Applications of Phase-Transfer Catalytic Reactions to Fatty Acids and Their Derivatives: Present State and Future Potential

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ABSTRACT: Phase-transfer catalysts (PTC), which accelerate reactions between liquid(organic)–liquid(water) and liquid–solid heterogeneous states, have been investigated and developed. Several processes with PTC have succeeded in industrial processes involving fatty acids and their derivatives. For example, preparation of fatty alkyl glycidyl ethers, from which fatty alkyl glyceryl ethers and their derivatives can be obtained, has been carried out with PTC. However, some problems remain to be solved. For example, preparation of the fatty alkyl glycidyl ether by a PTC reaction was considered, but typical problems to be solved included: (i) how to reuse or recover the catalysts; (ii) how to control the heterogeneous reaction without obstacles to produce useful chemical materials; (iii) how to satisfy the environmental requirements for the catalysts; and (iv) are there more effective catalysts? We address these problems based on our own experiences with phase-transfer catalytic Williamson ether syntheses of fatty alkyl glycidyl ethers. Moreover, we describe recent developments in phase-transfer catalytic reactions related to oleochemistry, such as transition metal-catalyzed reactions of long-chain olefins in liquid(organic)–liquid(water) or liquid–solid heterogeneous states. Based on these results, we have considered the potential of PTC as a synthetic tool in oleochemistry.
JAOCS 73, 831–839 (1996).

KEY WORDS: Fatty acid derivatives, fatty alkyl glycidyl ether, phase-transfer catalyst, quarts, quaternary ammonium salts, two-phase reaction, Williamson ether synthesis.

Catalytic reactions based on acidic, alkaline, and metallic catalysts or combinations of these have greatly contributed to produce many kinds of industrial useful chemicals. Catalysts can reduce high reaction temperatures or high pressures to moderate conditions and to accelerate reaction rates. The most important catalytic reactions in the chemical industry, polymerization of ethylene and stereospecific polymerization of propylene as discovered by Ziegler-Natta, are utilized worldwide on a large scale.

Heterogeneous catalysis from the early days through the end of World War II was surveyed in detail by Thomas (1). On the other hand, enzymes catalyze many processes that are essential to life in all living organisms at moderate temperatures, pressures, and pH conditions (2,3). Many chemists have contributed to the research and development of nature-like catalytic reactions, so-called "bio-mimetic reactions." Recently, bolaamphiphiles, which are simply defined as molecules in which two or more hydrophilic groups are connected by hydrophobic functionalities, have gained increasing attention because they may offer insight into micellar systems that can mimic enzymes (4).

One of the typical catalytic reactions that requires only moderate reaction conditions is the so-called phase-transfer catalytic reaction (5). These are reactions in which the reactants are present in different phases and brought into contact with a phase-transfer catalyst (PTC). PTC is now widely employed in organic preparations, both in the laboratory and on an industrial scale (6). The overall process emerging in textbooks is described in Scheme 1.

However, despite the usefulness of PTC, several problems still remain to be solved. Little has been reported on these subjects from an industrial standpoint, especially in relation to fatty acids and their derivatives. In the chemical industry,
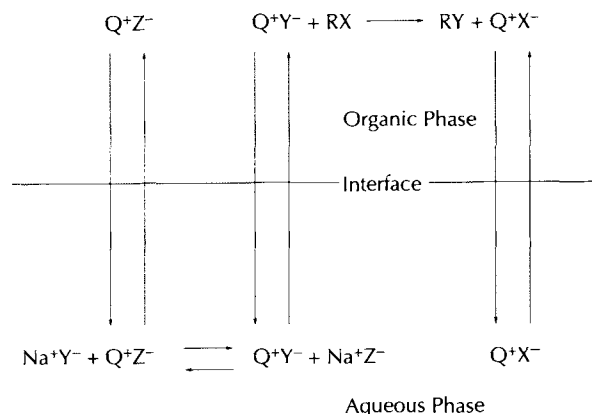
SCHEME 1

other factors, such as environmental safety requirements, should be considered, and problems have to be overcome.
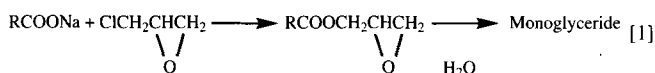
We will review industrial applications of PTC and discuss several problems to be solved. We also will look at future development of PTC as related to the oleochemical industry.

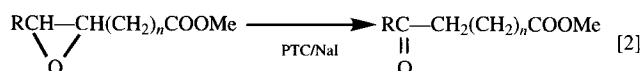## INDUSTRIAL APPLICATIONS OF PTC RELATED TO FATTY ACIDS AND THEIR DERIVATIVES

Several examples in oleochemical industrial applications of PTC have been reported in the literature, of which some will be reviewed in some detail.

During the past decade, Kao Corp. (Tokyo, Japan) has been producing fatty alkyl glycidyl ethers by the O-alkylation of fatty (C_{10}–C_{20}) alcohols with epichlorohydrin in an alkaline liquid–liquid(organic) two-phase reaction with a PTC. The thus-obtained fatty alkyl glycidyl ethers were transformed to fatty alkyl glyceryl ethers, $ROCH_2$ CH (OH) CH_2 OH, or to ceramide-like compounds, $ROCH_2$ CH (OH) CH_2 N (COR′) CH_2 CH_2 OH, as pharmaceutical, cosmetic, and emulsion-forming materials (Scheme 2) (7–9).

