

oxalate (purum, Fluka A.G.) and 2 vol. of pyridine ("Baker analyzed", Reagent, J. T. Baker Chemical Co.). After the chromatographic run, the plate was sprayed with a 3:1:1 mixture of petroleum ether, pyridine and epichlorohydrin (purum, Fluka A.G.) and stored exposed to vapours from the same solvent mixture in a closed chamber for about 1 h, after which it was photographed.

Results

Each keto acid gave rise to one spot when the chromatogram was run as described. The derivatives of oxalacetic and α -ketoglutaric acids migrated at the same rate, but the other components were satisfactorily separated. All the spots remained the same colour, yellow, for some time after they were sprayed. The first to change its colour to red was the derivative of oxalacetic acid, followed by the derivatives of pyruvic and α -ketoisocaproic acids. The chromatogram in Fig. 1 was photographed 1 h after being sprayed; the red-coloured spots are encircled by a continuous line, and the yellow spots by a broken line. All the components turned red within several hours except the derivative of levulinic acid which was the last to change. The structural isomers α -ketoisocaproic acid and α -keto- β -methylvaleric acid, whose dinitrophenylhydrazones are difficult to separate by thin-layer chromatography^{1,2}, can be identified in the form of the methyl esters of their dinitrophenylhydrazones on a thin layer on the basis of their different rates of staining despite the small difference in the R_F values.

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Thin-layer chromatography of tarry deposits resulting from the oxidation of aromatic hydrocarbons

In the study of certain gaseous reactions it is observed that some solid material is deposited on the walls of the reaction vessel and in the cooler parts of the tubing connecting the reactor to the rest of the apparatus. Typical examples of reactions forming these deposits are the pyrolysis of hydrocarbons¹ and their derivatives², and the oxidation of aromatic hydrocarbons³. The deposits generally account for only a small proportion of the reactants, and it is usual to regard them as the products of a relatively unimportant side-reaction.

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There have in the past been one or two attempts to study the nature of these deposits^{4,5}, but this has hitherto been a somewhat difficult task. The purpose of this note is to draw attention to the usefulness of thin-layer chromatography in work of this sort, and to report some preliminary findings on the nature of one type of deposit.

During the course of a detailed investigation, reported elsewhere⁶, of the oxidation of toluene in the gas phase a tarry deposit was deposited in the reactor and connecting tubing. Similar deposits have been observed in the oxidation of other aromatics, e.g. *p*-xylene³.

Small amounts of this material were dissolved in (a) benzene and (b) ethanol.

The solution in benzene exhibited an absorption spectrum suggestive of the presence of naphthalene, and was further examined by thin-layer chromatography on a kieselguhr plate using benzene as a solvent and a running time of 20 min. Three yellow spots were obtained at R_F values of 0.78, 0.58 and 0.34; of these the first and last gave rise to a blue fluorescence under ultra-violet light.

The first spot was scraped off and the material dissolved in ethanol; the absorption spectrum resembled that of dibenzyl, giving a characteristic absorption maximum at 207 $m\mu$.

Control experiments also showed that the yellow colour of this spot could have been due to *p*-benzoquinone which had an identical R_F value, and possibly to 1,4-naphthaquinone the R_F value of which was only slightly smaller.

The solution of the tarry material in ethanol was also examined by the thin-layer technique using ethanol as solvent and a single yellow spot at $R_F = 0.7$ was observed. When viewed under ultra-violet light this spot was seen to be composed of three parts which appeared blue, brown and green respectively. Control experiments showed that the blue fluorescence could have been due to diphenyl or to anthracene (or both) and the green fluorescence to naphthacene.

The general conclusion of these experiments is that the tarry deposits from the toluene-oxygen reaction contain, *inter alia*, quinones and aromatic hydrocarbons of several types. The technique is obviously well-adapted to the study of such deposits and further experiments are planned which, it is hoped, will throw more light on the nature of these materials.

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