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Stability of Quaternary Onium Salts under Phase-Transfer Conditions in the Presence of Aqueous Alkaline Solutions

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The parameters that affect the stability of a series of quaternary ammonium and phosphonium salts $R_4M^+Y^-$ under phase-transfer catalysis (PTC) conditions in a chlorobenzene–aqueous NaOH two-phase system have been defined. Quaternary ammonium salts are much more stable than phosphonium derivatives. When the quaternary cation R_4M^+ is the same, the stability is in the order $I > Br^- \gg Cl^-$. It dramatically increases either by diminishing the concentration of the base in the aqueous phase (from 50% to 15% aqueous NaOH) or by adding to the heterogeneous system a molar excess of the corresponding inorganic salt NaY. In all cases the degradation reactions are found to proceed in the organic phase via extraction of OH^- as $R_4M^+OH^-$, interfacial phenomena being unimportant. As a consequence quaternary onium salts are stable in the presence of aqueous alkaline solutions provided that the extractability and/or the reactivity of OH^- in the organic phase are minimized.

Lipophilic quaternary ammonium and phosphonium salts $R_4M^+Y^-$ are widely used in organic synthesis as phase-transfer catalysts.[1-4] They are soluble even in low polarity solvents like benzene, toluene, chlorobenzene, and cyclohexane. In these media they give rise to loose ion pairs, in which the anions are unsolvated and hence highly reactive.[2-4]

Under liquid–liquid phase-transfer catalysis (PTC) conditions in neutral or acid media, these salts are stable up to temperatures of 100–150 °C, the phosphonium salts being more stable than the corresponding ammonium ones. Their stability dramatically diminishes in aqueous–organic two-phase systems with strongly alkaline aqueous solutions; in this case the phosphonium derivatives are the less stable ones.[2-4]

The latter PTC conditions are usually employed for C-, O-, and N-alkylation reactions, alkene isomerization, H/D exchanges, α and β eliminations, etc...[2-6] In addition, concentrated aqueous alkaline solutions (50% aqueous NaOH, 60% aqueous KOH) were found to be an effective system for completely dehydrating the anions under liquid–liquid PTC conditions, thus affording anionic reactivities identical with those found under anhydrous homogeneous conditions.[5,7-9]

Highly effective phase-transfer agents, like lipophilic cryptands and crown ethers, are chemically stable even in the presence of concentrated aqueous alkaline solutions.[3,4,8] The use of these systems, however, is strongly limited by their relatively high cost and/or toxicity. Quaternary onium salts, on the contrary, are cheap and easily available, so that, in spite of their low stability, they are the catalysts of choice also under these latter conditions.[10]

Some authors pointed out that quaternary onium salts may be subject to degradation under PTC conditions,[2-4,7,13-17] without defining the parameters that determine the stability of these salts.[18]

Here we report a systematic study on the stability of a series of quaternary onium salts $R_4M^+Y^-$ in aqueous–organic two-phase systems in the presence of aqueous alkaline solutions as a function of: (i) the nature of the heteroatom, alkyl chain R, and counter ion Y^- associated with quaternary cation; (ii) the base concentration in the aqueous phase; (iii) the presence of a molar excess of the corresponding inorganic salt NaY; and (iv) the temperature.

Results

The onium salts examined are tetrahexyl-, tetraoctyl-, and tetrabutylammonium derivatives **1**–**3**, benzyltriethylammonium chloride (TEBAC) (**4a**) and bromide (TEBAB) (**4b**), benzyltrihexylammonium chloride and bromide (**5a**, **5b**), trioctylmethylammonium chloride (ALIQUAT) (**6a**), and tetrabutyl- and hexadecyltributylphosphonium derivatives (**7**, **8**). These salts are representative of those most widely used as phase-transfer catalysts.

$RN^+R'_3$
1–6

1, R = R′ = hexyl
2, R = R′ = octyl
3, R = R′ = butyl
4, R = benzyl; R′ = ethyl
5, R = benzyl; R′ = hexyl
6, R = methyl; R′ = octyl

a, $Y^- = Cl^-$
b, $Y^- = Br^-$
c, $Y^- = I^-$
d, $Y^- = MeSO_3^-$
e, $Y^- = OH^-$

$RP^+R'_3$
7, 8

7, R = R′ = butyl
8, R = hexadecyl, R′ = butyl

The stability of quaternary ammonium ($RN^+R'_3Y^-$) and phosphonium ($RP^+R'_3Y^-$) salts **1**–**6** and **7** and **8** was

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(18) Kinetic studies of the Hofmann degradation of tetrahexyl[5,19] and tetrabutylammonium hydrogen sulfate[20] under PTC conditions were recently done.

