# Gas-Phase Synthesis of Alkyl Iodides Promoted by Phase-Transfer Catalysts

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Phase-transfer catalysts (onium salts, crown ethers, cryptands) catalyze anion-promoted reactions both under aqueous-organic[1,2] and solid-organic[3,4] two-phase conditions; phosphonium salts also catalyze the nucleophilic substitution of gaseous substrates upon reaction with solid salts of nucleophiles[5]. We have now utilized this latter technique for the synthesis of alkyl iodides from gaseous alkyl chlorides or bromides and solid potassium iodide as the anion source, without the use of a solvent.

$$R-X_{(gas)} + KJ_{(solid)} \xrightarrow{\text{catalyst}} R-J_{(gas)} + KX_{(solid)}$$

The alkyl chloride or bromide is passed, by means of a peristaltic pump, through a column containing silica gel, potassium iodide, and tetrabutylphosphonium iodide. The column is heated at 160° and the pressure is reduced, if necessary, to keep the alkyl halide in the gaseous state. The resultant alkyl iodide is collected by cooling at the outlet of the column.

The halogen exchange was investigated for the conversion of 1-bromobutane into 1-iodobutane using different reagent beds at atmospheric pressure (Table 1). The results show that both the presence of an onium salt and of silica gel are important: the catalyst promotes the exchange between the reacted potassium halide and the not yet reacted potassium iodide, and the silica gel raises the rate of conversion by spreading the catalyst over a large surface, i.e., it plays the role of a "solid solvent" for the potassium iodide (this phenomenon has been utilized by other authors in three-phase syntheses[6]). Thus, with the combined use of phase-transfer catalyst and silica gel a higher conversion may be obtained using a lower ratio KJ/substrate.

The anionic surfactant sodium lauryl sulfate does not increase the conversion significantly.

The method might be of interest for the industrial-scale preparation of alkyl iodides since part of the usual safety precautions are not required: a solvent is not used and the solid catalytic mass permits simple handling of the reagents, products, and exhausted salts. It may be expected that performance of the reaction on a larger scale, i.e., the use of larger columns, will increase the reaction rates and yields due to longer contact times between the reacting phases.

The reaction products were fractionally distilled to give the pure alkyl iodides: no by-products (starting from primary alkyl halide) were detected either by distillation, or by $^1$H-N.M.R. or by G.L.C. (SE, 30 5% on Varaport) analysis.

If the product was passed several times through the same used column, the conversion increased, but the weight of the product collected decreased: the alkyl halides partly react with the silanol groups to give products chemically bonded to silica gel.

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**Table 1.** Conversion of 1-Bromobutane (28.02 g, 0.206 mol) into 1-Iodobutane with the Column filled with Different Reagent Beds[a]

| Entry | Material in the column | Conversion[b] [%] | Collected Product [g] |
|---|---|---|---|
| 1[c] | KJ | ~2 | 26.3 |
| 2[d] | KJ + $(n\text{-}C_4H_9)_4P^{\oplus}J^{\ominus}$ | 96 | 32.9 |
| 3[d] | KJ + $n\text{-}C_{12}H_{25}—O—SO_3^{\ominus}\ Na^{\oplus}$ | 11 | 27.9 |
| 4[e] | KJ + silica gel | 18 | 26.9 |
| 5[f] | KJ + silica gel | 50 | 29.1 |
| 6[g] | KJ + $(n\text{-}C_4H_9)_4P^{\oplus}J^{\ominus}$ + silica gel | 93 | 33.7 |
| 7[g] | KJ + $n\text{-}C_{12}H_{25}—O—SO_3^{\ominus}\ Na^{\oplus}$ + silica gel | 46 | 29.1 |

[a] Experimental conditions as given in the procedure for the synthesis of 1-iodobutane.

[b] Determined by $^1$H-N.M.R. analysis after test with standard mixture of authentic samples; integration of the central peaks of the triplets at $\delta = 3.38$ ppm ($—CH_2Br$) and 3.18 ppm ($—CH_2J$).

[c] Column completely filled with finely ground potassium iodide (340 g).

[d] Onium salt and anionic surfactant (0.016 mol) evenly distributed on finely ground potassium iodide (340 g).

[e] Silica gel (223 g) and finely ground potassium iodide (158 g), mixed mechanically.

[f] Silica gel (223 g) added to a solution of potassium iodide (158 g) in water and treated as described in Section: Catalytic Bed.

[g] Tetrabutylphosphonium iodide and anionic surfactant (0.016 mol), silical gel (223 g), and potassium iodide (158 g) treated as described in Sectim; Catalytic Bed.

