204. *The Heterogeneous Catalysis of Stereoisomeric Change in Oximes.*

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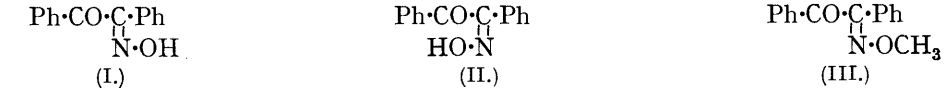
Taylor and Marks (*Nature*, 1930, **125**, 636; J., 1930, 2305) observed that α-benzilmonoxime (I) can be kept in hot alcoholic or benzene solution for long periods without undergoing any stereoisomeric change into the more stable geometrical isomeride β-benzilmonoxime (II), but that addition of a little animal charcoal to the solution causes this change to proceed to completion in a few minutes.



(I.) (II.) (III.)

Later work (Taylor, J., 1931, 2018) showed that this phenomenon was not peculiar to α-benzilmonoxime, since charcoal had the same effect on the less stable form of other oximino-ketones; nor is it peculiar to ketoximes, for β-cinnamaldoxime (m. p. 138·5°) can be recovered unchanged after its solution in benzene has been boiled for 1½ hours, but addition of animal charcoal brings about considerable change into the more stable α-aldoxime during the same period. Meisenheimer has also found the same effect with aldoximes ("Stereochemie," ed. Freudenberg, Leipzig, 1933, p. 988). In all these cases the stereochemical change is in the normal direction, the less stable isomeride being converted into the more stable, which is unaffected by any further treatment with charcoal. The charcoal is acting as a heterogeneous catalyst, and stereoisomeric change must take place more readily when the oxime molecules are adsorbed on its surface than when they are in the crystal lattice or in solution.

It was shown by Taylor and Roberts (J., 1933, 1439) that α-benzilmonoxime can be estimated quantitatively in alcoholic solution in the presence of the isomeric β-oxime by a volumetric method based on the great difference between the two isomerides in the ease of formation of a copper complex. By using this method, we have followed the rate of stereoisomeric change in alcoholic solution in the presence of various charcoals, and from the results have been able to obtain information about the mechanism of the catalysis.

It is first necessary to record two important experimental facts. (1) The phenomenon is peculiar to charcoal and could not be observed with any other adsorbent that was tested; gels of alumina, silica, and ferric oxide, kieselguhr, platinum-black, filter-paper pulp, glass-wool, and pumice under various conditions and after various treatments were all without action, even during long periods of time. Experiment showed that the amount of oxime adsorbed by these agents is small. (2) The catalysis of stereoisomeric change is peculiar to the oximes themselves and is not shared by their closely related *O*-methyl ethers, differing in this respect from the catalysis of the same change by a reagent such as hydrogen chloride, which is effective for both the oxime and its ether.

α-*O*-Methylbenzilmonoxime (III) was prepared by Brady and Perry's method (J., 1925, **127**, 2874). Solutions of the ether in alcohol and benzene were boiled for 1½ hours with the most active samples of blood charcoal; in both cases filtration and removal of the solvent left a residue of the unchanged α-ether. This ether is known to be less stable than the isomeric β-*O*-methyl ether since it is converted into the latter by the action of, *e.g.*, hydrogen chloride (von Auwers and Dittrich, *Ber.*, 1889, **22**, 2001). The absence of isomeric change is not due to the fact that the ether is not adsorbed by the charcoal, for experiment showed that the amount of adsorption from alcoholic solution by blood charcoal is of the same order as that of β-benzilmonoxime.

Preliminary experiments on the rate of change of α-benzilmonoxime into the β-isomeride showed that charcoals of different origin varied widely in their efficiency as catalysts, sugar charcoal, for example, being almost ineffective in comparison with blood charcoal. For the necessary initial work on the order of the reaction, a steam-activated coco-nut charcoal was chosen, and it was found that the rate of change varied with the rate of stirring, the size of the particles of the charcoal and the temperature; further, if these

factors were kept constant, it was almost independent of the concentration of oxime in the solution over the whole range that could be examined.

Materials.—All solvents and reagents were purified by the usual methods. The charcoals used were commercial samples of blood and animal charcoals, steam-activated coco-nut and palm-nut charcoals manufactured for use in respirators, and sugar charcoal prepared by carbonising pure sucrose. Since no two samples of any charcoal are alike (this is particularly true of the first two of the above kinds), a sufficiently large supply of each kind was taken, mixed thoroughly, and used throughout the work.

