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APPLICATION OF A COLOUR REACTION FOR THE IDENTIFICATION OF METHACRYLATE MONOMER AND POLYMER

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SUMMARY

The colour reaction described produces conclusive positive and negative results for the methacrylate and acrylate esters, respectively. However, the positive result is not restricted to the methacrylate esters but is applicable to other compounds examined, *i.e.* esters, amides, aromatic compounds, olefins, containing the $\text{CH}_2=\text{C}(\text{CH}_3)-$ structure or the $-\text{CH}=\text{C}(\text{CH}_3)-$ structure, where a conjugated situation with another double bond occurs.

The colour reaction is readily applied as a gas chromatographic effluent test but the limits of detection of the effluent tests are considerably greater than those of an acceptable spot test and identification of minor compounds on pyrolysis is not possible with this or other effluent tests.

INTRODUCTION

A colour reaction to distinguish polymers of methyl methacrylate from polyacrylates has been briefly noted by MANO¹. The test as described requires the depolymerisation of approximately 0.5 g of polymer in a tube protected against loss of the volatile degradation products. The monomer was diluted with several volumes of concentrated sulphuric acid and gently heated to obtain a pale yellow coloured solution. To the cooled solution was added half its volume of water and then zinc dust. A blue colour immediately develops if methacrylates are present. This colour can be layered to chloroform, the yellow colour not being extracted. When sodium nitrite replaces zinc the same colour is obtained.

This test has been used with some success with polymers of *n*-alkyl methacrylates which depolymerise substantially to monomer although some anomalous behaviour has been observed, while attempts at using the reaction as a gas chromatographic elution procedure have been less successful.

In this paper the general applicability of this reaction with a variety of unsaturated compounds experienced in polymers has been examined while the limits of detection for use on an effluent test procedure in gas chromatography have been determined.

EXPERIMENTAL

The reaction has been conducted essentially as described by MANO. Pyrolysis was carried out carefully in a long test tube ($6 \times 3/8$ in.) which acts as an air condenser such that possible absorption on filter paper was avoided.

The test was carried out in $2 \times 1/8$ in. micro test tubes using one drop of pyrolysis product and two drops of concentrated nitric acid. Heating was rarely required, a yellow-brown colouration normally being obtained on mixing. Zinc dust was replaced by a crystal of sodium nitrite, which was added to the acidic solution. In many cases a pale green or blue colouration was obtained and layering in two drops of added chloroform was essential to ensure that a positive test was obtained.

Gas chromatography was carried out using an F & M Model 810 R-19-29 Gas Chromatograph employing simultaneous thermal conductivity and flame ionisation detection equipped with a Leeds and Northrup twin-channel 0-1 mV Speedomax Recorder. Pyrolysis was carried out using a Philips Curie Point Pyrolyser. The following operating conditions were used:

Columns: matched each 10 ft. \times 1/4 in. O.D. aluminium packed with 10% methyl silicone polymer SE-30 on 60-80 mesh acid-washed Celite 560.

Injection temperature: 200°.

Carrier gas: helium, inlet pressure 40 p.s.i., flow rate 60 ml/min.

Thermal conductivity detector: maintained at 200° with a bridge current of 200 mA.

Column temperature: isothermal operation at 100°.

RESULTS AND DISCUSSION

While only the *n*-alkyl methacrylate polymers depolymerise to yield substantial yields of monomer the majority of polymers do produce some detectable monomer on degradation of such a large-sized sample. As degradation is necessary the principal studies have been concerned with monomers; many of the commercially available acrylic esters have been examined and the reactions observed are shown in Table I. The reactions of a selection of unsaturated compounds which have structures similar to that of the methacrylate esters are included in Table I.

A strong positive test was observed with all of the methacrylate esters, while conclusive negative results were observed with the acrylate esters and with other monomers not possessing a methyl group on the α -carbon atom.

Several other compounds containing the structure $\text{CH}_2=\text{C}(\text{CH}_3)-$ were examined and each produced a positive result, *i.e.* methacrylamide, α -methylstyrene, isopropenyl acetate, isobutylene, diisobutylene and 2-methyl-1-pentene.

Saturated derivatives of the methacrylate esters, the isobutyrate, *i.e.* methyl isobutyrate, *n*-butyl isobutyrate and isobutyric acid, yield respectively a green colour not extracted by chloroform, a completely negative yellow solution and a blue colour not extracted by chloroform.

