

Tritium Gas Exchange with Aromatic and Aliphatic Hydrocarbons Over Metal Containing ZSM-5 and Related Zeolites

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Abstract

Platinum and palladium containing Y-zeolite, mordenite and ZSM-5 catalyse efficient exchange at 100°C between elemental tritium and aromatic or aliphatic hydrocarbons, the tritium orientation in the organic molecule showing characteristics of both metal and zeolite catalysis. The hydrogen forms of the same zeolites (i.e. without metal) also activate elemental tritium for aromatic exchange at 120–150°C, which shows that a metal component is not necessary for activation of elemental hydrogen even at modest temperatures.

We report that zeolites containing noble metals are efficient for catalysing exchange between elemental tritium gas and both aromatic and aliphatic compounds at temperatures about 100°C. Substitution patterns have some of the characteristics of zeolite-induced exchange rather than noble-metal exchange and thus some novel specificities in the orientation of the isotope in the labelled compound may be obtained. Furthermore, and perhaps of greater mechanistic significance, is the observation that the hydrogen forms of the zeolites (i.e. in the absence of metal) also activate elemental tritium at temperatures of 130–150°C.

In a previous publication¹ the use of HY zeolite as a rapid and efficient hydrogen isotope exchange catalyst for the labelling of aromatic compounds was described. This exchange process involved the use of small quantities of high-activity tritiated water as the isotope source and exchange patterns were typical of electrophilic substitution reactions. This previous procedure¹ was not successful for labelling alkanes at temperatures up to 180°C.

We have now substituted elemental tritium for tritiated water as isotope source in the zeolite catalyst systems since higher specific activities are in general obtainable by gas exchange procedures. Results (Table 1) show that with the hydrogen forms of the zeolites, HY, ZSM-5 and Mordenite, a few per cent of the tritium gas were exchanged into toluene over periods of a week at 180°C. In contrast, platinum and palladium forms of the same zeolites at temperatures as low as 100°C exhibited relatively high activity for exchange of toluene with tritium gas. No detectable byproducts were formed. Alkanes exchanged at somewhat lower rates, and with the smaller pore zeolite, ZSM-5, some labelled byproducts were evident. Nevertheless pure high-activity alkanes may be consistently produced by exchange over PtY and PtMordenite.

¹ Long, M. A., Garnett, J. L., Williams, P. G., and Mole, T., *J. Am. Chem. Soc.*, 1981, **103**, 1571.

Table 1. Labelling of toluene by exchange with tritium gas over zeolites

Reaction conditions: *c.* 25 mg of zeolite, 200 μ l of hydrocarbon and 414 mCi of T₂ sealed in 20 ml ampoule and held at 100° for 96 h (except where otherwise indicated). Metal-zeolites prepared by bringing the H form into contact with a solution of either (NH₃)₄PtCl₂ or PdCl₂, drying, calcining at 350°C under nitrogen and reducing the metal at 350°C under hydrogen. Metal approx. 1% by weight

Catalyst	T incorp. (%) ^A	Distribution (% per H atom)			
		<i>ortho</i>	<i>meta</i>	<i>para</i>	Me
PtY ^B	67.8	14.6	6.0	42.0	5.6
PtMordenite	59.4	13.3	8.0	44.5	4.3
PtZSM-5	66.8	19.3	19.0	23.4	<1
PdY	60.7	3.0	<1	15.7	26.1
PdMordenite	66.2	10.3	2.6	19.0	18.4
PdZSM-5	62.8	20.6	19.0	20.8	<1
HY ^C	10.6	24.0	15.5	20.9	<1
HZSM-5 ^D	2.3	20.7	19.9	18.7	<1
H-Mordenite ^E	1.1				

^A Equilibrium represents *c.* 100% incorporation. ^B 72 h at 100°C. ^C 168 h at 150°C.

^D 168 h at 130°C. ^E 173 h at 125°C.

