Crystal Growth of Alkali-metal Halides during Gas-liquid Phase-transfer Catalysis

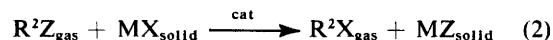Enrico Angeletti, Pietro Tundo,* and Paolo Venturello
Istituto di Chimica Organica dell'Università, Via G. Bidone 36, 10125 Torino, Italy
Marco Rubbo
Istituto di Mineralogia, Cristallografia, Geochimica dell'Università, Via San Massimo 22, 10123 Torino, Italy

The alkali-metal halide crystals produced during an organic synthesis carried out under gas-liquid phase-transfer catalysis (g.l.-p.t.c.) conditions grow in an unusual liquid medium by consuming the nucleophile salt; their habit depends on the catalyst used and on the reaction considered. The particular crystal habit, showing a cavity on one face only of the cube or on one corner only of the octahedron, illustrates some aspects of the crystal growth and gives information on the g.l.-p.t.c. mechanism.

When an organic synthesis is carried out under gas-liquid phase-transfer catalysis (g.l.-p.t.c.) conditions [1] [equation (1)], the metal halide (MX) is produced. We have previously reported that when this latter is used as a nucleophile source in a subsequent displacement reaction, carried out under g.l.-p.t.c. conditions [equation (2)], it shows a chemical reactivity higher than that of the corresponding commercially available salt.[2]

$$R^1X_{gas} + MY_{solid} \xrightarrow{cat} R^1Y_{gas} + MX_{solid} \quad (1)$$

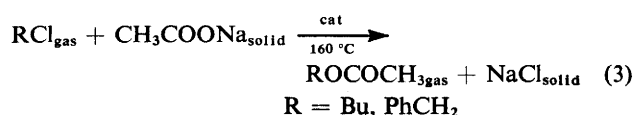$$R^2Z_{gas} + MX_{solid} \xrightarrow{cat} R^2X_{gas} + MZ_{solid} \quad (2)$$

The fairly high temperature used during the synthesis, the absence of stirring, and the slow and progressive exchange of the metal counterion during the catalytic process, provide particular conditions for the nucleation and the growth of the metal halide (MX), generally an alkali-metal halide. The reacting alkyl halide (R^1X or R^2Z) flows in the gaseous state into a column through a solid bed consisting of the nucleophile salt supporting a phase-transfer catalyst (phosphonium salt or crown ether). The produced salt (MX or MZ) remains in the column while the organic product (R^1Y or R^2X) is collected by cooling at the column outlet.

We have previously proposed that the molten catalyst promotes the reaction by continuously exchanging its anion with the 'underlying' solid phase and that, as it works in the liquid state, it also constitutes the medium in which the reaction occurs.

In order to investigate these processes (anionic activation of the organic reaction, attack and dissolution by the catalyst of the crystals of the MY salt, and the formation of the new MX species), we have performed a crystallographic and morphologic study of the salts produced during different g.l.-p.t.c. reactions.

Results and Discussion

We have, at the moment, paid particular attention to the sodium chloride crystals obtained according to equation (3), where an alkyl chloride is allowed to flow through solid sodium acetate in the presence of tetrabutylphosphonium bromide or of 18-crown-6 as catalysts. The X-ray powder

$$RCl_{gas} + CH_3COONa_{solid} \xrightarrow[160\ ^\circ C]{cat}$$
$$ROCOCH_{3gas} + NaCl_{solid} \quad (3)$$
$$R = Bu, PhCH_2$$

method of analysis did not show any differences between our diffraction spectra of NaCl and the reference ones.

Scanning electron micrography (s.e.m.) analysis showed the occurrence of crystals having cubic, octahedral, and cubic-octahedral (Figures 1—3) habits. The crystal size depends on the amount of catalyst, and the habit is a function of R in equation (3), as was verified by running the same reaction four times. When $R = PhCH_2$ cubes only are produced, while for $R = Bu$ mainly octahedra are generated.

Figures 4 and 5 show alkali-metal halides obtained during different syntheses under g.l.-p.t.c. conditions with different catalysts. The crystal habit changes as a function of both the reaction and the catalyst. Moreover, the crystal morphology, particularly that of the larger ones, presents a round-shaped cavity on one face only of the cube or only on one corner of the octahedron; in this case the external profile of the cavity belongs to a (100) face. The cavity itself is due to the growth around the contact area, as shown in the Scheme; moreover this confirms the mechanism suggested and gives new details of the g.l.-p.t.c. The nucleation takes place on the original solid bed, always on the (100) face of the alkali-metal halide. Successively the growth of the sodium chloride crystal that consumes the former salt is promoted by the phase-transfer catalyst that transfers both the nucleophile salt (from its solid phase to the liquid one constituted by the molten 'onium salt) and the alkali-metal halide (from the liquid phase to the crystals of NaY).