In fatty chemical production, reports also have included synthesis of: (i) monoglycerides of fatty acids from glycidyl esters, derived from the reaction of epichlorohydrin with fatty acids, by means of PTC (10,11):

$$RCOONa + ClCH_2CHCH_2 \longrightarrow RCOOCH_2CHCH_2 \xrightarrow{\ \ } Monoglyceride \quad [1]$$
$$\underset{O}{\diagdown/} \qquad \underset{O \quad H_2O}{\diagdown/}$$

Monoglycerides prepared by this method are not food-grade, but commercial monoglycerides for nonfood uses can be prepared by this improved method; (ii) the rearrangement reaction of an epoxidized fatty acid derivative to a keto fatty acid derivative with a PTC (12):

$$RCH—CH(CH_2)_nCOOMe \xrightarrow{PTC/NaI} RC—CH_2(CH_2)_nCOOMe \quad [2]$$
$$\underset{O}{\diagdown/} \qquad\qquad \underset{O}{\overset{\|}{}}$$

Keto fatty acid derivatives are reported to be useful as additives in polyvinyl chloride processing; (iii) long-chain 1,2-diols, recommended for use in cosmetics, are obtained by the hydrolysis reaction of 1,2-epoxides in the presence of PTC at relatively low temperatures and pressures (13):

$$R—CH—CH_2 + H_2O \xrightarrow{PTC} R—CH—CH_2 \quad [3]$$
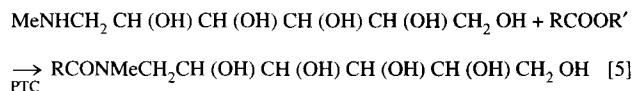$$\underset{O}{\diagdown/} \qquad\qquad \underset{OH \quad OH}{|\quad|}$$
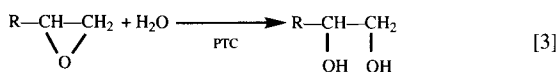
(iv) quaternary ammonium compounds that contain a long-chain alkyl can be derived from the addition reaction of quaternary ammonium salts with long-chain alkyl epoxides with a PTC in aqueous dispersion. The thus-obtained quaternary ammonium compounds are interesting for use in cosmetics, disinfectants, and in textile treatments as so-called softeners (14):

$$R—CH—CH_2 + R_3'NH^+X^- \xrightarrow{PTC} R—CH—CH_2N^+R_3' X^- \quad [4]$$
$$\underset{O}{\diagdown/} \qquad\qquad\qquad \underset{OH}{|}$$
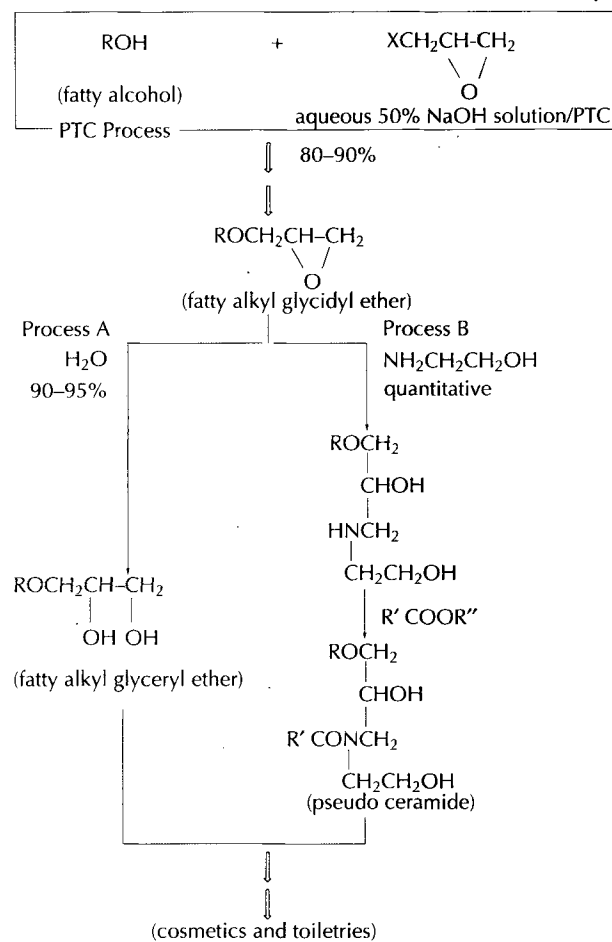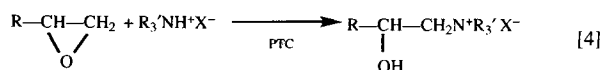
SCHEME 2

(v) manufacture of glucamide surfactants, useful as detergents for textiles or dishwashing, from N-alkyl-glucamines and fatty esters in the presence of a PTC (15):

$$MeNHCH_2 \ CH \ (OH) \ CH \ (OH) \ CH \ (OH) \ CH \ (OH) \ CH_2 \ OH + RCOOR'$$

$$\xrightarrow{PTC} RCONMeCH_2CH \ (OH) \ CH \ (OH) \ CH \ (OH) \ CH \ (OH) \ CH_2 \ OH \quad [5]$$

