Versatility of Zeolites as Catalysts for Ring or Side-Chain Aromatic Chlorinations by Sulfuryl Chloride

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Zeolites catalyze chlorination of aromatics by sulfuryl chloride SO_2Cl_2. It is possible by an appropriate choice of the catalyst to effect at will, with very high selectivity, either the ring or the side-chain chlorination. Zeolite ZF520 is the choice catalyst for the former, because of its high Brønsted acidity. Zeolite NaX (13X) is a fine catalyst for the latter, free-radical chlorination; the reaction is best effected in the presence of a light source; the catalyst can be reused many times with no loss in activity. Both reaction modes, the ionic (ring chlorination) and the radical (side-chain substitution), are likely to occur outside of the channel network in the microporous solid. The effects of various experimental factors—such as the nature of the solvent, the reaction time and temperature, the Brønsted acidity of the solid support, the presence of radical inhibitors, and the quantity of catalysts—were investigated. The procedures resulting from this study are very easy to implement in practice and are quite effective.

Introduction

Aromatic chlorides (ArCl) have a wide diversity of uses. They can serve as precursors for numerous functionalities, such as phenols, aromatic ethers and thioethers, amines, aryl hydrazines, benzonitriles, benzaldehydes, fluoro aromatics, silylated aromatics, and aromatic hydrocarbons.[1] There are two basic routes to effect these conversions. The one is through nucleophilic substitution of the halogen.[2] The other is through organometallic intermediates (ArLi, ArMgCl).[3]

We report here a preparation of aryl chlorides (ArCl) from sulfuryl chloride SO_2Cl_2. It has two assets: (1) catalysis by readily available zeolites; (2) the choice of the catalyst dictates whether the aromatic hydrocarbon starting material is ring chlorinated or side-chain chlorinated.

This feature of selectivity is obviously important to achieve. Yet, this is a nontrivial goal. Without added catalyst, chlorinations by sulfuryl chloride require high temperatures, and as such they are liable to be rather nondiscriminate reactions.[4] Take toluene as an example: the difficulty is to make selectively either benzyl chloride or chlorotoluenes.
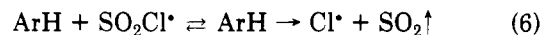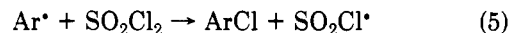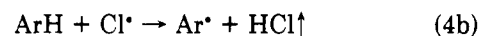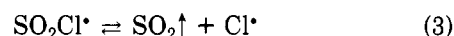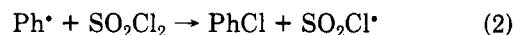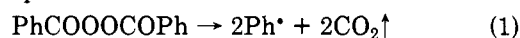
Our other objectives in this study were to design new processes that would require only low-cost ingredients (reagents, solvents), that would be parsimonious in the required amount of the catalysts, that would allow regeneration of the catalysts, and whose set up and workup procedures would remain very simple. Furthermore, these processes, besides being very selective, had also to lead to quantitative yields of the desired product.

We have had a measure of success in improving other important organic reactions by recourse to inorganic solid catalysts.[5] Such a methodology, we felt, would be likely to meet again with success.

An extremely encouraging indication that such optimism was well-founded came from rather unexpected quarters. It is well-known that fly ash from municipal incinerators is a favorable support for chlorinations leading to highly toxic waste chemicals such as polychlorinated aromatics

and dioxins. These reports[6] served as a strong inducement for us to run effective aromatic chlorinations on small solid particles serving as supports and as catalysts.

The Two Competing Mechanisms. Sulfuryl chloride can effect side-chain chlorinations such as the α-chlorination of toluene by a *radical pathway*. If for instance benzoyl peroxide is used as the free-radical initiator, a plausible sequence of events is:[7]

$$PhCOOOCOPh \rightarrow 2Ph^• + 2CO_2\uparrow \qquad (1)$$

$$Ph^• + SO_2Cl_2 \rightarrow PhCl + SO_2Cl^• \qquad (2)$$

$$SO_2Cl^• \rightleftharpoons SO_2\uparrow + Cl^• \qquad (3)$$

$$ArH + SO_2Cl^• \rightarrow Ar^• + HCl\uparrow + SO_2\uparrow \qquad (4a)$$

$$ArH + Cl^• \rightarrow Ar^• + HCl\uparrow \qquad (4b)$$

$$Ar^• + SO_2Cl_2 \rightarrow ArCl + SO_2Cl^• \qquad (5)$$

$$ArH + SO_2Cl^• \rightleftharpoons ArH \rightarrow Cl^• + SO_2\uparrow \qquad (6)$$

It is generally considered that an equilibrium exists between chlorine atom, sulfur dioxide, and the chlorosulfonyl radical (eq 3).[8] The latter can abstract hydrogen as well as chlorine atoms (eqs 4 and 5). With aromatic substrates or aliphatic substrates in aromatic solvents, however, molecular chlorine and sulfuryl chloride show similar behaviors. Russell suggested that in these cases the major abstracting species is neither the chlorine atom nor the chlorosulfonyl radical but the aromatic/chlorine atom π-complex (eq 6).[9]

The alternate pathway is *ionic* and it gives rise to ring chlorination, with Lewis acidic catalysts A such as $AlCl_3$, I_2, $SbCl_5$, etc.[10,11] At high temperature, sulfuryl chloride is decomposed thermally into sulfur dioxide and elemental chlorine:

$$SO_2Cl_2 \xrightarrow{\Delta} SO_2 + Cl_2 \qquad (7)$$
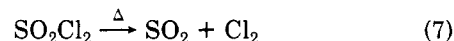
The latter, in the presence of the Lewis acidic catalyst,

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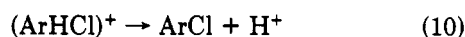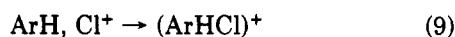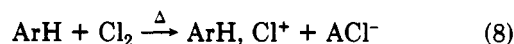(9) Russell, G. A. *J. Am. Chem. Soc.* 1958, *80*, 5002–5003.

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Table I. Comparison between Various Solid Catalysts (1 g) for the Thermal Chlorination of Toluene (0.47 mol) by Sulfuryl Chloride (0.12 mol) under Normal Lighting

| | | yields, % | | |
| | | α-chlorination | ring chlorination | |
run	catalyst			ortho:para
1	–	3	1	61:39
2	SiO$_2$	3	9	63:37
3	K10 montmorillonite	6	6	64:36
4	neutral Al$_2$O$_3$	11	53	58:42
5	xonotlite	20	34	59:41
6	benzoyl peroxide	80	0	–
7	zeolite FeX	2	9	59:41
8	zeolite HAB A40	69	1	74:26
9	zeolite NaX	74	0	–
10	zeolite NaY	81	0.4	–

Table II. Comparison between Various Zeolite Catalysts (1 g) for the Thermal Chlorination of Toluene (0.47 mol) by Sulfuryl Chloride (0.12 mol) during 30 min Using a 100-W "Solar" Lamp as a Source of Constant Intense Light

| | | yields, % | |
| | | α-chlorination | ring chlorination |
run	catalyst		
1	zeolite NaA	81	0
2	zeolite HAB A40	79	0.5
3	zeolite NaX	80	0.2
4	zeolite NaY	82	0.3