Under the conditions of all the reported syntheses, such a mass transfer is *ca.* 20 times higher than the amount of the catalyst and is made possible by the reaction that occurs in the liquid phase [equation (4)]. Accordingly, the 'onium salt reacts with the alkyl halide that, from the gaseous state, diffuses and dissolves into the liquid phase; the latter is an aprotic polar one that greatly promotes nucleophilic substitution reactions.

$$RX_{liquid} + QY_{liquid} \longrightarrow RY_{liquid} + QX_{liquid} \quad (4)$$

The growth of the crystal and the consumption of the nucleophile salt are hindered in the crystal-bed contact area: therefore the 'fingerprint' of the bed on one face of the cube or on one corner of the octahedron respectively is produced, while the crystal grows in that time. The nucleation may also occur in the liquid phase; in this case, crystals without a 'fingerprint' will be produced: these freely growing crystals are smaller in comparison and probably start to develop later.

The nature of the medium in which the crystal grows depends on the catalyst, on the nucleophile and on the electro-
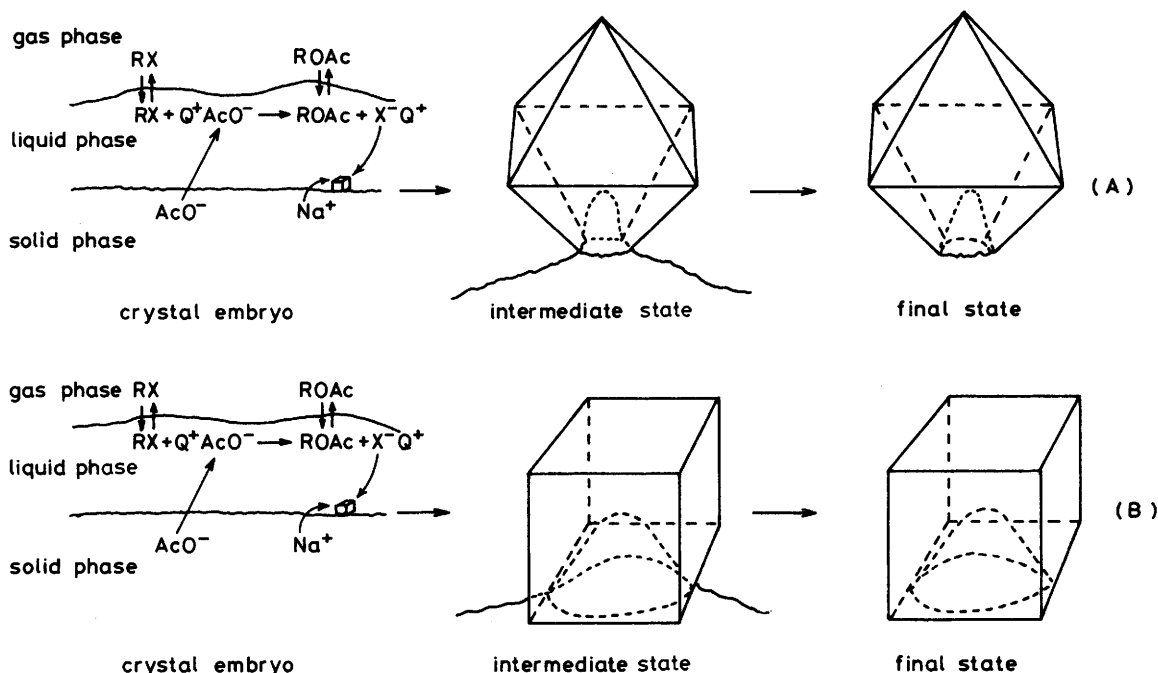
Scheme. Nucleation and growth on the (100) face of the octahedron (A) and of the cube (B) of the alkali-metal halides produced during a g.l.-p.t.c. reaction

phile. In reaction (3), for example, two different crystalline habits occur depending on whether benzyl chloride or butyl chloride, with their respective reaction products, are present in the organic phase.