Table I. Half-Life Periods ($t_{1/2}$) for Quaternary Onium Salts ($R_4M^+Y^-$) Degradation in a Chlorobenzene–50% Aqueous NaOH Two-Phase System under Phase-Transfer Conditions in the Absence (A)[a] and Presence (B)[b] of a Molar Excess of the Corresponding Inorganic Salt (NaY)

$R_4M^+Y^-$		T, °C	$t_{1/2}$, h		
R_4M^+	Y^-		A[a]	B[b]	entry
1a, $hexyl_4N^+$	Cl^-	25	35	*c*	1
			d,e		2
		60	0.4	8	3
			0.7[d]	1.5[d]	4
1b	Br^-	25	*f*	stable[g]	5
		60	13	stable[g]	6
			45[d]		7
		80	1	272	8
1c	I^-	25	stable[g]		9
		60	stable[d,g]		10
		80	136	stable[g]	11
2a, $octyl_4N^+$	Cl^-	60	0.25		12
2b	Br^-		3.5	stable[g]	13
3a, Bu_4N^+	Cl^-	25	18		14
4a, $benzylN^+Et_3$	Cl^-	25	6.7[h]	127[h]	15
4b	Br^-	25	240[h]	*h*, *g*	16
		35	96[h]		17
5a, $benzylN^+hexyl_3$	Cl^-	25	13		18
		60	0.05		19
5b	Br^-	25	432		20
		60	2.3		21
6a, $octyl_3N^+Me$	Cl^-	25	32		22
		60	0.7		23
7a, Bu_4P^+	Cl^-	25	0.03	0.3	24
7b	Br^-	25	3.5	220	25
		60	0.06	5.5	26
8a, $Bu_3P^+C_{16}H_{33}$	Cl^-	25	0.03	0.8	27
8b	Br^-	25	2	220	28
		60	0.25		29
			1.5[d]		30
8c	I^-	25	*i*	stable[g]	31

[a] A chlorobenzene solution (40 mL) of $R_4M^+Y^-$ (2–4 × 10^{-2} M) and 50% aqueous NaOH (40 mL). [b] Same amounts of PhCl, $R_4M^+Y^-$, and 50% aqueous NaOH as in *a*, in the presence of a molar excess (30 mol/mol $R_4M^+Y^-$) of NaY, partially as solid phase. [c] A 4% degradation after 6 days. [d] Reaction carried on in the ground NaOH–PhCl solid–liquid system: a chlorobenzene solution (40 mL) of $R_4M^+Y^-$ (2–4 × 10^{-2} M) and 50 mmol of solid NaOH. [e] A 5% degradation after 2 days. [f] An 8% degradation after 6 days. [g] No decomposition was observed after 6 days. [h] Reaction performed in the CH_2Cl_2–50% aqueous NaOH two-phase system. [i] An 8% decomposition after 3 days.

Table II. Effect of the Base Concentration in the Aqueous Phase on the Half-Life Periods ($t_{1/2}$) of Quaternary Salts 1a, 1b, and 8b in a Chlorobenzene–Aqueous NaOH Two-Phase System[a] at 60 °C

	$t_{1/2}$, h		
% NaOH	$hexyl_4N^+Cl^-$ (**1a**)	$hexyl_4N^+Br^-$ (**1b**)	$Bu_3P^+C_{16}H_{33}Br^-$ (**8b**)
10	78		
15	29	312	20
25	12		
30	6	30	4.5
40	0.75		
50	0.4	13	0.25

[a] A chlorobenzene solution (40 mL) of $R_4M^+Y^-$ **1a**, **1b**, or **8b** (2–4 × 10^{-2} M) and 40 mL of an aqueous NaOH solution.

Table III. Extractability (%) of OH^- in the Organic Phase as Quaternary Ammonium Hydroxide $R_4M^+OH^-$ by Tetrahexylammonium Halides 1a–c in a Chlorobenzene–50% Aqueous NaOH Two-Phase System in the Absence (A)[a] and Presence (B)[b] of a Molar Excess of the Corresponding Inorganic Salt (NaY) at 60 °C

	$R_4M^+OH^-$ (**1e**) (%)[c]	
Y^-	A[a]	B[b]
1a, Cl^-	10	≤1
1b, Br^-	≤1	undetectable
1c, I^-	negligible	

[a] A chlorobenzene solution (40 mL) of $R_4M^+Y^-$ **1a–c** (2–4 × 10^{-2} M) and 50% aqueous NaOH (40 mL). [b] Same amounts of PhCl, $R_4M^+Y^-$, and 50% aqueous NaOH as in *a*, in the presence of 30 molar equiv of NaY, partially as solid phase. [c] Expressed as $[R_4M^+OH^-]/[R_4M^+Y^-] + [R_4M^+OH^-] \times 100$.

