Mechanism of the Gas-Phase Isomerization of Dihalobenzenes over Zeolite β

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Abstract: The mechanism of the gas-phase isomerization of dihalobenzenes has been investigated over a wide pore zeolite β. A Langmuir–Hinshelwood rate law is obeyed, showing reaction in the adsorbed phase. Most of the products are formed according to a consecutive reaction scheme, as found in the homogeneous phase, with a small participation of a direct ortho $\rightleftharpoons$ para conversion. The electronic effect of substituents on the aromatic ring suggests a protonated intermediate, the isomerization of which is the rate-determining step. The influence of the acidity of the zeolite was studied by changing the Al content of the solid: the rate of isomerization goes through a maximum in function with the Al content, as expected for an acidic mechanism, but the rate of deactivation is not correlated with the Al content. The study of the adsorption of dichlorobenzene by CP-MAS–NMR and by FT-IR spectrometry confirms the existence of a protonated species, formed by interaction with the more acidic protons of the zeolite. Free radicals are detected by ESR upon adsorption of dichlorobenzene on the acidic zeolite. The participation of these radicals in the catalytic process could account for the particularities of the gas-phase reaction compared to liquid-phase catalysis.

Since the pioneer work of Venuto,[1] the application of zeolites as catalysts for the synthesis of fine chemicals has been growing rapidly. Van Bekkum, Kouwenhoeven,[2] and Hölderich[3] reviewed recently this field which is characterized by an overwhelming importance of patent literature. The acidic form of zeolites can catalyze any organic reaction subject to conventional proton catalysis. The use of a solid catalyst introduces many advantages such as the possibility to perform the reactions at higher temperatures than with liquid acids, the reduction of corrosion and environmental problems, and the possible regeneration of the catalyst. Whether the mechanism of the reaction is identical in heterogeneous and homogeneous phases is still to be established, and mechanistic studies are very scarce.

The present work deals with the isomerization of halobenzenes on zeolite β. Direct chlorination of benzene and chlorobenzene in the presence of metal halides always results in the formation of *o*- and *p*-dichlorobenzenes, the formation of the meta isomer being unfavored. The equilibrium mixture of dichlorobenzenes can be obtained by heating any of the isomers in the presence of AlCl₃[4,5] or BF₃·HF.[6] Water promotes the reactivity of aluminum chloride,[5] but the reaction is slow: by using a molar ratio of AlCl₃/substrate = 1/10 the equilibrium is reached after 20 h at 423 K. The isomerization proceeds by intramolecular 1,2-shifts of the halogen.[5,7] Disproportionation is negligible (<1%) at 423 K, but becomes notable at 473 K. Olah and co-workers[5,8] extended the study to dihalobenzenes and halotoluenes. They reached the conclusion that fluorine on the aromatic ring is unable to move under Friedel–Crafts isomerization conditions.

Isomerization of dihalobenzenes is interesting for the production of the meta isomer, which cannot be obtained directly. This isomer is the bulkier one and is thermodynamically favored at higher temperatures. Solid acids can be operated at high temperatures and constitute then an alternative to liquid-phase catalysts. Gas-phase isomerization of dichlorobenzenes over zeolite catalysts has been reported recently by Litterer,[9] who claimed a process that uses H-ZSM5 and H-mordenites of unspecified compositions, and by Toray Inc.[10] which uses ten-membered ring zeolites. In this case, deactivation of the catalyst in function of time was reported for the isomerization of chlorotoluenes at 573 K. This deactivation appears as the main problem for the practical use of heterogeneous catalysis. In the liquid phase, deactivation was reduced when processing a mixture of substituted halobenzenes with benzene or toluene. This positive effect of dilution suggests that coke deposit could occur through bimolecular processes, as usually accepted for hydrocarbon conversion on solid acids.

It is now well-known that small pore zeolites give rise to shape selectivity, which favors the formation of the less hindered product. In the classical case of xylene isomerization, ten-membered ring zeolites are used to increase para selectivity, whereas large pore zeolites yield equilibrium mixtures.[11] The aim of this work was to study the mechanism of dichlorobenzene isomerization; therefore, zeolite β was selected, since it is a large pore solid, which can be obtained with a broad range of chemical compositions.[12]

Experimental Section

1. Preparation and Characterization of the Catalyst. Zeolite β was synthesized by using tetraethylammonium hydroxyde (TEAOH) as the organic template and following the procedures described by Wadlinger et al.[12] The sample used for the kinetic studies had a chemical composition determined by elemental analysis: 0.38 Na₂O, 0.9 (TEA)₂O, 1 Al₂O₃, 15.9 SiO₂, 7.11 H₂O. The crystals appeared as spheroids with an average size of 0.6 μm.

This solid was calcined at 773 K, converted to the ammonium form by ion exchange in a 1 M solution of NH₄Cl at 333 K, and then calcined at 773 K to obtain the protonic form of the zeolite. After activation, the zeolite retained its crystallinity as evaluated from the X-ray powder diffraction pattern and exhibited a type I isotherm for the adsorption of nitrogen at 77 K. The adsorption capacities for nitrogen, *n*-hexane, and *o*-dichlorobenzene, listed in Table I, agree with literature data.[12,13]

2. Catalytic Tests. They were performed in a flow microreactor operated at atmospheric pressure. The catalyst was diluted in inactive alumina (zeolite/alumina = 2/1). Prior to any measurement, the catalyst was dehydrated in situ, under flowing N₂ at 723 K overnight. The reaction temperature ranged from 523 to 703 K.

