A New Series of Homogeneous Metal Catalysts for Very Rapid Hydrogen Isotope Exchange in Aromatic Compounds

By J. L. GARNETT, M. A. LONG, and R. F. W. VINING
(*The University of New South Wales, Kensington, N.S.W., Australia*)

and T. MOLE
(*C.S.I.R.O., Division of Applied Chemistry, Melbourne, Australia*)

Summary A range of metal halides catalyse, within a few minutes at room temperature, complete exchange of the aromatic hydrogen atoms between two molecules such as perdeuteriobenzene and toluene, this exchange not being subject to the steric effects and side reactions of the much slower conventional Pt catalysed deuterium labelling procedures.

WE have recently reported the use of organoaluminium dihalides as catalysts for the very rapid, specific exchange of protons in aromatic compounds.[1] Conventional homogeneous[2] and heterogeneous[3] catalysts normally require elevated temperatures and reaction times of hours or even days before equilibrium is attained. With the organoaluminium dihalides exchange between two aromatic compounds reaches equilibrium within minutes at room temperature.[1] We have now discovered a new range of highly active catalysts for these exchange reactions (Table) These new catalysts are generally non-organic metal halides as distinct from the organoaluminium catalysts previously reported and promote very rapid exchange at

20° between two aromatic compounds such as C_6D_6 and toluene.

In a typical reaction the catalyst (0·01 g) was added to a mixture of toluene (0·2 g) and C_6D_6 (0·2 g) under a dry nitrogen atmosphere and allowed to stand for several minutes at room temperature. If mass spectrometric analysis showed that limited exchange had occurred, the reaction was continued at 100° for one week to see whether ultimate equilibrium with some systems could be achieved.

TABLE *Deuterium exchange between toluene and perdeuteriobenzene.*

	% Approach to equilibrium	
	Room temp.	100 °C
Catalyst	5 min	1 week
$TaCl_5$	10%	100%
$MoCl_5$	10%	100%
WCl_6	5%	100%
BBr_3	0	100%
$AlCl_3$	50%	100%
$SbCl_5$	100%	100%

A wide range of metal salts have been examined in the present work, the most active being listed in the Table. $SbCl_5$ was the most efficient, virtually instantaneous exchange to equilibrium at room temperature being obtained. Generally where relevant the higher valence salts were significantly more active than the lower valence salts (*e.g.* $SbCl_5 > SbCl_3$).

The mass spectral analysis of the toluene in each case showed exchange of 5 protons only. N.m.r. analysis of the corresponding deuteriated benzoic acids obtained from oxidation of the deuteriated toluenes indicated a random distribution of deuterium in the aromatic ring. Exchange thus occurs with the aromatic protons only and is not subject to the steric effects observed in homogeneous platinum catalysed procedures.[4]

The mechanism by which the catalyst acts as a proton transfer agent is likely to involve the complexing of the two aromatic molecules in turn with the catalyst, possibly through a π-associative type species as proposed for other systems. Traces of dissolved water, usually accepted as being necessary to promote the activity of metal halide catalysts, may be involved in the proton transfer.

The immediate value of these catalysts will be in the very rapid and simple synthesis of deuteriated aromatic compounds using C_6D_6 as the most convenient isotopic source. The specificity of the technique towards aromatic proton exchange and the absence of steric effects and side-reactions as indicated in these preliminary studies, suggests that the present technique may also be used in a complementary way to present labelling methods. Thus, in addition to producing compounds such as ring labelled $[^2H_5]$-toluene, the present procedure will also give side-chain labelled $[^2H_3]$-toluene by back exchange with non-deuteriated benzene from $[^2H_8]$-toluene prepared by heterogeneous Pt exchange. Finally, the present metal salts can catalyse rapid exchange in a number of polycyclic aromatic hydrocarbons such as naphthalene at room temperature whereas other techniques require weeks at 150°.[5]

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