Crystal Growth Aspects.—The morphology and the growth habit of crystals of structural NaCl type are well known.[3] The ideal surface of the cube is characterized by an alternate distribution of charges of opposite sign; on the other hand, the surface of the octahedron presents a charge distribution of the same sign causing this crystal to be unstable in the gas phase. Therefore when such salts grow from the vapour they present only the cubic habit {100}. When they grow from polar solvents, other habits occur, particularly the {111}. The final habit depends on: (1) the nature of the solvent; (2) the supersaturation of the solution (defined as β, the ratio between the activities of the supersaturated and saturated solution); and (3) the crystal size, particularly in an unstirred medium. For a given solvent (Figure 6), there are in particular two critical values of the supersaturation parameter $\sigma' = \beta_c' - 1$ and $\sigma_c'' = \beta_c'' - 1$ at which the growth rate (r) is such that $\sqrt{3}r_{100} = r_{111}$ and $r_{111} = r_{100}/\sqrt{3}$, respectively. Thus when $\sigma < \sigma_c'$ only {100} is present, when $\sigma_c' < \sigma < \sigma_c''$ both habits coexist and lastly, when $\sigma > \sigma_c''$ only {111} survives.

Moreover, the solvent and/or other chemical species that are present in the solution, besides determining the β parameter, can also interfere with the crystal–solution interface; therefore by influencing the specific surface energy and the crystallization kinetics, they can modify the growth habit.

The growth of a crystal under g.l.-p.t.c. conditions may be considered as a diffusion process of Na$^+$ ion from the solid phase into the liquid, in which Cl$^-$ ion is continuously generated.
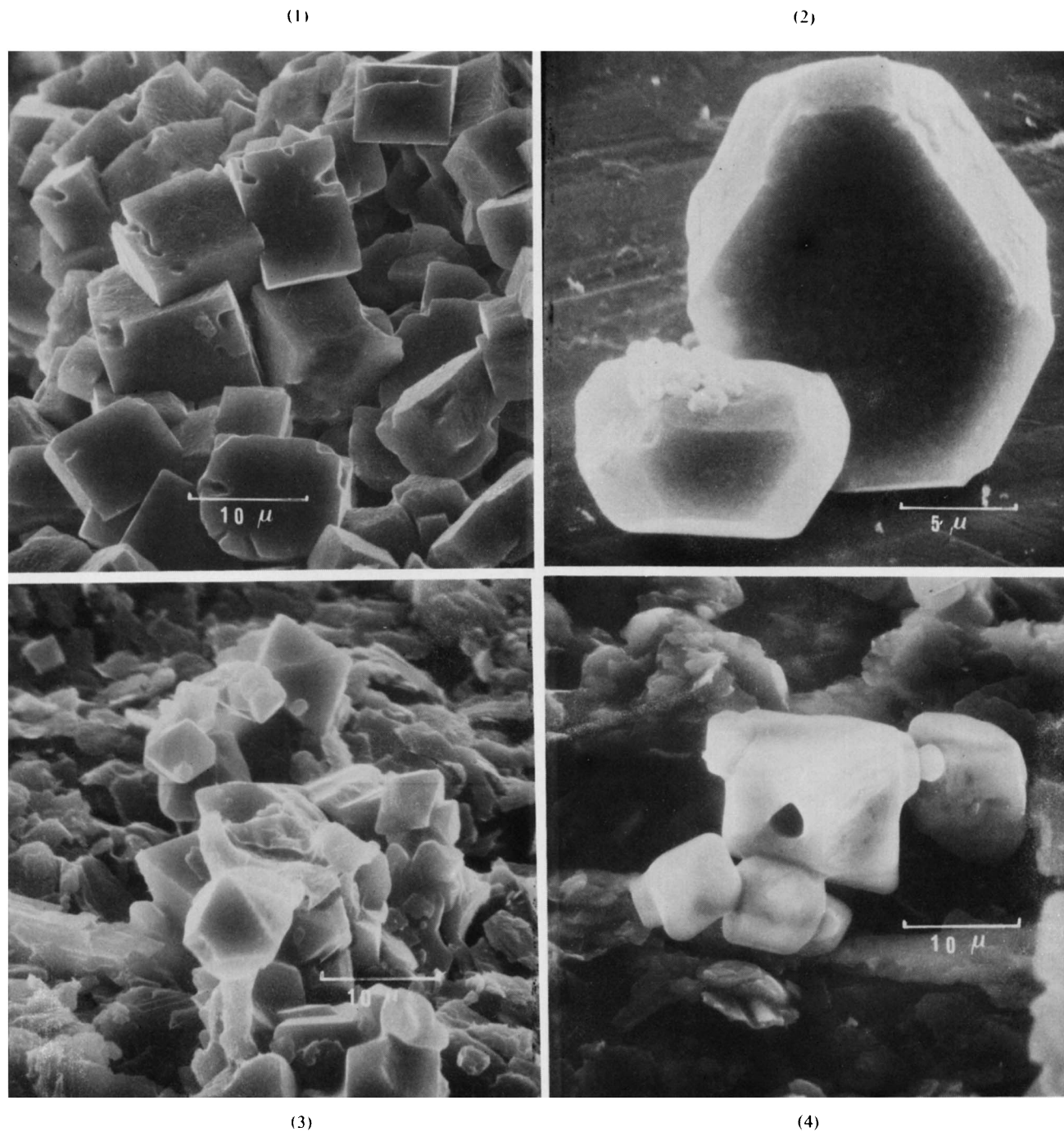
As regards the reaction between sodium acetate and benzyl chloride or butyl chloride [equation (3)], some considerations are suitable: (1) the salt is very poorly soluble in the liquid phase; (2) the average distribution size of the crystals is not broad; (3) both the reagents and the products have different
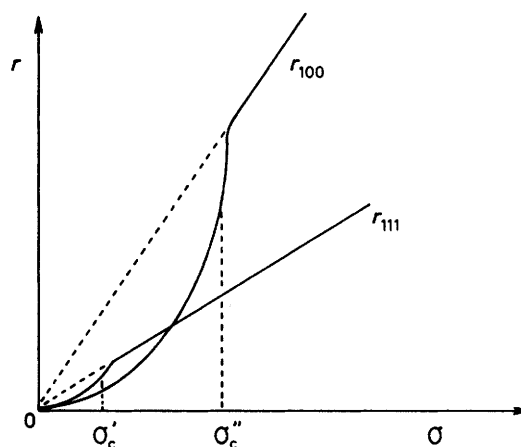
Figure 6. Growth rate (r) of the (100) and (111) face as a function of the supersaturation parameter $\sigma = \beta - 1$

