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On the Selectivity of the Bromination Reaction of Methylbenzenes on Zeolites

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Experimental and quantum chemical data show the electrophilic agent involved in the bromination reaction of benzene and methylbenzenes on zeolite Na–Y to be more active than that on H–Y, antibatic changes in substrate and positional selectivity of the reaction being observed.

A number of studies[1–5] (and references cited therein) have indicated the possibility of carrying out selective halogenation of aromatic compounds using zeolite catalysts. However, the nature of the electrophilic agents involved in the reaction is not quite clear as yet (*cf.* ref. 3). Such information is necessary for developing effective methods for selective halogenation of aromatic compounds which are acceptable from an ecological point of view.

For a detailed investigation of the mechanism of the bromination reaction of aromatic compounds on zeolite catalysts (*cf.* ref. 3) we have obtained data on the substrate and positional selectivities of bromination of some aromatic compounds (benzene **1**, toluene **2**, *o*-xylene **3** and *p*-xylene **4**) by bromine on zeolites Na–Y and H–Y.

The relative reactivities of **1**–**4** were determined under competitive conditions. A solution of bromine (weight ratio-

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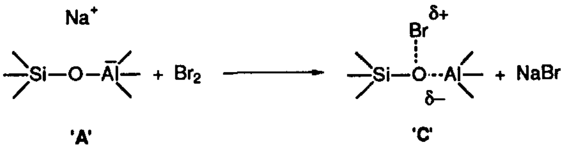
Table 1 Bromination of aromatic compounds

Conditions	Relative rate constants of bromination k_2/k_1	k_3/k_1	k_4/k_1	Ratio of bromotoluenes, *para/ortho*	Ref.
Br_2, Na–Y, CCl_4	6	4	5	13	[a]
Br_2, H–Y, CCl_4	202	923	330	2	[a]
Br_2, $FeBr_3$, $MeNO_2$	3.6	3.9	4.3	0.4	[6]
Br_2, $MeCO_2H$	605	5320	2520	2.0	[7]

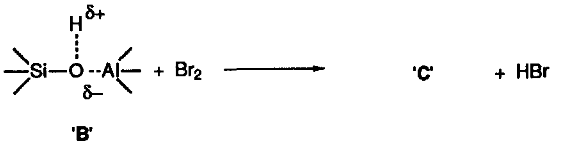
[a] This work.

zeolite/Br_2 = 30) in 10 ml of CCl_4 was added to a stirred suspension of 4–5 g of zeolite ($\approx$ 10–20 μm crystals, calcined at 500 °C) in 15 ml or CCl_4 at 30 °C. After 15 min stirring, a tenfold molar excess of an equimolar mixture of two competing substrates was added and stirring was continued for 1 h at 30 °C. After addition of aqueous NaOH and extraction with $CHCl_3$, the reaction mixture was subjected to GLC analysis.†

The results of the selectivity of bromination on zeolites Na–Y and H–Y are listed in Table 1, which gives for comparison the respective data on bromination in homogeneous media. It should be noted that there are large differences in substrate selectivity for the reaction on Na– *vs.* the decationized form of zeolite Y. The bromination on Na–Y gives relative rate values which are typical for the strongly electrophilic brominating agent $Br^+FeBr_4^-$.[6] Zeolite H–Y shows a much higher substrate selectivity, which is similar to that obtained in the case of bromination with molecular Br_2.[7] These facts may be rationalized by assuming that the bromine molecule being adsorbed on zeolite Na–Y is significantly polarized (*cf.* ref. 8) and subsequently dissociates to form an active brominating agent [eqn. (1)]. In the case of the decationized form, such a process [eqn. (2)] is assumed to be unfavourable and the reaction apparently proceeds *via* the less polarized and thus less active bromine molecule (*cf.* ref. 2). This assumption is consistent with calculations performed in molecular approximation by the *ab initio* STO-3G method (the active centres of zeolites Na–Y and H–Y were simulated by structures **A** and **B** respectively, structure **C** has been assumed for the brominating agent), which show process (1) to be ~ 10 kcal mol^{-1} more favourable than (2).‡



(1)



(2)

The decrease in the relative bromination rates of compounds **2–4** on passing from zeolite H–Y to Na–Y would result from their more difficult diffusion in zeolite channels as compared with benzene. However, the expected changes in relative rate constants due to diffusion limitations are probably negligible in the light of data indicating the absence of significant differences in the ability of the compounds examined to diffuse in zeolite Na–Y.[9,10]

It is noteworthy that, despite the low substrate selectivity, in the case of toluene bromination on zeolite Na–Y the *para/ortho* ratio is higher than that in the case of H–Y and in solution. This is probably due to the greater steric limitations imposed on the transition state of the reaction by an electrophile of type **C** which is more 'bulky' than Br_2 [eqn. (2)] and additional restrictions caused by the Na^+ ions, which are present in the cavities of zeolite Na–Y but not in those of H–Y.

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References

1 J. van Dijk, J. van Daalen and G. B. Paerels, *Recl. Trav. Chim. Pays-Bas*, 1974, **93**, 72.
2. T. M. Wortel, D. Oudijn, C. J. Vleugel, D. P. Roelofsen and H. van Bekkum, *J. Catal.*, 1979, **60**, 110.
3 J. Zabicky, I. Eger, A. Galun and M. Mhasalkar, *Zeolites*, 1987, **7**, 499.
4 F. de la Vega and Y. Sasson, *Zeolites*, 1989, **9**, 418.
5 F. de la Veta and Y. Sasson, *J. Chem. Soc., Chem. Commun.*, 1989, 653.
6 G. A. Olah, S. J. Kuhn, S. H. Flood and B. A. Hardie, *J. Am. Chem. Soc.*, 1964, **86**, 1039.
7 H. C. Brown and L. M. Stock, *J. Am. Chem. Soc.*, 1957, **79**, 1421.
8 R. P. Cooney and P. Tsai, *J. Raman Spectrosc.*, 1979, **8**, 195.
9 R. Burmeister, H. Schwarz and B. Boddenberg, *Ber. Bunsenges. Phys. Chem.*, 1989, **93**, 1309.
10 L. Forni and C. F. Visconti, *J. Catal.*, 1986, **97**, 480.

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† The yields of bromoaromatic compounds were > 70%. In the case of zeolite Na–Y formation of some dibromosubstituted products were observed, and the amount of these was taken into account in the calculation of relative rates.

‡ 1 cal = 4.184 J.