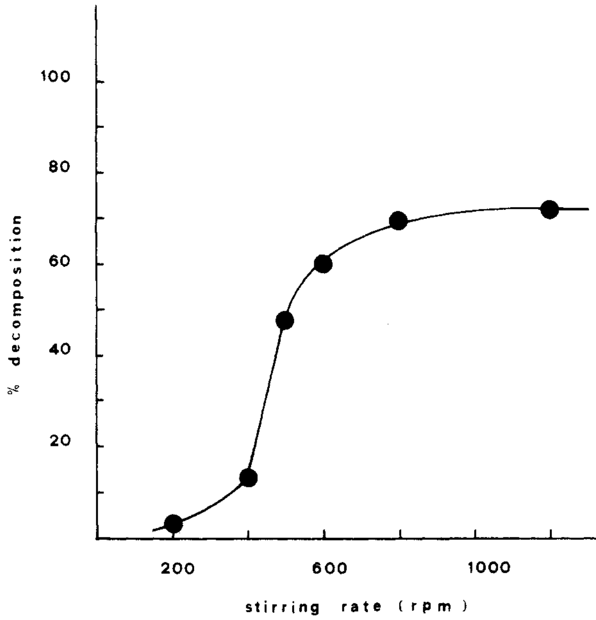

Figure 1. Effect of the stirring rate on the decomposition percent of $Bu_3P^+C_{16}H_{33}Br^-$ (**8b**) in the chlorobenzene–50% aqueous NaOH two-phase system, at 25 °C. Percent of decomposition evaluated after 4 h.

measured in a chlorobenzene–50% aqueous NaOH two-phase system. The experiments were performed at 25, 60, and 80 °C both in the absence and in the presence of a molar excess (30 molar equiv) of the corresponding inorganic salt NaY; the heterogeneous mixture was stirred at 1100 rpm. The stability of **1a–c** and **8b** was also checked in the ground NaOH–PhCl solid–liquid two-phase system at 25 and 60 °C.

The half-life times ($t_{1/2}$) for the degradation reaction of onium salts, determined by evaluating the $R_4M^+Y^-$ concentration present in the organic phase at different times, are reported in Table I.

The effect of the base concentration in the aqueous phase on the half-life periods ($t_{1/2}$) for the decomposition of quaternary salts **1a**, **1b**, and **8b** was measured in a chlorobenzene–aqueous NaOH two-phase system at 60 °C, in the concentration range 10–50% aqueous NaOH (Table II).

The amount of OH^-, extracted in the organic phase as $R_4M^+OH^-$, was measured (acid/base titration) for the series of tetrahexylammonium halides **1a–c** in the PhCl–50% aqueous NaOH two-phase system. These experiments were performed at 60 °C both in the absence and in the presence of a molar excess (30 molar equiv) of the corresponding inorganic salt NaY. The data are collected in Table III. The effect of the stirring speed on the decomposition reaction was studied for hexadecyltributylphosphonium bromide (**8b**) (Figure 1).

Reaction Products. The degradation of quaternary onium salts $RN^+R'_3Y^-$ **1–6** and $RP^+R'_3Y^-$ **7**, **8** was also performed on a preparative scale in chlorobenzene–, benzene–, or methylene chloride–50% aqueous NaOH two-phase systems. In all cases examined the mass balance was ≥90%, except for the reaction of benzyltriethylammonium chloride (**4a**), for which it was 86%. The product distribution depended on the nature both of the heteroatom M and the group R. The ammonium salts **1–3** decomposed, yielding quantitatively trialkylamines **9a–c** and alk-1-enes **11a–c**, according to the well-known Hofmann elimination (reaction 1).[2,4] The benzyltrialkyl- and

$$\underset{\mathbf{1\text{–}6}}{RN^+R'_3Y^-} + NaOH \xrightarrow[\text{50\% aqueous NaOH}]{\text{PhCl or PhH}} \underset{\mathbf{9a\text{–}d}}{R'_3N} + \underset{\mathbf{10a\text{–}c}}{R'_2NR} + \underset{\mathbf{11a\text{–}d}}{R''CH{=}CH_2} + NaY + H_2O \quad (1)$$