(1) Venuto, P. B.; Landis, P. S. *Advances in Catalysis*; Academic Press: London and New York, 1968; Vol. 18, p 259.

(2) Van Bekkum, H.; Kouwenhoeven, H. W. *1st International Symposium on Heterogeneous Catalysis and Fine Chemicals*; Poitiers, France, 1988; Elsevier: Amsterdam, 1988; p 45.

(3) Hölderich, W. F. *1st International Symposium on Heterogenous Catalysis and Fine Chemicals*; Poitiers, France, 1988; Elsevier: Amsterdam, 1988; p 83.

(4) Spryskov, A. A.; Erykalov, Yu. G. *Zh. Obshch. Khim.* **1959,** *29,* 2798.

(5) Olah, G. A.; Tolgyesi, W. S.; Dear, R. E. A. *J. Org. Chem.* **1962,** *27,* 3449.

(6) Japan Patent 11 809, 1971.

(7) Erykalov, Yu. G.; Chirtulov, V. G.; Filatov, V. M. *Zh. Org. Khim.* **1969,** *5,* 1438.

(8) Olah, G. A.; Meyer, M. W. *J. Org. Chem.* **1962,** *27,* 3464.

(9) Litterer, H. European Patent 140, 123, 1984.

(10) Toray, Inc., Japan Patent 58144, 330, 1982.

(11) Weisz, P. B. *Proceedings of the 7th International Congress Catalysis,* Tokyo, 1980; Seiyama, T., Tanabe, K., Eds.; Kodanska-Elsevier: Tokyo, 1981; p 3.

(12) Wadlinger, R. L.; Kerr, G. T.; Rosinski, E. J. U.S. Patent 3,308,069, 1967.

(13) Benslama, R.; Fraissard, J.; Albizane, A.; Fajula, F.; Figueras, F. *Zeolites;* **1988,** *8,* 196.

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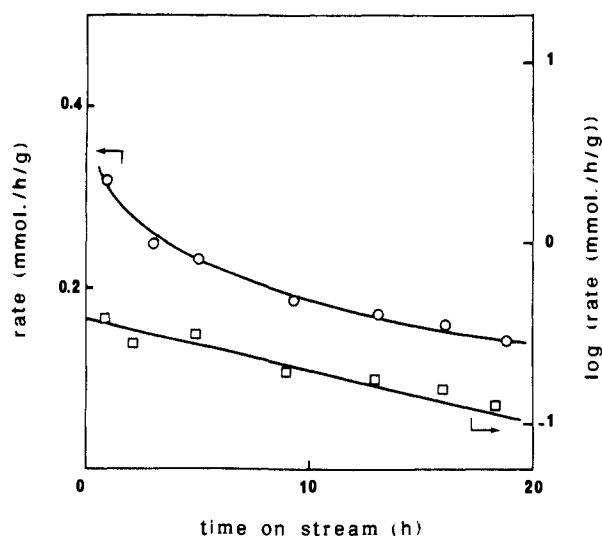1314   *J. Am. Chem. Soc., Vol. 112, No. 4, 1990*

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Figure 1. Activity as a function of time on stream for the isomerization of odCB over H-$\beta(8)$: reaction temperature, 643 K.

A carrier gas, usually N_2, was saturated with the vapor pressure of the reactant at a constant temperature and then passed through the reactor. The composition of the effluent was determined by sampling on line to a gas chromatograph equipped with a capillary column (30 m × 0.75 mm i.d.) bonded with an apolar phase. All connecting lines were placed in a hot box heated at 473 K in order to avoid condensations. The products were identified by GC-MS coupling.

In the course of the reaction, the catalysts suffer deactivation, as illustrated in Figure 1. Various models of decay were tested: the best fit is obtained with a first-order rate law; $dr/dt = -k_d r$, which takes the integrated form, $r = r_0 \exp(-k_d t)$, where r is the rate at time t, r_0 the initial rate (time = 0), and k_d the deactivation rate constant. This law has been reported for the cracking of n-dodecane over amorphous silica aluminas[14] and for the alkylation of chlorobenzene over ZSM5 zeolites[15] and seems characteristic of catalysts possessing a low density of sites.[14] This rate law was used to calculate r_0, the activity of the fresh catalyst, and the rate constant k_d which characterizes deactivation.

3. Characterization of the Adsorbed Phase. The nature of the adsorbed intermediate was investigated by ^{13}C CP-MAS–NMR, FT-IR, and ESR spectroscopies. The solid was first reactivated under flowing N_2 at 723 K, contacted with the vapor pressure of the reactant, and then analyzed by spectroscopy.