Replacement of the α -methyl group of the methacrylate ester by a chain, *i.e.* methyl α -ethylacrylate and methyl α -*n*-butylacrylate resulted in a negative test as did an olefin of similar structure, *i.e.* 2-ethyl-1-butene which produced a blue colour that was not extractable.

TABLE I
COLOUR REACTIONS OF UNSATURATED COMPOUNDS

Compound	Structure	Colour observed with sodium nitrate	Extracted colour	Result
Acrylate	$\text{CH}_2=\text{CH}-\text{COOR}^a$			
Methyl ester		yellow	yellow	neg.
Ethyl ester		yellow	yellow	neg.
Isopropyl ester		yellow	yellow	neg.
<i>n</i> -Propyl ester		yellow	yellow	neg.
<i>n</i> -Butyl ester		yellow	yellow	neg.
Isobutyl ester		yellow	yellow	neg.
2-Ethylhexyl ester		yellow	yellow	neg.
β -Ethoxyethyl ester		yellow	yellow	neg.
Glycidyl ester		yellow	yellow	neg.
2-Cyanoethyl ester		yellow	yellow	neg.
Acrylic acid		yellow	yellow	neg.
Methacrylates	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2=\text{C}-\text{COOR}^a \end{array}$			
Methyl ester		blue	blue	pos.
Ethyl ester		blue	blue	pos.
<i>n</i> -Propyl ester		blue	blue	pos.
<i>n</i> -Butyl ester		blue	blue	pos.
Isobutyl ester		green	blue	pos.
<i>n</i> -Pentyl ester		blue	blue	pos.
<i>n</i> -Hexyl ester		blue	blue	pos.
<i>n</i> -Nonyl ester		blue	blue	pos.
Decyl ester		blue	blue	pos.
Allyl ester		blue	blue	pos.
Hydroxyethyl ester		blue	blue	pos.
Hydroxypropyl ester		blue	blue	pos.
Methacrylic acid		blue	blue (fades)	pos.
Miscellaneous				
Acrylamide	$\text{CH}_2=\text{CH}-\text{CONH}_2$	yellow	yellow	neg.
Methacrylamide	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2=\text{C}-\text{CONH}_2 \end{array}$	blue	blue	pos.
Styrene	$\text{C}_6\text{H}_5-\text{CH}=\text{CH}_2$	yellow	yellow	neg.
α -Methylstyrene	$\begin{array}{c} \text{CH}_3 \\ \\ \text{C}_6\text{H}_5-\text{C}=\text{CH}_2 \end{array}$	green	blue	pos.
Vinyl acetate	$\text{CH}_3\text{COO}-\text{CH}=\text{CH}_2$	yellow	yellow	neg.
Isopropenyl acetate	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{COO}-\text{C}=\text{CH}_2 \end{array}$	green	blue-green	pos.
2-Methyl-1-pentene	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2=\text{C}-(\text{CH}_2)_2-\text{CH}_3 \end{array}$	green	blue	pos.
Methyl isobutyrate	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{CH}-\text{COOCH}_3 \end{array}$	green	yellow	neg.

TABLE I (continued)