partial pressure under the reaction conditions, and since they also have different affinities for the liquid phase, they show consequently different solubilities in it.

The two causes (β value and specific surface energy) affecting the crystal growth may be both present in g.l.-p.t.c. The experimental evidence at present does not allow an unequivocal interpretation. In the first case the crystalline habit may be determined by the relative growth rates of the cube and of the octahedron depending on the σ domains, owing to the different activity values of Na$^+$ and Cl$^-$ ions in the two different liquid phases: $Bu_4P^+Cl^- + Bu_4P^+AcO^- + PhCH_2Cl + PhCH_2OAc$, when R = PhCH$_2$ and $Bu_4P^+Cl^- + Bu_4P^+AcO^- + BuCl + BuOAc$, when R = Bu. In the second case, a component can be adsorbed during the NaCl crystal growth[3a] in a selective way on the cube (PhCH$_2$Cl + PhCH$_2$OAc) or on the octahedron faces (BuCl + BuOAc), affecting their specific surface energy.
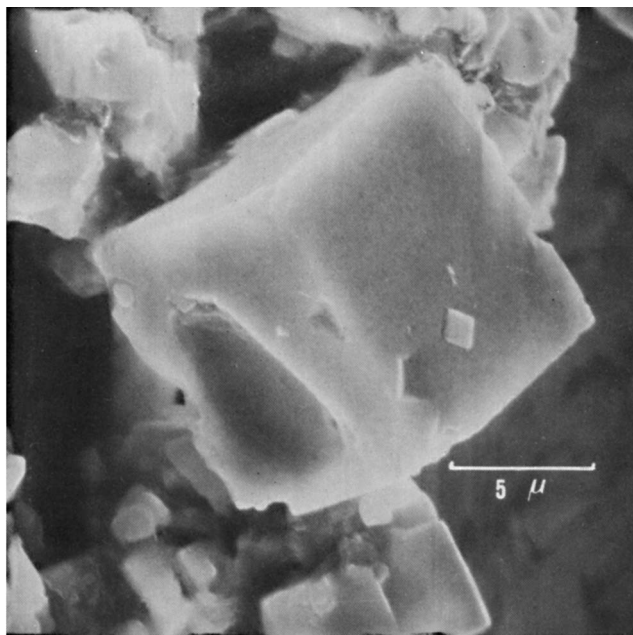
(1)

(2)

(3)

(4)