(vi) preparation of sulfur-containing fatty acids and their esters from halogeno-aliphatic carboxylate and aqueous sulfide solution with a PTC, which are useful as hair tonic agents, polymerization-controlling agents, antioxidants, metal surface-treating agents, and rubber additives (16):

$$X\text{-}CR^2 \ R^3 \ COOR^1 + Na_2 \ S \xrightarrow{PTC} S\text{-}[CR^2R^3COOR^1]_2 \quad [6]$$
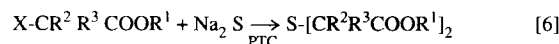
(vii) low-temperature saponification of fats, especially wool grease, by treating with alkali in an aqueous or water-solvent medium in the presence of a PTC (17):

$$RCOOR' + NaOH \xrightarrow{PTC} RCOONa + R' \ OH \quad [7]$$

RESULTS OF INDUSTRIAL APPLICATIONS OF PTC

In the following sections, several problems to be solved in industrial applications of PTC will be clarified and discussed.

But first, we will summarize the experiences we had in the preparation of fatty alkyl glycidyl ethers on an industrial scale.

Preparation of fatty alkyl glycidyl ether with a PTC. Fatty alkyl glycidyl ether can be prepared industrially at a high yield with our method by *O*-alkylation (Williamson ether synthesis) with a PTC as shown in Schemes 3 and 4 (18).

As PTC, tetraalkylammonium salts, such as tetrabutylammonium bromide, are available industrially. Scheme 3 shows that the PTC reaction requires an excess of 2–3 moles of reactants, such as epichlorohydrin and NaOH, based on 1 mol of fatty alcohol is used.

When the Williamson ether synthesis is carried out under PTC conditions, 50% aqueous NaOH solution is sufficient to deprotonate the alcohol ROH (19). The reaction usually involves a fivefold excess of NaOH over ROH. The concentration of the PTC is 3–5 mol% with respect to ROH. We also investigated the effect of the concentration of NaOH on the yield of the reaction product and have found that no less than a threefold excess of NaOH was needed to gain a yield of 80–90%, as shown in Scheme 3. However, the reaction can proceed under a mild temperature of 40–50°C, and the product separates from the upper organic layer upon standing without any difficulties.

The alkaline material. The rate-determining step of *O*-alkylation may be the formation of tetraalkylammonium alcoholates according to the interfacial mechanism reported (20). Thus, the selection of an alkaline source is the most important factor. In addition to this, industrial application of PTC requires the largest possible reduction in manufacturing cost. The most easily available sources of alkali are NaOH, KOH, K_2CO_3, $Ca(OH)_2$, and $CaCO_3$. In Table 1, the costs of these alkaline materials are listed for comparison.

In recent years, solid K_2CO_3 has become a popular alkaline reagent in PTC, both in solid/liquid and solid/liquid/gas systems (22). However, based on comparison of the cost of alkaline materials, we prefer NaOH to other alkalines. By the way, although $Ca(OH)_2$ is cheaper than NaOH, little has been reported on the application of calcium lime as alkali source in PTC reactions. Also, we have tried to utilize solid $Ca(OH)_2$ in the preparation of fatty alkyl glycidyl ether with a PTC. Unfortunately, calcium lime could not promote the ether formation as shown in Scheme 3. While solid NaOH was reported to accelerate alkyl glycidyl ether formation with a PTC (23,24), the use of solid NaOH requires a separation process to remove NaCl salts precipitated in the reaction mass and un-

ROH = Fatty Alcohol; R'X = CH₂CHCH₂Cl; Q⁺X⁻ = Bu₄N⁺Br(Cl)⁻

ROR' = Fatty Alkyl Glycidyl Ether; X = Br or Cl
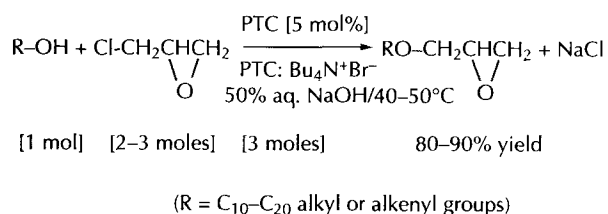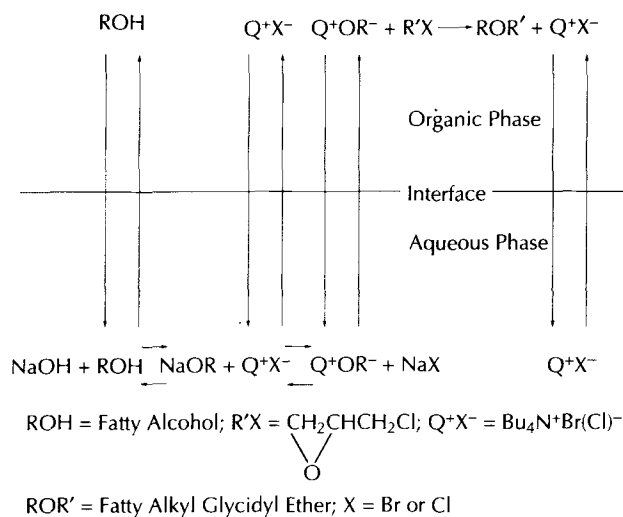
SCHEME 4

reacted NaOH. Moreover, no advantages could be observed with solid NaOH in the productive process of the fatty alkyl glycidyl ethers.

