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CatOnium

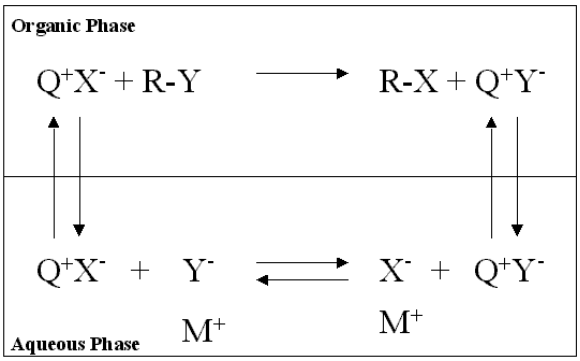
Phase Transfer Catalysts

Phase transfer catalysis is a phenomenon of rate enhancement of a reaction between reactants located in different phases (immiscible liquids or solid and liquid) by addition of a small quantity of an agent called phase-transfer catalyst that extracts one of the reactants, most commonly an anion, across the interface into the other phase so that reaction can proceed. Phase transfer catalysts (PTC) are salts of onium ions like tetraalkylammonium or tetraalkylphosphonium salts, or agents that complex inorganic cations such as crown ethers. The catalyst cation is not consumed in the reaction although an anion exchange does occur.

On commercial scale PTC are widely used in the production of monomers, polymers, agrochemicals, pharmaceuticals, dyes, flavours, fragrances, explosives, surfactants, petrochemicals, rubber, and wide variety of other commodity, specialty and fine organic chemicals. Phase transfer catalysis is also used in pollution prevention, pollution treatment and the removal or destruction of impurities in waste and product streams. Both cost reduction and pollution prevention as two powerful driving forces in the chemical industry are perfectly matched by the benefits provided by PTC technology.

Typical reactions where PTC's are employes as catalysts include, etherification, esterification, transesterification, N-alkylation, C-alkylation, S-alkylation, mercaptan reactions, dehydrohalogenation, Michael addition, aldol condensation, oxidation, epoxidation, chloromethylation, hydrohalogenation, hydrogenation, borohydride reduction, darzens condensation, carbene reactions, polymerization, polymer modification, displacements using: cyanide, fluoride, bromide, iodide, azide, thiocyanate, sulfide, other inorganic nucleophiles, benzyl chloride, allyl chloride, benzoyl chloride, methanesulfonyl chloride, epichlorohydrin, PCl_3, $POCl_3$ other alkyl halides, acyl halides, sulfonyl halides, phosphoro halides and anhydrides

The mechanism of phase transfer catalysis as proposed by Starks and depicted in the scheme below proceeds via the quaternary ammonium cation Q^+ that forms an ion pair with an anionic reactant X^-, which is in equilibrium between the organic and the aqueous or the solid phase. In the organic phase, because of the reduced hydration, the anion reacts quickly with a typical substrate RY forming the product RX and the anionic leaving group Y^- that pairs with the quaternary ammonium cation. In the aqueous or solid phase the catalyst exchanges the leaving group for another anionic reactant to complete the catalytic cycle.



By using PTC reactivity is enhanced sometimes by orders of magnitude, because once the anion or neutral compound is in the organic phase, it has very little hydration or solvation associated with it, thereby greatly reducing the energy of activation.

Chemical reaction and mass transfer control can be considered as two extreme cases that determine the reaction rate, the combination of both mostly occurring in practice. For both mechanisms the general rule is that the reaction rate is proportional to the catalyst concentration. In the case of chemical reaction control, the reaction rate increases by increasing the lipophylicity of the catalyst, decreasing of the polarity of the solvent and decreasing the hydration of the anionic reactant.
Mass transfer limited reactions are characterized by increased reactivity with increased accessibility of the positive charge of the quaternary nitrogen or phosphorus, increased agitation efficiency and increased polarity of the solvent used.

Related to the above, two empirical parameters “q-value” and “C #”, which give an indication for structure-activity relationships of a given PTC, are often used. The q-value reflects the accessibility of the positive charge of the quaternary onium compound. A q-value of 1.0 to 2.0 often gives high reactivity for "transfer rate limited" PTC reactions whereas a q-value of < 1 often gives high reactivity for PTC reactions which require a loose ion pair. The q-value is calculated by adding the reciprocals of the numbers of carbons on each of the four chains (the q-value for methyl tributyl ammonium cation for example will be 1/1 + 1/4 + 1/4 + 1/4 = 1.75. C# is simply the sum of all of the carbons of the quat and is a measure of the organophilicity of the phase transfer catalyst (the C# for the very same methyl tributyl ammonium cation will be 1 + 4 + 4 + 4 = 13). As the C# increases, the organophilicity increases and usually results in a higher concentration of the quat-anion pair in the organic phase. When the rate determining step is the organic phase reaction, C#'s in the range of 16 to 32 often provide desirable reactivity.

