

prepared with the hope in mind that it might prove of some interest to those working with zirconium, especially since the complete research will not appear for some months.

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HOWARD S. GABLE

THE ORTHO-PARA-HYDROGEN CONVERSION AT SURFACES

Sir:

Bonhoeffer and Harteck [*Z. physik. Chem.*, 4B, 113 (1929)] found that nickel possessed a negligible activity for the reconversion of para-hydrogen to the ortho-para mixture even at room temperatures. Still less might one expect it to function as an agent for para-hydrogen formation at liquid-air temperatures. The data of Benton and White [THIS JOURNAL, 52, 2325 (1930)] showed adsorption of hydrogen on nickel even at -110° in an activated form [Taylor, THIS JOURNAL, 53, 585 (1931)]. We have, therefore, carried out experiments on para-hydrogen formation with a very active nickel (10% nickel on kieselguhr) showing specific adsorptions for hydrogen of a much higher order of magnitude than the material employed by Benton and White. With this material we have shown it possible to produce the equilibrium concentration of 50% para-hydrogen at liquid-air temperatures as readily as on charcoal. That the surface activity was the important factor was readily shown by experiments with small fragments of nickel wire. With such, there was no measurable para-hydrogen formation.

We have extended these measurements to oxide surfaces since it has been found in adsorption studies [Garner and Kingman, *Nature*, 126, 352 (1930); Taylor and Williamson, THIS JOURNAL, 53, 813 (1931)] that below 0° there is no evidence of an activating adsorption of hydrogen but marked adsorption of molecular hydrogen. Our results on para-hydrogen conversion confirm this. Neither with an active zinc oxide nor with the more active hydrogenation agent zinc-chromium oxide is there any para-hydrogen formed at liquid-air temperatures even after fourteen hours' contact. On the contrary, in the temperature region where, on these surfaces, activated adsorption of hydrogen sets in, namely from 0° upwards, there is an immediate activity in the reconversion of the 50% para-hydrogen to the normal 1:3 mixture. The relative activities in this respect are exactly parallel with the influence of composition on the velocity of activated adsorption. Thus, with zinc-chromium oxide, the reconversion is complete in fifteen minutes' contact time at room temperature. With the less active zinc oxide it is barely perceptible in the same time at the same temperature and is not quite complete at 100° with the same time of con-

tact. We are extending further this interesting method of determining the nature of hydrogen adsorbed on surfaces.

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THE ALLOMERIZATION OF CHLOROPHYLL

Sir:

When an alcoholic solution of chlorophyll is allowed to stand, a process known as allomerization takes place.¹ Allomerized chlorophyll *a* differs from the original material in that the product of hot alkaline hydrolysis is a mixture of unstable chlorins instead of the normal product chlorin *e*. The same unstable chlorins are obtained from unallomerized chlorophyll or the magnesium-free compounds (phaeophytin *a* or methyl phaeophorbide *a*) by saponification with alcoholic alkali at room temperature or below. It has recently been established² that the essential change in both allomerization and low temperature saponification ("phase test" hydrolysis) is the dehydrogenation of the grouping —CHOHCO— to —COCO—. The fate of the two hydrogen atoms was, however, uncertain. We have now been able to show by very simple experiments that the hydrogen atoms are removed by the oxygen of the air. If allomerization or "phase test" saponification is carried out in a modified Warburg apparatus,³ the absorption of oxygen is easily measured. The amount absorbed corresponds to the removal of two hydrogen atoms with the formation of hydrogen peroxide.

The dehydrogenation of chlorophyll *a* or the magnesium-free compounds in the *a* or *b* series may also be brought about by the use of potassium molybdicyanide in acetone-pyridine solution. Two equivalents of reagent are required per mole. Dehydrogenated chlorophyll *a* thus prepared is identical with allomerized chlorophyll (the ultraviolet absorption spectrum is a satisfactory method of distinguishing the dehydro compound from the original material). After removal of the magnesium from allomerized chlorophyll or chlorophyll dehydrogenated with molybdicyanide, the absorption spectrum in the visible and the ultraviolet is identical in both cases and indistinguishable from that of methyl dehydrophaeophorbide. This latter substance we have prepared in quantity by the action of molybdicyanide on methyl phaeophorbide *a*; it yields the unstable chlorins on hot alkaline hydrolysis.

¹ Willstätter and Utzinger, *Ann.*, **382**, 129 (1911).

² Conant, Hyde, Moyer and Dietz, *THIS JOURNAL*, **53**, 359 (1931).

³ Hyde and Scherp, *ibid.*, **52**, 3359 (1930).