## 222. *Charcoal as a Catalyst of Stereoisomeric Change in Disulphoxides.*

By T. W. J. TAYLOR and W. C. J. COUGHTREY.

CERTAIN charcoals are very active catalysts for the conversion of the less stable of a pair of geometrically isomeric oximes into the more stable. It has been shown that the actual catalyst is the oxygen which is adsorbed on the charcoal in a reactive state (Taylor and Lavington, J., 1934, 980). The probable mechanism of the catalysis is an exchange of oxygen atoms between the charcoal surface and the oxime group; an oxygen atom can take up a position on the side of the carbon–nitrogen double bond opposite to the hydroxyl of the oxime group and, after migration of the hydrogen atom of the hydroxyl to this new oxygen atom, the oxime molecule can leave the surface in the more stable configuration, its original oxygen atom remaining behind. This view receives support from the fact that there is no catalysis of stereoisomeric change in the *O*-methyl ethers of the oximes, the methyl group unlike the hydrogen atom being incapable of migration. There is further support in the analogy with the exchange of the hydrogen isotopes between gaseous deuterium and benzene, which is only possible in the presence of a metallic surface which adsorbs hydrogen in a chemically reactive state (Horiuti, Ogden, and Polanyi, *Trans. Faraday Soc.*, 1934, **30**, 663).

If this view of the mechanism is correct, other cases of exchange phenomena between oxygen adsorbed on charcoal and oxygen combined in simple molecules are to be expected. If the oxygen atom involved in the exchange is one whose position determines which of two possible stereoisomeric configurations the molecule as a whole possesses, the exchange might become manifest by resulting in a change of configuration, as long as that change is accompanied by a diminution in free energy.

Such a case is that of the geometrically isomeric disulphoxides of cyclic systems containing two sulphur atoms, such as thianthren (I and II), in which the isomerism depends solely on the position of oxygen atoms. Either of these isomerides is known to give the same equilibrium mixture of both, if kept for some time above its melting point. The predicted catalysis by charcoal of the rate of this conversion to the mixture of lower energy content has been detected, although the conditions under which it takes place make it unsuitable for quantitative investigation.
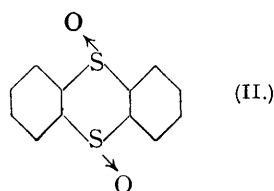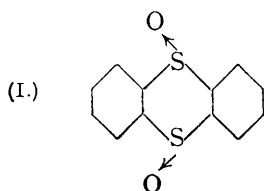
The α- (m. p. 284°) and the β- (m. p. 249°) disulphoxide were prepared by the methods of Fries and Vogt (*Ber.*, 1911, **44**, 756). The equilibrium mixture of the two, obtained from either isomeride if kept above its m. p. for some time, melts somewhat indistinctly, but the final clearing point, 276°, is easily observed. During the conversion of the β-compound into the equilibrium mixture, the m. p. falls from its initial value of 249° to a eutectic, m. p. about 226°, and then rises to 276°.

The occurrence of isomeric change was detected by the m. p.'s of the samples. Specimens of the disulphoxides were subjected to the various treatments described below, and in each case a second sample was subjected to the same treatment with the omission of the charcoal. The m. p.'s of the two products were taken concurrently in the same bath with a short-stem thermometer together with one of the untreated starting material. All the experiments were repeated several times.

No stereoisomeric change could be detected if either isomeride were kept in boiling benzene for 2 hours either in the presence or in the absence of small quantities of blood charcoal. Nitrobenzene was unsuitable for work at higher temperatures, since it seemed to react slightly with the disulphoxides at 180°. Tetralin proved to be a very suitable solvent : either isomeride could be kept in it for 2 hours at 180° and crystallised with unchanged m. p. on cooling.