Method of Measurement.—The reaction vessel was a 250 c.c. wide-necked Pyrex flask mounted in a gas-heated thermostat. Through the rubber bung in the neck of the flask, a small paddle-shaped stirrer passed which was driven by a motor through a reducing gear; the rate of revolution could be altered by a sliding resistance, and was observed by counting the revolutions of the more slowly moving axle of the gear; it is these rates which are quoted below. The rate was checked two or three times during each experiment.

In an experiment, a weighed amount of charcoal was placed in the flask, the stirrer started, and at a noted time a known volume of an alcoholic solution of pure α-benzilmonoxime, of known concentration and kept in the same thermostat, was run on to the charcoal. In the initial experiments the reaction was stopped after a measured interval (5—30 minutes) by running into the flask excess of an aqueous solution of copper acetate; the α-oxime which remained unchanged combined with this to give the insoluble copper complex, which, after standing for ½ hour after dilution with water, was determined in terms of 0·05*N*-sodium thiosulphate solution (Taylor and Roberts, *loc. cit.*). This procedure, however, introduces an error, since the charcoal is present with the copper complex and adsorbs copper acetate from the solution; this copper is not removed from the charcoal surface by repeated washings with hot water or alcohol, but is removed completely by the glacial acetic acid necessary to decompose the oxime–copper complex. The quantity of copper in solution before the final titration is thus greater than that corresponding to the amount of oxime present, since it includes the copper which has been adsorbed by the charcoal; in the case of charcoals of low adsorptive power the error introduced is negligible, but with, *e.g.*, animal charcoal it is serious; 1 g. of this charcoal will adsorb from 0·05*N*-copper acetate solution an amount of copper equivalent to 15·7 c.c. of 0·05*N*-thiosulphate solution. No reagent could be found which would either remove the adsorbed copper from the charcoal without attacking the oxime–copper complex or dissolve the complex without removing the adsorbed copper. It is thus necessary to filter the charcoal from the oxime solution before the addition of the copper acetate in the estimation of the remaining oxime. This procedure, however, introduces an uncertainty in the time of reaction, since filtration is not instantaneous and the separated charcoal must be washed. This difficulty was partly overcome in the determinations of the activities of the various charcoals given later by adopting a standard procedure; 6 mins. after the beginning of the reaction the whole reaction mixture was poured on to a Buchner filter and filtered directly into the required amount of aqueous copper acetate; the filter was then immediately washed with alcohol and water. The time taken by the operation was usually 45 secs. and never exceeded 60 secs.; the total time of reaction is thus referred to as 6—7 mins.

In each experiment the analytical method gives the amount of α-oxime which has not undergone stereoisomeric change, expressed in c.c. of 0·05*N*-thiosulphate; hence the amount of change that has taken place is conveniently taken as the difference between this value and the 0·05*N*-thiosulphate titre of the original α-oxime solution and is shown thus in the results recorded. Since the oxime–copper complex is (Ph·CO·C:NOPh)CuOH, 1 c.c. corresponds to 5×10^{-5} g.-mol. of α-oxime.

Effect of Particle Size.—A sample of the coco-nut charcoal was ground in a mortar and passed through a series of sieves ranging from 60 to 120 meshes to the inch, five samples of different particle size being thus obtained; these are referred to as, *e.g.*, 80—100, which means that the sample passed through the 80- but was retained by the 100-mesh sieve.

With a constant rate of stirring (66 r.p.m.) the amount of change brought about by 0·1000 g. of each sample was measured at 23° :

Grade of charcoal	120	100—120	80—100	60—80	60
Amount of change per min.	0·50	0·34	0·26	0·21	0·11

The results show that the effect of particle size is very great, and that for the middle samples,

which are the better defined, the amount of change is proportional to the mesh number of the retaining sieve.

Effect of the Amount of Charcoal.—With grade 100—120 coco-nut charcoal at 23° with constant rate of stirring (92 r.p.m.) the following results were obtained with different weights of charcoal in 10 c.c. of the same oxime solution :

Charcoal, g.	0·1134	0·2207	0·3329	0·4448
Amount of change in 6—7 mins.	2·8	5·5	7·2	8·9

The results show that within the limits of accuracy of the method the amount of change is proportional to the weight of charcoal taken.