^{13}C CP-MAS–NMR spectra were recorded, at 75.47 MHz, on a AM 300 Bruker spectrometer equipped with a double-bearing probe. The samples were spun at 4 kHz in a rotor made of zirconia. The contact time between proton and carbon was 5 ms. Free induction decays (2000–10000) were accumulated per sample at a repetition time of 30 s which was long enough to ensure a complete relaxation of the carbon atoms.

The infrared measurements were performed on a Nicolet 320 FT-IR spectrometer. The solids were compressed under 200 MPa pressure into self-supporting wafers (10 mg per cm²). The resulting wafer was introduced in a cell equipped with KBr windows and connected via a stopcock with a vacuum line where the treatment of the catalyst was performed.

ESR signals were recorded on a Bruker ER.200D instrument. The activated solid was contained in a quartz tube connected to a vacuum line. After activation and adsorption of the substrate, the tube was sealed and transferred in the spectrometer.

Results

1. Kinetics of the Reaction. A preliminary study was done for the determination of conditions ensuring the absence of external diffusion limitations. The influence of the partial pressure of o-dichlorobenzene (odCB) on the rate, determined at 613 K, is reported in Figure 2. The reaction order decreases from 1 at low pressure to zero above 6.6 kPa, and it can then be concluded that the reaction occurs in the adsorbed phase. The kinetic results on Figure 2 can be fitted by a Langmuir–Hinshelwood law:

$$r = k\lambda P/(1 + \lambda P) \qquad (1)$$

(14) Abbot, J.; Wojciechowski, B. W. *J. Catal.* **1989**, *115*, 537.
(15) Chen, F. R.; Coudurier, G.; Naccache, C. *Proceedings of the 7th International Zeolite Conference*, Tokyo, 1986, Murakami, Y., Ijima, A., Ward, J. W., Eds.; Kodansha-Elsevier: Tokyo, 1986; p 733.

Table I. Surface Areas and Adsorption Capacities (g of Adsorbate for 100 g of Solid) of the Protonic Form of Zeolites β Determined at 300 K, at Two Different Partial Pressures (P/P_0)

sample	adsorption capacity at $P/P_0 = 0.95$		adsorption capacity at $P/P_0 = 0.2$		BET surface area (m²/g)
	n-hexane	odCB	n-hexane	odCB	
H-$\beta(8)^a$	25	21	16.7	14	633
H-$\beta(12)^a$			16.6		
H-$\beta(13)^a$			18.7		497

^{a} H-$\beta(x)$: x refers to the Si/Al ratio of the sample.

Table II. Rates of Isomerization of the Three Dichlorobenzene Isomers at 613 K^a

substrate	reaction rate (mol/h/g × 10^5)	conversion (%)	initial selectivity	activation energy (kJ/mol)
odCB	0.79	2	meta/para = 11	104
mdCB	0.89	1.9	para/ortho = 2.5	103
pdCB	1.39	6	meta/ortho = 25	89

^{a} Reactant pressure, 133 Pa.

in which λ is the adsorption constant of odCB on zeolite β, and k is the rate constant of the surface reaction. At 613 K these constants take the values $k = 2 \times 10^{-6}$ mmol/h/g and $\lambda = 1.6 \times 10^{-4}$ Pa^{-1}.

The activation energy determined in the zero-order range is $E_0 = 129$ kJ/mol. Erykalov et al.[7] reported 46 kJ/mol for the isomerization of o-dichlorobenzene by $AlCl_3$ in the liquid phase. The higher value obtained here reflects the lower activity of the zeolite compared to $AlCl_3$.

At low pressure, the kinetic equation reduces to $r = k\lambda P$, and the apparent activation energy is then $E_1 = -d(\log r)/d(1/T) = E_0 + \Delta H_a$ where ΔH_a stands for the enthalpy of adsorption of the reactant. The value $E_1 = 104$ kJ/mol was determined; therefore, an estimation of $\Delta H_a = 25$ kJ/mol can be obtained.

The products of the reaction are m- (mdCB) and p-dichlorobenzenes (pdCB). Only trace amounts of chlorobenzene (CB) were detected. For a typical conversion of 3% at 613 K, the distribution of products was as follows: mdCB; 2.6%; pdCB; 0.3%; CB; 0.08%. At 703 K, for a conversion of 37%, the distribution was as follows: mdCB, 26%; pdCB; 9%; CB, 1.6%; trichlorobenzenes, 0.18%.

The selectivity in the zeolite-catalyzed reaction then differs slightly from that expected from the liquid-phase results, since disproportionation is minimized. The amount of CB is small but higher than that of trichlorobenzenes, and the pdCB isomer appears as a primary product, formed even at very low conversion.

However, the ratio mdCB/pdCB in the products decreases when increasing the conversion, as illustrated in Figure 3, and then pdCB is formed mainly by the successive mechanism proposed by Olah et al.[5] The rates of isomerization of m- and p-dichlorobenzenes were measured at 613 K, in the first-order range of the kinetic law. The initial reaction rates and selectivities are listed in Table II for the isomerization of the three dichlorobenzenes. A small but noticeable interconversion is then observed between ortho and para isomers.