The variety of chemical reactions and environments in which they take place created the need for large number of different PTC’s. To meet the requirements of our customers we supply more than 100 different PTC’s. The most common phase transfer catalysts are quaternary ammonium salts containing either alkyl or mixed alkyl/aryl groups. In some cases their applicability is restricted by the thermal stability which is limited to about 100^0C. We supply broad range of quaternary ammonium halides, with F^-, Cl^-, Br^- and I^- as counter anions, and limited number of quaternary hydroxyl ammonium compounds, with an OH^- group as counter anion. Phosphonium salts are used in the cases in which the use of ammonium compounds because of their thermal instability is not suitable. The thermal stability of the quaternary phosphonium salts is quite good in a range between 120-150^0C, with indications that they can be also use at temperatures up to 200^0C. The last group of PTC’s in our program includes a range of quaternary pyridinium salts that are very effective at high temperatures.

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Quaternary Ammonium Halides

	Abbre-viation	Product	CAS No.	Structure	C#	q-value
		Fluorides				
1	TMAF	Tetramethyl ammonium fluoride	373-68-2	$(CH_3)_4NF$	4	4,00
2	TEAF	Tetraethyl ammonium fluoride	665-46-3	$(C_2H_5)_4NF$	8	2,00
3	TPAF	Tetrapropyl ammonium fluoride		$(C_3H_7)_4NF$	12	1,33
4	TBAF	Tetrabutyl ammonium fluoride	429-41-4	$(C_4H_9)_4NF$	16	1,00
		Chlorides				
5	TMAC	Tetramethyl ammonium chloride	75-57-0	$(CH_3)_4NCl$	4	4,00
6	TEAC	Tetraethyl ammonium chloride	56-34-8	$(C_2H_5)_4NCl$	8	2,00
7	TPAC	Tetrapropyl ammonium chloride	5810-42-4	$(C_3H_7)_4NCl$	12	1,33
8	TBAC	Tetrabutyl ammonium chloride	37451-68-6	$(C_4H_9)_4NCl$	16	1,00
9	MTEAC	Methyl triethyl ammonium chloride	10052-47-8	$CH_3(C_2H_5)_3NCl$	19	1,50
10	MTPAC	Methyl tripropyl ammonium chloride		$CH_3(C_3H_7)_3NCl$	28	1,33
11	MTBAC	Methyl tributyl ammonium chloride	56375-79-2	$CH_3(C_4H_9)_3NCl$	13	1,75
12	MTOAC	Methyl trioctyl ammonium chloride	5137-55-3	$CH_3(C_8H_{17})_3NCl$	25	1,38
13	MTOAC	Methyl trioctyl ammonium chloride solution	5137-55-3	$CH_3(C_8H_{17})_3NCl$	25	1,38
14	PTMAC	Propyl trimethyl ammonium chloride		$C_3H_7(CH_3)_3NCl$	6	3,33
15	BTMAC	Butyl trimethyl ammonium chloride		$C_4H_9(CH_3)_3NCl$	7	3,25
16	DDTMAC	Dodecyl trimethyl ammonium chloride	112-00-5	$C_{12}H_{25}(CH_3)_3$ NCl	15	3,08
17	TDTMAC	Tetradecyl trimethyl ammonium chloride	4574-04-3	$C_{14}H_{29}(CH_3)_3$ NCl	17	3,07
18	HDTMAC	Hexadecyl trimethyl ammonium chloride	112-02-7	$C_{16}H33(CH_3)_3$ NCl	19	3,06
19	BZTMAC	Benzyl trimethyl ammonium chloride	56-93-9	C_6H_5- $CH_2(CH_3)_3NCl$	10	3,14
20	BZTEAC	Benzyl triethyl ammonium chloride	56-37-1	C_6H_5-$CH_2(C_2H_5)_3NCl$	13	1,64
21	BZTBAC	Benzyl tributyl ammonium chloride	23616-79-7	C_6H_5-CH_2 $(C_4H_9)_3NCl$	19	0,89
22	PHTMAC	Phenyl trimethyl ammonium chloride	138-24-9	$C_6H_5(CH_3)_3NCl$	9	3,17
23	DEEAC	N , N-diethyl ethanol ammonium chloride		$(C_2H_5)_2(C_2H_5OH)NHCl$	n.a.	n.a.
24		**Bromides**				
25	TMAB	Tetramethyl ammonium bromide	64-20-0	$(CH_3)_4NBr$	4	4,00
26	TEAB	Tetraethyl ammonium bromide	71-91-0	$(C_2H_5)_4NBr$	8	2,00
27	TBAB	Tetrabutyl ammonium bromide	1643-19-2	$(C_4H_9)_4NBr$	16	1,00