Figure 1. Electron micrography of NaCl cubic crystals produced in the reaction between $PhCH_2Cl$ and CH_3COONa with $Bu_4P^+Br^-$ as catalyst (5% mole : mole, with respect to the sodium acetate) at 150 °C

Figure 2. Electron micrography of NaCl cubic-octahedral crystals produced in the reaction between BuCl and CH_3COONa with 18-crown-6 as catalyst (5% mole : mole, with respect to the sodium acetate) at 170 °C

Figure 3. Electron micrography of NaCl octahedral crystals produced in the reaction between BuCl and CH_3COONa with $Bu_4P^+Br^-$ as catalyst (2% mole : mole, with respect to the sodium acetate) at 170 °C

Figure 4. Electron micrography of NaCl crystals produced in the reaction between BuCl and CH_3COONa with $Bu_4P^+Br^-$ as catalyst (5% mole : mole, with respect to the sodium acetate) at 160 °C

Figure 5. Electron micrography of KBr crystals produced in the reaction between BuBr and $CH_3COCH_2COOC_2H_5$ in the presence of K_2CO_3 with $Bu_4P^+Br^-$ as catalyst (5% mole : mole, with respect to the potassium carbonate) at 170 °C

Conversion of NaCl into NaBr according to equation (5), as a function of the catalyst and of the salt source [a]

	Conversion (%) [b]		
NaCl source	No catalyst	$Bu_4P^+Br^-$ [c]	18-Crown-6 [c]
Cube [d,e]	0.0	4.2 (45) [f]	
Octahedron [e,g]	0.0	2.4	
Cube [h]	3.8	74	22
Octahedron [h]		53	~2

[a] NaCl (0.10 mol); BuBr (0.50 mol); flow (liquid), 21 ml h^{-1}; T 150 °C. [b] By potentiometric titration. [c] 0.01 mol equiv. with respect to NaCl. [d] C. Erba NaCl. [e] Sieved through 125—250 μ mesh. [f] Mechanically ground to an average size <75 μ. [g] Crystallized from formamide. [h] NaCl obained according to equaton (3).

Reactivity of the NaCl *Crystals produced under G.l.-p.t.c. Conditions.*—In order to estimate the chemical reactivity of the sodium chloride obtained according to equation (3), the salt crystals were washed with methylene dichloride to remove the former catalyst and placed, with further catalyst, to react with BuBr under g.l.-p.t.c. conditions, according to equation (5).

$$NaCl_{solid} + BuBr_{gas} \xrightarrow[150\ °C]{cat} NaBr_{solid} + BuCl_{gas} \quad (5)$$
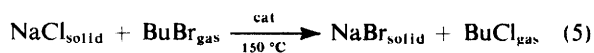
For comparison the same reaction was run employing sodium chloride obtained in cubic or octahedral habit by a standard crystallization method.[3d] The extent of the conversion of the solid sodium chloride according to equation (5), was determined, after washing the bed with methylene dichloride to remove the catalyst, by selectively titrating the Br$^-$ and Cl$^-$ content of the bed.

The crystals of sodium bromide generated according to equation (5) always showed a cubic habit in both cases, when sodium chloride had a cubic or an octahedral habit. This fact may imply a low supersaturation of sodium bromide (low β value) in the catalyst phase.

The reactivity of the sodium chloride crystals, besides the presence of the catalyst, is affected also by their size and therefore only between crystals of the same size and of well defined morphology can a strict comparison be made. Moreover, the contact area between liquid and solid phase changes as a function of the crystal surface area. Indeed the ratio between the surface areas of a cube and of an octahedron passing through a mesh of size s is *ca.* 2.3. So the conversions in the Table do not represent true kinetic values, but only comparable qualitative trends. In this connection the observed higher reactivity of the cube (100) in comparison with that of the octahedron (111) face may be attributed to the higher surface area of the cubic habit.

As reported for the ester synthesis,[2] in this case also the tetrabutylphosphonium bromide is more reactive than the 18-crown-6 as a g.l.-p.t.c. agent, although more attention was paid to the latter as an agent able to attack the crystalline skeleton of the salt, transferring the reactive anion in the organic phase. The lower activity of the 18-crown-6, in comparison with that of the phosphonium salt, can be attributed in g.l.-p.t.c., as in l.l.- and s.l.-p.t.c.,[4] to the incomplete cation complexation and to its lower anion activation.