The $AlCl_3$-catalyzed reaction follows a consecutive reaction scheme[5]

Scheme I

$$odCB \rightleftharpoons mdCB \rightleftharpoons pdCB$$

and the ionic mechanism rules out the possibility of a direct path between odCB and pdCB. However, the zeolite-catalyzed reaction is better described by a triangular scheme (see Scheme II).

The conversion was increased up to 65% at a reaction temperature of 703 K. The two kinetic models, represented by Schemes I and II, were compared with the experimental results, taking the set of rate constants reported in Table III. The best fit (Figure 4) was obtained assuming a small participation $(k_3/k_1 = 0.04, k_{-3}/k_1 = 0.09)$ of a direct odCB $\rightleftharpoons$ pdCB interconversion.
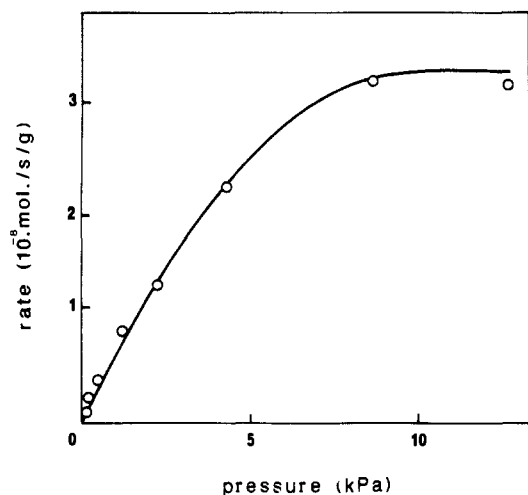
Figure 2. Influence of the partial pressure of odCB on the reaction rate of odCB isomerization at 613 K.
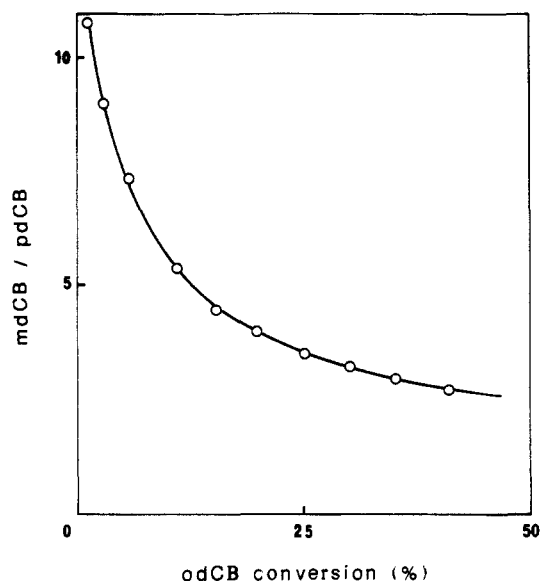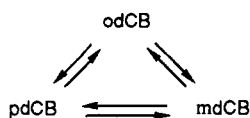

Figure 3. Selectivity ratio mdCB/pdCB as a function of odCB conversion at 643 K over H-β(8).

Scheme II

This set of constants can be used to compute the equilibrium composition of the reaction mixture, defined as d(odCB)/dt = d(mdCB)/dt = d(pdCB)/dt = 0. The composition thus obtained at 703 K was mdCB/odCB/pdCB = 0.47/0.37/0.16 which compares reasonably well with the composition 0.45/0.36/0.19 obtained from the thermodynamic data.[16]

Before reaching any conclusion concerning the mechanism of the reaction, we must be aware that diffusional limitations can modify the distribution of products, mainly in the case of microporous solids. When substantial diffusion resistance exists, most molecules remain in the crystallite long enough for several reaction steps to occur, and the products are mostly multistep products. Wei and Prater[17] have shown that in such a case, the consecutive reaction Scheme I changes to the more complex triangular Scheme II, due to diffusion-disguised rate constants. This model has been successfully applied by Chutoransky and

(16) Stull, D. R.; Westrum, E. F., Jr.; Since, G. C. *The Chemical Thermodynamics of Organic Compounds*; Wiley: New York, 1968; p 533.
(17) Wei, J.; Prater, C. D. *Advances in Catalysis*; Academic Press: London and New York, 1962; Vol. 13, p 203.

Table III. Relative Rate Constants for the Isomerization of Dichlorobenzenes over H-β(Si/Al = 8), at Three Different Temperatures[a]

temp (K)	k_1	k_{-1}	k_2	k_{-2}	k_3	k_{-3}
		Consecutive Scheme				
613	1	0.32	0.8	1.74	0	0
643	1	0.39	0.98	1.55	0	0
703	1	0.3	0.8	0.91	0	0
		Triangular Scheme				
613	1	0.35	0.87	1.83	0.07	0.09
643	1	0.43	1.07	1.63	0.06	0.09
703	1	0.32	0.75	1.02	0.04	0.09

