

LETTERS TO THE EDITORS

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Activation of Metallic Copper by Oxidation and Reduction

THE activation of copper by repeated oxidation and reduction is ascribed by previous authors to an increase in surface area¹, and our experiments have confirmed this conclusion. In the activated state, as measured by the interference colours produced during oxidation, the area is at least five to ten times as great as the measured area.

Copper oxide films on active metal, when reduced by hydrogen at 300° C., gradually lighten in colour as the reaction proceeds, but do not show interference colours. The reduction is evidently not simply a reversal of the process of oxidation. A marked feature of the reduction is an induction period during which the decrease in pressure of hydrogen is proportional to the square of the time. This indicates that metallic nuclei are produced at a number of active points and increase in diameter as the first power of the time. Separate nuclei cannot be seen, so that their number must be considerable. The extent of the growth of these nuclei is limited, probably because the film is finely subdivided by gaps in the material. Before the whole of the oxide is completely converted to metal, a second type of nucleation appears which is visible. These nuclei increase in diameter linearly with time, and this is believed to be due to the recrystallization of small copper nuclei by a process analogous to sintering, and also to those processes observed by Kornfeld² in the recrystallization of stretched aluminium wire. The recrystallization of the copper in a mixture of crystals of metallic copper and oxide may lead to the formation of inclusions of oxide in the resultant metal, and the phenomena observed by Ransley³ during the reduction of oxide inclusions in metallic copper might be expected to occur.

Ransley showed that in the reduction of oxide inclusions in massive copper by hydrogen at 700–800° C., hydrogen diffused through the metal to the oxide, and water was produced at such high pressures that its escape caused cracks and blistering of the surface, producing the well-known embrittlement. A similar blistering has been observed during the activation of copper. Reduction of the inclusions by carbon monoxide did not occur by the same mechanism, since this gas, being insoluble in copper, cannot diffuse to the oxide. The reduction in this case took place, without embrittlement, by the diffusion of oxygen, possibly as ions, from the inclusions to the surface, where it reacted with the carbon monoxide. This difference between the mechanisms of the reactions of carbon monoxide and hydrogen is paralleled by their behaviour in experiments on the activation of copper.

If, after a series of reductions with hydrogen, carbon monoxide is used to reduce copper oxide, the rate for the first reduction is very similar to that with hydrogen. A second reduction following oxidation in the normal manner is, however, very slow and erratic, and cannot be completed at 300° C. in a reasonable time. The oxidation and reduction with hydrogen must be repeated before the carbon monoxide reduction goes smoothly. During the first

reduction with carbon monoxide, the activation produced by hydrogen is very largely destroyed.

In the reduction of the oxide with carbon monoxide, metallic nuclei are formed very rapidly and in large numbers. In general, patches of metallic copper are formed on the surface long before reduction is complete. Under certain conditions, a complete covering of metal is formed on the oxide within a few minutes. The metallic film formed on the surface during the first reduction with carbon monoxide must be very porous, and the reaction continues because gas can diffuse to the oxide down numerous cracks in the metal.

The following sequence of events probably occurs during the reduction and oxidation reactions. During the reduction of the oxide by hydrogen, oxide particles will be enclosed in the metal which is formed. The reduction of these inclusions leads to embrittlement and the formation of a cracked metal film. This, it is suggested, is the process whereby the film is activated. This film expands on oxidation and the cracks are partly healed; but sufficient capillary passages remain to facilitate a subsequent reduction by hydrogen. However, after a carbon monoxide reduction, the metal film is much more compact, because embrittlement of the metal will not have taken place. Hence, on oxidation an oxide film is formed which is more perfect than when hydrogen is used. If a second reduction with carbon monoxide be now attempted, the film, being relatively free from cracks, is impermeable to the reducing gas, and the reaction is brought to a standstill.

These results indicate that there is some specific action by hydrogen which is absent when carbon monoxide is used, and is responsible for the activation of copper. This may be an effect analogous to that causing the embrittlement of massive copper on reduction with hydrogen.

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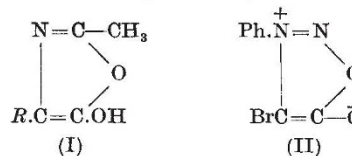
¹ Hinshelwood, *Proc. Roy. Soc., A*, 102, 318 (1922). Constable, *Proc. Roy. Soc., A*, 115, 570 (1927); *A*, 107, 278 (1925).

² Kornfeld, *Phys. Z. Sowjet Union*, 7, 432 (1935); 12, 301 (1937).

³ Ransley, *J. Inst. Metals*, 65 (1939).

Structure of the Sydnones

THE communication from Prof. Wilson Baker and his collaborator¹ prompts us to intimate that we also have concerned ourselves with the sydnones, but from the point of view that their formation might be related to the racemization of α -acetylamino-carboxylic acids by acetic anhydride. Bergmann and Zervas² adduced evidence that this change depended on enolization of the anhydro-compound to I.



Accordingly, we have resolved N-nitroso-N-phenyl alanin by means of brucine, and from the *brucine salt*, m.p. 147–149°, less soluble in acetone or benzene, have prepared the *dextro-rotatory form* of the acid,