Catalytic Halide Exchange in Hydrocarbons Promoted by Aluminas Coated with Phosphonium Salts

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Summary Passing a mixture of two different alkyl halides, in the gas phase, through a column filled with alumina and a phosphonium salt, gives halide-exchange products which are collected at the outlet by condensation; the process is catalytic and allows transformations to be carried out in a continuous flow process.

RECENTLY, we reported that phase-transfer catalysis[1] is highly efficient even when one of the reagents is gaseous, the second reagent (the source of the nucleophile) is a solid salt,[2–4] and the catalyst, a molten phosphonium salt, is placed at the interface between the two phases. The nucleophile is consumed during the reaction, and a continuation of the reaction requires preparation of new solid reagent.

We report here the results obtained in making the process in the column definitely catalytic (*i.e.* devising a system in which the nucleophilic exchange may proceed continuously). Such a system is only possible with compounds containing substituents that can at the same time be both leaving- and entering-groups, such as the alkyl halides [reaction (1)].

$$\text{R–Hal} + \text{R}'\text{–Hal}' \overset{\text{cat.}}{\rightleftharpoons} \text{R–Hal}' + \text{R}'\text{–Hal} \qquad (1)$$

On passing a mixture of reagents through a suitable column, the exchange reaction between these and the catalyst coating the solid support makes it possible for the overall reaction (1) to take place.[2] This should provide a route to a large range of unusual aklyl halides.

The products collected at the outlet show that the reaction is controlled by kinetic factors (if the gas flow rate is too high for the catalyst to operate efficiently) and/or by thermodynamic factors (free-energy of the four halides and partition coefficients of each between the molten catalyst and the gas phase).

Reaction (2) (written non-stoicheiometrically), showing all

$$CH_2Cl_2 + C_2H_5Br \overset{\text{cat.}}{\rightleftharpoons} CH_2ClBr + CH_2Br_2 + C_2H_5Cl \qquad (2)$$

possible exchange products, was selected as a test reaction for evaluating the efficiency of various catalytic beds. A mixture of dichloromethane (1·0 mol. equiv.) and bromoethane (2·0 mol. equiv.) was passed at a rate of 28 ml h^{-1} over 200 g of a fixed bed contained in a column (length 50 cm, diameter 2·5 cm) at 170 °C. The reaction mixture condensed at the outlet was assayed by n.m.r. spectroscopy.

Analysis of the data in Table 1 shows that the limited flow of 28 ml h^{-1} is sufficient to discriminate between the solid supports not containing a quaternary salt, their relative activities being $4 > 3 > 2 \gg 1$. The reaction is kinetically controlled, as a thermodynamic equilibrium between the five compounds was not achieved for any of the solid supports. Operating with the same flow rate, addition of the

TABLE 1 Catalytic conversion of CH_2Cl_2 into CH_2ClBr and CH_2Br_2 by means of C_2H_5Br [a]

Expt	Catalytic bed[b]	Product yields (%)	
		CH_2ClBr	CH_2Br_2
1	Silica gel	1	0
2	Basic Al_2O_3	33	2
3	Neutral Al_2O_3	48 (66)[c]	6 (14)[c]
4	Acidic Al_2O_3	52	21
5	Silica gel + $Bu^n_4P^+Br^-$	50 (25)[d]	23 (1)[d]
6	Basic Al_2O_3 + $Bu^n_4P^+Br^-$	50 (50)[d]	24 (24)[d]
7	Neutral Al_2O_3 + $Bu^n_4P^+Br^-$	48 (50)[d]	22 (21)[d]
8	Acidic Al_2O_3 + $Bu^n_4P^+Br^-$	49 (50)[d]	25 (12)[d]

[a] $CH_2Cl_2 : C_2H_5Br = 1:2$ (mol/mol), continuous flow rate of 28 ml h^{-1} with a peristaltic pump, $T = 170$ °C, atmospheric pressure, conversions were established by n m r integrations of the corresponding singlets, efficiency does not diminish after passage of about 500 ml of the reacting mixture [b] 200 g for the aluminas and 110 g for silica gel, beds containing phosphonium salt (10% by weight with respect to the inorganic support) were prepared by dissolving the phosphonium salt in methanol, adding the solids removing the solvent, and drying at 130 °C for 15 h, silica gel and aluminas were Merck reagent (70–230 mesh), code numbers, respectively, 7734 1076 1077, 1078 [c] $CH_2Cl_2 : C_2H_5Br = 1.5$ (mol/mol) [d] Flow rate 200 ml h^{-1}

TABLE 2 Reactions carried out in a continuous flow process, promoted by acidic Al_2O_3 coated with $Bu^n_4P^+Br^-$ (10% by weight) [a]

R–Hal + R′–Hal′ (molar ratio)	Products (% conversion from the parent halide)[b]		
$CHCl_3 + C_2H_5Br$ (1:5)	$CHBrCl_2$ (9 5)	$CHBr_2Cl$ (0 5)	$CHBr_3$ (0)
$CH_2Cl_2 + CHBr_3$ (3:2)	CH_2BrCl (33) $CHBrCl_2$ (7)	CH_2Br_2 (6) $CHCl_3$ (1)	$CHBr_2Cl$ (28)
n-$C_3H_7Br + CH_3I$ (1:3)		n-C_3H_7I (66)	
$CH_2{=}CHCH_2Cl + CH_3I$ (1:3)		$CH_2{-}CHCH_2I$ (75)	

[a] Flow rate 28 ml h^{-1}, for the reaction conditions see footnotes,[a,b] Table 1 [b] Established by n m r integration of the corresponding signals, after the observed conversion remained constant for at least 50 ml of collected product

phase-transfer catalyst tetra-n-butylphosphonium bromide produces equally efficient conversion for all beds, since thermodynamic equilibrium is secured in all cases (possibly the 50% yield of exchanged chlorine is not purely accidental, as the initial Br : Cl ratio was 1 : 1) On the other hand, increasing the flow rate about 10-fold produced a support-dependent discrimination, the observed relative efficiencies being in the order 6 > 7 > 8 ≫ 5 which is, for the tested aluminas, the reverse of that obtained in the absence of the catalyst

Addition of the phosphonium salt therefore allows the exchange rate to increase several times, differently, however, for different supports

In Table 2, the catalytic activity of acidic alumina containing 10% tetra-n-butylphosphonium bromide in other exchange reactions is reported These results indicate the versatility of the method, although the yields are dependent on the alkyl halides used

While it is relatively simple to describe a mechanism for the reaction that takes place in the presence of a cationic catalyst, which exchanges its anion with gaseous halides diffusing over it, it is far more difficult to explain the activity of the supports in the absence of a catalyst and the differences that show up between aluminas that are very similar to each other These systems, however poorly investigated for the present, might be considered to be on the borderline between phase-transfer catalysis and catalysis promoted by highly porous inorganic materials, alternatively two different mechanisms may be operative, one when the onium salt is present and the other in its absence

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[4] For the use of a reactor consisting of three phases [two liquids (aqueous and organic phases) and an insoluble solid (the catalyst bound to a polystyrene resin)] see V Ragaini and G Saed, *Z Phys Ch -W* , 1980, **119**, 117