If the α-disulphoxide is heated for the same period and at the same temperature in tetralin with a little blood charcoal, the sample recovered shows m. p. 270—276° (blank 283—284°) and is the equilibrium mixture of the two disulphoxides. This is shown by analysis (Found : C, 58·2; H, 3·3. Calc. for $C_{12}H_8O_2S_2$: C, 58·1; H, 3·2%), by mixed m. p. with the equilibrium mixture obtained by keeping either isomeride at 290° for a short time, and by the resemblance in solubilities to that authentic equilibrium mixture. Similarly, if the β-disulphoxide is heated under the same conditions with blood charcoal, the m. p. of the recovered sample is 242° (blank 249°). That the catalysis of isomeric change is not homogeneous and is not due to substances extracted from the charcoal by the solvent was shown by heating 0·2 g. of the same sample of blood charcoal with 5·5 g. of tetralin for $2\frac{1}{2}$ hours at 180° and, after removing the charcoal, heating the α-disulphoxide with this tetralin for a further 2 hours; the recovered sulphoxide melted at 284°.

Since no sufficiently accurate method could be found for the quantitative analysis of mixtures of the two disulphoxides, it was impossible to explore the catalysis as was done in the case of α-benzilmonoxime. Points of resemblance between the two cases could, however, be shown. In the charcoal catalysis of the stereoisomeric change of α-benzilmonoxime, blood charcoal is about 100 times as active as sugar charcoal. Two samples, each of 0·4 g., of the α-disulphoxide were heated in the same bath for $2\frac{1}{2}$ hours at 180°, one with 0·15 g. of blood charcoal and the other with the same amount of pure sugar charcoal; the m. p. of the recovered sulphoxide in the first case was 270—276° and in the second 282—283°; hence, as with the oxime, sugar charcoal is relatively inactive as a catalyst. Again, in the case of the oxime the activity of blood charcoal is very much diminished if the charcoal is poisoned by boiling it with an aqueous solution of potassium cyanide. Two samples of the α-disulphoxide, each of 0·4 g., were heated at 180° for $2\frac{1}{2}$ hours in the same bath, the one with 0·2 g. of blood charcoal poisoned by 5 hours' boiling with a concentrated solution of cyanide and then thoroughly washed with water, and the other with the same amount of the same charcoal which had been boiled for the same time with water; the m. p. of the recovered sulphoxide in the first case was 282—283°, showing that hardly any isomeric change had taken place, and in the second case 273—276°.

The close parallelism between the effects observed with the oximes and the sulphoxides is evidence for the view that the essential mechanism of the catalysis is the same in the two cases and is an exchange of oxygen atoms between the active oxygen adsorbed on the charcoal and that combined in the sulphoxide. The only other type of explanation that seems possible is that actual reduction or oxidation is involved. For instance, the following equilibrium might be set up on the charcoal surface, thianthren disulphoxide $\rightleftharpoons$ thianthren + adsorbed oxygen, and this might lead to the conversion of the α-disulphoxide into the more stable equilibrium mixture. Such a mechanism is, however, excluded by the fact that thianthren can be heated to 200° in tetralin with very large amounts of blood charcoal and free access of oxygen without undergoing any observable oxidation to the sulphoxide equilibrium mixture. Similarly, the alternative mechanism depending on the reversibility of the change disulphoxide + adsorbed oxygen $\rightleftharpoons$ disulphone (or sulphoxide–sulphone) is extremely unlikely. The sulphone group is very difficult to reduce; diphenylsulphone distils unchanged from zinc dust, and hence it is improbable that a sulphone would give up its oxygen to charcoal. Further, the disulphone of thianthren is a very sparingly soluble substance (its m. p. is 324°), but if the α-disulphoxide

is boiled with charcoal with free access of oxygen, no disulphone can be found in the product.

The exchange mechanism accounts satisfactorily for the observed facts without introducing these improbable oxidation or reduction processes. It may be compared with the results obtained by Horiuti, Ogden, and Polanyi (*loc. cit.*), which show that exchange of hydrogen atoms takes place between gaseous deuterium and benzene even when the metal catalyst is unable to reduce the benzene to *cyclo*hexane.

THE DYSON PERRINS LABORATORY, OXFORD.   [*Received, March* 12*th,* 1935.]