28	TOAB	Tetraoctyl ammonium bromide	14866-33-2	$(C_8H_{17})_4NBr$	32	0,50
29	DDTMAB	Dodecyl trimethyl ammonium bromide	1119-94-4	$C_{12}H_{25}(CH_3)_3$ NBr	15	3,08
30	TDTMAB	Tetradecyl trimethyl ammonium bromide	1119-97-7	$C_{14}H_{29}(CH_3)_3NBr$	17	3,07
31	HDTMAB	Hexadecyl trimethyl ammonium bromide	57-09-0	$C_{16}H33(CH_3)_3$ NBr	19	3,06
32	BZTMAB	Benzyl trimethyl ammonium bromide	5350-41-4	C_6H_5-$CH_2(CH_3)_3NBr$	10	3,14
33	BZTEAB	Benzyl triethyl ammonium bromide	5197-95-5	C_6H_5-$CH_2(C_2H_5)_3NBr$	13	1,64
34	BZTBAB	Benzyl tributyl ammonium bromide	25316-59-0	C_6H_5-CH_2 $(C_4H_9)_3NBr$	19	0,89
35	PHTMAB	Phenyl trimethyl ammonium bromide	16056-11-4	$C_6H_5(CH_3)_3NBr$	9	3,17
		Iodides				
36	TMAI	Tetramethyl ammonium iodide	75-58-1	$(CH_3)_4NI$	4	4,00
37	TEAI	Tetraethyl ammonium iodide	68-05-3	$(C_2H_5)_4NI$	8	2,00
38	TPAI	Tetrapropyl ammonium iodide	631-40-3	$(C_3H_7)_4NI$	12	1,33
39	TBAI	Tetrabutyl ammonium iodide	311-28-4	$(C_4H_9)_4NI$	16	1,00
		Acetates				
40	TMAA	Tetramethyl ammonium acetate	10581-12-1	$(CH_3)_4CH_3COOH$	4	4,00
41	TEAA	Tetraethyl ammonium acetate	1185-59-7	$(C_2H_5)_4CH_3COOH$	8	2,00
42	TBAA	Tetrabutyl ammonium acetate	10534-59-5	$(C_4H_9)_4CH_3COOH$	16	1,00
		Bisulfates				
43	TMABS	Tetramethyl ammonium bisulfate	103812-00-6	$(CH_3)_4NHSO_4$	4	4,00
44	TEABS	Tetraethyl ammonium bisulfate	16873-13-5	$(C_2H_5)_4NHSO_4$	8	2,00
45	TPABS	Tetrapropyl ammonium bisulfate	56211-70-2	$(C_3H_7)_4NHSO_4$	12	1,33
46	TBABS	Tetrabutyl ammonium bisulfate	32503-27-8	$(C_4H_9)_4NHSO_4$	16	1,00

Quaternary Ammonium Hydroxides

	Abbre-viation	Product	CAS No.	Structure	C#	q-value
1	TMAH	Tetramethyl ammonium hydroxide	75-59-2	$(CH_3)_4NOH$	4	4,00
2	TEAH	Tetraethyl ammonium hydroxide	77-98-5	$(C_2H_5)_4NOH$	8	2,00
3	TPAH	Tetrapropyl ammonium hydroxide	4499-86-9	$(C_3H_7)_4NOH$	12	1,33
4	TBAH	Tetrabutyl ammonium hydroxide	2052-49-5	$(C_4H_9)_4NOH$	16	1,00
5	BZTMAH	Benzyl trimethyl ammonium hydroxide	100-85-6	C_6H_5-$CH_2(CH_3)_3NOH$	10	3,14
6	DDTMAH	Dodecyl trimethyl ammonium hydroxide		$C_{12}H_{25}(CH_3)_3NOH$	15	3,08

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Quaternary Phosphonium Halides