For reactions initiated by solid bases (e.g., KOH, NaOH), Bentley *et al.* (25) reported that solvents (e.g., H_2O, ROH, polyethylene glycol, MeCN, Me_2SO) may act as solid–liquid PTC (e.g., for C–H, N–H, or O–H alkylation). Also, they have found that a weaker base, such as K_2CO_3 or $Ca(OH)_2$, does not cause deprotonation in solid–liquid phase-transfer catalytic reactions to initiate the intended reaction.

Investigation of effective catalysts. As PTC, several kinds of surfactants and salts were investigated. That is, anionic surfactants, cationic surfactants, betaine compounds, quaternary ammonium salts, or nonionic surfactants were applied to the fatty alkyl glycidyl ether formation. A comparison of the catalytic activities of these catalysts is shown for oleyl glycidyl ether formation (Table 2).

The data in Table 2, as expected, show that catalytic activities decreased in the order of cationic surfactants ≈ quaternary ammonium salts > betaines > nonionic surfactants ≈ anionic surfactants. Among cationic surfactants, some unique surfactant containing polyoxyethylene chains, $C_{18}H_{37}N^+Me[(CH_2CH_2O)_4H]_2$ Cl⁻ or $C_{18}H_{37}N^+Me_2$-$[(CH_2CH_2O)_4H]Cl^-$, also catalyzed Williamson ether formation; likewise, tetraalkyl-substituted ammonium salts (also

PTC [5 mol%]

R–OH + Cl-CH₂CHCH₂ $\xrightarrow[\text{50% aq. NaOH/40–50°C}]{\text{PTC: Bu₄N⁺Br⁻}}$ RO–CH₂CHCH₂ + NaCl

[1 mol] [2–3 moles] [3 moles] 80–90% yield

(R = C₁₀–C₂₀ alkyl or alkenyl groups)

SCHEME 3

TABLE 1
Cost Difference of Alkaline Materials (Ref. 21)[a]

Alkaline	MW	Mol/kg	Cost $/kg	Cost $/Mol
NaOH	40	25	1.0	0.04
KOH	56	18	2.0–2.5	0.11–0.14
K_2CO_3	138	7	2.0–2.5	0.29–0.36
$Ca(OH)_2$	74	13	0.25	0.02
$CaCO_3$	100	10	0.5	0.05

[a]MW, molecular weight.

TABLE 2
Preparation of Oleyl Glycidyl Ether with Phase-Transfer Catalyst (PTC)

PTC[a]	Yield (%)
$Bu_4N^+Br^-$	82
$Bu_4N^+HSO_4^-$	84
$C_{10}H_{21}N^+Me_3Cl^-$	75
$C_{18}H_{37}N^+Me_3Cl^-$	72
$C_{18}H_{37}N^+Me[(CH_2CH_2O)_4H]_2Cl^-$	80
$C_{12}H_{25}N^+Me_2CH_2CO_2^-$	75
$C_{18}H_{37}N^+Me_2CH_2CO_2^-$	60
$C_{16}H_{33}OSO_3^-Na^+$	35
$C_{12}H_{25}O(CH_2CH_2O)_6H$	42
None	15

[a]Reaction conditions were as follows: alcohol 1.0 mol, 50% aqueous NaOH solution (3.0 moles as NaOH), epichlorohydrin (2.0 moles), PTC (0.05 moles), and n-hexane (500 mL) were reacted at a temperature of 40–50°C for 6 h.

called "quats") or cationic surfactants containing long alkyl radical(s) (also called "long alkyl quats") (26). The presence of polyoxyethylene units in long alkyl quats as the most effective PTC and the combination of quats and polyethyleneglycol (co-catalytic effect) have been reported (27,28).

However, in our studies on the catalytic behavior of cationic surfactants, containing polyoxyethylene chains, for preparation of fatty alkyl glycidyl ethers on a large scale, both drawbacks and advantages were observed. Typical advantages included both an acceleration of the reaction and a facility for oil/water phase separation at the stage of termination of the reactions. Both acceleration of the reaction and acquisition of the operation time needed for phase separation after completion of the reaction are shown in Table 3, compared with cationic surfactants containing a long-chain alkyl group (26).

On the other hand, a drawback was the unexpected and sudden increase of the viscosity of the reaction mixture at the initial stage of the reaction.