However, a lower capacity to attack the crystalline lattice should be also considered for the crown ether. In fact it was demonstrated, both under vacuum and in the molten state, that the (100) NaCl face shows a double layer distribution of Cl$^-$ and Na$^+$ ions, the outermost being Cl$^-$.[5] Such a surface

conformation makes it difficult for the 18-crown-6 to take out a Na$^+$ ion from the crystalline lattice. On the other hand the phosphonium salt can more easily exchange its counterion with the anion of the crystal, since the nucleophilic activity of Br$^-$ is higher when it is the counterion of the bulky Bu_4P^+ cation rather than of the [Na$^+$ $\subset$ 18-crown-6].[4]

Studies on dissolution and growth of the crystals under g.l.-p.t.c. conditions make it possible to get specific information about the mechanism of the catalysis and about the solid surface–liquid phase interaction. At present other reactions and other crystals of different salts are under consideration.

Experimental

All reagents were ACS grade and were used without further purification. Tetrabutylphosphonium bromide was prepared as previously described.[6] Cubic NaCl crystals were supplied by C. Erba (code 479686); octahedral crystals were obtained by crystallization from formamide.[3a] Scanning electron micrographs were run on an Siemens Autoscan.

Argentometric titrations (0.1N-AgNO$_3$) were carried out in water solution on a Metrohm-Herisau Multi Dosimat E-451 potentiometer, with a combined silver electrode in the presence of nitric acid.

The crystal of sodium chloride and of the other salts shown in Figures 1—5 were obtained as previously reported. Potassium bromide in Figure 5 was obtained during the acetoacetic ester synthesis, allowing ethyl acetoacetate and butyl bromide to flow through a column consisting of potassium carbonate and $Bu_4P^+Br^-$ as catalyst.

Syntheses according to equation (3) were run as previously described. In particular, sodium acetate, containing tetrabutylphosphonium bromide (0.02 mol. equiv.), was placed in a column heated at 150 °C; with a flow (liquid) rate of 40 ml h^{-1} the alkyl halides were forced through: these were benzyl chloride (2.0 mol. equiv. with respect to the carboxylate, at 20 Torr) and butyl chloride (5.0 mol. equiv. with respect to the carboxylate, at atmospheric pressure). After cooling, the solid bed was suspended in methylene dichloride, filtered, and washed with fresh methylene dichloride to remove the catalyst completely. The purity of the obtained sodium chloride was determined by argentometrically titrating its Cl$^-$ content: it was 100% (molar) for the reaction with benzyl chloride and 76% (molar) for that with butyl chloride, the remaining 24% being unchanged AcONa.

Reaction between NaCl *and* BuBr.—Sodium chloride (0.10 mol, 5.84 g) was added to a solution of the catalyst [1.0 mmol; tetrabutylphosphonium bromide (0.34 g); 18-crown-6 (0.26 g)] in methylene dichloride (15 ml). The solvent was completely removed under vacuum; the obtained solid bed was then placed in the column (50 cm in length and 2 cm in diameter) thermostatted at 150 °C. During 2.6 h butyl bromide (0.50 mol, 53.7 ml) was introduced at atmospheric pressure. At the end of the addition, the last traces of the organic product were removed under vacuum and the solid bed was washed, after cooling, with methylene dichloride to remove the catalyst. The Cl$^-$ and Br$^-$ content of the bed was then determined potentiometrically. The data of the Table, line 4, were corrected for the presence of NaBr from the reaction between BuBr and AcONa.

References

1 (a) P. Tundo, *J. Org. Chem.*, 1979, **44**, 2048; (b) P. Tundo and P. Venturello, ' Synthetic Reactions by Gas-liquid Phase-transfer Catalysis,' in ' Crown Ethers and Phase Transfer Catalysis in Polymer Science,' Plenum, New York, and references therein.

2 E. Angeletti, P. Tundo, and P. Venturello, *J. Chem. Soc., Perkin Trans. 1*, 1982, 993.

3 (a) R. Boistelle, Thesis, Nancy University, 1966; (b) I. R. Stranski, *Z. Phys. Chem. B*, 1932, **17**, 127; (c) R. Kern, *Bull. Soc. Fr. Minèral, Cristallogr.*, 1953, **76**, 325; (d) P. Hartman, *ibid.*, 1963, **86**, 427.

4 D. Landini, A. Maia, F. Montanari, and F. M. Pirisi, *J. Chem. Soc., Perkin Trans. 2*, 1980, 46.

5 E. J. W. Verwey, *Recl. Trav. Chim. Pays-Bas*, 1946, **65**, 521.

6 P. Tundo and P. Venturello, *Synthesis*, 1979, 952.