9a, R′ = hexyl
9b, R′ = octyl
9c, R′ = butyl
9d, R′ = ethyl
10a, R = benzyl; R′ = ethyl
10b, R = benzyl; R′ = hexyl
10c, R = methyl; R′ = octyl
11a, R″ = butyl
11b, R″ = hexyl
11c, R″ = ethyl
11d, R″ = H

trioctylmethylammonium salts **4**, **5**, and **6** afforded a more complex mixture. In particular, in the case of $PhCH_2N^+Et_3Y^-$ (TEBA) (**4**), the main reaction product was the benzyldiethylamine (**10a**) (80%), together with minor amounts of triethylamine (**9d**) (6%) and dibenzyl ether (**13a**) (~3%). The formation of ethylene in the crude was not checked. The benzyltrihexylammonium derivatives (**5**) gave benzyldihexylamine (**10b**) (77%), hex-1-ene (**11a**) (65%), trihexylamine (**9a**) (23%), and dibenzyl ether (**13a**) (9%). Methyltrioctylammonium salts (**6**) decomposed, affording the methyldioctylamine (**10c**) (18%), oct-1-ene (**11c**) (18%), and trioctylamine (**9c**) (72%). The presence of the expected dimethyl ether (**13b**) in the reaction mixture was not checked.

The trialkylamines **10a–c** and alkenes **11a,c,d** are the expected reaction products of the Hofmann degradation of the onium salts **6** (reaction 1). Alternatively the amines **9a–d** and ethers **13a,b** clearly derive from a preliminary attack of OH^- on the benzylic CH_2 and methyl group of the salts **4**, **5**, and **6**, respectively, followed by the reaction of $PhCH_2O^-$ or MeO^-, formed in situ, with the starting materials (reactions 2, 3).[4,13]

$$\underset{\mathbf{4\text{–}6}}{RN^+R'_3Y^-} + 2NaOH \xrightarrow[\text{50\% aqueous NaOH}]{\text{PhCl orCH}_2\text{Cl}_2} \underset{\mathbf{12a,b}}{RONa} + \underset{\mathbf{9c,d}}{R'_3N} + NaY + H_2O \quad (2)$$

$$\underset{\mathbf{4\text{–}6}}{RN^+R'_3Y^-} + RONa \xrightarrow[\text{50\% aqueous NaOH}]{\text{PhCl or CH}_2\text{Cl}_2} \underset{\mathbf{13a,b}}{R_2O} + \underset{\mathbf{9c,d}}{R'_3N} + NaY \quad (3)$$

12a, R = benzyl
12b, R = methyl
13a, r = benzyl
13b, r = methyl

The phosphonium salts **7** and **8**, in the PhCl–50% aqueous NaOH two-phase system decomposed via an already well-known reaction,[2,4,15,21,22] affording trialkylphosphine oxides and alkanes (reaction 4). In particular **7** gave tributylphosphine oxide (**14a**) (96%) and butane (**16**) (not isolated). Hexadecyltributylphosphonium salts (**8**)[23] afforded tributylphosphine oxide (**16**) (22%), hexadecyldibutylphosphine oxide (**14b**) (73%), hexadecane (22%), and butane (**16**) (not isolated). The ratio 3:1 between phosphine oxides **14b** and **14a**, respectively, was that expected from a statistical distribution of the two compounds.

$$\underset{\mathbf{7,8}}{RP^+R'_3Y^-} + NaOH \xrightarrow[\text{50\% aqueous NaOH}]{\text{PhCl}} \underset{\mathbf{14a,b}}{R'_2RP{=}O} + \underset{\mathbf{16}}{R'H} + \underset{\mathbf{17}}{RH} \quad (4)$$

7, R = R′ = butyl
8, R = hexadecyl; R′ = butyl
14a, R = R′ = butyl
14b, R = hexadecyl; R′ = butyl
16, R′ = butyl
17, R = hexadecyl

Effect of Nature of the Heteroatom M, Alkyl Group R, and Anion Y^-. In the chlorobenzene–50% aqueous NaOH two-phase system all the quaternary ammonium salts **1–6** examined are much more stable than the phosphonium derivatives **7** and **8**. The highest differences of decomposition half-lives ($\Delta t_{1/2}$) were found for onium chlorides ($\Delta t_{1/2}$ = 1200–220) (Table I, entries 1, 14, 15, 18, 22, 24, and 27).