Table III. Effect of Light on Percent Yields for Chlorination of Toluene (0.47 mol) by Sulfuryl Chloride (0.12 mol) with Zeolite NaX as Catalyst (0.5 g) under Reflux for 30 min

conditions[b]	yield,[a] %
i	54
ii	72–78
iii	83

[a] Almost exclusive α-chlorination. [b] (i) Total darkness; (ii) normal lighting in the laboratory, a combination of daylight and of fluorescent light; (iii) intense light from a 250-W mercury vapor lamp standing 10 cm away from the reaction flask.

cleaves heterolytically, and the positive halogen serves as the electrophile for the aromatic substitution:

$$\text{ArH} + \text{Cl}_2 \xrightarrow{\Delta} \text{ArH, Cl}^+ + \text{ACl}^- \quad (8)$$

$$\text{ArH, Cl}^+ \rightarrow (\text{ArHCl})^+ \quad (9)$$

$$(\text{ArHCl})^+ \rightarrow \text{ArCl} + \text{H}^+ \quad (10)$$

An encounter complex is first formed (eq 8). It evolves into a Wheland intermediate (eq 9), which deprotonates into the reaction product.[12] Alternatively, when reactions are performed at room temperature, results from several kinetic studies strongly indicate that molecular sulfuryl chloride itself is the electrophile.[13]

Clearly, the free-radical mechanism demands the presence of a radical chain initiator. Its side-chain selectivity stems from the greater stability and lifetime of benzyl as compared to phenyl radicals. The ionic mechanism, conversely, will be favored by the use of polar solvents[14] that will help the formation of the loose ion pairs in eq 8, and its ortho–meta–para regioselectivity will be governed in the usual manner, either by atomic orbital coefficients in the hydrocarbon substrate or by the stability of the isomeric Wheland intermediates, depending on whether one is dealing with an early or a late transition state.[15]

Results

Reasons for the Zeolite Option. We elected as our test reaction the chlorination of toluene. In these exploratory runs, the substrate was its own solvent (50 mL). Sulfuryl chloride (10 mL) was introduced together with 1 g of a solid catalyst. This suspension was heated to reflux during 30 min. The resulting yields for α and for nuclear chlorination are shown, together with product distribution for the ring substitution,[16] in Table I. These results overall are encouraging. All these solids catalyze chlorination of toluene. In the absence of a catalyst, substrate conversion is a mere 4% after 30 min of reaction (run 1). This finding

is consonant with the results of an earlier study: under similar conditions, reaction times of 7 h are necessary to obtain satisfactory yields.[7] Silica favors ring chlorination (run 2). This agrees with a report of the specific conversion of toluene into chlorotoluenes, with no concomitant formation of benzyl chloride.[17] In order to achieve such a high level of selectivity the solid had been introduced in excess (107% w/w with respect to the reagents). When it is added in lesser quantities, as here, the selectivity drops, even though ring chlorination continues to be favored over side-chain chlorination. The K10 acidic montmorillonite (run 3) gives equipartition between the two reaction modes, equally mediocre. Neutral alumina (run 4) and the basic xonotlite silicate[18] (run 5) are much more selective. They favor the ring reaction, with product distributions deviating a little from the quasistatistical ortho–para ratios (2:1) in runs 1–3. With the exception of the ferric ion-exchanged X zeolite (Si/Al = 1.25) (run 7) that gives poor results, rather similar to those with the K10 montmorillonite, which also contains substantial amounts of ferric ions,[19] the other zeolite catalysts (runs 8–10) definitely orient the chlorination reaction to the side chain.

We deemed these initial results promising enough for further study, since they combined overall yields in the range 70–80% with rather impressive selectivities for α-chlorination (at least 70:1).

Side-Chain Chlorination. With toluene serving again as the substrate, we have sought to effect the clean, selective α-chlorination, avoiding ring chlorination in so doing. To guide the choice of a zeolite to catalyze the free-radical side-chain chlorination, we argued to ourselves that the O$_3$SiOAlO$_3$ network is more likely to undergo homolytic opening into O$_3$SiO$^•$ + O$_3$Al$^•$, thus generating silyloxy radicals. These would serve as the catalytic centers to initiate radical chain reactions. The greatest density of such centers is to be expected with aluminum-rich zeolites. Hence, a zeolite with as low as possible a Si/Al ratio is called for. Indeed, with a similar experimental set

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(16) For these and all the subsequent chlorinations of toluene, the GC analysis conditions we routinely adopted did not allow us to distinguish para and meta isomers. However, each time we specifically searched for this latter product in our reaction mixtures, its proportion was found to be two or three percents, as compared with o- and p-chlorotoluenes.

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(19) Typical dry basis composition of this solid is (in wt %): SiO$_2$, 80.4%; Al$_2$O$_3$, 7.4%; Fe$_2$O$_3$, 4.75%; CaO, 1.14%; MgO, 0.38%; TiO$_2$, 0.83% (Dr. A. Mathy, personal communication).

Table IV. Effect of Light with an Incandescent Lamp 10 cm Away from the Reaction Flask in the Presence or Absence of Zeolite NaX as the Catalyst (Other Conditions as in Table III)

		yields, %		
lamp	amt of cat., g	α-chlorination	ring chlorination	ortho: para
200 W[a]	0	2	0.4	58:42
200 W[a]	0.5	81	0	–
100 W[b]	0	2	0.4	58:42
100 W[b]	1	80	0.2	59:41

[a] Normal Joule effect incandescent bulb. [b] "Solar" lamp with a spectrum similar to that of daylight.

up as previously, 30-min reaction time in refluxing toluene, only complemented with light irradiation (see below), benzyl chloride was formed specifically (Table II) and in high, ca. 80% yield using as catalyst zeolites NaA (4A) (Si/Al = 1), HAB A40 (Si/Al = 1), NaX (13X) (Si/Al = 1.25), or NaY (Si/Al = 2.5). These positive results are all the more gratifying that the catalysts can be used with no special care. There is no need, for instance, for a prior dehydrative activation.

The influence of light, conversely, is very definite. Our initial experiments, in the presence of zeolites NaX or NaY as catalysts, had nonreproducible or unexpected results. These led us to suspect operation of a noncontrolled parameter. In particular, the amount of light entering the reaction flask depended on sunshine, on the size of the reflux condenser surmounting the reaction mixture, etc. Thus, we did a first test, by chlorinating toluene (i) in the dark, (ii) under normal illumination, and (iii) under strong photochemical irradiation (Table III). The results show an important role for light, whose absence decreases significantly the yield for the chlorination. However, photochemical irradiation is not an absolute must. Decent yields are achieved already under the normal lighting conditions in the laboratory. We sought therefore a simple, low-cost alternative that could guarantee a high yield while dispensing with a photochemical apparatus (Table IV).

We found that illumination of the reaction mixture with an inexpensive "solar" lamp was sufficient to achieve yields almost as good as under bona fide photochemical irradiation. This type of incandescent bulb emits a visible spectrum similar to that of sunlight, with a constant intensity, that gave highly reproducible results. Alternatively, an ordinary "cold white" fluorescent tube or bulb lamp have also been used. In all cases, the selectivity is extremely high, up to 400:1 in favor of the benzylic substitution, as compared to the ring chlorination. The influence of the catalyst is blatant: in its presence, the yield shoots up 40-fold!