Typical examples are as follows. In the course of the addition of epichlorohydrin (2–3 moles) to the reaction mixture comprising fatty alcohol (1 mol), aqueous NaOH (3 moles), and cationic surfactants (0.05 moles) containing polyoxyeth-

TABLE 3
Comparison of Functionalities for Cationic Surfactants[a]

Starting alcohol	Cationic surfactant[b]	Yield (%)	Reaction time (h)[c]	Time for phase separation[d]
Oleyl alcohol	A	80	2	10 min
Oleyl alcohol	B	72	6	12 h
Isostearyl alcohol	A	78	1.5	10 min
Isostearyl alcohol	B	70	4	12 h

[a]That contain polyoxyethylene chains to those that contain tetraalkyl (including long-chain alkyl) in the preparation of glycidyl ether (Ref. 26). Isostearyl alcohol: 2-methylheptadecanol, $C_{18}H_{37}OH$ (Ref. 30), and reaction conditions were generally the same as shown in Table 2.
[b]A: $C_{18}H_{37}N^+Me[(CH_2CH_2O)_4H]_2Cl$; B: $C_{18}H_{37}N^+Me_3Cl^-$.
[c]Reaction time: overall reaction time required until the alcohol disappeared completely.
[d]Time for phase separation: time required until the organic/water two-phase separated completely.

ylene chains as mentioned above, the viscosity of the reaction mixture changed gradually from ca. 10 cps (at the initial point of the reaction) to 6000 cps and caused great difficulty in stirring the reaction mixture homogeneously. After completion of the addition of epichlorohydrin, the viscosity of the reaction mixture dropped to about 50 cps, and stirring could be conducted more smoothly. This increase in the viscosity causes a great loss in product yield if poor agitating mechanics are supplied.

This phenomenon of viscosity increase was thought to have been induced by phase inversion. Phase inversion, as the name implies, is the process whereby the internal and external phase of an emulsion are suddenly inverted, e.g., oil/water to water/oil or vice versa. The viscosity of an emulsion, at a given emulsion concentration, gradually increases as the phase volume increases, but at a certain point, there is a sudden decrease in the viscosity (29).

An effective treatment to avoid this sudden increase in the viscosity was to increase the concentration of PTC, such as to 0.08–0.1 moles per 1.0 mol of alcohol used (8–10 mol%). At a concentration of 8–10 mol% of cationic surfactant, containing a polyoxyethylene chain, there was no more viscosity increase during the reaction and the reaction proceeded more smoothly.

However, removal of the PTC from the products, either by distillation or extraction, was unsuccessful. Because of the high lipophilicity of the PTC, it remained almost always in the organic phase and could not be extracted into the water phase. Moreover, the relatively high molecular weight of the PTC made its distillation more difficult.

A similar phenomenon to that of viscosity increase of the reaction mixture also was observed with long-alkyl quaternary ammonium salts, such as stearyltrimethylammonium chloride. On the other hand, quats, such as tetrabutylammonium bromide or tetrabutylammonium hydrogensulfate, did not induce an increase in the viscosity while the reaction proceeded.

The optimum PTC were the quats, such as tetrabutylammonium bromide or tetrabutylammonium hydrogensulfate, as shown in Scheme 3. Long-chain alkyl cationic surfactants were not suitable. Because the latter are more lipophilic than the former, they may remain almost in the organic phase and make reuse of the PTC difficult.

The range of applicable reactants. Reactants such as fatty alcohols, used in preparation of the fatty alkyl glycidyl ethers by means of PTC, were freely selected from linear alcohols or highly branched alcohols, such as $C_6H_{13}OH-C_{20}H_{41}OH$. Among some highly branched alcohols, such as Guerbet alcohols (2-alkyl substituted alcohols), which are now commercially available [for example, 2-heptylundecanol or 5,7,7-trimethyl-2-(1,3,3-trimethylbutyl)octanol], can undergo O-alkylation to give the corresponding fatty alkyl glycidyl ethers at high yields (Table 4). Moreover, a cholesteryl glycidyl ether also can be obtained by the reaction of cholesterol with epichlorohydrin in the presence of PTC in the same manner (31).

Alcohol	Yield of alkyl glycidyl ether (%)
5,7,7-Trimethyl-2-(1,3,3-trimethylbutyl)octyl alcohol: $C_{18}H_{37}OH$	78
2-Heptylundecyl alcohol: $C_{18}H_{37}OH$	75
2-Methylheptadecyl alcohol: $C_{18}H_{37}OH$[b]	72
2-Ethylhexyl alcohol: $C_8H_{17}OH$	82

[a]Reaction conditions were generally the same as shown in Table 2 except for the PTC: $Bu_4N^+Br^-$ (0.05 moles). See Table 2 for abbreviation.
[b]Reference 30.

PROBLEMS TO BE SOLVED

Based on our studies on the application of PTC to the preparation of fatty alkyl glycidyl ethers, further problems to be solved include: (i) how to reuse PTC; (ii) how to meet the environmental safety requirements; and (iii) are there more effective catalysts? Several solutions thus far reported in regard to these problems are briefly reviewed in the following section.

How to reuse the catalysts. The first trial toward solving the problem of how to reuse PTC was the application of an insoluble polymer-supported (32) or polymer-immobilized PTC (33–37). For example, quaternary ammonium and phosphonium salts of acryloyl monomer can be grafted onto an ultra-thin nylon capsule membrane, which acts as PTC-accelerating reaction between substrates in the inner organic phase and water-soluble anions in the outer phase (38). Other immobilized PTC were tetraalkylammonium and tetraalkylphosphonium salts immobilized on a 2% cross-linked polystyrene matrix. Their catalytic activity has been compared with that of the best soluble PTC (39). The modification of silica, alumina with ammonium, or phosphonium active groups also produced heterogeneous PTC, which are already used on an industrial scale for heterogeneous catalysis (40,41). Such fixation of catalysts on organic polymers or inorganic material, such as ceramics, solved the problem of separation during product isolation and made it possible to reuse PTC repeatedly.