[a]The partial pressure of reactants was 133 Pa. Rate constants defined in Schemes I and II.
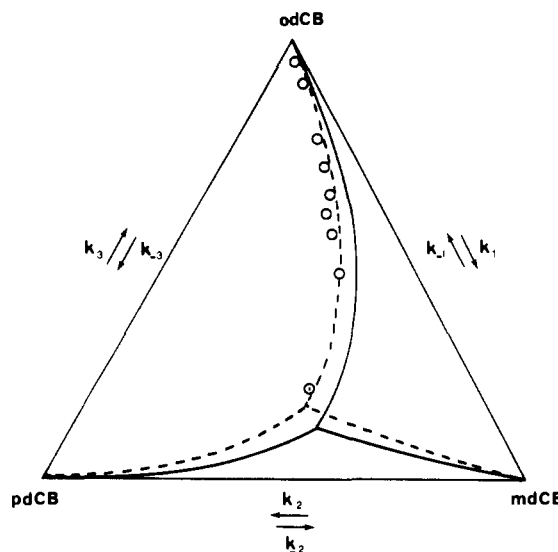

Figure 4. o-Dichlorobenzene isomerization reaction paths: (O) experimental compositions; compositions calculated assuming a triangular scheme (dotted line) or a linear scheme (dark line); and (⊙) equilibrium composition at 703 K.

Dwyer[18] to interpret the direct interconversion between the ortho and para isomers in the isomerization of xylenes over zeolites. Depending on the size of the crystals, these authors observed either the consecutive mechanism on small particles (0.2–0.4 μm), in the absence of diffusional control, or the triangular scheme on large particles (2–4 μm) in the presence of strong diffusional limitations.

The interpretation of the results in terms of reaction Scheme I, therefore, depends on the importance of diffusional limitations. The modified Thiele modulus, $\Phi = R(r/D_{\text{eff}})^{1/2}$, was calculated from the size of the crystals ($R = 0.3$ μm) and the highest rate measured at 703 K ($r = 3 \times 10^{-7}$ mol/s/g). The intracrystalline diffusion coefficient, D_{eff}, for configurational diffusion around 600 K is typically 10^{-12} cm^2/s.[11] This is most probably a lower limit, since Chutoransky and Dwyer[18] report $D_{\text{eff}} = 10^{-7}$ cm^2/s for the effective diffusion coefficient of o-xylene in a medium pore zeolite at 500 K. The value of the Thiele modulus obtained with this set of values is $\Phi = 0.02$, which ensures that diffusion resistance is negligible.

The direct odCB ⇌ pdCB interconversion, which is not an artefact introduced by diffusional limitations, cannot, however, be reconciled with the ionic mechanism. This small contribution to the overall process can be attributed to a radical process, as will be discussed further.

2. Effect of Substituents on the Rate. The mechanism proposed by Olah[5] can be written as
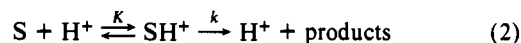
$$S + H^+ \underset{}{\overset{K}{\rightleftharpoons}} SH^+ \overset{k}{\longrightarrow} H^+ + \text{products} \qquad (2)$$

(18) Chutoransky, P.; Dwyer, F. G. ACS Symp. Ser. **1973**, *121*, 540.

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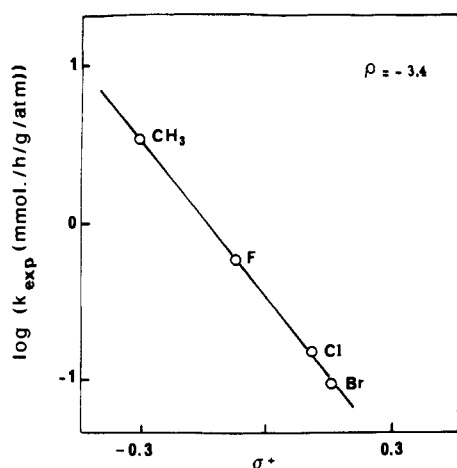
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Figure 5. Effect of the substituents on the rate for the isomerization of para-substituted bromobenzenes over H-β(8): reaction temperature, 613 K; reactant pressure, 133 Pa; $k_{exp} = r/P$.

in which S stands for the substrate, K the equilibrium constant for protonation, and k the rate constant of the halogen shift elementary step. In turn, the rate law can be deduced as

$$r = k[SH^+] = kK[H^+][S] \tag{3}$$

which appears similar to the kinetic law obtained in the heterogeneous phase since in the first-order range eq 1 reduces to

$$r = k\lambda P \sim kK[H^+][S] \tag{4}$$

Protonation of the substrate, which follows electrophilic directing effects in aromatic substitutions, will be affected by the electron-withdrawing effect of the substituents. This effect can be investigated by using the Hammett equation applied to the protonation step. This equation takes the form log r = constant + $\sigma\rho$, in which σ characterizes the type of substituent and ρ the nature of the reaction.

The influence of substituents was investigated with para-substituted bromobenzene, because bromine is easily shifted at low temperature. The reactions were carried out at 613 K under 133 Pa of reactant partial pressure, in order to ensure a first-order rate law, and a reaction rate below 10^{-6} mol/s/g to avoid diffusional limitations.

The results are reported in Figure 5 and in Hammett coordinates

$$\log r = -3.39\sigma^+ - 0.48 \tag{5}$$

The negative value of ρ reflects the development of a positive charge in the transition state, as expected for this reaction.