Effect of Temperature and of Rate of Stirring.—Experiment showed that with a constant weight of coco-nut charcoal the amount of change increased with rise of temperature and of rate of stirring. If the latter exceeded 130 r.p.m., the results were erratic because a part of the charcoal tended to be thrown out of the solution; in consequence, lower stirring rates were used throughout. It is difficult to disentangle the two effects of temperature and stirring rate, because at a higher temperature the viscosity is smaller and thus stirring at the same rate does not produce the same effect. The approximate value of the temperature coefficient of the reaction velocity, however, calculated from results at different temperatures with equal stirring rates, is 1·1—1·3, as would be expected for a reaction whose rate is governed by diffusion.

Effect of Concentration of α-Oxime in Solution.—With 0·0184 g. of 80—100 grade coco-nut charcoal at 23° and constant stirring rate (109 r.p.m.), the amount of change in solutions of α-oxime of different concentrations was measured :

Original concn. of oxime, *M*	0·0131	0·0222	0·0383	0·0928
Amount of change per min.	0·28	0·29	0·29	0·31

The amount of change is hardly altered by seven-fold increase in the concentration of α-oxime, and hence the reaction is of zero order. Presumably, at lower concentrations the reaction rate will be affected by the concentration in the solution, but it is impossible to work with more dilute solutions with the method of analysis, which is the only one available.

By these experiments it was established that under the conditions used the reaction is of zero order, and hence in order to compare the catalytic efficiencies of a series of charcoals the correct measure to take is the amount of α-oxime converted into its isomeride by 1 g. of the charcoal under standard conditions of temperature, rate of stirring, and time. The catalytic activities of the charcoals (ground to pass a 120-mesh sieve) were measured as described above at 23° with a stirring rate of 120 r.p.m. for 6—7 mins. With some, it was impossible to obtain accurately reproducible results, partly because of unavoidable inhomogeneity of the samples and partly because of the time error discussed above. Hence the measurements were repeated several times and the mean results are given in Table I.

The most obvious difference between the charcoals which must be connected with their different catalytic activities is the extent to which they adsorb the oxime from solution. Hence a series of measurements was made to enable the catalytic activity to be compared with the adsorbing power. The adsorption of the α-oxime itself by the charcoals cannot be measured because, as the above results indicate, even at room temperature the rate of stereoisomeric change is too high. Hence some other compound must be used for determining the adsorbing power of a charcoal. Benzilic acid was first chosen since it has approximately the same molecular weight as the oxime, but contains a carboxyl group which facilitates its volumetric determination. The adsorption of this acid on blood charcoal, however, is abnormally small (see p. 987), so β-benzilmonoxime, which contains identically the same groups as the α-oxime, was taken as standard substance in all the adsorption measurements.

It was found that none of the charcoals used contained any substance soluble in alcohol. The method of measuring the adsorption was to take a known volume of an alcoholic solution of the β-oxime of known concentration, add to it a known weight of a charcoal, and allow adsorption equilibrium to be established. The mixture was then centrifuged, and from the clear supernatant liquid samples of known volume were removed with a pipette and their

content of β-oxime obtained by evaporation to dryness on the water-bath; all determinations were carried out in duplicate. The adsorbing powers are quoted as the weight of β-oxime adsorbed by 1 g. of the charcoal from a solution of the oxime which was originally 0·05*N*. Strictly, the comparison should be made between the weights adsorbed from solutions which are at the same concentration at adsorption equilibrium, but such determinations take a long time, and errors introduced by the simpler method are not material for the present purpose.

TABLE I.

Charcoal.	Catalytic activity.	Adsorbing power.	Activity after treatment with KCN.
Blood	490 (mean of 3)	0·110	67
Animal	280 (,, 4)	0·071	30
Palm-nut	33 (,, 4)	0·050	—
Coco-nut	33 (,, 10)	0·048	35
Sugar	6·5 (,, 4)	0·010	5

It will be seen from Table I that the charcoals fall into two groups: (1) the " normal " charcoals, comprising the last three, where the activity is simply proportional to the adsorbing power, and (ii) the " abnormal " charcoals, the first two, where the activity is very greatly in excess of that proportional to the adsorbing power; as judged by the first class, blood charcoal should have an activity of 60—70 instead of 490. The abnormal charcoals are those which are known to contain mineral impurities, and the extra activity may be due to these. In consequence, experiments were carried out to find the effect of treatment by chemical reagents on the activity of the abnormal charcoals.