The second trial was the application of cationically charged polymeric PTC, which can be prepared from polymerizable cationic surfactants. Some reported polymerizable cationic surfactants are as in Scheme 5 [Ref. 42 (top panels); Ref. 43 (bottom panel)].
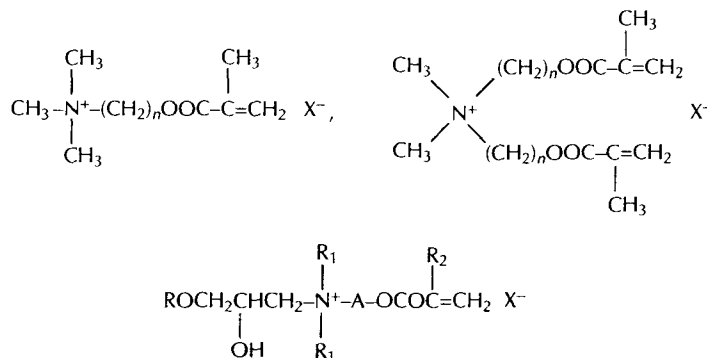
No attempts were made to apply polymer-supported PTC or cation-charged polymeric PTC from polymerizable cationic surfactants to catalyze fatty alkyl glycidyl ether formation with PTC (Scheme 5). However, these polymeric PTC may be able to catalyze alkyl glycidyl ether formation more effectively.

Wang and Engberts (44) reported on cross-linked polysoaps, which were synthesized by free-radical cyclo(co)polymerization of decylmethyldiallylammonium bromide monomers with a small amount of N,N'-methylene-*bis*-acrylamide in aqueous solution. They exhibited higher catalytic activities for the decarboxylation of 6-nitro-benzisoxazole-3-carboxylate than the corresponding noncross-linked copolymer analogues. Polysoap-catalyzed reactions may mimic reactions analogous to micelles formed by ordinary surfactants.
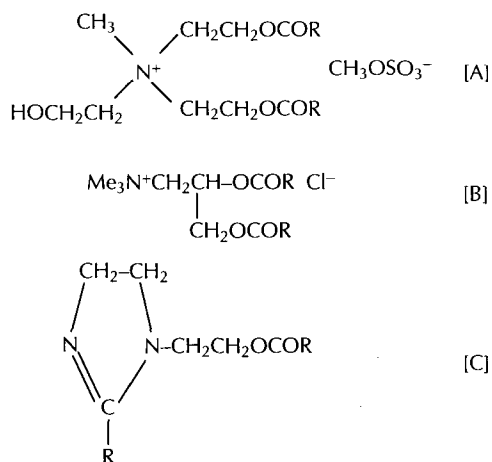
How to meet environmental safety requirements. Cationic surfactants with long-chain alkyls have been used as textile softeners, which prevent the build up of electrostatic charges so that not only do synthetic fabrics no longer crackle, emit sparks, or cling, but the tendency for soil to be redeposited is decreased.

However, a number of cationic surfactants with long-chain alkyl groups have poor biodegradability under practical sewage-plant conditions. They also are irritating to the skin and/or the eyes. Based on these facts, using environmentally compatible substances is recommended. Some attempts at discovering suitable substitutes for the abovementioned long-chain alkyl surfactants presented the following substances: N-methyl-N,N-*bis*[2-(C_{16}/C_{18}-acyloxy)ethyl]-N-(2-hydroxyethyl)ammonium-methosulfate [**A**], N,N,N-trimethyl-N-[1,2-di-($C_{16/18}$-acyloxy)propyl]ammonium chloride [**B**], and1-[($C_{16/18}$-acyloxy)ethyl]-2-($C_{15/17}$-alkyl)imidazoline [**C**] (Scheme 6) (Ref. 45). These environmentally compatible cationic surfactants may be applicable as PTC.

Other types of cationic surfactants, which are less irritating to the skin and/or the eyes, were reported: A, ethoxylated methyl glycoside hydroxypropyldimethyldodecyl ammonium

SCHEME 5

CH$_3$ CH$_2$CH$_2$OCOR
N$^+$ CH$_3$OSO$_3^-$ [A]
HOCH$_2$CH$_2$ CH$_2$CH$_2$OCOR

Me$_3$N$^+$CH$_2$CH–OCOR Cl$^-$ [B]
                 |
            CH$_2$OCOR

CH$_2$–CH$_2$
/   \
N   N-CH$_2$CH$_2$OCOR   [C]
\\   /
   C
   |
   R

SCHEME 6

chloride (46); B, quaternary ammonium salt of castor oil (47); C, diethylaminopropyl lanolic acid-benzyl ammonium chloride (48); D, triethyl-aminopropyl lanolic acid-ethosulfate (48); or E, quaternary ammonium salt of jojoba oil (49). Structures of these less-irritating surfactants (A–E) are summarized in Scheme 7. However, little has been reported on the catalytic activities of these cationic surfactants as PTC. However, they can be expected to catalyze phase-transfer catalytic reactions.