Having thus established a direct relationship between the efficiency of the side-chain chlorination and the presence of a light source, it was tempting to postulate intervention of a free radical mechanism. Accordingly, we made a test with radical inhibitors. Free-radical traps belong to one of three groups:[20] (1) stable radicals that can combine rapidly to the reaction intermediates: they include dioxygen,[21] the Koelsch radical,[22] and 2,2-diphenylpicrylhydrazyl (DPPH);[23] (2) compounds of this

Table V. Effect of Free-Radical Traps on Toluene Chlorination by Sulfuryl Chloride under Reflux for 1 h (Other Conditions as in Table III)

			yields, %	
run	catalyst	inhibitor (0.01 mol)	α-chlorination	ring chlorination
1	BzOOBz[a]	I₂	0.3	1
2	NaX[b]	I₂	1	3
3	BzOOBz[a]	benzoquinone	0.3	0
4	NaX[b]	benzoquinone	45	1
5	BnzOOBz[a]	O₂	7	0.3
6	NaX[b]	O₂	64	0
7	BzOOBz[a]	N₂ (control)	81	0
8	NaX[b]	N₂ (control)	83	0

[a] Benzoyl peroxide, 0.5 g. [b] Zeolite NaX, 1 g; 40-W "cold white" fluorescent tube added as a light source.

Table VI. Influence of the Temperature on the Chlorination of Toluene Using Zeolite NaX as a Catalyst (Other Conditions as in Table I)

		yields, %		
temp	reaction time, h	α-chlorination	ring chlorination	ortho:para
room temp	24	0.5	0.6	54:46
reflux	0.5	74	0	–

second type react by transfer of a hydrogen or a halogen atom: they include iodine,[24] thiols,[25] and 1,8-dihydroanthracene;[26] (3) molecules capable of stabilizing other radicals by addition: quinones,[27] styrene, or other vinylic monomers.[28] We chose to use one representative from each of these groups, viz. dioxygen, iodine, and benzoquinone (Table V).

When the free-radical chlorination is initiated by the decomposition of benzoyl peroxide, addition of an inhibitor has a pronounced effect: the reaction is blocked (entries 1, 3, 5, and 7). These observations confirm the well-established free-radical chlorination[7] that operates under such conditions. The results are less clear cut with the NaX zeolite as the catalyst. Since we are now shining light on the reaction mixture, the effect of the free-radical inhibitors is offset somewhat with the countervailing influence from the lamp. Only iodine blocks effectively the free-radical chlorination (entries 2 and 8).

On the other hand, the influence of the temperature is definite: thermal activation is required to carry out side-chain chlorination with the NaX zeolite as the catalyst. This can be deduced from the results given in Table VI. Whereas chlorination at room temperature is negligible, even after 24 h, refluxing the reaction mixture half an hour is sufficient for a 74% yield of benzyl chloride in the absence of any irradiation.

Another line of evidence in support of a free-radical pathway is the occurrence of successive multiple chlorination (Table VII). In order to maximize mono-, di-, or trichlorination, a combination of varying the relative amounts of the reactants and catalyst and lengthening the reaction time gives the required leeway. Yet, as can be seen from the vigorous conditions used (large excess of sulfuryl chloride, prolonged heating in a high boiling point

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Table VII. Multiple Chlorination of Toluene in the Joint Presence of the NaX Zeolite as a Catalyst and a 100-W "Solar" Lamp as a Light Source in Refluxing Chlorobenzene as Solvent

reaction conditions	yield, %	product distribution		
		$PhCH_2Cl$	$PhCHCl_2$	$PhCCl_3$
toluene[a]/SO_2Cl_2 (2:1), zeolite NaX, 1 g, 1 h, chlorobenzene, 50 mL	79	100	0	0
toluene[b]/SO_2Cl_2 (1:4), zeolite NaX, 2.5 g, 20 h, chlorobenzene, 50 mL	82	8	79	13
toluene[b]/SO_2Cl_2 (1:8), zeolite NaX, 5 g, 24 h, chlorobenzene, 100 mL	76	2	16	82

[a] 0.2 mol. [b] 0.1 mol.

Table VIII. Side-Chain Chlorination of Aromatics and of Cyclohexane (0.5 mol) by Sulfuryl Chloride (0.12 mol), in the Joint Presence of Zeolite NaX (1 g) as Catalyst and a 40-W "Cold White" Fluorescent Tube as a Light Source

substrate	reaction time, h	yield, %	product(s)
o-xylene	3	68	2-methylbenzyl chloride
m-xylene	0.5	70	3-methylbenzyl chloride
p-xylene	0.5	77	4-methylbenzyl chloride
ethylbenzene	3	83	(1-chloroethyl)benzene
		15	(2-chloroethyl)benzene
tert-butylbenzene	1	70	1-chloro-2-methyl-2-phenylpropane
m-chlorotoluene	3	62	3-chlorobenzyl chloride
p-chlorotoluene	3	39	4-chlorobenzyl chloride
p-nitrotoluene[a]	3	0	–
cyclohexane	0.5	94	chlorocyclohexane

[a] 0.2 mol in 0.5 mol of CH_2Cl_2.

Figure 1. Hammett plot for the chlorination of substituted toluenes by sulfuryl chloride in benzene at 80 °C using the NaX zeolite as a catalyst.

solvent, increased amount of catalyst), substitution by more than one chlorine on the same carbon is difficult. These observations are fully consistent with earlier studies of the rate of chlorination of benzal and benzyl chlorides compared with toluene.[29]

We have probed the generality of the side-chain chlorination on a number of other alkyl aromatics and on cyclohexane (Table VIII). These unoptimized results are altogether satisfactory. Almost quantitative yields are observed with cyclohexane and with ethylbenzene as substrates. With the latter, the product distribution is almost identical with that observed with UV light as an initiator.[30] Fluorene and indan give rise to complex mixtures of products. Under similar conditions, we have reacted also various other polymethylbenzenes, viz. mesitylene, 1,2,4-trimethylbenzene, 1,2,4,5-tetramethylbenzene, and penta- and hexamethylbenzene. They are all transformed into chlorinated derivatives. However, coexistence of mono- and dichlorination on different methyl groups occurs. We strove to make these reactions more selective by introduction of a solvent, decrease of the amount of sulfuryl chloride reagent, etc., so far without success, presumably due to the high reactivity of these polyalkylaromatics toward free-radical chlorination. Conversely, introduction of a chlorine substituent in the toluene ring considerably diminishes its reactivity and leads to lower yields, particularly in case of a para-disubstitution. The p-nitrotoluene no more undergoes the zeolite-catalyzed reaction with sulfuryl chloride than with benzoyl peroxide as the initiator. Inhibition by the nitro group is well-known to prevent the reaction entirely.[7]

Experiments to determine relative reactivities of substituted toluenes toward chlorination were carried out. Thus, two toluenes were made to compete for a deficiency of sulfuryl chloride in benzene at 80 °C using the NaX zeolite as catalyst. The relative rates were obtained from
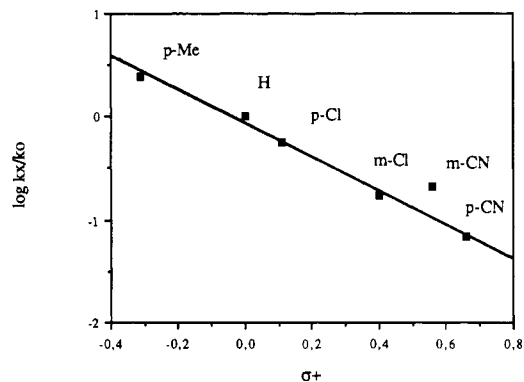
Table IX. Relation between Zeolite Structure and Percent Yield for Chlorination of Toluene (0.47 mol) by Sulfuryl Chloride (0.12 mol) at Reflux (30 min), in the Joint Presence of a Zeolite Catalyst (1 g) and a 100-W "Solar" Lamp as a Light Source

run	zeolite type	cation	Si/Al	opening, Å	yield,[a] %
1	A	K^+	1	3	84
2	A	Na^+	1	4	83
3	A	Ca^{2+}	1	5	80
4	X	Na^+	1.25	ca. 10	83
5	Y	Na^+	2.5	ca. 10	82