The activity of blood charcoal was found to be somewhat reduced by drying in the steam-oven or over concentrated sulphuric acid; the results obtained after this treatment were irregular, and it is possible that this deactivation is due to a partial cohesion of the particles which alters the extent of the available surface. An effect of roughly the same magnitude was caused by washing with benzene, water, dilute or concentrated hydrochloric acid, or concentrated hydrofluoric acid; in each case, the charcoal was washed free from the reagent by water and dried in the steam-oven. Treatment with concentrated potassium cyanide solution, however, had a very much greater effect (see Table II).

TABLE II.

Blood charcoal, original activity 490.

Treatment.	Observed activities.	Mean.
Drying, 4 hrs. steam-oven	156, 194	175
Conc. HCl	175, 315	245
Conc. HF	233, 169	201
Conc. KCN	98, 42	70

Further experiment showed that the poisoning by potassium cyanide was a slow process, but after 5 hours' boiling of the charcoal with concentrated aqueous potassium cyanide no further diminution in activity occurred. All the charcoals were treated in this fashion, and after being thoroughly washed and dried, their activities were redetermined (see Table I): the " normal " charcoals are unaffected, but the abnormally high activities of blood and animal charcoals have given place to one proportional to their adsorbing powers, within the limits of experimental error.

These results present a close and surprising analogy to those of Warburg and Brefeld (*Biochem. Z.*, 1924, **145**, 461) on the oxidation of amino-acids on charcoal surfaces by oxygen and to those of Rideal and Wright (J., 1926, 1813; 1927, 2323, 3182) and of Wright (*ibid.*, p. 2323) on the similar oxidation of aliphatic acids. In both these cases blood and animal charcoals show an abnormally high efficiency as heterogeneous catalysts which disappears to a large extent after poisoning with potassium cyanide; and these authors have clearly demonstrated that the high activity is due to the iron content of these charcoals.

The same phenomena occur in the catalytic decomposition of hydrogen peroxide by iron salts adsorbed on graphite (Kuhn and Wassermann, *Annalen*, 1933, **503**, 232). It thus appears highly probable that the enhanced activity of blood and animal charcoals

as catalysts for the stereoisomeric change arises from the small quantity of iron which they are known to contain.

Now, Kuhn and Wassermann (*Ber.*, 1928, **61**, 1550) have pointed out that cases such as these must be divided into two classes, *viz.*, those where the iron salt is active when simply adsorbed on the charcoal, as in hydrogen peroxide decomposition, and those where simple adsorption is insufficient and the iron must be in a state which they describe as "Einbettung"; this must be some particular state of chemical combination since, in order to bring it about, the charcoal, as Warburg and Brefeld have shown, must be made from a substance which contains nitrogen, and the charcoal and iron salt must be heated together for some time. Warburg and Brefeld's amino-acid oxidation is an example of the latter class; they found it impossible to endow sugar charcoal with enhanced activity by treatment under any conditions with iron salts, but charcoals made from nitrogenous compounds (Bismarck-brown and hæmin) could be made more active by treating them with ferric chloride, heating to redness, and washing with dilute hydrochloric acid and water. This extra activity was destroyed by treating the charcoal with potassium cyanide.

That the extra activity of blood and animal charcoals in catalysing the stereoisomeric change is due to "bedded-in" iron, and that there is a complete parallel between the catalysis of stereoisomeric change and of oxidation was proved by a series of experiments similar to those of Warburg and Brefeld.

Charcoal from pure sucrose (original activity 6·5) was made into a paste with ferric chloride solution, dried on the water-bath, and heated to redness in a closed crucible; after cooling, it was extracted with boiling *N*-hydrochloric acid, washed free of acid, dried in a steam-oven, and passed through a 120-mesh sieve. Its activity was then 6·6, 4·3, mean 5·5. There is thus no further activation of sugar charcoal by iron.

