cavity) CaY-82 on the conversion of bromobenzene. (O) blank; (Δ) methanol; (□) pyridine; (▲) 2,6-dimethylpyridine; (X) triethylamine.

TABLE 4
Solvent Effect in the Bromination of Bromobenzene^a

Reaction temperature (°C)	Solvent	<i>t</i> _{50%} (min)	<i>p/o</i> -50%
25	CH ₂ Cl ₂	>600	23
40	CH ₂ Cl ₂	400	23
40 ^b	CH ₂ Cl ₂	360	35
25	CHCl ₃	300	17
40	CHCl ₃	80	17
40 ^b	CHCl ₃	45	20
65	CHCl ₃	15	17
25	CCl ₄	60	12.5
40	CCl ₄	30	12.5
40 ^b	CCl ₄	12	16
65	CCl ₄	<6	12.5

^a Bromobenzene (30 mmole), bromine (45 mmole), CaY-82 (1 g, *T*_{act} 400°) were stirred in 25-ml solvent.

^b NaHCO₃ (5 g) and KA (2.5 g) added.

Compared to the excess catalyst method the *p/o* selectivity has further improved by a factor of 2.5. In both methods an increase in halobenzene/catalyst ratio resulted in lower *p/o* selectivities.

Mechanistic Considerations

Experiments with different organic reactants, showing an order of reactivity in zeolite-catalyzed bromination

toluene > benzene > fluorobenzene
> chlorobenzene > bromobenzene

TABLE 5
Solvent-free Bromination^a

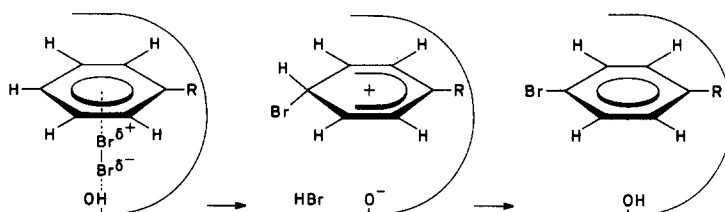
X	C ₆ H ₅ X/cat. (mmole/g)	Br ₂ /cat. (mmole/g)	Catalyst	Conv. ^b (%)	<i>p/o</i>
Br	2.0	2.3	NaY	79	>100
Br	0.8	1.0	NH ₄ Y-59	65	34
Br	2.6	3.4	NH ₄ Y-59	87	8
Br	1.3	1.4	MgY-67	70	70
Br	2.6	2.9	MgY-67	81	45
Br	2.2	3.5	CaY-82	99	53
Br	2.2	3.0	CeY-62	98	52
Cl	1.3	1.6	CaY-82	85	>70
F	1.8	1.6	CaY-82	87	>100

^a Halobenzene and bromine were adsorbed from the gas phase. After 0.5- to 2-hr reaction the zeolite was treated with 4-N KOH and the slurry extracted with carbon tetrachloride.

^b Conversion.

together with the *p/o* orientation observed, suggest an electrophilic character of the attacking species which makes a route to an anion radical (23) less probable. Generally electrophilic aromatic bromination involves the formation of a charge-transfer complex (21), the addition of Br^+ and the elimination of H^+ . Conventional aromatic brominations show no significant primary kinetic isotope effect proving that proton loss has made little progress in the transition state (22). From experiments in which bromobenzene and bromobenzene- d_5 were subjected to zeolite-catalyzed bromination (on CaY-82) a similar small isotope effect $k_{\text{H}}/k_{\text{D}} = 1.4$ was obtained showing that here the addition step is also rate deter-

mining. In this connection it may be noted that the zeolite favors the formation of the *p*-isomer although this is less strongly adsorbed than the *o*-isomer. The observed relation between Brønsted acidity and catalytic activity of the zeolite indicates activation of bromine (which may be already in interaction with the aromatic nucleus) by acidic OH-groups as visualized below. Molecular models show that the bromine-halobenzene charge-transfer complex (21) can be subject to simultaneous adsorption at two opposite walls of the cavities. This location would make the aromatic *p/o* substitution prone to steric influence by the zeolite walls. For the



rapid fall in selectivity as the reaction proceeds the hydrogen bromide formed is considered responsible. This product may interfere by changing the character of the inner surface or by its strong adsorption preventing optimal adsorption of the bromine/bromobenzene complex during the first step of the reaction or by crystallinity loss of the zeolite. Removal of HBr by adding NaHCO_3 and KA substantially improves the *p/o* ratio.

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