[a] Almost exclusive α-chlorination (see Table II).

initial and final concentrations of the substrates. They follow the sequence: p-$CH_3C_6H_4CH_3$ (2.44) > $C_6H_5CH_3$ (1.00) > p-$ClC_6H_4CH_3$ (0.56) > m-$CNC_6H_4CH_3$ (0.21) > m-$ClC_6H_4CH_3$ (0.17) > p-$CNC_6H_4CH_3$ (0.07). This reveals a polar character of the transition state. Introduction of an electron-withdrawing group on the aromatic ring substantially decreases the rate of α-chlorination while an electron-donating group increases it. One is dealing with an *electrophilic radical* having a tendency to abstract electron-rich hydrogen atoms.[31] Indeed the Hammett equation gave slightly better correlation using the Brown and Okamoto σ[+] constants[32] than with σ values.[33] The former give a straight line with a slope of −1.65 and a correlation coefficient of 0.997 for five points (Figure 1). Only the toluene/m-tolunitrile competition gave a discordant point which was excluded from the linear regression calculations. A comparison of the ρ value obtained with literature data will be presented in the General Discussion. It can already be mentioned that van Helden and Kooyman reported a closely related ρ value of −1.5 for chlorinations by sulfuryl chloride in benzene at 80 °C. Their experimental conditions differed from those we adopted by the catalyst, viz. 2,2′-azobisisobutyronitrile.[34]

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H
|
O   O   :O   O
\ / \ / \ / \
Si Al Si
/ \ / \ / \
O O O O   O O   [HB]⁺

+ B
↑   O   O (-) O   O
| ———→   \ / \ / \ / \
| Si Al Si
↓   / \ / \ / \
                      O O O O   O O

H
| (+)
O   O (-) O   O
\ / \ / \ / \
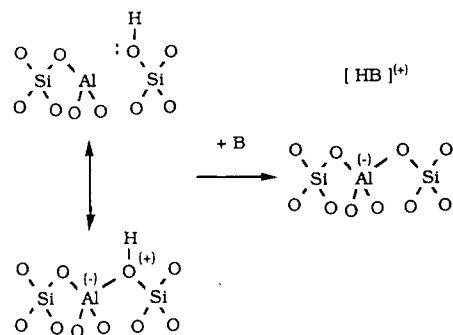Si Al Si
/ \ / \ / \
O O O O   O O

Figure 2. A Brønsted acidic site in a zeolite and its interaction with a base.

Another important result, in view of the discussion to come, is the localization of the catalytic activity for the free radical chlorination *on the outer surface of the zeolite*. We reached this conclusion from the data in Table IX. The dual observation that a 3-Å zeolite (KA), much too small for penetration of aromatic rings, is active and that the catalytic activity is near-invariant upon occupation of the channels by K⁺, Na⁺, or Ca²⁺ ions (entries 1–3) is consistent only with the substitution occurring exclusively on the outer surface of the microporous solid.

Nuclear Chlorination. Electrophilic aromatic chlorination is liable both to general Lewis and to general Brønsted acid catalysis.[35] Binding of the acidic particle to a lone pair on a chlorine atom polarizes the sulfuryl chloride molecule and thus favors its heterolytic dissociation; that produces the required positive chlorine as the electrophile. We felt accordingly that the Brønsted acidity might be an important component of the activity of the solid catalysts. Since the results in Table I had made us opt for zeolites as catalysts, and because these microporous solids have Brønsted acidities (Figure 2) that are linked to the Si/Al ratio,[36] we looked for a highly acidic zeolite in order to direct sulfuryl chloride to chlorinate in the ring positions of an aromatic substrate. We chose thus the ZF520 zeolite as the catalyst, because of its high silicon-to-aluminum ratio, a factor of 20. This is a zeolite of the faujasite class.[37] The results were gratifying. Under similar conditions as in Table I, the yields for the α-chlorination and for the side-chain chlorination of toluene were 5% and 74%, respectively. The latter corresponded to an ortho–para ratio of 60:40, near-statistical distribution. Furthermore, it was sufficient to run the reaction in the dark with the same ZF520 catalyst to cut drastically the amount of side-chain chlorination. The yields then became 1% (α) and 73% (ring), with a barely altered product distribution for the latter (61:39). We shall come back to this rather surprising absence of regioselectivity in the presence of such high chemiselectivity: the channels and the supercages of the ZF520 faujasite have dimensions big enough for the entry of aromatic rings, and yet no shape selectivity is apparent, under our experimental conditions.

We have probed the generality of the nuclear halogenation on other aromatics than toluene (Tables X and XI). To avoid side-chain substitution, chlorinations of alkylbenzenes were performed in the dark. Substitution of activated hydrocarbons such as ethylbenzene, *tert*-butyl-

Table X. Nuclear Chlorination of Monosubstituted Benzenes (0.5 mol) by Sulfuryl Chloride (0.12 mol) under Reflux in the Presence of Zeolite ZF520 (2 g)

substrate	reaction time, h	yield, %	product(s)	ortho: meta: para
benzene	2	24	chlorobenzene	–
ethyl-benzene	2	84	chloroethyl-benzenes	54:3:43
tert-butyl-benzene	2	77	*tert*-butylchloro-benzenes	22:13:65
chloro-benzene	2	22	dichlorobenzenes	34:0:66
nitro-benzene	2	0	–	
anisole[a]	0.5	81	chloroanisoles	26:0:74
phenol[b]	1	57	chlorophenols	48:0:52

[a] 1 g of catalyst. [b] 0.1 mol in 0.5 mol of CCl_4.

Table XI. Nuclear Chlorination of Xylenes and Naphthalene in the Presence of Zeolite ZF520 (Other Conditions as in Table X)

substrate	reaction time, h	yield, %	product(s)
o-xylene	2	33	1-chloro-2,3-dimethylbenzene
		50	4-chloro-1,2-dimethylbenzene
m-xylene	2	24	2-chloro-1,3-dimethylbenzene
		62	1-chloro-2,4-dimethylbenzene
p-xylene	2	84	2-chloro-1,4-dimethylbenzene
naphthalene[a]	1	76	1-chloronaphthalene

[a] 0.1 mol in 0.5 mol of CCl_4, 1 g of catalyst.