Charcoal was prepared by carbonising a specimen of pure Bismarck-brown mixed with a little pure potassium chloride. It was extracted with *N*-hydrochloric acid, washed, and dried. It was divided into a number of samples; one was made into a paste with distilled water and then treated as described for the sugar charcoal above, and the others (each weighing 2 g.) were treated in the same manner except that 0·7 c.c. of solutions of various analytically pure metallic salts (1 mg. of metal per c.c.) was used instead of distilled water. The charcoals were finally ground and passed through a 120-mesh sieve. Under the microscope, the particle size seemed fairly regular and about the same as that of ordinary blood charcoal. The catalytic activities of the charcoals were measured, and in some cases the poisoning effect of potassium cyanide. Since the treatment may have altered the adsorbing power of the charcoals, and this factor in itself will alter their catalytic activities, the amount of β-benzilmonoxime adsorbed by some of the charcoals was also measured (see Table III).

TABLE III.

Bismarck-brown charcoal.

Treatment.	Activity.	Mean.	Adsorbing power.	Treatment.	Activity.	Mean.	Adsorbing power.
Water	6·7, 7·4	7·0	0·011	$NiCl_2$	5·1, 7·9	6·5	0·018
,, , then KCN...	5·3, 6·1	5·7	0·011	$CuSO_4$	8·5, 7·8	8·1	—
$FeCl_3$, ...	21·5, 21·9	21·7	0·011	$CoSO_4$	11·2, 11·7	11·5	—
,, , then KCN ...	3·5, 3·5	3·5	0·018	$Mn(OAc)_2$ ...	12·2, 14·2	13·2	—
$CrCl_3$	21·8, 17·7	19·7	—				
,, , then KCN ...	14·4, 10·0	12·5	—				

The results show that the charcoal from Bismarck-brown, if treated with water alone, is identical in both catalytic activity and adsorbing power with charcoal from pure sucrose, but differs from it in that treatment with certain metallic salts endows it with an increased activity while leaving its adsorbing power unchanged. This extra activity is sensitive to potassium cyanide. Since the Bismarck-brown iron-activated charcoal shows a behaviour similar to that of blood and animal charcoals, it appears almost certain that the activity of these charcoals which is in excess of their adsorbing power arises from their iron content.

A point of some importance emerges from the rough comparison of the extra activity

of Bismarck-brown charcoal brought about by the different metals; an exact comparison is impossible since there is no guarantee that the metals are present in the charcoals in equivalent quantities. It will be seen that the most marked increase is caused by iron and chromium, somewhat less by manganese and cobalt, and none by copper and nickel. This suggests that the function of the metal in catalysing the stereoisomeric change is not connected with the formation of co-ordination complexes between the metal and oxime; α-benzilmonoxime forms such complexes very readily with both ferrous iron and copper, but the latter is quite ineffective in activating the charcoal. In general, such an explanation of the action of the metal is improbable, since it is already known that β-benzilmonoxime does not itself combine with metals (Taylor and Ewbank, J., 1926, 2818), but is converted by certain metallic salts into the complex of the α-oxime, a stereochemical change in the reverse direction to that catalysed by the charcoals. The other obvious explanation of the action of the metals in these particular charcoals is that they act in a manner somewhat similar to that in Warburg and Brefeld's experiments, *i.e.*, as oxidation catalysts. Kuhn and Wassermann (*loc. cit.*) have shown clearly that the catalysis of the decomposition of hydrogen peroxide by iron adsorbed on graphite is due to the fact that iron can exist in the ferrous and the ferric state; the essence of the mechanism is a repeated oxidation and reduction of the iron. That something similar is happening here, unlikely as it may seem at first sight, is suggested by the comparison of the metals iron, cobalt, and nickel, the most active being that where the two valency states are most marked, and the inactive one being that whose tervalent derivatives are unknown.

This fact and the whole parallel to oxidation catalysis led us to investigate the effect of freeing the charcoals from the oxygen which, since they had been in contact with air, they must contain.

The charcoals, in a quartz tube, were heated in a stream of washed and dried cylinder hydrogen in an electric furnace to a bright red heat for a measured time. The stream of hydrogen was continued during cooling, after which the tube was closed and the charcoal kept in hydrogen until used. To determine the activity, the charcoal was tipped into a weighing bottle and weighed as rapidly as possible in air. The period of exposure to air at this stage was found, within limits, to have little effect on the measured activity. A few experiments were performed in which the charcoal was heated in a closed tube originally full of air. Since profound changes in catalytic activity were observed, the adsorbing power of certain of the charcoals was redetermined after the treatment.