Among ammonium salts, benzyltrialkyl derivatives **4** and **5** are the less stable ones. The currently used trioctylmethylammonium chloride (**6a**) (ALIQUAT) showed a stability comparable to that of the other symmetrical tetraalkylammonium derivatives **1a**, **2a**, and **3a**, which are the most stable ones (Table I, entries 1, 3, 5, 6, 12–14, 22, and 23).

The quaternary cation R_4M^+ being the same, the stability of the onium salts strongly depends on the counter anion Y^-, increasing in the order chlorides ≪ bromides < iodides (Table I). In particular, at 25 °C, $t_{1/2}$ for degradation of hexadecyltributylphosphonium derivatives **8a,b** are 2 min and 2 h for chloride **8a** and bromide[23] **8b**, respectively. An 8% decomposition was found after 3 days for iodide **8c** (Table I, entries 27, 28, and 31). The same behavior was observed for tetrabutylphosphonium chloride and bromide (**7a**, **7b**) (Table I, entries 24 and 25).

In the case of tetrahexylammonium salts **1**, $t_{1/2}$ at 25 °C for chloride **1a** was 35 h, the degradation of bromide **1b** was 8% after 6 days, while iodide **1c** was recovered unchanged after the same reaction time (Table I, entries 1, 5, and 9). Onium salts **2**, **4**, and **5** behaved similarly (Table I, entries 12, 13, 15, 16, and 18–21).

Effect of NaOH Concentration, Added Inorganic Salt (NaY), and Temperature. The stability of all the onium salts **1–8** dramatically increases by decreasing the NaOH concentration in the aqueous phase. As showwn in Table II, on changing the base concentration from 50% to 15%, $t_{1/2}$ of decomposition for tetrahexylammonium chloride (**1a**) and bromide (**1b**) and for hexadecyltributylphosphonium bromide (**8b**) is enhanced of 73, 24, and 80 times, respectively.

The addition to the PhCl–50% aqueous NaOH two-phase system of a molar excess of the corresponding inorganic salt NaY also contributes to enhance the stability of quaternary salts (Table I). Tetrahexylammonium chloride (**1a**), which at 25 °C decomposed by 50% after 35 h, in the presence of 30 molar equiv of NaCl was recovered almost unchanged after 6 days (entry 1). At 60 °C, $t_{1/2}$ of **1a** was 8 h and 15 min in the presence and in the absence of the inorganic salt, respectively (entry 3). No decomposition was observed when tetrahexyl- and tetraoctylammonium bromide (**1b** and **2b**) were reacted

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(23) It has been reported[13] that hexadecyltributylphosphonium bromide (**8b**) was recovered unchanged after 16 h at 100 °C under PTC conditions in the presence of concentrated NaOH.

at 60 °C in the presence of NaBr for 6 days (entries 6 and 13).

The half-life time ($t_{1/2}$) of decomposition of TEBAC (**4a**) increased by ~20 times by adding a molar excess of NaCl (entry 15).

The addition of NaY produced similar enhancement of $t_{1/2}$ in the case of phosphonium salts **7a**,**b** and **8a**,**b** (110–10 times) (Table I, entries 24–28).

As shown in Table I, the stability of all the salts increased by diminishing the reaction temperature according to an expected kinetic effect.

Stability under Solid–Liquid PTC Conditions. Quaternary onium salts were found to decompose also in the ground NaOH–PhCl solid–liquid two-phase system (Table I, entries 2, 4, 7, and 10). Under the latter conditions, $t_{1/2}$ slightly increase with respect to liquid–liquid ones (2–7 times), while the effect of the added salt NaY is less pronounced. No degradation was observed when **1a** was reacted for 3 days at 60 °C in the presence of solid K_2CO_3 instead of NaOH.

Discussion

Under liquid–liquid PTC conditions the degradation of quaternary onium salts promoted by hydroxide ion (reactions 1–4) could, in principle, occur in the organic phase via extraction of OH^- in the latter phase as $R_4M^+OH^-$ (eq 5 and 6) or at the phase boundary (eq 7).[24]

$$(R_4M^+Y^-)_{org} + (OH^-)_{aq} \rightleftharpoons (R_4M^+OH^-)_{org} + (Y^-)_{aq} \quad \text{(both phases)} \quad (5)$$

$$(R_4M^+OH^-)_{org} \rightarrow \text{reaction products} \quad \text{(organic phase)} \quad (6)$$

$$(R_4M^+Y^-)_{org} + (OH^-)_{aq} \rightarrow \text{reaction products} \quad \text{(phase boundary)} \quad (7)$$

All the experimental facts are consistent with the extraction mechanism depicted by eq 5 and 6. In particular the independence[4,25] of reaction time on the stirring speed above ~900 rpm (Figure 1) shows the unimportance of interfacial phenomena (eq 7). Moreover, the presence of a certain amount of OH^- as $R_4M^+OH^-$, found in the organic phase (Table III), is direct evidence that the decomposition reaction takes place in this phase.