Table XII. Chlorination of Toluene (0.2 mol) by Sulfuryl Chloride (0.1 mol) at Reflux in Various Solvents (0.5 mol) in the Presence of Zeolite ZF520 (1 g) in the Dark

			yields, %		
run	solvent	reaction time, h	α-chlori-nation	ring chlorina-tion	ortho:para
1	dichloromethane	3	0.2	84	63:37
2	chloroform	1	0.5	15	62:38
3	carbon tetra-chloride	1	0.3	86	58:42
4	benzene	3	0.3	81	61:39
5	chlorobenzene	1	0.3	84	64:36
6	carbon disulfide	2	0.2	84	64:36
7	nitromethane	1	0.2	66	56:44
8	nitrobenzene	1	1.5	57	61:39

benzene, xylenes, and naphthalene leads to high yields of chlorinated products, whose distributions are similar to those obtained with molecular chlorine under homogeneous conditions.[38] Selective monochlorination of anisole and phenol is also achieved without any evidence of polyhalogenation. This corroborates earlier studies showing that sulfuryl chloride is a relatively weak electrophile, as compared with chlorine.[39] One should therefore expect a considerable yield lowering when substrates devoid of activating substituents are chlorinated under the same conditions. Indeed, benzene and chlorobenzene give a mere 22–24% yield after 2 h, and the strongly deactivated nitrobenzene shows no sign of reaction during the same period of reflux, despite its higher boiling point (210 °C).

As a consequence, benzene, chlorobenzene, and nitrobenzene could serve as reaction media for the chlorination of toluene besides various other solvents (Table XII). Since activated hydrocarbons are attacked much faster than un- or deactivated rings, good yields of chlorotoluenes

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Table XIII. Influence of the Temperature on the Chlorination of Toluene Using Zeolite ZF520 as a Catalyst (Other Conditions as in Table I)

| | | yields, % | | |
temp	reaction time, h	α-chlori-nation	ring chlorina-tion	ortho:para
room temp	24	0.6	44	70:30
reflux[a]	0.5	1	73	61:39

[a] In the dark.

Table XIV. Effect of the Amount of Zeolite ZF520 on the Thermal Chlorination of Toluene (Other Conditions as in Table I)

| | yields, % | | |
amount of catalyst, g	α-chlori-nation	ring chlorination	ortho:para
1	5	74	60:40
2	0.1	82	62:38
5	0.05	80	63:37

can be obtained with no concomitant formation of other chlorinated derivatives (runs 4, 5, 8). Reaction times necessary to reach completion vary from 1 to 3 h, depending upon the solvent. The best results were obtained with carbon tetrachloride (run 3). Surprisingly, reaction in chloroform does not progress anymore after 1 h and is limited to a 15% yield (run 2). So far, we have not found a satisfactory explanation for this observation. The proportion of benzyl chloride is kept to a low level throughout the trials except with nitrobenzene (run 8). Rapid degradation of the ZF520 catalyst when refluxed in this high boiling point solvent (it turns to a black material) may be related to the disappointing 59% overall yield (including 1.5% of benzyl chloride). Inactivation of acidic sites under these drastic conditions should thwart the benefit of a strongly polar medium. It inhibits electrophilic aromatic substitution while allowing a thermal radical chlorination to occur to some extent. We note in passing the attractiveness of nitromethane as the solvent, combining a decent 66% yield and a product distribution deviating markedly from the statistical (run 7).

We investigated the influence of the reaction temperature on the chlorination of toluene (Table XIII). While the reaction, when run 24 h at ambient temperature gave no better yield than 45%, at toluene reflux temperature (111 °C) the observed yield for ring chlorination was nearly 75% with the above mentioned high selectivity (73:1). Whereas this preference for nuclear substitution is quite unaltered at room temperature, where it slightly decreases to (68:1), the isomer distribution underwent a more pronounced change, with a drop in the ortho/para ratio from 70/30 to 61/39 on warming.

Using again toluene as a probe-substrate, we increased the amount of catalyst used for the thermal reaction from 1 to 2 or to 5 g (Table XIV). This has a tremendous effect on the chemiselectivity. The predominance of nuclear over side-chain chlorination goes up to 1600:1. It also slightly increased the yield but did not modify significantly the ortho–para distribution, which drew nearer to the statistical (67:33) value. Such a lack of influence strongly suggests that reaction occurs on the outer surface of the catalyst, as the less hindered para isomers are expected to form preferentially with an intracrystalline process.[40–42]

Table XV. Chlorination of Toluene (0.2 mol) by Sulfuryl Chloride (0.1 mol) at Reflux for 1 h in Various Solvents (0.5 mol) (Other Conditions as in Table VIII)

| | | yields, % | | |
run	solvent	α-chlori-nation	ring chlorina-tion	ortho:para
1	dichloromethane	81	0	–
2	chloroform	78	0	–
3	carbon tetrachloride	74	0	–
4	benzene	83	0	–
5	chlorobenzene	79	0	–
6	carbon sulfide	70	0	–
7	nitromethane	1	55	53:47
8	nitrobenzene	3	35	54:46

Table XVI. Chlorination of Toluene (0.47 mol) by Sulfuryl Chloride (0.12 mol) at Reflux (30 min), in the Presence of Ion-Exchanged Zeolite Catalysts (1 g) (Other Conditions as in Table XIII)

| | yield, % | | |
catalyst	α-chlori-nation	ring chlorination	ortho:para
NaX	80	0.2	59:41
HNaX[a]	23	22	58:42
FeX[b]	0.5	12	59:41
NiX[c]	40	15	61:39

[a] Zeolite NaX partially exchanged with protons. [b] Zeolite NaX exchanged with ferric ions. [c] Zeolite NaX exchanged with nickel-(II) ions.

Another piece of evidence in support for this suggestion is the close similarity of regioselectivities obtained in homogeneous and in heterogeneous conditions, as further commented upon in the General Discussion.

Competition between the Two Mechanisms. When toluene serves as its own solvent, exclusive α-chlorination occurs with zeolite NaX as catalyst. Because polar solvents are expected to favor the ionic mechanism that leads to predominant ring chlorination,[14] we set about exploring the influence of the nature of the solvent on the outcome of the reaction (Table XV). The results are eloquent and clear cut, demonstrating a nice dichotomy between these nonpolar (albeit polarizable) solvents (entries 1–6) that serve as abodes for the radical mechanism and the polar nitrosolvents (entries 7 and 8) in which the preferred course of the reaction switches to the electrophilic aromatic substitution. As previously noted with the ZF520 catalyst (cf. Table XII), the highest proportion of the para isomer is reached in nitromethane. Correcting for the statistical factor 2 in favor of the ortho position, the para selectivity is up to 1.77 in this solvent.

Another way in which to favor nuclear over side-chain chlorination is by boosting the Brønsted acidity on the outer surface of the zeolite catalyst (Table XVI). This can be done by partial or total replacement of the sodium counterions with protons or with transition-metal cations. The latter, introduction of divalent and trivalent Lewis acids, is well-known to enhance Brønsted surface acidity of aluminosilicates.[43] A recent NMR investigation from these laboratories has shown conclusively that it is explained by the high polarization of the surface layer of water molecules.[44] These are pinched between negative charges on surface oxygens, to which they are attached by hydrogen bonds, and the Lewis acidic high-valent cation coordinated on one of their lone pairs.

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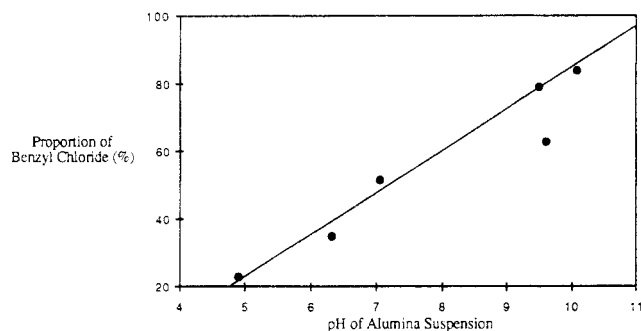
Figure 3. Influence of the surface acidity of alumina on the ratio of side-chain to ring chlorination of toluene.

