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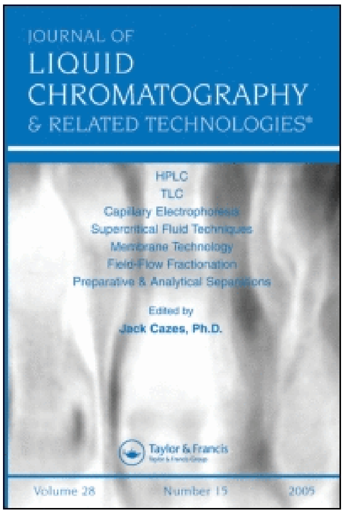

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DIRECT MONITORING OF REACTION PROCESSES WITH MICRO-HPLC TECHNIQUE

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ABSTRACT

A simple scheme was developed by utilization of a micro-HPLC technique in order to monitor synthetic reactions in-situ. The application of this system for the organic reaction of bromination of toluene was successfully presented.

INTRODUCTION

The monitoring of reaction processes for optimization of reaction conditions in organic synthesis by chromatographic techniques (e.g., TLC, HPLC or GC) has been widely used, although there are some limitations in terms of volatility and thermal stability of materials. Also, conventional chromatographic techniques sometimes require appreciable amounts of precious crude reaction mixtures and series of time-consuming procedures.

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Micro-HPLC techniques recently developed (1)-(5) have the advantage of drastically reduced consumption of mobile phases and sample; this will provide the possibility of monitoring synthetic reaction processes in-situ for which a scheme is as follows; the reactants and products, i.e., the crude mixture, are automatically picked up from the reaction vessel, using a microfeeder combined with a micro loop injector, and the chromatograms of reactants and products are continuously measured at intervals during the reaction without tedious procedures. All that is required is manipulation of a loop injector.

This communication describes the preliminary results of testing this system, in which the reaction studied is a bromination of toluene.

EXPERIMENTAL

Figure 1 shows the block diagram of this system. The micro-HPLC system used here comprised a microfeeder, MF-2 (Azuma Electric, Co. Ltd., Tokyo, Japan), A, as a pump with a Uvidec 100-II ultraviolet spectrophotometer (Jasco, Tokyo, Japan) operating at 254 nm. The "picking-up" system was a microfeeder MF-2, B, with a micro loop injector M_L-422 (0.08 μl)(Jasco, Tokyo, Japan) (6). With this injector, the crude mixture can be picked up from the reaction vessel and transferred to the chromatographic system via teflon tubing without stopping the mobile phase flow. The "picking-up" rate of the crude mixture can be controlled by adjusting the gear of the microfeeder-B. The chromatographic conditions are as follows;

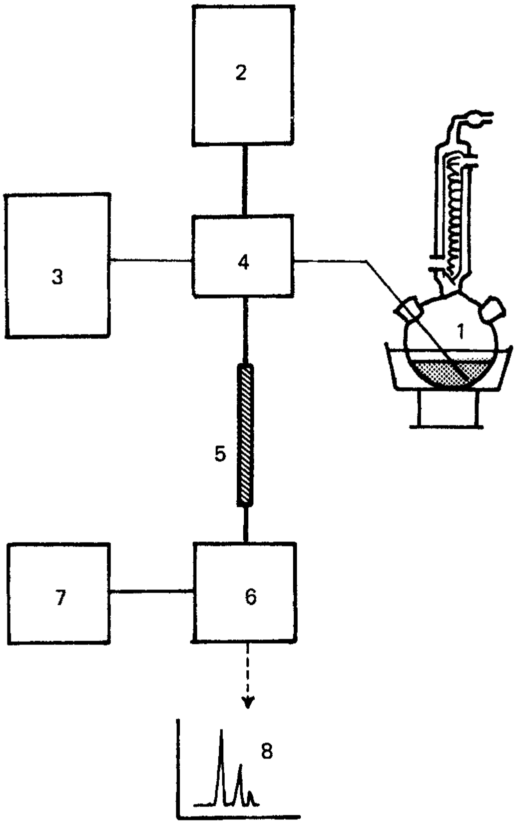


Figure 1 Schematic Diagram of the Direct Monitoring System for Reaction Processes
1: reaction vessel, 2: microfeeder-A,
3: microfeeder-B, 4: micro loop injector,
5: micro-HPLC column, 6: UV detector,
7: integrator, 8: chart recorder

Mobile phase: acetonitrile/water= 70/30

Flow rate of mobile phase: 10 µl/min.