A second series of experiments was done with para-substituted fluorobenzenes. Fluorine cannot be displaced from the ring,[5,8] and the reaction rate is then controlled by the facility to break the Ar–X bond. The results obtained at 613 K and 133 Pa of partial pressure for the reactant are reported in Figure 6. They show a good correlation between the rate of reaction and the strength of the Ar–X bond. This relationship suggests that the slow step of the reaction is the splitting of the Ar–X bond in the transition intermediate, in agreement with the mechanism proposed for the AlCl₃-catalyzed reaction.[8]

The effect of the substituents therefore agrees nicely with the formation of a protonated intermediate, the decomposition of which yields the products.

3. Effect of the Al Content of the Zeolite. It is widely agreed that the acid strength of zeolites increases with the Si/Al ratio of the framework.[19] Zeolite β can be synthesized in a wide range of compositions and then permitted to investigate the effect of the Al content on catalytic properties. The small size of the crystals is, here also, a good protection against diffusional limitations. The results of this study are summarized in Figure 7: a volcano curve is observed, as with many other organic reactions.[20]
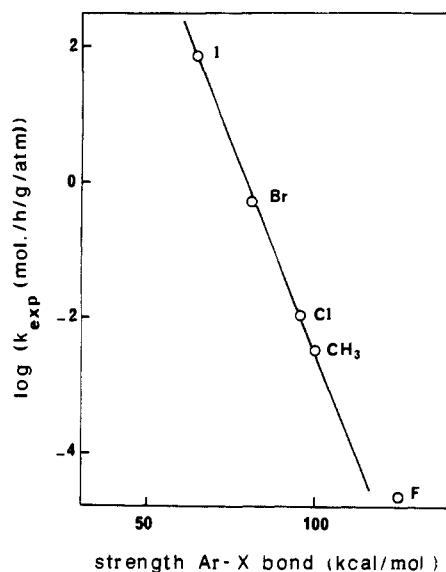
(19) Barthomeuf, D. *Mat. Chem. Phys.* **1987**, *17*, 49.

strength Ar-X bond (kcal/mol)

Figure 6. Effect of the substituents on the rate for the isomerization of para-substituted fluorobenzenes over H-β(8): reaction temperature, 613 K; reactant pressure, 133 Pa; $k_{exp} = r/P$.
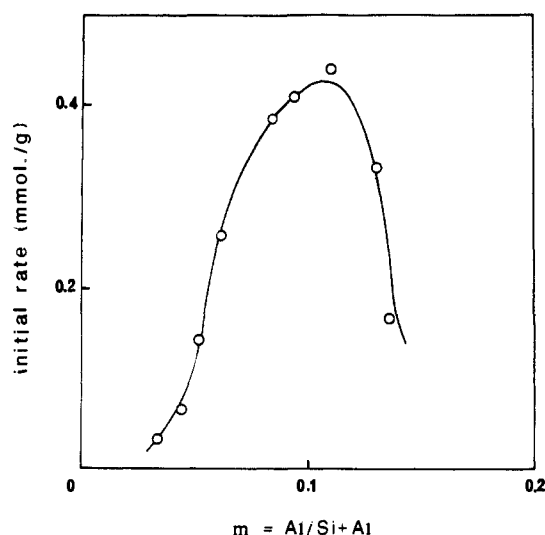

m = Al/Si+Al

Figure 7. Catalytic activity, as r_0, of H-β for the isomerization of odCB at 643 K as a function of aluminum content.

This behavior agrees with current ideas concerning the acidity of zeolites.

Barthomeuf[19] proposed that such a change of catalytic activity with the Al content reflects the influence of α_0, the efficiency coefficient of the site, and of its acid strength. These two factors have parallel variations with the Al content because zeolites are both an acid and the solvent of this acid. At high Al content the interactions between AlO₄⁻ tetrahedra decrease both the efficiency and the strength of the sites. Upon dealumination, the decrease in the number of sites is overbalanced by the increase in α_0 and strength, up to a point where all the sites will be isolated. Beyond this point, α_0 and the acid strength should be the highest and constant; then activities on a per weight basis are expected to decrease as observed. Selectivities depend only on the conversion and not on the composition of the zeolite.

It is interesting to notice that both deactivation and chlorobenzene formation show no correlation with the Al content of the zeolite and thus with acidity. It was previously observed that deactivation of mordenites[21] was faster in the presence of air and

(20) Coq, B.; Durand, R.; Fajula, F.; Moreau, C.; Finiels, A.; Chiche, B.; Figueras, F.; Geneste, P. *1st International Symposium on Heteregeneous Catalysis and Fine Chemicals*; Poitiers, France, 1988; Elsevier: Amsterdam, 1988; p 241.
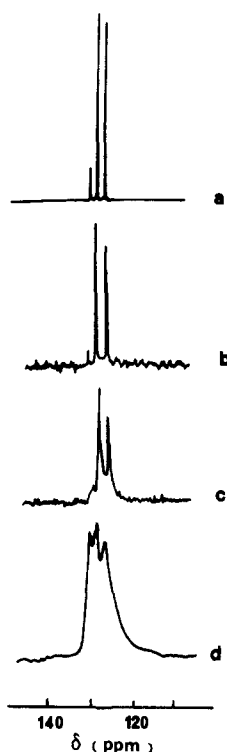
Figure 8. NMR spectra of liquid odCB (a) and of odCB adsorbed on (b) silica, (c) Na-β(8), and (d) H-β(8).