The amount of OH^- extracted depends on the nature of the anion Y^-. As reported in Table III for tetrahexylammonium halides **1a–c**, it increases in the order $R_4M^+I^- < R_4M^+Br^- < R_4M^+Cl^-$. This sequence reflects the well-known selectivity coefficients $K_{Y/X}^{sel}$ for the extraction of anions in low polarity solvents by lipophilic quaternary onium cations: $OH \ll Cl^- < Br^- < I^-$.[2-4,26]

Extractability data of OH^- in the organic phase by quaternary salts **1a–c** (Table III) account for the dramatic differences in half-life times of degradation found in the order $R_4M^+Cl^- \ll R_4M^+Br^- < R_4M^+I^-$ (Table I).

The increased stability of all the $R_4M^+Y^-$ salts by the addition of an excess of the corresponding inorganic salt is explained along the same lines. As expected, under these conditions, the amount of $(R_4M^+OH^-)_{org}$ noticeably decrases until becoming almost negligible (Table III).

It should be pointed out that, in very important base-promoted reactions such as C-, O-, and N-alkylation, α and β eliminations,[2-4] etc., leaving groups like Cl^-, Br^-, and I^- etc... (generated in situ during the process) themselves prevent the degradation of the catalyst.

The effect of the base concentration in the aqueous phase on the stability of onium salts $R_4M^+Y^-$ can be explained by the different hydration state and, hence, reactivity, of the hydroxide ion present in the organic phase as $R_4M^+OH^-$ (Table II). As previously reported,[5] in the chlorobenzene–aqueous NaOH two-phase system, an increase in NaOH concentration (from 15% to 50%) reduced the OH^- hydration sphere of the tetrahexylammonium hydroxide (**1e**), dissolved in chlorobenzene, from 11 to 3.5 molecules of water. This produced a dramatic rate enhancement of the Hofmann degradation of **1e** (up to 10^4 times).

The data as a whole indicate that a number of quaternary onium salts can be currently used as phase-transfer agents under PTC conditions even in the presence of alkaline aqueous solutions. When concentrated base solutions (50% NaOH–60% KOH) are used, the catalysts of choice are quaternary ammonium salts. Among these, quaternary iodides[27] are stable up to 60 °C while bromides, at the same temperature, do not decompose for days, providing that they are in the presence of the corresponding inorganic salt. Under the latter conditions the degradation rate of quaternary chlorides is negligible only at room temperature.

Phosphonium salts can also be used as PTC agents in base-promoted reactions, but under much milder conditions [i.e., low temperatures ($\leq$25 °C), moderate aqueous base concentrations ($\leq$15%)] and, eventually, in the presence of the inorganic salt.

In all cases reaction conditions should be realized which prevent the extractability of OH^- in the organic phase or minimize its reactivity.

Experimental Section

General Methods. Potentiometric titrations were carried out with a Metrohm Titroprocessor E636 by using silver or glass and calomel electrodes, the latter isolated with a potassium sulfate bridge. Proton NMR spectra (in δ) were recorded on a Varian EM-390 90-MHz spectrometer with tetramethylsilane as internal standard. GC data were obtained on a Varian 3700 gas chromatograph, equipped with a 50 × $^1/_8$ in. OV-101 5% on Chromosorb GHP 100–120-mesh column and were evaluated with a Varian Model 401 data system by the internal standard method.

Materials and Solvents. All inorganic salts were Analar grade commercial products, used without further purification. Quaternary onium salts **1a–c**, **2b**, **3a**, **4a**,**b**, **6a**, **7a**,**b**, and **8b**,**c** were commercially available, used without further purification. The tetraoctylammonium chloride (**2a**) and hexadecyltributylphosphonium chloride (**8a**) were obtained from the corresponding methanesulfonates, $R_4M^+MeSO_3^-$ **2d** and **8d**, by exchange with Cl^- anion.[7,30] The benzyltrihexylammonium salts **5a**,**b** were prepared according to the literature,[31] by refluxing trihexylamine with the appropriate benzyl halide in acetone. They had the following melting points: **5a**, mp 105–107 °C; **5b**, mp 101–103 °C (from ethyl acetate) (lit.[31] mp not given). Chlorobenzene, benzene, and methylene chloride were Analar grade chemical solvents, used after fractional distillation.