TABLE IV.

Charcoal.	Original activity.	Activity after heating in H_2.	Activity after heating in closed tube.	Adsorbing power, original.	Adsorbing power, heated in H_2.
Blood	490	20 (5½ hrs.)	29 (5 hrs.)	0·110	0·110
Animal.....	280	15 (7 ,,)	58 (7 ,,)	0·071	—
Coco-nut	33	12 (3 ,,); 13 (13 hrs.)	13 (3 ,,)	0·048	0·050
Sugar	6·5	2 (6 ,,)	—	0·010	—

The results indicate that the cause of the catalytic activity of a charcoal lies in the oxygen which it contains. Heating in hydrogen deactivates all the charcoals, some to an enormous extent, without bringing about any parallel change in their adsorbing power. The charcoals after this treatment show a small activity which is proportional to their adsorbing power. All the extra activity of blood and animal charcoals has disappeared. If the results are simply due to the removal of oxygen, it should be possible to reactivate the deactivated charcoals by restoring oxygen to them. Standing in air at room temperature or at 70° for 24 hours had little effect, but washing thoroughly with water and drying in the steam-oven brought about marked reactivation. A more effective way was to boil the charcoal with a dilute solution of hydrogen peroxide; this caused complete reactivation of blood charcoal and gave a product which, in catalytic activity, adsorbing power, and extent of poisoning by potassium cyanide, was exactly the same as the original charcoal before it was heated in hydrogen (see Table V). Blank experiments showed that hydrogen peroxide itself is incapable of converting the α- into the β-oxime, even when illuminated with ultra-violet light.

TABLE V.

Charcoal.	Original activity.	Poisoned by KCN.	Heated in H_2.	Reactivated by H_2O.	Reactivated by H_2O_2.	Then poisoned by KCN. (H_2O).	Then poisoned by KCN. (H_2O_2).
Blood	490	68	20	63	490	78	63
Animal.....	280	30	15	98	131	30	—
Coco-nut	33	35	12	64	69	—	—
Sugar	6·5	5	1·5	3	3	—	—

The results, and especially those with blood charcoal where the changes in catalytic activity are large and are thus less obscured by the errors of the measurements, confirm the view that the main catalytic activity of all the charcoals is due to the oxygen adsorbed upon them or combined with them. There are two points which are not easy to explain. (i) It was never found possible to cause animal or sugar charcoals which had been deactivated by heating in hydrogen to regain their original activities, as could be done with blood charcoal. (ii) Coco-nut charcoal, on the other hand, after being heated in hydrogen could be easily reactivated to a markedly larger activity than it originally possessed; this behaviour was confirmed several times and seems to be peculiar to this charcoal; it may be connected with its structure, which, being derived from the cellular structure of a plant, is different from that of the other charcoals investigated. The small activities observed in all the charcoals after heating them in hydrogen may be due to the oxygen adsorbed by them during the exposure to the atmosphere which it is impossible to avoid in determining the activity; there may well be a rapid initial stage in oxygen adsorption by a charcoal, followed by a slow approach to saturation which has been accelerated in our experiments with hydrogen peroxide. On the other hand, the possibility remains that there is a true residual activity of a charcoal independent of its oxygen content; this would seem unlikely, and in any case such a residual activity would form only a small fraction (4—5%) of the total activity of the more active charcoals.

The disappearance on heating in hydrogen of the " extra " activity of blood and animal charcoals, that part which, as the above experiments indicate, arises from their iron content, is most probably due to the reduction of the iron to the metallic state. With blood charcoal this extra activity can be restored completely by simple oxidation with hydrogen peroxide, a fact which suggests that the iron is catalytically active when it is present as oxide.