Figure 9. IR spectra of activated and evacuated H-β(8) (a) and after adsorption of odCB at 298 K (b) and 348 K (c).

lower in hydrogen or wet nitrogen. A radical mechanism was then suggested. The results obtained on pillared clays support this proposal: these solids show a low activity above 673 K, deactivate very fast, and catalyze disproportionation as the main reaction. Pillared clays possess strong acid sites and contain 4.6 wt% Fe_2O_3. These experimental facts suggest the possibility of radical mechanisms initiated by the reduction of Fe^{3+} ions.

4. Adsorption of Dichlorobenzenes. The ^{13}C NMR spectrum of liquid *o*-dichlorobenzene is reported in Figure 8a. Two intense lines corresponding to the carbons which bear hydrogen appear as well as a weak line due to the resonance of the carbons bearing chlorine. The lower intensity of this resonance reflects the higher relaxation time of quaternary carbon atoms.[22] The adsorption of odCB on silica, or on nonacidic Na-β, does not perturb dramatically the ^{13}C spectrum obtained by CP-MAS-NMR (Figure 8 (parts b and c)). The traces of paramagnetic impurities present in the Na form of the zeolite are unable to change the relaxation of the quaternary carbon atoms. The weak intensity of the peak of the quaternary carbons then mainly results from the low polarization transfer to these carbons which may exist due to the absence of close protons. By contrast, this peak is much more intense when odCB is adsorbed on the protonic form of the zeolite (Figure 8d) which evidences a direct interaction between protons and the quaternary carbons. A significant broadening of all resonance lines is moreover observed, due to the reduced mobility of the adsorbate in the protonic zeolite. In liquid phase, Olah et al.[8] reported ring deuteration accompanying isomerization of dichlorobenzenes with D_2O pretreated aluminum chloride as catalyst. They then proposed a σ-complex type intermediate. The present NMR results of gas-phase adsorption are then consistent with this intermediate.

The infrared study of adsorption has been performed by using *p*-dichlorobenzene as substrate. Among the three isomers, para is the most symmetric and therefore possesses the simplest spectrum. The acidic form of the H-β zeolite, evacuated overnight at 1.3 × 10^{-3} Pa and 673 K, shows the IR spectrum reported in Figure 9a. This spectrum presents some common features with
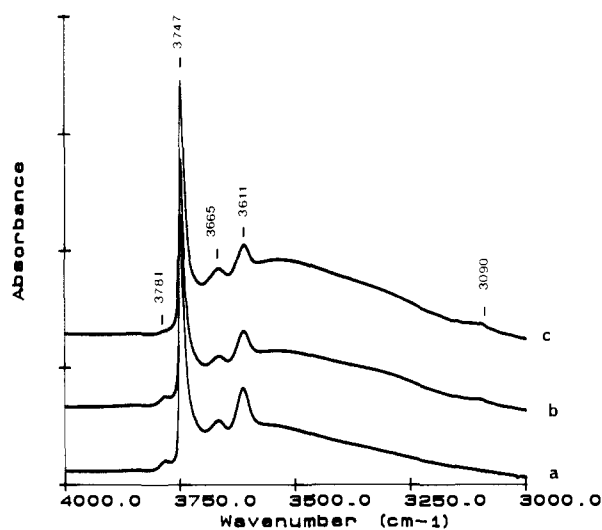
that of Na-TEA-β reported by Corma et al.[23] After decomposition of the organic template in vacuum, the Na form of the zeolite develops three bands in the OH region: a band at 3745 cm^{-1} assigned to nonacidic silanol groups, a 3680-cm^{-1} band assigned to OH groups bonded to extraframework Al species, and a band at 3615 cm^{-1} assigned to framework acidic OH groups. This spectrum is reproduced on the Na form of our sample obtained by calcination of the original sample in air. By exchange of the Na$^+$ ions, the IR spectrum is modified since the 3615-cm^{-1} band shifts to 3610 cm^{-1} and the 3680-cm^{-1} band to 3665 cm^{-1}, and a new small band, not reported for Y zeolites,[24] appears at 3782 cm^{-1}. The shift of the framework OH band toward lower wave numbers is evidence of an increase of the acid strength upon ion exchange, which is well-known on Y zeolites.[24]

Upon adsorption of a small amount of *p*-dichlorobenzene (133 Pa, at room temperature) the acidic OH band decreases, the 3747-cm^{-1} band remains unaffected, and a broad band around 3400 cm^{-1} appears (Figure 9b). The decrease of the 3782-cm^{-1} band suggests that these OH groups also interact with the substrate. A longer contact time, after heating at 343 K, induces a strengthening of this tendency (Figure 9c). Simultaneously, the sharp peaks of the adsorbate appear (not shown) at their normal position compared with the liquid phase, excepted the 3100-cm^{-1} band which is shifted by 10 cm^{-1} toward higher frequencies.