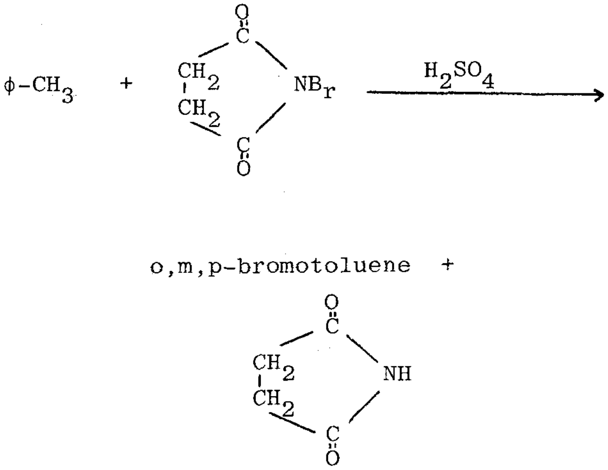
Column: Chemcosorb (Chemco, Osaka, Japan) ODS/H,
7 µm, 0.5 mm i.d. x 15 cm

Column temperature: 20 °C

All of chemicals used in this work were reagent grades commercially available.

RESULTS

The reaction scheme is



The reaction courses were checked by measuring the chromatograms of toluene and bromine-substituted toluenes.

The chromatographic pre-run of the components included in this reaction system was performed, and the retention data for each constituents were obtained to identify the peaks in the chromatogram measured during the reaction. They are listed in Table 1.

The crude reaction mixtures were then injected directly into the micro-HPLC system using the system developed here with a few minutes' interval between them.

Table 1

Retention Data for Components Included in the Bromination of Toluene

Compound	capacity factor, k'
chloroform	0
succinimide	- 0.24
N-bromosuccinimide	- 0.27
surfuric acid	- 0.28
toluene	0.37
bromotoluenes (o,m,p-)	0.86

In Figure 2, the ratio of the peak area of toluene to that of bromotoluenes are plotted with the reaction time for three reaction temperatures. In these instances, the ratio increases with increase of the reaction time and that value levels off at the time when the reaction should be nearly completed. This behavior shows the reaction progress depends on the temperature; also, the data obtained can be used to indicate the optimum reaction conditions.

It is apparent from above results that the monitoring of the reaction processes can be followed accurately by the use of the technique proposed in this communication.

The product-isomers (o,m,p-bromotoluenes) in this instance separated by the chromatographic system could be

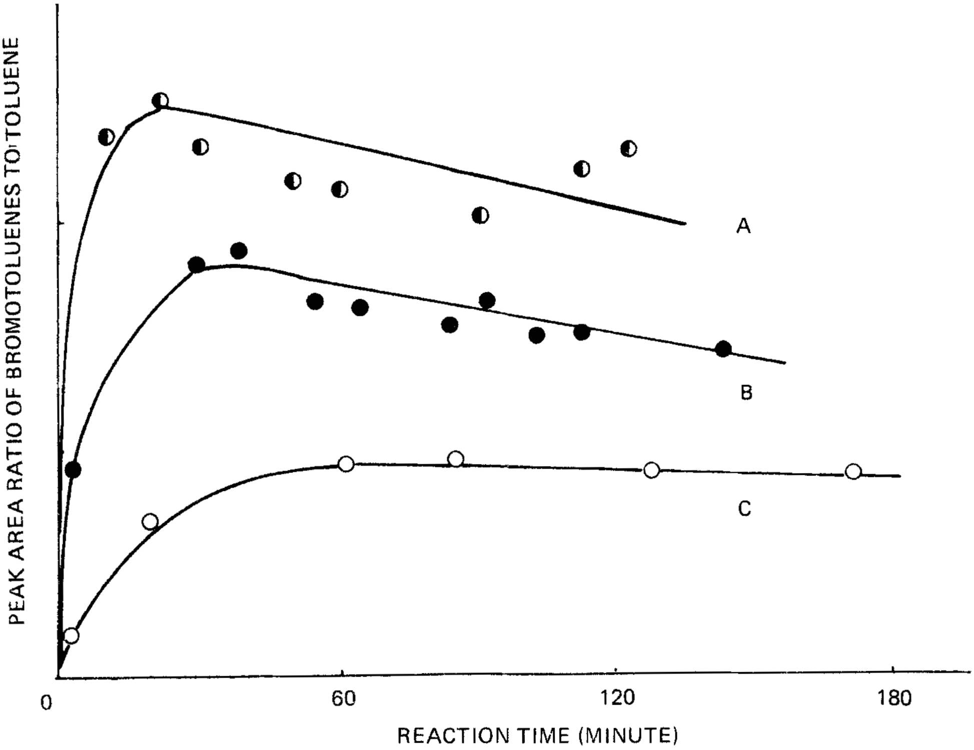


Figure 2 Peak Area Ratio of Bromotoluene to Toluene v.s. Reaction Time

A: reaction temperature 50 °C
B: reaction temperature 25 °C
C: reaction temperature 0 °C

identified with a recently developed KBr buffer IR memory technique (7)-(10).

This system will be useful not only for organic synthesis reactions, but also polymerization reactions in the gel permeation chromatography mode.

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