In seeking for an explanation of the main problem, the actual mechanism of the stereoisomeric change, the fact must be borne in mind that the catalysis of stereoisomeric change does not occur in the oxime ethers, but only in the oximes themselves. This makes it very improbable that the catalysis is in essence an interaction between the catalyst and the carbon–nitrogen double bond which diminishes the torsional rigidity of that bond and thus facilitates normal stereoisomeric change. Effects of this kind certainly exist, as was shown by Taylor and Roberts (*loc. cit.*) in the homogeneous catalysis of the same stereoisomeric change by hydrogen chloride; the latter, however, unlike the charcoals, is a catalyst for stereoisomeric change in oxime ethers as well as in the oximes. This consideration rules out any explanation of the main problem such as that molecular oxygen is the catalyst and acts in virtue of its paramagnetic properties. Such an explanation would bring the phenomenon in line, to some extent, with Kuhn's suggestion as to the action of paramagnetic molecules and free atoms in catalysing stereoisomeric change in the parallel case of carbon–carbon double-bond geometrical isomerides (Solvay Report, " Molécules organiques," 1931, p. 361 *et seq.*); but the evidence is against any view of this kind, since there is no reason why the oxime ethers should not be affected.

The true explanation is clearly one which can account for the catalysis occurring in the oximes alone and also for the very close parallel, especially in the effect of small quantities of metals of variable valency, to true oxidation reactions. The most probable explanation is that oxygen is present on the charcoal in a state in which it is able to effect true oxidation reactions, and that it is this same oxygen which is the actual catalyst of the stereoisomeric change. Then, just as in nitrogen-containing charcoals we know that the availability of the oxygen for oxidation reactions is increased by the presence of metals such as iron, so we find that iron will increase the catalytic activity for stereoiso-

meric change of such a charcoal, since this depends simply on the availability of the oxygen. The available or active oxygen does not bring about an oxidation, because the product is the isomeric oxime which is not changed any further. The mechanism of the catalysis is most probably an exchange phenomenon; if an available oxygen atom can become attached to the nitrogen atom of the oxime grouping, it can only do so on the opposite side of the double bond to the hydroxyl group already there. The hydrogen atom of the hydroxyl group could migrate to this new oxygen atom, and the whole molecule leave the surface with the more stable configuration of the β-oxime, the stereoisomeric change having taken place by means of an exchange of oxygen atoms, the one originally on the surface now forming part of the oxime group, and the other, originally in the oxime group, remaining on the surface. The absence of the effect in the oxime ethers is then accounted for by the fact that the migration of the methyl group from one oxygen atom to the other is very unlikely to take place, just as a migrating methyl group is a rare type of tautomerism, so that the exchange of oxygen atoms cannot proceed. The driving force of the whole process is, of course, the lowering of free energy which accompanies the change from the α- to the β-configuration, and it is this factor which prevents the reverse change of the β- into the α-oxime.

Note on the Adsorption of Benzilic Acid (with Miss G. M. PRICE).—As mentioned above, the adsorption of benzilic acid by blood charcoal is abnormally low. The following results were obtained for the amount of acid adsorbed at room temperature by 1 g. of charcoal from an alcoholic solution which was originally 0·0557*M*.

Charcoal.	Benzilic acid, g.-mol. × 10^4.	β-Benzilmonoxime, g.-mol. × 10^4.
Blood	2·52	4·92
Animal	4·50	3·18
Palm-nut	3·54	2·24
Coco-nut	3·86	2·07
Sugar	0·96	0·45

When compared with the corresponding results for β-benzilmonoxime, these figures show that the amount of the acid adsorbed by blood charcoal is less than half that to be expected. This fact was confirmed by measuring the adsorption isothermals at room temperature from alcoholic solution of both the acid and the β-oxime :

Benzilic acid.

G.-mol./l. in solution at equilm.	0·0233	0·0238	0·0266	0·0466	0·0504	0·0523
G.-mol. × 10^4 adsorbed per g. charcoal	0·60	1·44	1·75	2·42	2·50	2·52
G.-mol./l. in solution at equilm.	0·0952	0·0966				
G.-mol. × 10^4 adsorbed per g. charcoal	2·54	2·55				

β-Benzilmonoxime.

G.-mol./l. in solution at equilm.	0·0130	0·0147	0·0178	0·0235	0·0268	0·0293
G.-mol. × 10^4 adsorbed per g. charcoal	2·18	2·40	2·60	2·90	2·91	3·03
G.-mol./l. in solution at equilm.	0·0308	0·0341	0·0373	0·0401	0·0458	
G.-mol. × 10^4 adsorbed per g. charcoal	3·07	3·22	3·26	3·45	3·52	

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THE DYSON PERRINS LABORATORY, OXFORD. [*Received, May 1st*, 1934.]