Temperature-programming in the Study of Catalytic Reactions. The Exchange of *m*-Xylene with Deuterium Oxide on Zeolites

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Summary Temperature-programming provides an effective technique for obtaining kinetic data for catalytic reactions, particularly exchange reactions of compounds containing different types of hydrogen atoms.

USEFUL indications about the mechanism of reactions on catalysts have been obtained from studies of the relative rates of exchange with deuterium of the different types of hydrogen atoms in molecules such as *m*-xylene.[1] If conventional methods are used, several experiments may be needed at a range of temperatures to obtain a full comparison of the various exchange rates. We have now shown that the use of temperature-programming can provide equivalent information in a single experiment.

The exchange of *m*-xylene with deuterium oxide was studied on 0·1 g. samples of X-type zeolites in a static system with a capillary leak to a mass spectrometer giving a continuous analysis of the isotopic composition of the xylene throughout each run.[2] Concentrations of *m*-xylene and deuterium oxide corresponded to 2·0 and 11·1 molecules per supercage of the zeolite and a linear increase of temperature was used.

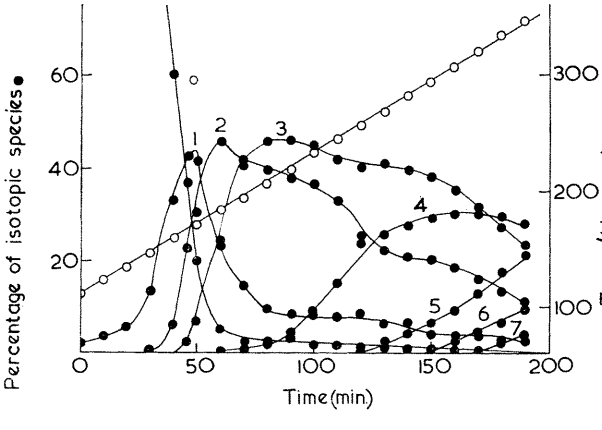

FIGURE 1. *The composition of the isotopic* m-*xylenes during temperature-programmed exchange on a cobalt X-zeolite. The heating rate was* 1·23° *min.*$^{-1}$ *and numbers on the curves refer to the number of deuterium atoms in the* m-*xylene.*

The composition of the xylenes during exchange in a cobalt X-zeolite (52% of the Na^+ ions replaced by Co^{2+}) is given in Figure 1. The results show that three hydrogen atoms exchanged more rapidly than the fourth which, in turn, reacted faster than the remaining six atoms. This last group of atoms must be those on the two methyl groups. Further details about the nature of the exchange of the first three atoms was obtained from the data in the Table.

Experimental and calculated percentage distributions of products during the early stages of exchange

	Number of D atoms in molecule				
	0	1	2	3	4
Experimental[a]	20·6	41·8	30·6	7·0	0·0
Calculated[b]	20·2	42·7	30·1	7·0	—

[a] At the stage of exchange on cobalt X-zeolite when the average deuterium content had reached 1·24 atoms molecule^{-1} (50 min. in Figure 1).

[b] Assuming a random (binomial) distribution of 1·24 D atoms over three positions.

The agreement between the experimental distribution and one calculated assuming random exchange of three positions is evidence[3] that the first three atoms exchanged at equal rates by a step-wise process. A similar type of comparison at later stages in the reaction showed that the last six hydrogen atoms in the molecule also exchanged with equivalent rates by a step-wise process.

Analysis of the change of the isotopic composition of the xylenes at reasonably close intervals of time, by methods which were similar to those used for conventional experiments,[4] gave approximate values of the *initial* rates of exchange of the different groups of hydrogen atoms at a series of temperatures. The Arrhenius plots, so obtained, are given in Figure 2 and they indicate the marked differences in the reactivity of the three groups of hydrogen atoms; temperatures of 140°, 226°, and 290°, respectively corresponded to an initial rate of exchange of 1% min.$^{-1}$ (0·1 g. of catalyst)$^{-1}$ for the three processes which had apparent activation energies of about 140, 140, and 105 kJ mole^{-1}.

The same pattern of behaviour was observed on a cerium X-zeolite (86% of the Na^+ ions replaced by Ce^{3+}) but reaction occurred at lower temperatures (74°, 148°, and 245°, respectively for the standard initial rates for the three processes) and the apparent activation energies were all about 85 kJ mole^{-1}.

The results do not indicate which of the ring hydrogen atoms exchanged more slowly than the other three. The position *meta* to the side groups should be unreactive if electrophilic attack by deuterium ions is involved but, if steric effects are important, the position *ortho* to both side groups would be most hindered. The first alternative is considered more likely on the basis of other work with these catalysts.[5]

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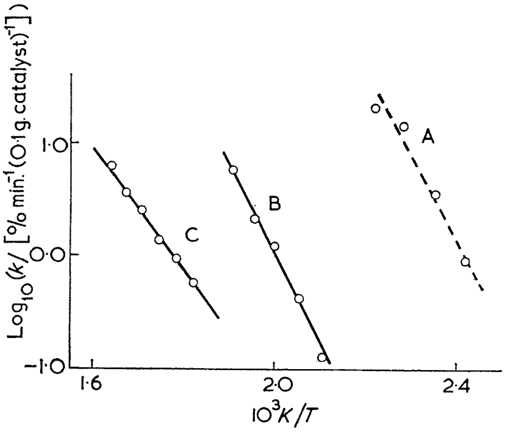

FIGURE 2. *Arrhenius plots derived from the results in Figure* 1. k *is the initial rate of reaction in % min.*$^{-1}$ (0·1 *g. of catalyst*)$^{-1}$ *and A, B, and C refer to the exchange of the first three, the fourth, and the remaining six hydrogen atoms in* m-*xylene.*

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