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The preparation of 2-methyl-4-chlorophenoxyacetic acid and 2,3,6-trichlorobenzoic acid methyl esters by pyrolysis of their tetramethylammonium salts

The preparation of methyl esters by heating the tetramethyl ammonium salts of carboxylic acids was reported by PRELOG AND PICENTANIDA in 1936[1]. In this reaction heat causes trimethylamine to be driven off leaving the methyl ester. The reaction was applied to the direct production of a number of aryl and alkyl acid esters in the injection port of a gas chromatograph by ROBB AND WESTBROOK[2]. It was found that while a quantitative yield of ester could be determined, the temperature of the injection port was critical. Even so the response of the acids to treatment was somewhat variable and quantitative conversion was not attained in many cases. DOWNING[3] modified the ROBB AND WESTBROOK procedure so that it could be applied to most simple organic acids. The essential feature of his modification was the removal of water before pyrolysis, which had the advantage that the efficiency of the conversion to methyl esters was unaffected by sample size or concentration. The yields were also largely insensitive to reagent concentration or to variation, within wide limits, of injection port temperature.

BAILEY[4], again working with non-aqueous conditions, showed that the method could be applied to the determination of mono- and dibasic aromatic acids when present as major components in mixtures containing non-acidic components, and to similar mixtures containing mono- and dibasic aliphatic acids and esters.

This paper describes an attempt to apply the findings of these workers to the determination of the phenoxy aliphatic and substituted benzoic acids normally used in herbicidal formulations.

Experimental

The apparatus used throughout this work was a Perkin Elmer Model F.11 gas chromatograph fitted with the analytical module appropriate to the column selected. In all cases the flame ionisation detector was used to monitor column effluents. The columns used were either a 2-m glass ($\frac{1}{4}$ in. O.D.) or a 2-m stainless steel ($\frac{1}{8}$ in. O.D.). Both columns were packed with 10% Silicone Oil SE-30 on 80–100 mesh Chromosorb W. The temperature of the oven was maintained at 150° and the nitrogen carrier gas inlet pressure was kept constant at 1.0 kg/cm² throughout these experiments. The temperature of the injection block and oven were measured using the Perkin Elmer temperature readout attachment.

For the purpose of these experiments two acids were used, viz. pure 2-methyl-4-chlorophenoxyacetic acid (MCPA) and pure 2,3,6-trichlorobenzoic acid (TBA).

Use of the glass column. A glass column was prepared as outlined above and the inlet arm was packed with quartz wool to increase the area available for heat transfer. The injection block was maintained at a temperature of 380°. The sample was prepared by dissolving a known weight of MCPA in methanol and adding a calculated 50% excess of tetramethylammonium hydroxide in methanol solution. Aliquots of this solution were injected onto the quartz wool at a point just above the hottest zone of the injection block. A typical chromatogram is reproduced in Fig. 1.
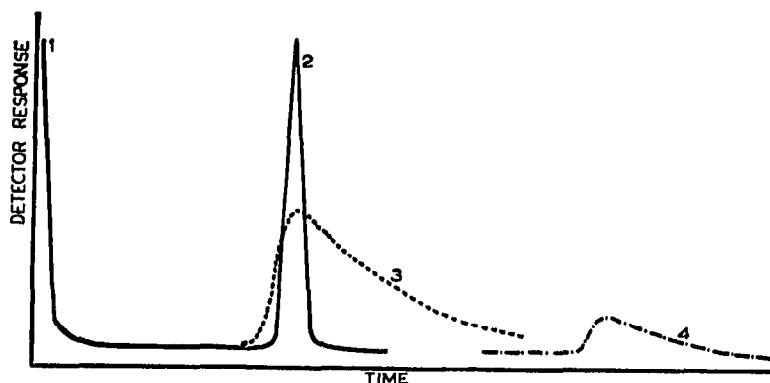
Fig. 1. Typical chromatograms obtained from pure MCPA (4), MCPA methyl ester (2) and MCPA tetramethylammonium salt (3). 1 = solvent.

Also shown in Fig. 1 are typical peaks obtained from prepared methyl ester of MCPA and MCPA free acid. This work was not continued because it was felt that the tailing of the peak was due to the small length of the heating zone being insufficient for the pyrolysis reaction to go to completion.

A similar experiment was carried out using a solution of TBA in methanol containing a 50% excess of tetramethylammonium hydroxide, but no conversion to the methyl ester was achieved.

Use of the stainless steel column. Methanolic solutions of MCPA in excess tetramethylammonium hydroxide were gas chromatographed at a number of different injection block temperatures. The analytical module for the stainless steel columns has a much longer injection block heating zone and consequently the sample has more time to undergo pyrolysis before being swept into the column. It was found that the temperature of the pyrolysis was critical. Too high a temperature resulted in a considerable quantity of 4-chlorocresol being produced by pyrolytic decomposition of the MCPA, whereas too low a temperature resulted in a poor yield of MCPA methyl ester. The rate of production of MCPA methyl ester and 4-chlorocresol at different injection block temperatures is shown in Table I. This table shows that a maximum production of methyl ester occurs at about 240°.

TABLE I

MCPA METHYL ESTER PRODUCED BY PYROLYSIS OF THE TETRAMETHYL AMMONIUM SALT AT VARIOUS INJECTION BLOCK TEMPERATURES

Injection block temperature (°C)	Methyl ester produced (%)	4-Chlorocresol (%)
150	72	—
210	86	—
240	96	—
270	94	Trace
305	85	1
335	81	2

The percentage ester produced was determined by comparing the peak area obtained from a known weight of MCPA in tetramethylammonium hydroxide with that obtained from the same weight of pure MCPA converted to the methyl ester by treatment with diazomethane and chromatographed at an injection block temperature of 175°. The amount of 4-chlorocresol was estimated as a percentage of the methyl ester peak assuming the same response factor. The production of 4-chlorocresol at relatively low injection block temperatures was not anticipated and in order to see if this was due to decomposition of the free acid or the methyl ester, a separate experiment was carried out.

A known weight of MCPA was converted to the methyl ester by treatment with diazomethane and chromatographed at a series of different injection block temperatures. The results again showed formation of 4-chlorocresol at temperatures above 270°. It is evident from this that careful control of injection block temperature is essential even during routine gas chromatographic analyses of MCPA methyl esters if decomposition is to be avoided.

Similar experiments were carried out with TBA but again the conversion to the methyl ester was minimal. The reason for this is almost certainly steric hindrance since it is well known that di-*ortho* substituted benzoic acids are resistant to all but the strongest methylating agents.

Conclusion

In the experiments described above it is evident that the temperature of pyrolysis is highly critical. With the simple control of injection block temperature available on the gas chromatograph used, the fine temperature control necessary for reproducible conversions is not likely to be achieved.

The method appears to work qualitatively in the case of MCPA but not for TBA, probably on the grounds of steric hindrance. This method of preparing methyl esters does not, however, lend itself to the quantitative determination of phenoxyacetic acids on a routine basis.

In addition, it has been demonstrated that the methyl ester of MCPA is decomposed at injection block temperatures above 270°. The effects of high injection block temperatures in the decomposition of the methyl esters of other herbicidally active acids is at present under investigation.

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