

The acceleration of indium ion reduction in perchloric acid by thiourea may successfully be employed in analytic routine of indium determination. The calibration curve for determination indium in perchloric acid in the indium concentration range from 1×10^{-6} to 5×10^{-4} M are straight lines. Thiourea concentrations should be at least 5 g/L so that the limiting current could be well developed.

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Simultaneous Determination of Chloride, Bromide, and Iodide by Gas Chromatography

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During a recent investigation of the electrochemical reduction of succinimide (1) it was discovered that injection of an acetonitrile solution of tetra-*n*-butylammonium succinimide into a gas chromatograph resulted in the formation of *N*-*n*-butylammonium succinimide in excellent yield. Decimolar solutions of tetra-*n*-butylammonium bromide (TBAB) and tetra-*n*-butylammonium iodide (TBAI) were also sampled and the percentage reaction occurring in the gas chromatograph, according to eq 1 was 76% for the bromide and 79% for the



iodide. It thus became apparent that mixtures of quaternary ammonium bromides, iodides, and possibly chlorides could be determined simultaneously as alkyl halides by this method provided that (1) the alkylation reaction is largely complete in the injection port of the gas chromatograph and (2) the alkyl halides, RX, are separated on the column.

A literature survey revealed that, in fact, this general procedure has been utilized previously on at least two occasions. Cation exchange was employed to convert aqueous sodium or potassium halides (Cl, Br, I) into tetramethyl-, tetraethyl-, or tetrapropylammonium halides (2). Another approach involved extracting aqueous halide solutions with toluene-alcohol solutions of tetraheptylammonium carbonate to yield tetraheptylammonium halides (3). In both of these studies, injection of the quaternary ammonium halide solutions into a gas chromatograph resulted in the on-column preparation of the corresponding haloalkanes, according to eq 1, which were determined. These methods (2, 3) share the inherent limitations imposed by the use of quaternary ammonium cations as alkylating agents; in particular, the derivatization reactions were incomplete and trialkylamines which derive from thermal decomposition of quaternary ammonium ions can interfere with the gas chromatographic analysis.

The present study was undertaken in order to seek improvements in the general method of analyzing halide mixtures by alkylation in a gas chromatograph. In particular, it was desired to improve the yield of the alkylation reactions for chloride, bromide, and iodide in the gas chromatograph and to eliminate the trialkylamine interference. Both of these improvements were realized when *n*-butyl tosylate was employed as an alkylating agent.

EXPERIMENTAL SECTION

Reagents. Tetra-*n*-butylammonium bromide (TBAB) and tetra-*n*-butylammonium iodide (TBAI) were products of Aldrich

Chemical Co. Tetra-*n*-butylammonium fluoborate (TBAF) was obtained by reacting fluoboric acid with TBAB (4). Benzyltriethylammonium chloride was prepared by refluxing benzyl chloride and triethylamine in acetone (5) and its purity was assayed by Volhard titration. *n*-Butyl *p*-toluenesulfonate (*n*-butyl tosylate) was obtained by reacting *p*-methylbenzenesulfonyl chloride with 1-butanol in pyridine (6). 1-Halobutanes were obtained from Eastman Kodak Co. and were distilled before use.

Apparatus. Most halide determination runs were made by using a Varian Aerograph Model 2720 gas chromatograph equipped with a thermal conductivity detector and stainless steel columns (6 ft \times 1/4 in.) packed with Porapak Q or poly-*m*-phenyl ether (six-ring) on 80-100 mesh H-P Chromosorb W. Several runs were also made by using a Hewlett-Packard Model 5840A gas chromatograph equipped with a flame ionization detector and a 6 ft \times 1/8 in. stainless steel column containing Porapak Q. Each of these instruments was equipped with a conventional heated injection port.

Procedures. This procedure for simultaneous determination of chloride, bromide and iodide involved simply adding excess *n*-butyl tosylate to the halide-containing solution and injection of an aliquot into a gas chromatograph. The system was calibrated by prior injection of known mixtures of the three 1-halobutanes. The injection port was flushed periodically with acetone to remove traces of salt residues. The injection of these salt-containing solutions into the gas chromatograph resulted in no obvious deleterious effects upon either the column or instrument.