Infrared studies of the interaction of many organic molecules with zeolite surfaces have been reviewed by Ward,[24] and this earlier work provides a simple interpretation of the results. The decrease in intensity of the 3610-cm^{-1} band shows the interaction of the substrate with the more acidic protons of the zeolite. The infrared band characteristic of OH groups is shifted toward lower frequencies and broadened, which accounts for the appearance of the 3400-cm^{-1} band. The C–H stretching frequencies that are in the plane of the aromatic ring are shifted by 10 cm^{-1} toward higher frequencies as a result of the decrease in the electron density upon adsorption. The infrared study of adsorption is then consistent with the general scheme since it suggests a protonated intermediate formed by interaction with the strong Brönsted sites of the solid.

The ESR spectrum of H-β after activation is reported in Figure 10a: a small signal is observed close to $g = 2$ which could be attributed to some graphitic residues formed by the incomplete combustion of the organic template used for the synthesis of the zeolite. In addition, a weak signal attests to the presence of Fe^{3+} ions in the sample. Upon adsorption of odCB (133 Pa) at room

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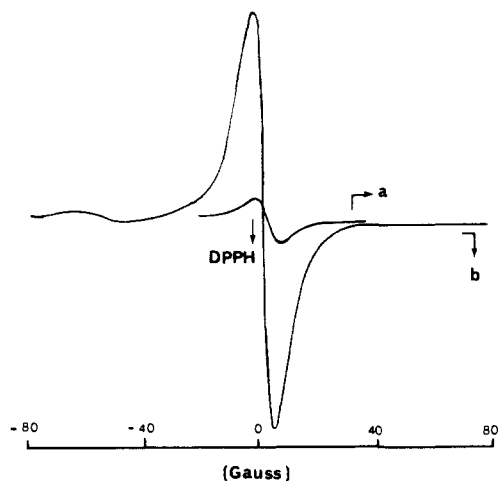
Figure 10. ESR spectra of activated and evacuated H-β(8) (a) and after adsorption of odCB at 298 K (b).

temperature, a sharp and intense line develops, showing the formation of a radical (Figure 10b). Heating the sample at 643 K after adsorption results in an increase (×16) and narrowing of the signal. By further increase in the pressure of the adsorbate at room temperature the intensity is lowered. Since no hyperfine structure could be obtained, the identification of this radical is speculative, but it is clearly formed from o-dichlorobenzene and then validates the proposal of the intervention of radical mechanisms in some steps of the process.

Discussion

The mechanism observed in the zeolite-catalyzed conversion of halobenzenes presents many analogies with the homogeneous reaction catalyzed by AlCl$_3$. In both cases the ionic mechanism predominates. It accounts for the effect of substituents on the substrate and of the composition of the zeolite on the rate. Moreover this mechanism is consistent with results obtained by NMR and IR studies of the adsorbed phase. However a small discrepancy appears, due to a little contribution (<5.%) to the rate of a nonionic mechanism accounting for a direct odCB $\rightleftarrows$ pdCB interconversion. This interconversion is not an artefact introduced by diffusional limitations, and the ESR evidence of the formation of free radicals validates the proposal of a radical mechanism for that reaction.

Indeed radical mechanisms are known on zeolites: benzene chlorination at 423 K has been reported to occur by an ionic process (electrophilic substitution) on aluminum-rich Y zeolites, whereas a radical addition process was observed on high silica materials.[25] Moreover, halogenation of aromatics by Cu halides[26] and dehalogenation of halobenzenes[27] have been demonstrated to follow a radical mechanism. Following these ideas, this direct ortho–para conversion could be described as a dehalogenation, followed by rehalogenation at the ortho or para position. It is interesting to notice that radical processes could account for catalyst deactivation too. The absence of correlation between the rate of deactivation and the Al content of the catalyst, the faster deactivation in the presence of air and of iron-containing clays, and the detection of biphenyls in the carbon residue extracted from the catalyst after dissolution in HF[21] suggest that coke formation could be, for the main part, a radical process initiated by the reduction of the Fe^{3+} impurities contained in the solid. The presence of ferric ions can be ascertained on the basis of the elemental analysis which shows that the various samples contain 500–1000 ppm of iron and a very weak ESR signal around $g = 4$ which can be attributed to Fe^{3+} ions.

Another characteristic of the gas-phase reaction on zeolite β is the inhibition of disproportionation, which may be attributed to the steric constraints introduced by the size of the pores. This restriction is lowered on pillared clays, and disproportionation then appears as the main reaction.

Conclusion

The ionic character of the mechanism of the AlCl$_3$-catalyzed isomerization of dichlorobenzenes is preserved when the reaction is performed in the gas phase over zeolite β as catalyst. However, the number of strongly acidic protons per gram of catalyst is much lower in a zeolite than in AlCl$_3$·H$_2$O. This reduced number of sites requires an increase of the reaction temperature up to 700 K. After contacting the substrate and the catalyst at this temperature, ESR gives direct evidence for the generation of free radicals, most likely by reduction of the Fe^{3+} impurities of the solid. These radicals participate in the catalytic process, and their role is probably important in deactivation.

Registry No. odCB, 95-50-1; mdCB, 541-73-1; pdCB, 106-46-7.

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