**Table 2.** Alkyl Iodides from Alkyl Bromides (0.206 mol, 0.67 mol equiv relative to KJ in the column)[a]

| Educt R—X | Collected Product [g] | Conversion[b] [%] | Yield[c] [%] | b.p./torr found | b.p./torr reported |
|---|---|---|---|---|---|
| $n\text{-}C_3H_7—Cl$ | 21.5 (16.5)[d] | 56 (69)[d] | 44 | 102–103°/760 | 102.5°/760[7] |
| $n\text{-}C_3H_7—Br$ | 29.2 | 74 | 64 | 102–103°/760 | 102.5°/760[7] |
| $H_2C{=}CH—CH_2—Br$ | 28.4 | 78 | 67 | 102–103°/760 | 102–103°/760[8] |
| $n\text{-}C_4H_9—Cl$ | 28.1 (24.4)[d] | 57 (72)[d] | 52 | 130–132°/760 | 130–132°/760[9] |
| $n\text{-}C_4H_9—Br$ | 33.7 | 93 | 83 | 130–132°/760 | 130–132°/760[9] |
| $n\text{-}C_8H_{17}—Cl$[e] | 39.0 (36.9)[d] | 56 (70)[d] | 53 | 106–107°/19 | 103–105°/15[10] |
| $n\text{-}C_8H_{17}—Br$[e] | 44.2 | 82 | 69 | 106–107°/19 | 103–105°/15[10] |
| $n\text{-}C_5H_{11}—CHBr—CH_3$[e] | 17.1 | [f] | | | |
| $C_6H_5—CH_2—Cl$[e] | 37.1 | 81 | 71 | 102–103°/16 | 98–102°/14[11] |

[a] Conditions as described for 1-iodobutane.

[b] See Table 1, footnote b.

[c] Yield of distilled product.

[d] Collected product and conversion upon two passages of the reaction product through the same column under the same conditions.

[e] Conversion carried out at 15 torr.

[f] Elimination products are also formed; product mixture: heptenes (mainly *trans*-2-heptene), 21%; 2-bromoheptane, 7%; 2-iodoheptane, 72% [determined by G.L.C. analysis (SE 30, 5% on Varaport) by comparison with authentic samples].

**Tetrabutylphosphonium Iodide**[12]:

Equimolar amounts of tributylphosphine and 1-iodobutane are mixed and the mixture is allowed to stand at 20° for 3 days. The phosphonium iodide crystallizes spontaneously. It is recrystallized from tetrahydrofuran/diethyl ether; yield: 82%; m.p. 98–99° (corr.).

Tetrabutylphosphonium iodide can also be prepared by shaking a solution of tetrabutylphosphonium bromide[13] in dichloromethane with a saturated aqueous solution of potassium iodide, according to Brändström[14].

Tetrabutylphosphonium iodide is sufficiently stable at high temperatures: after 12 h at 160°, no change was observed either in its melting point or in its $^1$H-N.M.R. spectrum.

**Catalytic Bed and Column used in Halogen/Iodine Exchange:**

*Preparation of the Catalytic Bed (2000 g of solid reagent bed):* Silica gel (Merck Kieselgel 60, 70–230 mesh, pore diameter 60 Å, specific surface area 500 m$^2$/g; 1115 g) is added to a solution of potassium iodide (788 g) and tetrabutylphosphonium iodide (96.5 g) in water/methanol (7/3) with stirring. The solvents are removed under reduced pressure using a rotary evaporator and the resultant powder is dried in a stove for 12 h at 110°. With this procedure, a homogeneous composition of the catalytic bed is ensured and no visible crystals of potassium iodide are present.

All syntheses reported in Table 2 were carried out using the catalytic bed thus prepared; preliminary tests showed that small changes can occur in the conversion using a different preparation. The solid reagent bed may be kept at 160° for a long time without loss of activity.

*Column:* The solid reagent [130 g, corresponding to 51.25 g (0.309 mol) of potassium iodide and 6.27 g (0.016 mol) of tetrabutylphosphonium iodide; molar ratio $Q^{\oplus}/J_{total}$: 0.05] is placed in a horizontal glass column (length: 50 cm, ∅: 2.5 cm) enclosed in a glass jacket in which liquid paraffin is kept at 160° by means of a heating device. During heating, the support releases silica gel-adsorbed water which is removed by a stream of nitrogen.

**1-Iodobutane; Typical Procedure:**

1-Bromobutane (28.02 g, 0.206 mol; molar ratio KJ/1-bromobutane: 1.50) is introduced into the column at atmospheric pressure within ~30 min by means of a peristaltic pump (Masterflex, model n° 7013) using a flow rate of 0.8 ml/min. The 1-bromobutane is vaporized in the column and the product is collected at the outlet of the column by cooling with a condenser. The last portions of product are removed from the column by a stream of nitrogen; yield: 33.7 g; conversion: 93% (according to $^1$H-N.M.R. analysis). The product is purified by fractional distillation (Fischer, Spaltrohr-System); yield: 31.5 g (83%); purity: 98% (determined by G.L.C. analysis; SE 30 5% on Varaport, and FFAP 5% on Varaport); b.p. 102–103°; $n_D^{20}$: 1.5000 (Ref. [9], $n_D^{20}$: 1.5003).

**Benzyl Iodide; Typical Procedure:**

Benzyl chloride (26.08 g, 0.206 mol) is introduced into the column in which the pressure is 15 torr. This operation requires ~35 min. The product is collected by cooling; yield: 37.1 g; conversion: 81% [according to $^1$H-N.M.R. ($CCl_4$) analysis; $\delta = 4.44$ ppm ($C_6H_5-\underline{CH_2}-Cl$) and 4.30 ppm ($C_6H_5-\underline{CH_2}-J$)]. The product is purified by fractional distillation in vacuo; yield: 31.9 g (71%); b.p. 102–103°; m.p. 24° (Ref. [11], m.p. 24.5°).

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