Table XVII. Recycling of the NaX Zeolite Catalyst by Various Means and Its Effectiveness in Consecutive Reactions (Other Conditions as in Table VIII)

run	prior catalyst treatment (see text)	yield in benzyl chloride, %
1	none	70
2	a	75
3	e	75
4	a	73
5	a	73
6	f	70
7	a	73
8	c	72
9	b	76
10	d	71

In order to confirm the key role of Brønsted acidity in making the reaction selective for ring chlorination of toluene, we also measured the ratio of side-chain to ring chlorination using aluminas with variable surface acidities (Figure 3). Indeed, it is possible to span the whole range of 20–90% α-chlorination merely by changing the acidic-basic character of the alumina. Increasing the acidity leads to increased nuclear chlorination. The only point deviating significantly from the correlation curve was obtained with anhydrous γ-alumina, whose metastable structure[45] differs from the other α varieties used.

Regeneration of the Catalysts. The zeolite catalysts differ in their profiles for reuse, as can be seen from the rather dramatic contrast between zeolites ZF520 (Figure 4A) and NaX (Figure 4B). The activity of zeolite ZF520 decreases with each successive run until it becomes negligible after five consecutive reactions. Conversely, the activity of the NaX zeolite remains intact and at a consistently high level after 10 successive runs. Furthermore, no special care or reactivation procedure is necessary to maintain the resiliency of this zeolite. This can be deduced from a detailed examination of the 10 runs of toluene chlorination with the same catalyst (Table XVII). Between two successive reactions, after the solid catalyst had been recovered by filtering, these were the various treatments that were applied to it: (a) washing with toluene and direct reuse; (b) washing with toluene, followed by air drying; (c) washing with toluene, followed by hot air drying; (d) washing with methanol, followed by hot air drying; (e) washing with toluene, followed by air drying and by 2-h storage in a dessicator with phosphoric anhydride; (f) same as (e) but with a 5-day storage in the P_2O_5 dessicator. The performance of the NaX catalyst remained consistently high whatever treatment was applied to it. Neither the high temperature (a reflux at ca. 110 °C, with potential overheating of the solid accumulated at the bottom of the flask) nor the acidic conditions (hydrochloric acid is con-
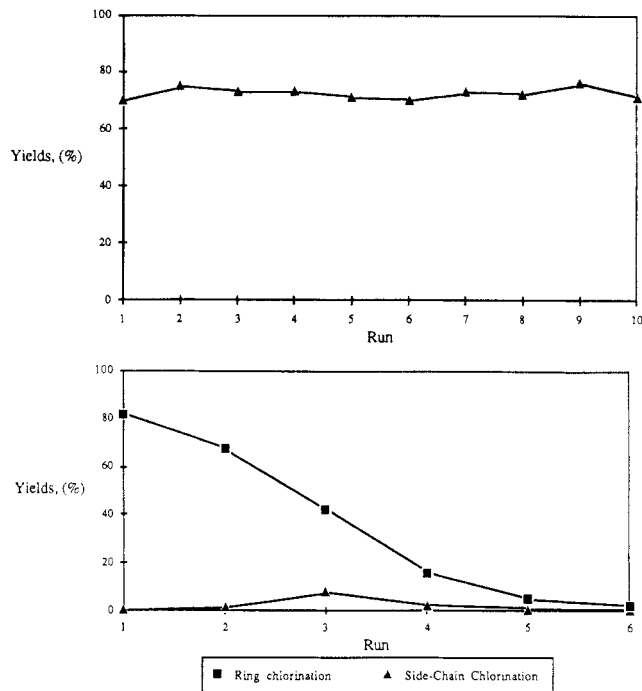

Figure 4. (A) Recycling of the NaX zeolite catalyst in consecutive chlorinations of toluene. (B) Recycling of the ZF520 zeolite catalyst in consecutive chlorinations of toluene.

stantly evolved as the reaction proceeds) affect the catalytic prowess of the zeolite, even after 10 consecutive uses. The slight variations observed should not be overinterpreted. They reflect probably the systematic errors in the weighing of the reagents and in the chromatographic analysis of the products formed.

To return to the impoverishing of zeolite ZF520 as a catalyst, the first cause that comes to mind is a gradual poisoning of the surface acidic centers. However, attempts to rejuvenate the catalyst by washing it with mineral acid (such as 0.1 N hydrochloric acid) failed. Furthermore, X-ray analyses indicate structural changes in spent NaX and ZF520 zeolites. Detailed examination of these phenomena is currently underway and will be reported in due course.

General Discussion

Sulfuryl chloride is a convenient chlorinating agent of marked versatility.[46] As a laboratory reagent, it possesses several advantages over molecular chlorine. Its liquid nature (bp 69.5 °C) facilitates handling and allows easy control of introduced quantities and rates of admission. Furthermore, chlorinations with sulfuryl chloride do not proceed with the violence that such reactions unleash when carried out with free chlorine.[47]

The use of SO_2Cl_2 to chlorinate side chains of aromatic hydrocarbons was pioneered mostly by Kharasch and Brown.[7] They found that benzoyl peroxide was an efficient catalyst for these reactions and first proposed a free-radical mechanism. Following these findings, other peroxides, 2,2'-azobisisobutyronitrile (AIBN),[48] or light[30,49] were also used as initiators. More recently, transition-metal complexes such as $Pd(PPh_3)_4$ have been reported to promote homolytic dissociation of SO_2Cl_2 and formation of benzyl chlorides.[50] As far as we know, recourse to inorganic solids

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Table XVIII. Product Distributions for the Chlorination of 1-Chlorobutane under Various Conditions

		site of chlorination					
reagent	conditions	CH₃———	CH₂———	CH₂———	CH₂———	Cl	ref
Cl_2	$h\nu$, 68 °C	20	49	23	8		53
Cl_2	reflux, darkness	22	52	21	5		54
SO_2Cl_2	BzOOBz, reflux	24	47	22	7		55
SO_2Cl_2	NaX, reflux	25	46	23	6		this work

to catalyze side-chain chlorination of aromatic hydrocarbons has not been reported yet. In a related matter, it has been observed that, when applying ZSM-5 type zeolites to the gas phase chlorination of benzene, addition and not substitution prevailed, leading to a mixture of hexachlorocyclohexanes. Evidently, ZSM-5 induced a free-radical reaction, which, in view of the molecular dimensions of hexachlorocyclohexanes (diameter ±8 Å), takes place on the external surface and/or at the pore opening of the zeolite (diameter ±5.5 Å).[51] Shape selectivity has been achieved in the photochlorination of n-alkanes adsorbed on pentasil zeolites. Thus, dodecane for example gave mainly 1-chlorododecane, as adsorption within the channels of the zeolite protects the backbone methylene groups from attack by chlorine atoms.[52] Results gathered in Table IX have already led us to conclude that our chlorinations by sulfuryl chloride in the presence of NaX zeolite occur on the outer surface of the solid.