Stability Measurements. In a typical procedure, the reaction flask was thermostated at the appropriate temperature and charged with 40 mL of a standardized chlorobenzene solution of

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[24] The possibility that the reaction occurs in the aqueous phase is ruled out since in the PhCl (CH_2Cl_2)–aqueous NaOH two-phase system all quaternary salts examined are entirely partitioned into the organic phase.

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[27] It should be emphasized that quaternary onium iodides are scarcely used as phase-transfer agents due to the well-known "catalyst poisoning" by I^- under PTC conditions.[2-4,26,28,29]

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quaternary salt $R_4M^+Y^-$ (2–4 × 10^{-2} M) and 40 mL of 50% NaOH solution already thermostated. Stirring and timing were started. Samples (2–3 mL) of organic phase were withdrawn at various times by stopping the stirrer for 40–60 s to allow adequate separation. These were quenched in ice-cold MeOH (50 mL), and the quaternary halide was determined by using 0.01 N silver nitrate (potentiometric titration).

Extractability of Hydroxide Ion in the Organic Phase. The extractability of OH^- in the organic phase as quaternary hydroxide $R_4M^+OH^-$ 1e was determined by stirring for 2–5 min 40 mL of a standardized chlorobenzene solution of $R_4M^+Y^-$ (2–4 × 10^{-2} M) with 40 mL of 50% NaOH solution both in the absence and presence of 30 mmol of the appropriate inorganic salt NaY (Y = Cl, Br, I) in a flask thermostated at 60 °C. Stirring was stopped and aliquots (5–8 mL) of the organic phase were withdrawn and added to an aqueous NaBr solution (0.5 g of inorganic salt in 50 mL of water). The heterogeneous mixture was stirred for 5 min in order to obtain a complete OH^- extraction in the aqueous phase and than titrated with 0.01 N HCl (potentiometric titration). In this way the amine eventually derived from the partial decomposition of $R_4M^+Y^-$ remains in the organic phase and the hydroxide ion can be selectively titrated.

Reaction Products. The reaction products were checked in the case of quaternary onium salts **1**–**6a** and **7**,**8b**. In a typical procedure the flask used for degradation runs, thermostated at 40 or 60 °C, was charged with 50 mL of a 50% aqueous NaOH solution and with 30 mL of a chlorobenzene, benzene, or methylene chloride solution of the appropriate quaternary onium salt (0.4 M) and decane (0.2 M) (as GLC internal standard). The heterogeneous mixture was stirred for 10–60 h. The progress of the reaction was monitored by potentiometric titration of the halide ion. The organic layer was separated, washed with water, dried over Na_2SO_4, and analyzed by GLC (50 cm × $^1/_8$ in. in OV-101-5% Chromosorb GHP 100–120-mesh column, in a program temperature from 40 to 250 °C). At 100% conversion the mass balance was $\geqslant$90%, except for the reaction of **4a**, for which it was 86%. The solvent was evaporated and reaction products were isolated by fractional distillation, column chromatography, and/or crystallization. They were analyzed by NMR and GLC, and their physical properties were identical with those of authentic samples prepared according to the literature. The distribution of reaction products is reported in the Results section. The reaction time, temperature, and products for the degradation of various onium salts are the following:

Tetrahexylammonium chloride (1a): chlorobenzene; 60 °C; 10 h; trihexylamine (**9a**); bp 158–160 °C (12 mm) [lit.[32] bp 165–170 °C (16 mm)]; NMR δ 0.92 (t, 9 H), 1.10–1.60 (m, 24 H), 2.4 (t, 6 H); hex-1-ene (**11a**), identified via oxidation to the corresponding pentanoic acid (**18**), as described below.

Tetraoctylammonium chloride (2a): benzene; 60 °C; 10 h; trioctylamine (**9b**); bp 166–168 °C (0.7 mm) [lit.[32] bp 225–230 °C (16 mm)]; NMR δ 0.93 (t, 9 H), 1.08–1.63 (m, 36 H), 2.41 (t, 6 H); oct-1-ene (**11b**), identified as eptanoic acid (**19**) (see below).

Tetrabutylammonium chloride (3b): chlorobenzene; 60 °C; 10 h; tributylamine (**9c**); bp 210–212 °C (760 mm) [lit.[33] 212 °C (761 mm)]; NMR δ 0.98 (t, 9 H), 1.10–1.60 (m, 12 H), 2.43 (t, 6 H); but-1-ene (**11c**) was not isolated from the reaction mixture.

