Journal of Chromatography, 107 (1975) 393–395

CHROM. 8154

Note

Separation of polysulphides by thin-layer chromatography

R. W. HILEY and A. CAMERON

Lubrication Laboratory, Department of Mechanical Engineering, Imperial College of Science and Technology, London SW7 2BX (Great Britain)

(Received January 6th, 1975)

It has been common practice for many years to add sulphurised olefinic compounds to lubricating oils in order to reduce friction at high temperatures. This sulphurisation process usually involves simple heating of unsaturated material with sulphur, and produces a complex mixture of compounds, most of which are polysulphides[1]. The investigation of such systems requires a technique for separating different polysulphides with the same end groups.

In their recent paper[2] concerning the separation of many classes of sulphur compounds Nakamura and Tamura report only two polysulphides higher than a disulphide. In their only chromatogram showing two polysulphides with the same end group (2,4,5-trichlorophenyl disulphide and trisulphide), these are barely separated. Coates, in an excellent exposition[3] of the uses of thin-layer chromatography (TLC) in the analysis of lubricating oils, has reported the chromatographic separation of commercial polysulphide mixtures. Unfortunately, since it was not his purpose, he made no attempt to characterise the actual compounds involved. When his chromatographic system for sulphur compounds was tried on the dibenzyl polysulphides no significant separation was achieved. A search of other literature has revealed no other separations of polysulphides on the basis of sulphur chainlength by TLC. This paper describes such a separation.

EXPERIMENTAL

The chromatography was conducted on 20 cm × 20 cm glass plates coated with silica gel GF_{254} (Merck, Darmstadt, G.F.R.). The layer thickness was nominally 0.25 mm but was measured as 0.28 mm on a dry layer. The plates were activated for at least 30 min at approximately 60°. Spots were applied in the usual way either in toluene or methanol solution. The amount spotted was approximately 0.1 μmoles. Chromatograms were developed in a simple lined tank, singly, and at room temperature to a line scribed 10 cm from the spotting line. The eluent was, in all cases, carbon disulphide.

The spots were visualised by spraying the entire chromatogram with a 1% solution of palladium(II) chloride in equal volumes of dilute hydrochloric acid and acetone, as suggested by Coates. This revealed the polysulphides and other sulphur-containing compounds in various colours against a pale buff background. On warming the plates for about 30 min the spots all darkened to a grey-brown colour and became much more distinct. Where the compounds had been heated as a solution in hexadecane a 3-ml portion of this solution was shaken with 0.5 ml of methanol and a 5-μl portion of the methanolic extract spotted onto the chromatogram. Using these proportions a sample of approximately 0.1 μmole was again obtained.

The dibenzyl monosulphide, trisulphide and tetrasulphide were all synthesised by one of the authors. The monosulphide was synthesised from toluene-α-thiol and benzyl chloride, via the sodium thioate. The trisulphide and tetrasulphide were synthesised from sulphur dichloride and sulphur monochloride, respectively, by reaction with toluene-α-thiol[4]. All three compounds were recrystallised from ethanol and had melting points in agreement with the literature. The disulphide used was a microanalytical standard grade from Hopkin and Williams (Chadwell Heath, Essex, Great Britain).

RESULTS

Good separation of the four polysulphides was obtained when they were spotted as a mixed solution. In this mixture, the R_F values of the trisulphide and tetrasulphide were raised considerably, however, and the R_F values quoted in Table I are those for separate spots of each compound.

Several other solvent systems were tried before the toxic and unpleasant carbon disulphide. Although it was possible to separate, for example, diphenyl disulphide and dibenzyl disulphide with a mixture of acetic acid and isooctane, no convincing separation of the dibenzyl polysulphides was obtained with this or several other solvent systems. It is felt by the authors that the success of carbon disulphide in this context must be related to its well known excellence as a solvent for polysulphides and sulphur.

It was of significance with regard to lubrication and corrosion to know the effect of heat upon dilute solutions of the higher polysulphides in oils. Thus, 1% solutions of the trisulphide and tetrasulphide in hexadecane were heated for 30 min at 200°. TLC of methanolic extracts from the resultant solutions showed the expected disproportionation. The trisulphide solution gave three spots, corresponding to disulphide, trisulphide and tetrasulphide, respectively. The tetrasulphide produced a large trisulphide spot, a barely visible disulphide spot and two spots at R_F values of

TABLE I

R_F VALUES AND SPOT COLOURS FOR THE DIBENZYL POLYSULPHIDES AND SOME OTHER COMPOUNDS

Compound	*Approximate R_F value × 100*	*Spot colour*
Dibenzyl sulphide	20	light green
Dibenzyl disulphide	35	yellow
Dibenzyl trisulphide	40	yellow-brown
Dibenzyl tetrasulphide	45	brown
Toluene-α-thiol	45	bright yellow
Diphenyl disulphide	70	red-brown
Sulphur	90	very dark grey-brown

0.52 and 0.59 as well as its own spot. The two higher spots have been ascribed to dibenzyl pentasulphide and hexasulphide, respectively, formed by disproportionation of the tetrasulphide. Both compounds have been reported in the literature[5].

DISCUSSION

The study of sulphurisation reactions has been hampered in the past by the lack of suitable, simple methods for analysis of the products. The various forms of chromatography offer an obvious solution to this problem, especially since they can be conducted at room temperature to prevent any disproportionation. TLC has been shown to be capable of resolving polysulphides on the basis of sulphur chainlength and, if resolutions can be improved, it may be possible to use column or preparative-layer chromatography to isolate long-chain polysulphides.

The dibenzyl polysulphides were chosen for study because they are all readily obtainable or easily prepared as crystalline solids. It would be interesting to obtain some long-chain aliphatic polysulphides or perhaps even cyclic polysulphides as pure compounds and to study their behaviour in the same chromatographic system. Few such compounds are available but their preparation should not prove too difficult.

ACKNOWLEDGEMENT

We are much indebted to the Quaker Chemical Corporation, whose sponsorship made this research possible.

REFERENCES

1 L. Bateman and C. G. Moore, in N. Kharasch (Editor), *Organic Sulphur Compounds*, Vol. I, Pergamon, Oxford, 1961, p. 210.
2 H. Nakamura and Z. Tamura, *J. Chromatogr.*, 96 (1974) 211.
3 J. P. Coates, *J. Inst. Petrol., London*, 57 (1971) 209.
4 Y. Minoura, *Nippon Kagaku Zasshi (J. Chem. Soc. Jap., Pure Chem. Sect.)*, 73 (1952) 131.
5 J. Tsurugi and T. Nakabayashi, *J. Org. Chem.*, 24 (1959) 807.