219. *The Relation between General Absorption and Residual Affinity: Heterocyclic Compounds.*

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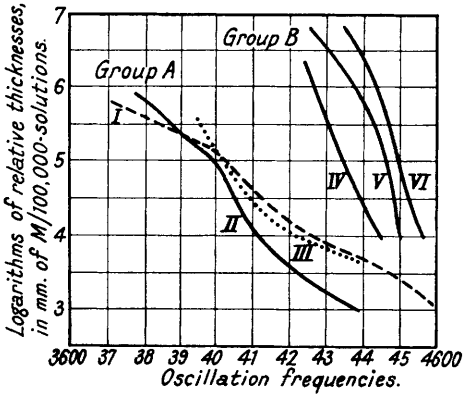
IN earlier work (Gibson, Graham, and Reid, J., 1923, **123**, 874) certain open-chain and cyclic sulphur-containing compounds were examined spectrographically, mainly in relation to the valency and mode of linkage of the sulphur atom. It is now shown that increase in residual affinity as measured by chemical reactivity is accompanied by increased light absorption. The following compounds have been compared spectrographically: pentamethylene sulphide and oxide, 1 : 4- and 1 : 3-dioxan, 1 : 4-thioxan, and 1 : 4-dithian, *cyclo*hexane being included for comparison.

The compounds were prepared by the known methods and carefully purified before use. Alcoholic solutions were used for the spectrographic examination, and an iron arc was the source of radiation.



I. 1 : 4-*Thioxan.* IV. cyclo*Hexane.*
II. 1 : 4-*Dithian.* V. 1 : 4-*Dioxan.*
III. *Pentamethylene sulphide.* VI. 1 : 3-*Dioxan.*

Inspection of the absorption curves (see fig.) shows that they fall into two groups. That marked A shows the greater absorption and contains the curves of the three sulphur compounds. Group B includes the curves of the compounds containing oxygen. This general result is in agreement with the work of Purvis, Jones, and Tasker (J., 1910, **97**, 2287), who found that the thiocarbonates, thio-oxalates, etc., were more absorptive than the corresponding oxygen compounds.

Reference to Group B curves shows that 1 : 4- is more absorptive than 1 : 3-dioxan, and it is more reactive chemically, readily yielding addition compounds with picric acid, mercuric chloride, sulphuric acid, etc., whereas 1 : 3-dioxan, although forming a mercuric chloride compound, gives only an unstable picrate. Pentamethylene oxide, like 1 : 3-dioxan, is chemically inert, and although its absorption is considerable at high concentrations, yet it falls off very rapidly with dilution. It would appear that the compound possessing the greater residual affinity has the greater absorptive power.

From the positions of the curves in Group B, it is seen that the absorptive power of the oxygen-containing compounds is less than that of *cyclo*hexane. The introduction of one or two oxygen atoms into the ring system depresses the absorption.

Over the greater part of the dilution range the curves in Group A lie unchanged in order of decreasing absorption, *viz.*, 1 : 4-dithian, pentamethylene sulphide, 1 : 4-thioxan, *i.e.*, the replacement of a sulphur atom or a methylene group in the ring system by an oxygen atom brings about a decrease in absorption. This is what might be expected from the relative positions of the curves of the oxygen compounds of Group B. From measurements of the rate of addition of bromoacetophenone to the sulphur atoms in these three compounds, Clarke (J., 1912, **101**, 1788) found their reactive powers to be: 1 : 4-dithian very high, pentamethylene sulphide high, 1 : 4-thioxan low. The absorption curves of the compounds are seen to be in this same order.

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