	Abbre-viation	Product	CAS No.	Structure	C#	q-value
		Chlorides				
1	MTPC	Methyl triphenyl phosphonium chloride	1031-15-8	$CH_3(C_6H_5)_3PCl$	19	1,50
2	ETPC	Ethyl triphenyl phosphonium chloride	896-33-3	$(C_6H_5)_3C_2H_5PCl$	20	1,00
3	PTPC	Propyl triphenyl phosphonium chloride		$(C_6H_5)_3C_3H_7PCl$	21	0,83
4	BTPC	Butyl triphenyl phosphonium chloride	13371-17-0	$(C_6H_5)_3C_4H_9PCl$	22	0,75
5	DDTPC	Dodecyl triphenyl phosphonium chloride	15510-55-1	$C_{12}H_{25}ClP\text{-}(C_6H_5)_3$	30	0,58
6	TDTPC	Tetradecyl triphenyl phosphonium chloride		$C_{14}H_{29}ClP\text{-}(C_6H_5)_3$	32	0,57
7	HDTPC	Hexadecyl triphenyl phosphonium chloride	14866-43-4	$C_{16}H_{33}ClP\text{-}(C_6H_5)_3$	34	0,56
8	ATPC	Allyl triphenyl phosphonium chloride	18480-23-4	$CH_2{=}CH\text{-}CH_2ClP\text{-}(C_6H_5)_3$	21	083
9	BZTPC	Benzyl triphenyl phosphonium chloride	1100-88-5	$C_6H_5\text{-}CH_2ClP\text{-}(C_6H_5)_3$	25	0,64
		Bromides				
10	TBPB	Tetrabutyl phosphonium bromide	3115-68-2	$(C_4H_9)_4PBr$	16	1,00
11	HDTBPB	Hexadecyl tributyl phosphonium bromide	14937-45-2	$C_{16}H_{33}(C_4H_9)_3BrP$	28	0,81
12	MTPB	Methyl triphenyl phosphonium bromide	1779-49-3	$(C_6H_5)_3CH_3PBr$	19	1,50
13	ETPB	Ethyl triphenyl phosphonium bromide	1530-32-1	$(C_6H_5)_3C_2H_5PBr$	20	1,00
14	PTPB	Propyl triphenyl phosphonium bromide	15912-75-1	$(C_6H_5)_3C_3H_7PBr$	21	0,83
15	BTPB	Butyl triphenyl phosphonium bromide	1779-51-7	$(C_6H_5)_3C_4H_9PBr$	22	0,75
16	DDTPB	Dodecyl triphenyl phosphonium bromide	15510-55-1	$C_{12}H_{25}BrP\text{-}(C_6H_5)_3$	30	0,58
17	TDTPB	Tetradecyl triphenyl phosphonium bromide	15510-55-1	$C_{14}H_{29}BrP\text{-}(C_6H_5)_3$	32	0,57
18	HDTPB	Hexadecyl triphenyl phosphonium bromide	14866-43-4	$C_{16}H_{33}BrP\text{-}(C_6H_5)_3$	34	0,56
19	ATPB	Allyl triphenyl phosphonium bromide	1560-54-9	$CH2{=}CH\text{-}CH2BrP\text{-}(C_6H_5)_3$	21	0,83
20	BZTPB	Benzyl triphenyl phosphonium bromide	1449-46-3	$C_6H_5\text{-}CH_2BrP\text{-}(C_6H_5)_3$	25	0,64
21	TPHTPB	Tetraphenyl phosphonium bromide	2751-90-8	$(C_6H_5)4PBr$	24	0,67
		Iodides				
22	MTPI	Methyl triphenyl phosphonium iodide	2065-66-9	$CH_3IP\text{-}(C_6H_5)_3$	19	1,50
23	ETPI	Ethyl triphenyl phosphonium iodide	4736-60-1	$(C_6H_5)_3C_2H_5PI$	20	1,00
24	PTPI	Propyl triphenyl phosphonium iodide		$(C_6H_5)_3C_3H_7PI$	21	0,83
25	BTPI	Butyl triphenyl phosphonium iodide		$(C_6H_5)_3C_4H_9PI$	22	0,75

Quaternary Pyridinium Halides

	Abbre-viation	Product	CAS No.	Structure	C#	q-value
		Chlorides				
1	MPC	Methyl pyridinium chloride		$C_5H_5NCH_3Cl$	6	1,2
2	EPC	Ethyl pyridinium chloride		$C_5H_5NC_2H_5Cl$	7	0,70
3	BPC	Butyl pyridinium chloride		$C_5H_5NC_4H_9Cl$	9	0,45
4	DDPC	Dodecyl pyridinium chloride	104-74-5	$C_5H_5NC_{12}H_{25}Cl$	17	0,28
5	TDPC	Tetradecyl pyridinium chloride		$C_5H_5NC_{14}H_{29}Cl$	19	0,27
6	HDPC	Hexadecyl pyridinium chloride	6004-24-6	$C_5H_5NC_{16}H_{33}Cl$	21	0,26
		Bromides				
7	MPB	Methyl pyridinium bromide		$C_5H_5CH_3Br$	6	1,20
8	EPB	Ethyl pyridinium bromide		$C_5H_5C_2H_5Br$	7	0,70
9	PPB	Propyl pyridinium bromide		$C_5H_5C_3H_7Br$	8	0,53
10	BPB	Butyl pyridinium bromide		$C_5H_5C_4H_9Br$	9	0,45
11	DDPB	Dodecyl pyridinium bromide	104-73-4	$C_5H_5NC_{12}H_{25}Br$	17	0,28
12	TDPB	Tetradecyl pyridinium bromide		$C_5H_5NC14H_{29}Br$	19	0,27
13	HDPB	Hexadecyl pyridinium bromide	140-72-7	$C_5H_5NC_{16}H_{33}Br$	21	0,26