Frequently, a portion of a quaternary ammonium PTC is converted to a nitrosamine by-product during PTC reactions. To reduce the formation of nitrosamine, heterocyclic quaternary ammonium salts, such as N,N-di-n-butylpiperidinium bromide, were invented. These salts are excellent PTC for the preparation of aromatic ethers. In aromatic ether formation by the invented PTC, only 3.5 ppm of di-n-butyl-nitrosamine was found (a control run with the same proportion of tetrabutylammonium bromide as PTC produced 11 ppm of the same nitrosamine) (50).

Catalytic amounts of α- and β-cyclodextrins act as PTC in the simple nucleophilic displacement between cyano ion, iodide, and thiocyanate ions and octyl bromide in a liquid/liquid two-phase system. This shows the potential of cyclodextrin compounds based on natural sources as environmentally suitable PTC (51).

Is there any possibility of obtaining more effective catalysts? Many attempts have been made to discover other more effective and readily available PTC (52). In the course of the syntheses of biodegradable surfactants, tailor-made quaternary ammonium salts with a dioxolane group, which were prepared by the reaction of alkoxy acetone with epihalohydrin and subsequent quaternization, were more effective than conventional PTC (53,54). Such tailor-made quaternary ammonium salts catalyzed the replacement reaction of octyl bromide with NaI at higher yields (50–80%) than tetrabutylammonium bromide, which gave only a 14% yield (Scheme 8).

In recent years, a newer quaternary ammonium ion dendrimer (PE-PMA 36) was reported as having catalytic effects

analogous to those of other colloidal and polymeric quaternary ammonium ions (55).
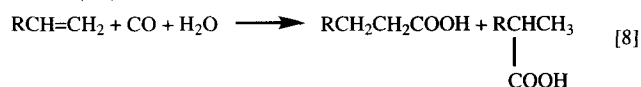
NEWER APPLICATIONS OF PTC: PRESENT STATUS

In the last two decades, both in the laboratory and in industry, many attempts to utilize PTC for organic syntheses have been made. PTC has increased the extent of our knowledge and skill concerning the control of chemical reactions under mild conditions, especially in an aqueous solution.

Some newer applications of PTC, related to fatty acids and their derivatives, are presented below.

Transition metal-catalyzed formation of long-chain carboxylic acids with PTC. As transition metal-catalyzed reactions with PTC, two types of applications are possible. The first one is to carry out the reactions under liquid(organic layer)–liquid(water) two-phase conditions in the presence of a PTC. The other one is to use water-soluble transition metal complexes that contain water-soluble ligands and carry out the reactions in liquid–liquid phases in a similar manner as ordinary PTC-catalyzed reactions.

Examples of the former type include: (i) preparation of long-chain carboxylic acids by the reaction of α-olefin with CO in the presence of a Co-carbonyl catalyst. The well-studied hydrocarboxylation reaction was catalyzed by Co-carbonyl in polar solvents. Recently, common surfactants of various structures as PTC favored the hydrocarboxylation reaction in two-phase olefin/water systems. The yield and selectivity of the desired products were markedly improved by the presence of special surfactants, such as cationic surfactants (56).

RCH=CH$_2$ + CO + H$_2$O $\longrightarrow$ RCH$_2$CH$_2$COOH + RCHCH$_3$ [8]
                                                                  |
                                                                COOH

(ii) In the Wacker-type oxidation of long-chain olefins to carbonyl compounds by the use of PdCl$_2$/heteropolyacid/surfactants as PTC in an aqueous solution, solubility problems of olefin caused a reduction in the reaction rate. These problems have been solved by resorting to PTC techniques and the addition of a suitable surfactant (57).

RCH=CH$_2$ $\longrightarrow$ RCCH$_3$ [9]
 ||
                           O
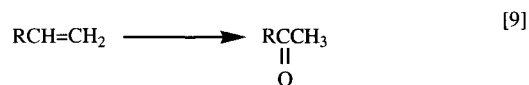
In the latter cases, the key technology is to discover water-soluble transition metal catalysts, which are useful for the simple separation of catalysts from the reaction products and have both high activity and selectivity. Typical examples are palladium complexes that contain water-soluble polyether- or crown ether-substituted phosphine ligands with phase-transfer ability (58). It was also reported that water-soluble rhodium catalysts with sulfonated or carboxylated triphenylphosphine as water-soluble ligand catalyzed the hydroformylation of long-chain olefins to produce long-chain aldehydes. This reaction has been performed on an industrial scale for the manufacture of aldehydes for the fine oleochemicals market (59,60).
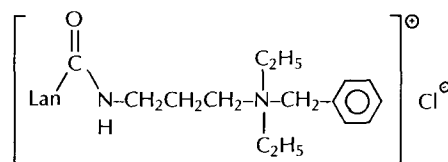
$$W + X + Y + Z = 10$$