Table 2. Labelling of n-hexane and cyclohexane by exchange with tritium gas over zeolites

Reaction conditions as in Table 1

Compound	Catalyst	T incorp. (%) ^A	Distribution (% per H atom)		
			C1,6	C2,5	C3,4
n-Hexane	PtY	31.5	5.6	7.8	8.8
	PtMordenite	13.5	5.0	9.2	8.3
	PtZSM-5	13.6 ^B			
	PdY	43.1	7.4	6.7	7.2
	PdZSM-5	53.9	8.2	4.0	8.7
Cyclohexane	PtY	19.7			
	PtMordenite	8.3			
	PtZSM-5	25.7 ^B			

^A Equilibrium represents *c.* 100% incorporation. ^B Byproducts accounted for *c.* 18% of organic activity.

³H n.m.r. spectroscopy^{2,3} shows that the distribution of the isotope within the exchanged molecules is influenced by both the guest metal and the particular zeolite. In toluene, methyl exchange and 'ortho deactivation'⁴ are phenomena associated with catalysis by metals such as platinum⁵ and palladium,⁶ while *ortho/para* predominance is typical of H-zeolites.^{1,7} With the metallic forms of ZSM-5 no alkyl exchange was observed and this is assumed to reflect the constraints imposed by

² Garnett, J. L., Long, M. A., and Odell, A. L., *Chem. Aust.*, 1980, **47**, 215, and references therein.

³ Elvidge, J. A., Jones, J. R., Chambers, V. M. A., and Evans, E. A., in 'Isotopes in Organic Chemistry' (Eds E. Buncl and C. C. Lee) Vol. 4, Ch. 1 (Elsevier: Amsterdam 1978).

⁴ Garnett, J. L., *Catal. Rev.*, 1971, **5**, 229.

⁵ Garnett, J. L., Long, M. A., and Lukey, C. A., *J. Chem. Soc., Chem. Commun.*, 1979, 634.

⁶ Harper, R. J., and Kembal, C., *Proc. 3rd Int. Congr. Catal.*, 1965, **2**, 1145, and references therein.

⁷ Venuto, P. B., Wu, E. L., and Cattanach, J., 'Molecular Sieves' (Society of Chemical Industry: London 1968).

the particular pore geometry of the zeolite. The necessarily high temperatures and long reaction times of the H-zeolite runs led to scrambling reactions which largely obscured the specificity.

The relative exchange rates at different positions within n-hexane (Table 2) also depend slightly on the particular metal-zeolite, the observed slight preference for secondary hydrogen replacement over primary hydrogen being in agreement with that observed in deuterium gas exchange studies over platinum metal films.⁸

The present results, together with additional studies in which we have shown that the hydrogen forms of a variety of zeolites are inactive in promoting alkane exchange at temperatures below 180°C, leads to the conclusion that the metal component within the zeolite is necessary for the efficient activation of hydrogen (tritium) gas and alkanes at 100°C. 'Spillover' as recently described by Dmitriev *et al.*⁹ in discussion of their observation of exchange between deuterium gas and surface hydroxy groups in PtY zeolite, is a likely process by which the acidic protons of the zeolite may gain isotope and promote the characteristic electrophilic-type exchange pattern of H-zeolites. Nevertheless, the noble metal component of the zeolites is not necessary for the activation of elemental tritium at slightly higher temperatures since slow exchange into toluene occurs with the hydrogen forms of zeolites.

This single-step exchange procedure represents a clean and efficient method of tritiation of both aromatic and aliphatic hydrocarbons to high specific activities, the level of which is limited only by the amount of tritium gas which is devoted to the exchange step. The unique type of specificity observed for toluene labelled over PdY, i.e. where tritium is confined almost entirely to *para* and *methyl* positions, could only be achieved with conventional catalysts if a combination of exchange steps were used.

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⁸ Long, M. A., Moyes, R. B., Wells, P. B., and Garnett, J. L., *J. Catal.*, 1978, **52**, 206.

⁹ Dmitriev, R. V., Steinberg, K. H., Detjuk, A. N., Hofman, F., Bremer, H., and Minachev, K. M., *J. Catal.*, 1980, **65**, 105.