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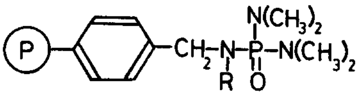
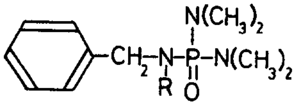
POLYMER-SUPPORTED PHOSPHORIC TRIAMIDES AS CATALYSTS FOR PHASE-TRANSFER REACTIONS

M. Tomoi*, M. Ikeda, and H. Kakiuchi
Department of Applied Chemistry, Faculty of Engineering,
Yokohama National University, Yokohama 232, Japan

Aqueous organic two-phase reactions are known to be catalyzed by quarternary ammonium or phosphonium salts,[1] crown ethers,[2] cryptands,[3] α-phosphoryl sulfoxides,[4] and phosphoric triamides.[5,6] Recently, the onium salts,[7—10] crown ethers,[8,9,11] and cryptands[8] immobilized on polymer supports were found to catalyze the two-phase reactions. The advantage of using polymer-supported catalysts is that products can be easily separated from the reaction mixture, and the catalysts separated are reusable.

We wish to report the preparation and catalytic behavior of phosphoric triamides immobilized on polymer supports. Polymer-supported phosphoric triamide (I) was prepared by the reaction of sodium salt of pentamethylphosphoric triamide[12] with chloromethylated polystyrene resin cross-linked with 10% divinylbenzene (macroreticular type; 4.6 mequiv. of Cl per g of polymer) in tetrahydrofuran at a reflux temperature under a nitrogen atmosphere. Catalyst (I) contained 1.6 mmol. of P=O group per g of polymer. Polymer-supported phosphoric triamide (II) was prepared by the reaction of sodium salt of N,N,N',N'-tetramethylphosphoric triamide[13] with chloromethylated polystyrene resin cross-linked with 30% divinylbenzene (macroreticular type; 5.6 meqiv. of Cl per g of polymer) in hexamethylphosphoric triamide at 100°C under a nitrogen atmosphere. Catalyst (II) contained 0.48 mmol. of P=O group per g of polymer.


(I) R=CH_3 ; (II) R=H


(III) R=CH_3; (IV) R=H

The aqueous organic two-phase reactions were carried out, under magnetic stirring, in the presence of 0.01—0.10 mol. equiv. of the polymer-supported catalyst (See Table). The polymer-supported phosphoric triamides were found to be highly effective catalysts for the two-phase reactions. The most remarkable characteristics of the results obtained in this study are as follows. (1) In contrast to observations on the immobilized onium salts or crown ethers,[8] the polymer-supported phosphoric triamides are better catalysts than the corresponding non-immobilized phosphoric triamides (III and IV).[5,6] (2) The catalytic activity of (II) was considerably higher than that of (I). This fact could be explained by

Table. Phase-Transfer Reactions Catalyzed by Polymer-Supported Phosphoric Triamide

Substrate	Reagent	Solvent	Catalyst	[P=O]/[Substrate]	Temp °C	Time hr	Yield[a] %	Product
$C_8H_{17}Br$	KI[b]	None	None	—	80	24	<5	$C_8H_{17}I$
"	"	"	(I)	0.08	"	8	>95	"
"	"	"	(II)	0.08	"	1	95	"
"	"	"	(III)	0.08	"	8	33	"
"	"	"	(IV)	0.08	"	8	73	"
"	"	"	(II)	0.01	"	8	94	"
"	"	"	(II)[c]	0.01	"	8	>95	"
$C_8H_{17}Br$	$NaCN$[d]	None	None	—	80	24	11	$C_8H_{17}CN$
"	"	"	(I)	0.02	"	8	82	"
"	"	"	(II)	0.02	"	8	>95	"
"	"	"	(II)[c]	0.02	"	4	>95	"
$PhCOCH_3$[e]	$NaBH_4$[f]	Benzene	None	—	Room temp	8	10	$PhCH(OH)CH_3$
"	"	"	(I)	0.10	"	3	>95	"
"	"	"	(I)	0.02	"	8	>95	"
"	"	"	(II)	0.02	"	4	88	"
$C_6H_{13}COCH_3$[e]	$NaBH_4$[f]	Benzene	None	—	Room temp	24	3	$C_6H_{13}\underset{OH}{CH}(CH_3)$
"	"	"	(I)	0.10	"	3	>95	"
"	"	"	(I)	0.02	"	6	>95	"
"	"	"	(II)	0.02	"	3	>95	"

a) By g.l.c. analysis. b) Saturated aqueous solution, 5.0 mol. equiv.
c) Recovered catalyst. d) 8 M aqueous solution, 2.0 mol. equiv.
e) 25.5 Mmol; benzene (4 ml), 1% aqueous NaOH (1 ml). f) 0.76 Mol. equiv.

assuming that the anionic moieties of inorganic reagents interact with the hydrogen of NH in (II) through hydrogen bonding, and therefore the inorganic reagents are efficiently extracted from the aqueous phase to the organic phase. (3) The activity of the recovered catalysts was higher than that of the original catalysts. The immobilized catalysts are ground under magnetic stirring. This is considered to induce an increase in the surface area of the catalysts and thereby an increase in the catalytic activity.

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