For determination of the rate of the reaction between bromide ion and *n*-butyl tosylate, bromide ion concentration was followed by linear-sweep voltammetry with a platinum disk working electrode. A PARC Model 170 electrochemistry system was employed with standard PARC electrochemical accessories for this experiment. An initial voltammogram was obtained in acetonitrile containing 0.05 M TBAB and 0.1 M TBAF. The *n*-butyl tosylate (0.1 M) was then added and the decrease in bromide ion concentration was followed by recording linear-sweep voltammograms periodically. The peak current for the first bromide oxidation wave at $E_p = +0.75$ V vs. SCE was proportional to bromide ion concentration. The second-order rate constant was determined by standard procedures (7).

RESULTS AND DISCUSSION

Initial experiments were performed with solutions of TBAI in acetone; 1-iodobutane and tri-*n*-butylamine were formed in the gas chromatograph according to eq 1, where R = *n*-butyl and X = iodide. The extent to which this derivatization reaction proceeded was determined by comparing the peak areas of the derived 1-iodobutane with 1-iodobutane standards. As expected, the percent reaction was increased by raising the injection port temperature as well as by the addition of TBAF

Table I. Reaction of Iodide Ion with Tetra-*n*-butylammonium Ion in a Gas Chromatograph^a

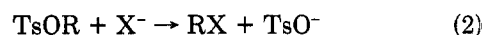
| run | sample composition | | injector temp, °C | % reaction ^b |
|-----|--------------------|----------------|-------------------|-------------------------|
| | TBAI concn, mM | TBAF concn, mM | | |
| 1 | 5.82 | 0 | 280 | 12 |
| 2 | 6.38 | 10 | 280 | 16 |
| 3 | 6.34 | 100 | 280 | 40 |
| 4 | 5.02 | 100 | 320 | 62 |
| 5 | 10.03 | 100 | 320 | 67 |
| 6 | 20.10 | 100 | 320 | 72 |
| 7 | 50.15 | 100 | 320 | 77 |
| 8 | 50.15 | 0 | 320 | 62 |

^a Runs were carried out by injecting 1 μ L of sample or standard 1-iodobutane solution into a gas chromatograph equipped with a 6 ft \times 1/8 in. column containing poly-*m*-phenyl ether at 80 °C and FID temperature = 300 °C.

^b Percentage reaction according to eq 1 was determined by comparing sample peak areas with those derived from standard 1-iodobutane solutions.

to the TBAI solutions; the percentage derivatization also increased somewhat with increasing TBAI concentration, but even under the best conditions, the formation of 1-iodobutane was significantly less than 100% (see Table I). When the derivatization reaction is incomplete, halide salt residues are left in the injection port and the likelihood of sample contamination from prior runs exists. This may account for the rather large percent average deviation (8%) obtained for the peak areas of 1-iodobutane derived from decomposition of TBAI while the corresponding figure for 1-iodobutane standards over the same concentration range was 3%. Tri-*n*-butylamine is also formed by thermal decomposition of TBAI and the oven temperature was raised periodically in order to elute it from the column more rapidly.

In order to render this gas chromatographic method feasible for the simultaneous determination of halide ions, we sought a better alkylating agent. Since *p*-toluenesulfonate (tosylate) derivatives are excellent alkylating agents (8) and also since the *n*-butyl halides are readily determined by gas chromatography, the efficiency of *n*-butyl tosylate was investigated. An acetone solution containing 0.05 M TBAB and 0.10 M *n*-butyl tosylate was injected into the gas chromatograph, and a single product peak was present in the chromatogram which had a retention time identical with authentic 1-bromobutane on poly-*m*-phenyl ether and Porapak Q columns; on the basis of a comparison of peak areas for sample and standards, the formation of 1-bromobutane in the gas chromatograph was quantitative. Moreover, the width of the derivative peak was identical with that of authentic material, even when a modest injection port temperature of 210 °C was employed. This result implied that the reaction of bromide with *n*-butyl tosylate to form 1-bromobutane and tosylate, according to the generalized equation



takes place rapidly either in solution upon mixing or in the injection port of the gas chromatograph. Identical results were obtained when acetonitrile replaced acetone as the solvent.