Benzyltriethylammonium chloride (4a): methylene chloride; 40 °C; 60 h; (in this case a methylene chloride solution of **4a** (0.05 M) was used) benzyldiethylamine (**10a**); bp 208–210 °C (760 mm) [lit.[33] bp 209–210 °C (757 mm)]; NMR δ 1.70 (t, 6 H), 2.56 (q, 4 H), 3.57 (s, 2 H), 7.14–7.40 (m, 5 H); ethylene (**11d**) was not checked in the reaction mixture; dibenzyl ether (**13a**) bp 158–160 °C (10 mm) [lit.[34] bp 198–200 °C (55 mm)]; NMR δ 4.52 (s, 4 H) 7.18–7.37 (m, 10 H).

Benzyltrihexylammonium chloride (5a): chlorobenzene; 60 °C; benzyldihexylamine (**10b**); bp 183–185 °C (14 mm) [lit.[32] bp 185–195 °C (30 mm)]; NMR δ 0.92 (t, 6 H), 1.08–1.65 (m, 16 H), 3.53 (s, 2 H), 7.08–7.24 (m, 5 H); trihexylamine (**9a**);[32] dibenzyl ether (**13a**);[34] hex-1-ene (**11a**).

Trioctylmethylammonium chloride (6a): benzene; 60 °C; 60 h; methyldioctylamine (**10c**); bp 156–158 °C (10 mm) [lit.[32] bp 158 °C (10 mm)]; NMR δ 0.91 (t, 6 H) 1.08–1.57 (m, 24 H) 2.18–2.44 (m, 7 H); trioctylamine (**9b**);[32] oct-1-ene (**11b**).

Tetrabutylphosphonium bromide (7b): chlorobenzene; 60 °C; 24 h; tributylphosphine oxide (**14a**) mp 61–63 °C (from CCl_4) [lit.[35] mp 62–63 °C (from CCl_4)]; NMR δ 0.93 (t, 9 H), 1.22–1.83 (m, 18 H); butane (**16**) was not isolated from reaction mixture.

Hexadecyltributylphosphonium bromide (8b): chlorobenzene; 60 °C; 24 h; tributylphosphine oxide (**14a**);[36] hexadecyldibutylphosphine oxide (**14b**) mp 62–63 °C (from hexane); NMR δ 0.92 (t, 9 H), 1.10–1.80 (m, 42 H) [Anal. Calcd for $C_{24}H_{51}PO$: C, 74.55; H, 13.30. Found: C, 74.58; H, 13.37]; hexadecane (**17**) bp 284–286 °C (760 mm) lit.[36] bp 286.5 °C (760 mm); NMR 0.80 (t, 6 H), 1.05–1.45 (m, 28 H); butane (**16**) was not isolated from reaction mixture. Compounds **14a**,**b** and **17** were separated from crude by column chromatography on silica gel using light petroleum, methylene chloride, and a mixture of methylene chloride and methanol as eluants.

Oxidation of Alkenes 11a and 11b to Pentanoic and Heptanoic Acids (18 and 19), Respectively. The alkenes **11a** and **11b** were separated from the other components of the reaction mixture by distillation together with the reaction solvent (benzene or chlorobenzene) as head fraction. From the latter, **11a** and **11b**, oxidized by $KMnO_4$ under PTC conditions according to a previously reported procedure,[37] gave the corresponding pentanoic acid (**18**) [bp 184–186 °C (760 mm) [lit.[38] bp 184 °C (768 mm)]; NMR δ 0.92 (t, 3 H) 1.17–1.86 (m, 4 H), 2.4 (t, 2 H), 11.86 (s, 1 H)] and heptanoic acid (**19**) [bp 221–223 °C (760 mm) [lit.[38] bp 222 °C (764 mm)]; NMR δ 0.95 (t, 3 H), 1.12–1.82 (m, 6 H), 2.39 (t, 2 H), 11.45 (s, 1 H)], respectively.

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Registry No. **1a**, 5922-92-9; **1b**, 4328-13-6; **1c**, 2138-24-1; **2a**, 3125-07-3; **2b**, 14866-33-2; **3a**, 1112-67-0; **4a**, 56-37-1; **4b**, 5197-95-5; **5a**, 62017-60-1; **5b**, 31280-89-4; **6a**, 5137-55-3; **7a**, 2304-30-5; **7b**, 3115-68-2; **8a**, 41272-12-2; **8b**, 14937-45-2; **8c**, 56772-64-6; NaOH, 1310-73-2.

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