A
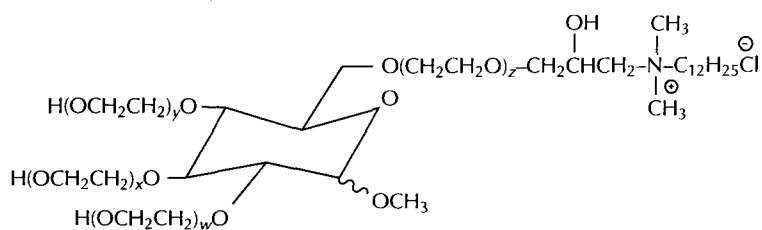
Ethoxylated (10 moles) Methyl
Glucoside Hydroxypropyl
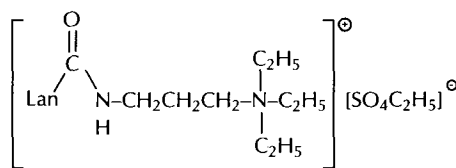Dimethyldodecyl Ammonium Chloride
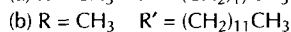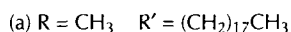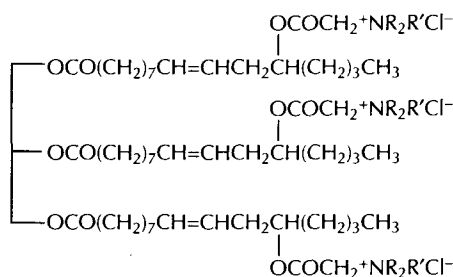
B

(a) R = CH₃   R' = (CH₂)₁₇CH₃
(b) R = CH₃   R' = (CH₂)₁₁CH₃
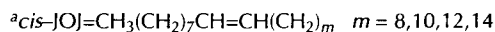
quaternary ammonium salt of castor oil

C

Diethyl-aminopropyl lanolic acid-benzyl-ammonium chloride

D

Triethyl-aminopropyl lanolic acid-ethosulfate

E

^{a}cis-]O]=CH₃(CH₂)₇CH=CH(CH₂)ₘ   m = 8,10,12,14
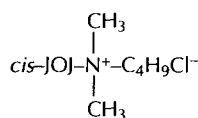
quaternary ammonium salt of jojoba oil

SCHEME 7

Stereospecific interesterification process in the presence of PTC. Cast *et al.* (61) studied the interesterification of trilaurin with methyl palmitate and NaOMe in coexistence with sev- eral kinds of quaternary ammonium salts. They found that the highest stereospecific conversion (*ca.* 12%) of trilaurin (LaLaLa) into 1,2-di-lauroyl-3-palmitin (LaLaPa) occurred

$$R_1 \quad O{-}CH_2$$
$$\diagdown C \diagup \quad |$$
$$\diagup \quad \diagdown$$
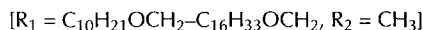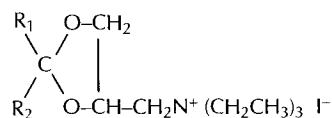$$R_2 \quad O{-}CH{-}CH_2N^+\,(CH_2CH_3)_3 \ \ I^-$$

$[R_1 = C_{10}H_{21}OCH_2{-}C_{16}H_{33}OCH_2, R_2 = CH_3]$

SCHEME 8

in the presence of tetrahexylammonium bromide. This showed that the possibility of using the traditional route for the modification of oils and fats still remained.

PRESENT STATE AND FUTURE POTENTIAL OF PTC IN OLEOCHEMISTRY

As already reviewed, the applications of PTC as organic synthetic tools are widely spread in many chemical fields, such as those of cosmetics and toiletries, surfactants and emulsifiers. The functionality of PTC reactions may be more effective when they are used as one of the building blocks to construct total reaction processes. As typical examples of industrial applications of PTC, we have described the PTC-catalyzed synthesis of fatty alkyl glycidyl ethers, from which the alkyl glyceryl ethers and their derivatives can be prepared on an industrial scale (Scheme 2) (7–9). Another possible application of PTC to synthetic organic reactions can be found in relation to natural resources. Examples include: (i) 2,5-Disubstituted furan compounds as intermediates of synthetic pyrethroids were prepared by dehydrating saccharides with hydrochloric acid in a mixture that contain water, organic solvent, and a catalytic amount of surface active agent as PTC (62). (ii) Several cyclic monosaccharides, such as glucose, galactose, mannose, and linear monosaccharides, such as mannitol, both containing di-O-isopropylidene groups, could be alkylated in Williamson ether syntheses with a PTC at high yields. The thus-obtained O-alkylated cyclic and linear monosaccharides, which both contained di-O-isopropylidene groups, were changed to corresponding O-alkyl ether compounds by acidic hydrolysis. These O-alkylated cyclic or linear monosaccharides were useful as nonionic surfactants derived from natural resources (63,64).

The phase-transfer catalytic reactions occur between heterogeneous multi-phases, comprising liquid(organic phase), liquid(water phase), and/or solid phase, and open up new areas, both in industrial and laboratory organic synthesis. Reports on the application of PTC to industrial organic synthesis have been limited compared to those for small-scale laboratory syntheses. As has been discussed above, it is necessary to solve several problems to fulfill the requirements of industrial application of PTC.

Because of availability and moderate reaction conditions, PTC should be recommended for application in the chemical industry. Recently, several attempts have been made to find more catalytically active PTC. Compounds that exhibit high

catalytic activity, selectivity, high environmental suitability, and reasonable availability suggest some of the potential PTC for further developments.

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