The second-order rate constant for the reaction between bromide and *n*-butyl tosylate in acetonitrile containing 0.1 M TBAF was determined to be near $1.5 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ by measuring the decrease in peak height of the first oxidation wave due to bromide at +0.75 V vs. SCE by linear-sweep voltammetry. The reaction between bromide and *n*-butyl tosylate thus proceeds slowly in solution and must, therefore, take place rapidly in the injection port of the gas chromatograph.

In separate experiments, 0.05 M solutions of benzyltriethylammonium chloride and TBAI were prepared in acetone containing 0.1 M *n*-butyl tosylate and microaliquots of these solutions injected into the gas chromatograph resulted in a quantitative conversion to 1-chlorobutane and 1-iodobutane, respectively. It was thus demonstrated that chloride, bromide, and iodide each reacts with *n*-butyl tosylate to yield the corresponding 1-halobutane in stoichiometric fashion.

Then four solutions were prepared in acetone, each containing a known amount of quaternary ammonium chloride, bromide, and iodide as well as excess *n*-butyl tosylate and the chromatographic peaks for the three 1-haloalkanes on Porapak Q were well separated. As Table II shows, chloride, bromide, and iodide were accurately determined in these mixtures; hence, each of the three individual derivatization reactions proceeded without interference under these conditions. A typical gas chromatogram obtained with a solution containing the three quaternary ammonium halides and excess *n*-butyl tosylate is shown in Figure 1A and compared to a trace obtained with similar concentrations of the authentic 1-halobutanes (Figure 1B). Other than the much larger water peak in Figure 1A (a small amount of water was added to the acetone to aid in dissolving the benzyltriethylammonium chloride), Figure 1A and Figure 1B are quite similar. The peaks for 1-halobutanes derived from halide ion and *n*-butyl tosylate were virtually identical in width to the corresponding 1-halobutane standard, suggesting that the derivatization reactions are all rapid and probably complete in the injection port. Calibration plots constructed for each of the halides (0.007–0.07 M) from data obtained by injecting known halide mixtures containing excess *n*-butyl tosylate were all linear; linear regression correlation coefficients were 0.99958, 0.99207, 0.99858 for chloride, bromide, and iodide, respectively. With the derivatization reactions complete in the injection port, the average deviations of sample and standard 1-halobutane peak area measurements were less than 2%. The sensitivity of this method depends, of course, upon the type of detector employed in the gas chromatograph. The sensitivity limit for bromide ion determination in acetone was approximately 10 ppm when a flame ionization detector was employed. The formation of 1-bromobutane, according to eq 2, was still near

Table II. Simultaneous Determination of Chloride, Bromide, and Iodide in Acetone Containing 0.25 M *n*-Butyl Tosylate^a

| run | amt of halide taken, μ g | | | amt of halide found, ^b μ g | | | recovery, ^b % | | |
|-----|------------------------------|------|------|---|------|------|--------------------------|-----|------|
| | Cl | Br | I | Cl | Br | I | Cl | Br | I |
| 1 | 6.76 | 14.9 | 22.3 | 6.65 | 15.2 | 22.3 | 98.4 | 102 | 100 |
| 2 | 10.1 | 22.4 | 33.4 | 9.84 | 22.6 | 33.4 | 97.4 | 101 | 100 |
| 3 | 17.0 | 37.2 | 55.7 | 16.4 | 37.9 | 55.2 | 96.8 | 102 | 99.1 |
| 4 | 23.8 | 52.1 | 78.0 | 22.7 | 52.1 | 76.3 | 95.3 | 100 | 97.8 |

^a Determinations were made by injecting a 10- μ L aliquot of sample or standard solution into a gas chromatograph equipped with 6 ft \times 1/4 in. column packed with Porapak Q; the column temp was 210 °C, injector = 225 °C, and TCD = 235 °C. The halides were in the form of quaternary ammonium salts. ^b Halide found (and hence percent recovery) was determined by comparing the sample peak areas derived from Cl, Br, and I with peak areas for standard solutions of the corresponding 1-halobutane.