In order to collect further evidence in support of this statement, we investigated the chlorination of 1-chlorobutane (Table XVIII). Free-radical chlorination of this aliphatic substrate is well-documented. The fixation of chlorinating agents can occur on four different carbons and has widely been used to test the selectivity of attacking radicals.[29] The isomer distributions obtained with sulfuryl chloride in homogeneous (peroxide initiator) or in heterogeneous conditions are closely parallel. Selectivity in favor of the terminal methyl group, especially, is not enhanced as would be expected if restrictions of diffusion into the channels of the solid were encountered. Intracrystalline reaction can therefore be rejected with a high degree of certainty. Comparison of the results obtained with molecular chlorine shows only a small discrepancy in the relative proportions of 1,3- and 1,4-dichlorobutanes. This could be due to the plausible intervention of chlorosulfonyl radicals besides chlorine atoms when sulfuryl chloride is the chlorinating agent. Evidence for the existence of $SO_2Cl\cdot$ radicals has been provided by Kharasch and Zavist in related reactions.[56] The data in our hands is insufficient, however, to indicate if this radical is involved in the chlorination of aliphatic substrates with the NaX zeolite. In the case of aromatic chlorination, on the contrary, it can be assumed that an aromatic/chlorine atom π-complex is the major hydrogen abstracting species. The involvement of such a complex was first suggested by Russell and Brown for photochlorinations by Cl_2 in 1955.[57] It was

found to afford a suitable explanation for various experimental observations. For example, Russell reported that molecular chlorine and sulfuryl chloride gave different product distributions when neat 2,3-dimethylbutane was chlorinated at 25 °C but not in benzene solution. The tertiary-to-primary selectivity (on a per hydrogen basis) increased from 4.2 (with Cl_2) or 12 (with SO_2Cl_2) in the pure liquid alkane to 49 or 53, respectively, in 8 M benzene.[9] This increase in selectivity was attributed to the formation of a benzene/chlorine atom π-complex. The aromatic ring is the electron donor, and the chlorine atom is the electron acceptor; the complex has thus a certain charge-transfer character (eq 11). Bühler first identified

$$\bigcirc + Cl\cdot \longrightarrow \overset{\delta^+ \quad \delta^-}{\bigcirc\hspace{-0.3em}-\hspace{-0.3em}Cl\cdot} \qquad (11)$$
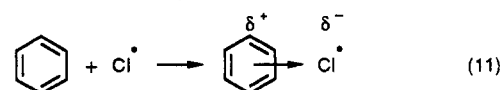
its transient absorption in the pulse radiolysis of benzene in carbon tetrachloride.[58] More recently, ultraviolet/visible spectra of arene/chlorine atom complexes have been recorded under laser flash photolysis using five different sources of chlorine atoms.[59] The involvement of such complexes is the zeolite-catalyzed α-chlorinations—at least when run in benzene—is supported by the ρ Hammett constant obtained in competitive halogenations of substituted toluenes in benzene at 80 °C. The −1.65 ρ value is significantly more negative than those for the uncomplexed chlorine atom determined in carbon tetrachloride ($\rho = -0.56$ at 40 °C using $SO_2Cl_2/h\nu$;[60] $\rho = -0.48$ at 60 °C using $Cl_2/AIBN$[61]). A much more selective chain carrier appears to be present. Comparison with the values obtained in other aromatic media at 80 °C ($\rho = -0.80$ in the neat substrates using $SO_2Cl_2/AIBN$;[62] $\rho = -0.78$ in chlorobenzene using $Cl_2/AIBN$;[61] $\rho = -0.53$ in benzonitrile using $Cl_2/AIBN$;[61] $\rho = -0.50$ in nitrobenzene using $Cl_2/AIBN$[61]) confirms the great influence of the solvent and its ability to act as an electron donor.

Although less common than their side-chain counterparts, aromatic nuclear chlorinations have also been performed with sulfuryl chloride. Anhydrous aluminum chloride is an efficient catalyst for the monochlorination of benzene.[10] Addition of sulfur monochloride S_2Cl_2 as a cocatalyst further increases the activity of the reagent, thus allowing easy access to polychlorinated derivatives.[63] With a very high concentration of the catalysts, it is even possible to accomplish total perchlorination of toluene or of p-xylene, including the hydrogen atoms from the side chains.[64] Activated substrates have been monochlorinated at room temperature in the absence of a catalyst.[13] With sulfuryl chloride, these reactions are much slower, however,

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than with molecular chlorine. To our knowledge, silica gel has been the only heterogeneous catalyst used to perform chlorinations with sulfuryl chloride before this report. For example, warming at 70 °C a mixture of toluene, sulfuryl chloride and silica gel (107% w/w with respect to the reagents) in carbon tetrachloride leads, after 5 h, to an 81% yield of chlorotoluenes with an almost equimolar distribution between the ortho and para isomers.[17] Much higher para selectivities can be reached using molecular sieves and other chlorinating agents. Thus, treatment with chlorine of toluene or chlorobenzene entirely adsorbed within the CaX zeolite gives ortho/para ratios of (17:83) and (4:96), respectively. The nuclear disubstituted derivatives are contaminated with significant amounts of polyhalogenated compounds. Furthermore, chlorination of alkylbenzenes gives large amounts of benzyl chlorides as side products.[40] Such drawbacks could be avoided in the halogenation of chlorobenzene. Using modified Y-type zeolites, only dichlorobenzenes are formed but the para selectivity does not exceed 85%.[41] The most impressive shape-selective aromatic chlorinations are those by the Smith group in Swansea. With *tert*-butyl hypochlorite in the presence of partially proton-exchanged NaX zeolite, the (o/p) regioselectivities for chlorotoluenes and dichlorobenzenes are 9:91 and 3:97, respectively. No other products could be detected in the chlorinations of toluene and chlorobenzene.[42] These reactions require however vast amounts of solid, 60 g of zeolite for 0.1 mol of aromatic substrate. Furthermore, both the chlorinating agent and the ion-exchanged zeolite need to be prepared in the laboratory before use.

By contrast, our procedure requires only a trifling quantity of catalyst. The aromatic serves as its own solvent. The absence of shape selectivity is therefore not surprising; it is the price paid for the ease of implementation.

Experimental Section

General Information. All the organic reagents and solvents were commercial products of the highest purity available, used without any further purification. Sulfuryl chloride was freshly distilled under a slow stream of nitrogen before use, until a colorless fraction (bp 69–70 °C) was obtained. Zeolite powders NaX (13X), NaA (4A), KA (3A), and CaA (5A) were purchased from Aldrich. Zeolite NaY was purchased from Ventron. Zeolites ZF520 and HAB A40 were respectively gifts from Zeocat (Montoir de Bretagne) and Degussa (Hanau) (see Table XIX). Other ion-exchanged zeolites were prepared according to previously published procedures.[40,42]

Philips 100-W "solar" incandescent bulb (S100W), Sylvania 40-W W "cold white" fluorescent tube (IRSCW40), or an ordinary 60-W incandescent bulb were the light sources.

Analyses of products were performed with Intersmat IGC 121FL/ICR-1B or Varian 3300/4400 gas chromatographic systems equipped with flame ionization detectors and capillary columns (length 25 m, inside diameter 0.32 mm, stationary phase OV-1701). Product identifications were performed by comparing retention times with those of authentic commercial samples. Yields are determined with internal standards.

Chlorination without Added Solvent: Typical Procedure. Unless otherwise stated in the tables, a suspension of a catalyst (1 g) in toluene (50 mL, 0.47 mol) and sulfuryl chloride (10 mL, 0.12 mol) was refluxed 30 min. Irradiation by a 100-W "solar" incandescent bulb or a 40-W "cold white" fluorescent tube placed 10 cm away from the Pyrex reaction flask was possibly applied. The solid was then filtered off and washed with two portions of toluene (5 mL each). 1,4-Dichlorobenzene was added as an internal standard, and the reaction mixture was analyzed by GC.