Compound	Structure	Colour observed with sodium nitrate	Extracted colour	Result
<i>n</i> -Butyl isobutyrate	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{CH}-\text{COOC}_4\text{H}_9 \end{array}$	yellow	yellow	neg.
Isobutyric acid	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{CH}-\text{COOH} \end{array}$	blue	yellow	neg.
Methyl α -ethylacrylate	$\begin{array}{c} \text{C}_2\text{H}_5 \\ \\ \text{CH}_2=\text{C}-\text{OOCH}_3 \end{array}$	yellow	yellow	neg.
Methyl α -butylacrylate	$\begin{array}{c} \text{C}_4\text{H}_9 \\ \\ \text{CH}_2=\text{C}-\text{COOCH}_3 \end{array}$	yellow	yellow	neg.
4-Methyl-pent-3-en-2-one	$\begin{array}{c} \text{CH}_3 \quad \text{O} \\ \quad \\ \text{CH}_3-\text{C}=\text{CH}-\text{C}-\text{CH}_3 \end{array}$	blue	blue	pos.
2-Ethyl-1-butene	$\begin{array}{c} \text{C}_2\text{H}_5 \\ \\ \text{CH}_2=\text{C}-\text{CH}_2-\text{CH}_3 \end{array}$	blue	yellow	neg.
Ethyl crotonate	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}=\text{CH}-\text{COOC}_2\text{H}_5 \end{array}$	yellow	yellow	neg.
Isoamyl crotonate	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}=\text{CH}-\text{COOC}_5\text{H}_{11} \end{array}$	green	yellow	neg.
3-Methyl-2-butenic acid	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{CH}=\text{C}-\text{CH}_2-\text{COOH} \end{array}$			
6-Methyl-hept-5-en-2-one	$\begin{array}{c} \text{CH}_3 \quad \text{O} \\ \quad \\ \text{CH}_3-\text{C}=\text{CH}-(\text{CH}_2)_2-\text{C}-\text{CH}_3 \end{array}$	yellow	yellow	neg.
Acrylonitrile	$\begin{array}{c} \text{CN} \\ \\ \text{CH}_2=\text{CH} \end{array}$	yellow	yellow	neg.
Divinyl benzene	$\text{CH}_2=\text{CH}-\text{C}_6\text{H}_4-\text{CH}=\text{CH}_2$	yellow	yellow	neg.
Ethyl vinyl ether	$\text{CH}_2=\text{CH}-\text{O}-\text{C}_2\text{H}_5$	yellow	yellow	neg.
Isobutylene	$\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{CH}_2=\text{C} \\ \diagdown \\ \text{CH}_3 \end{array}$	green	green	pos.
Diisobutylene	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{CH}_2=\text{C}-\text{CH}_2-\text{C}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	blue	green	pos.

* Appropriate substituent.

With the methyl group on the β -carbon atom, *i.e.* ethyl and isoamyl crotonate, yellow and green solutions were obtained but the colours were not transferred into chloroform. With a methyl group on each side of the double bond, *i.e.* 3-methyl-2-butenic acid a green colour was observed but was not transferred into chloroform. 6-Methyl-hept-5-en-2-one with two methyl groups on the chain ends results in a yellow solution while with 4-methyl-pent-3-en-2-one a positive result was obtained.

The results indicate that a positive reaction is not restricted to the methacrylate esters but also can be obtained with the other compounds examined that contain the $\text{CH}_2=\text{C}(\text{CH}_3)-$ structure, *i.e.* ester, amide, aromatic compound and olefin. The possible anomaly with 4-methyl-pent-3-en-2-one may be explained by the presence of a conjugated system between the olefinic double bond and the carbonyl group, while with the two similar compounds, *i.e.* 3-methyl-2-butenic acid and 6-methyl-hept-5-en-2-one, one and two methylene groups separate the two double bonds. The crotonates are similar in structure to the anomalous compound in that a conjugated system occurs but these produce negative results. The α -carbon atom of the olefinic double bond with the crotonates is not completely substituted and is apparently of importance as all of the compound examined that produce positive results are of this structure.

The limit of detection as an effluent test was determined firstly by injection of methyl methacrylate monomer into the chromatograph. The effluent collector consisted of an 1/8 in. Swagelok nut screwed on to the exit of the thermal conductivity detector and fitted with a silicone rubber septum through which passed a glass capillary tube. Capillaries made from syringe needles of electroplated steel were unsuitable as minor reaction with the nitric acid reagent produced a green colour. Using the micro tubes as receivers a good positive test was obtained with 0.25 μl while an inconclusive result was obtained with 0.20 μl . Pyrolysis of samples of polymethyl methacrylate and poly-*n*-butyl methacrylate equivalent to 0.25 μl , *i.e.* 250 μg , similarly produced a satisfactory test. To achieve reproducible pyrolysis chromatograms small sample size is essential. The use of approximately 10 μg of acrylic polymers deposited on the ferromagnetic wire by evaporation of a solution has been shown to be very satisfactory² and it is apparent that application of the effluent test with routine pyrolysis with these quantities of sample is not possible. Examination of a larger sample of the pyrolysis residue may be successfully conducted.

Effluent colour reactions for detection of the principal types of compounds have been reported by WALSH AND MERRITT³. The sensitivity, *i.e.* minimum detectable amount, varied between 20 and 100 μg and it is apparent that while effluent tests are often of considerable value, their sensitivity does not approach that of the classical spot tests, where a limit of 5 μg is expected.

REFERENCES

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