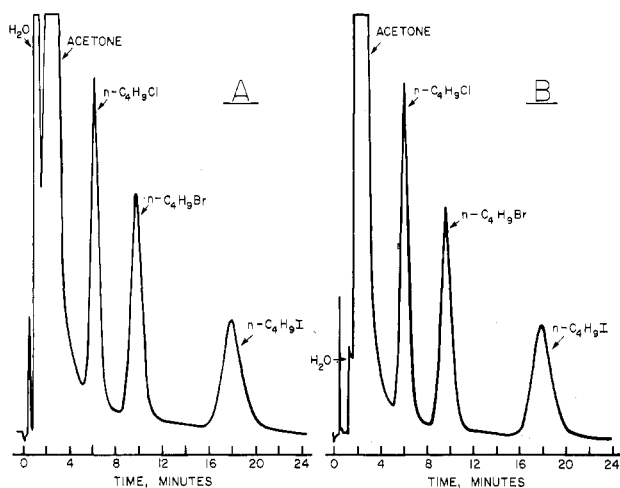


Figure 1. Comparison of gas chromatograms for acetone solutions containing: 0.0672 M benzyltriethylammonium chloride, 0.0652 M TBAB, 0.0615 M TBAI, and 0.25 M *n*-butyl tosylate (A) and 0.0671 M 1-chlorobutane, 0.0652 M 1-bromobutane, and 0.0615 M 1-iodobutane (B). Experimental conditions were the same as those described at the bottom of Table II.

100% at this relatively low concentration.

These experiments demonstrate that the simultaneous determination of quaternary ammonium chlorides, bromides, and iodides is feasible in nonaqueous solvents such as acetone, acetonitrile, and methanol in which the halide salts and *n*-butyl tosylate are mutually soluble. The determination of these halide ions in aqueous solution by this procedure, however, would probably require that the halides first be extracted into a nonaqueous solution containing *n*-butyl tosylate and was not attempted here. Matthews et al. (3) attempted to extend the sensitivity limit of their extraction-

gas chromatographic method to the parts-per-billion range using an electron capture detector, but the detector became unresponsive after the foil and walls became coated with triethylamine which derived from decomposition of tetraheptylammonium cation. If *n*-butyl tosylate was employed as the alkylating agent in a similar procedure, however, the nonvolatile tetraheptylammonium tosylate decomposition products should not deactivate the electron capture detector and low-parts-per-billion-level sensitivity for simultaneous halide determinations in water might be possible. When attempting to extend the use of this method to other systems such as to the determination of inorganic halides or to the determination of other nucleophiles, it should first be verified that the derivatization reaction (eq 2) proceeds rapidly and quantitatively in the injection port of the gas chromatograph.

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Optically Transparent Thin-Layer Electrode for Organic Solvents

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Optically transparent thin-layer electrodes (OTTLE) have been used in voltammetry, coulometry, and spectroelectrochemistry (1). OTTLEs are generally constructed by bonding two microscope slides (optical flats) together with a transparent minigrad sandwiched between (see Figure 1, ref 1). Applications of the OTTLE in nonaqueous solvents have been limited because of solvent attack on the bonding adhesive. Since electrochemistry in nonaqueous solvents is common, an OTTLE possessing long-term resistance to commonly used organic solvents would have wide appeal. In this paper, we describe the construction of an OTTLE that is resistant to materials that do not attack quartz and gold.

In our laboratory, electrochemical experiments with a conventional OTTLE in solvents such as propylene carbonate, *N,N*-dimethylformamide (DMF), and acetonitrile show that after a dozen or so experiments or lengthy exposure to these solvents, particularly DMF, the bonding material deteriorates and the optical flats separate. Attempts at mechanically

binding the OTTLE together with miniature C-clamps which are subsequently covered with a silicone rubber adhesive (a bonding material relatively resistant to attack by many organic solvents but mechanically weak) have been unsuccessful because of the inability to form a uniform seal at the OTTLE edges. Because glass sealing compounds that form vacuum seals when sufficiently heated are available (Vitta Corp., Wilton, CT), an attractive alternative is to make all solvent surfaces of glass. Quartz was selected because of its excellent transmission qualities.

The OTTLE, along with an enlargement illustrating the edge detail, is shown in Figure 1. One optical flat is made from a quartz Beckman cuvette cut in half lengthwise. (This process actually produces two optical flats from which two OTTLEs can be made.) The cut sides are ground parallel to the flat to a depth of 0.1 mm, measured from the ground surface to inner face of the flat (edge c in Figure 1). A slot, which serves as a port to draw in new solution when the