Chlorination in a Solvent: Typical Procedure. Unless otherwise specified in the tables, a small portion of a catalyst (1 g) was added to a solution of toluene (21 mL, 0.2 mol) and sulfuryl chloride (8 mL, 0.1 mol) in a solvent (0.5 mol). The mixture was

refluxed for 1 h. Irradiation conditions and workup treatment were the same ones as above.

Large-Scale Chlorination: Preparation of 4-Methylbenzyl Chloride. To a solution of sulfuryl chloride (81 mL, 1 mol) and *p*-xylene (490 mL, 4 mol) was added 5 g of NaX zeolite. The suspension was refluxed 1 h under irradiation by a 40-W "cold white" fluorescent tube placed 10 cm away from the Pyrex reaction flask. The solid was then filtered off and washed with two portions of *p*-xylene (10 mL each). The filtrate was distillated under reduced pressure. The fraction of boiling range 45–48 °C (1 mm) consisted of 97% pure 4-methylbenzyl chloride according to GC analysis. Yield is 101 g (72%).

Competitive Chlorination of Toluenes. To a solution of toluene, a substituted toluene, and sulfuryl chloride (0.1 mol each) in 45 mL of benzene (0.5 mol) was added 1 g of NaX zeolite. The flask was fitted with a reflux condenser and quite completely immersed in an oil bath at 80 ± 5 °C. Its contents were magnetically stirred, and they were illuminated by a 60-W incandescent bulb placed 10 cm away. After 1–3 h, depending upon the substrate reactivities, an internal standard was added and the supernatant solution was analyzed by GC.

Chlorination of 1-Chlorobutane. To a solution of sulfuryl chloride (8 mL, 0.1 mol) in 1-chlorobutane (52 mL, 0.5 mol) was added 1 g of NaX zeolite. The suspension was refluxed 2 h under irradiation by a 60-W incandescent bulb placed 10 cm away from the Pyrex reaction flask. An internal standard was then added, and the reaction mixture was analyzed by GC. The overall yield of dichlorobutanes was 70% (see Table XVIII for the isomer distribution).

Determination of the Surface Acidity of Aluminas. 10% w/w aqueous suspensions of aluminas were prepared by stirring 2 g of a solid in 20 mL of purified water. After equilibrium was set up (1 h to one night), the pH was measured at 20 °C using a combined glass electrode and a digital pH meter. The following solids were used: acidic aluminum oxide type 504C (Fluka), weakly acidic aluminum oxide type 506C (Fluka), neutral aluminum oxide (Macherey Nagel), basic aluminum oxide (Riedel de Haen), anhydrous γ-alumina (Merck), and aluminum oxide pellets (Ventron).

Conclusions

The procedures that have been evolved in this study commend themselves for their simplicity of set up and of workup. It suffices to react the aromatic hydrocarbon with sulfuryl chloride, with or without a solvent, in the presence of the appropriate catalyst: the zeolite ZF520 if nuclear substitution is desired; the zeolite NaX if chlorination is wanted on the side chain. The reaction mixture is brought to reflux for 30 min to a few hours. After filtering off the solid catalyst—if ZF520, a fresh sample is preferable for another reaction; if NaX, it is reusable—it suffices to distill off the solvent to recover a near-quantitative yield of the desired chlorinated product. Truly catalytic amounts of the solid catalysts are required and there is no need for any preliminary activation. The practical value of our methodology is illustrated by the molar-scale preparation of 4-methylbenzyl chloride. The progress of the reaction is conveniently followed by noting the evolution of acidic gas (SO_2 + HCl) or by checking the loss in weight of the reaction flask after completion of the chlorination.

It remains to underscore two interesting aspects of this work. Contrary to many uses of zeolite catalysts, especially for industrial applications,[65] shape selectivity within the supercages and the channels of the microporous solid was not a factor. Both the nuclear and the side-chain chlorinations occur on the outer surface of the zeolite catalysts. Thus, there is no size restriction operative against reactant or product molecules. This first point is of particular significance in view of possible application of our proce-

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Table XIX. Typical Dry Basis Composition of Zeolites Used in This Work (wt %)

zeolite	composition (wt %)				
	SiO$_2$	Al$_2$O$_3$	Na$_2$O	K$_2$O	CaO
KA (3A)	38.98	33.08	5.02	22.92	–
NaA (4A)	42.30	35.89	21.81	–	–
CaA (5A)	44.76	36.46	5.54	–	15.04
HAB A40	42.31	35.90	21.79	–	–
NaX (13X)	47.46	32.68	19.86	–	–
NaY	64.03	22.37	13.60	–	–
ZF520	95.87	4.07	0.06	–	–

dures to the synthesis of fine chemicals. In fact, many of the target molecules to be prepared in multistage syntheses are too bulky to be built in or to desorb from the zeolite pore systems, as the presently available structures peak at about 10-Å pore dimension.[66] Secondly, the properties of the NaX zeolite as a free-radical initiator for chlorinations in like and as efficient manner as benzoyl peroxide brings in a new dimension. It complements their common use as acidic catalysts. This is due to a useful attractive structural feature, the presence of oxy radical centers O$_3$M-O$^•$ (M = Al or Si) on the outer surface. Other aluminosilicates such as clays are known to have a wealth of such centers on their surface. A number of authors have drawn attention to them,[67–69] in particular Friedemann

Freund in a very recent study.[67] The density of such centers is controllable to some extent; it can be increased by dehydrative activation of the surface alanol and silanol groups. Contact with these centers of aromatic molecules leads to radicals and to radical cations.[68,69] We had taken advantage of their presence already for designing effective aromatic nitrations[70] and for catalysis of the radical-cation mediated Diels–Alder reaction.[71] This new success at catalysis of aromatic chlorination is another illustration of the promise for chemistry inherent in these metal–oxy radical centers on the surface of inorganic solids. It has not escaped our attention that other chemical processes present a dichotomy between an ionic and a radical pathway, leading to different products or to differing product distributions. We plan to explore the potential of zeolite catalysts, such as the ZF520 and the NaX, respectively, to channel such reactions into one or the other of the two coexisting routes. Yet more generally, preparative organic chemistry in academic laboratories has much to gain from borrowing zeolites from their industrial birthplace.

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Norrish Type I and Type II Reactions of Ketones as Photochemical Probes of the Interior of Zeolites[†,‡]

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The Norrish type I and type II reactions of alkylbenzoin ethers, alkyldeoxybenzoins and α-alkyldibenzyl ketones included within the microporous structures of zeolites X and Y have been investigated. Product distributions varied significantly from that observed in benzene. In addition, it differed between various alkali-metal cation-exchanged samples. These variations are interpreted to result from the restriction offered by the zeolite micropores on the motions of the adsorbed organic molecule. Although this study is restricted to ketones, the knowledge gained is expected to be of general value.

Introduction

Photochemical and photophysical properties of organic molecules are considerably altered when they become part of an organized or constrained structure.[1] In this context,

the internal structure (pores and cages) of zeolites have attracted recent attention.[2–4] This paper presents a study

† Part of the series on Modification of Photochemical Reactivity by Zeolites. For other members of the series, see ref 4.
‡ Contribution no. 5419.

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