

NOTES

A Method for Separating Para-hydrogen from Oxygen and Carbon Monoxide

By E. BERGMANN, L. FARKAS AND L. SANDLER

Para-hydrogen has often been used as a research tool for elucidating reaction mechanisms. In order to analyze the para-ortho ratio in the hydrogen, the hydrogen has to be separated from all gases taking part in, or formed by, the reaction, so that the ortho-para ratio is not changed by this process. In most cases satisfactory separation can be achieved by the use of liquid or solid air which freeze out most of the common gases. In two important cases, however, *viz.*, when oxygen or carbon monoxide is present, liquid hydrogen had to be used for the separation process. Since liquid hydrogen is not always available and its preparation is very expensive, we have tried to substitute a chemical method of separation for the physical one. For this purpose, solutions had to be found which absorb the above gases quantitatively without causing any appreciable para-ortho conversion during the absorption process.

Absorption of Oxygen.—To the quantitative absorption of oxygen a method was adapted which has been devised for the purification of nitrogen by Schlenk,¹ and which is based on the fast and complete reaction of triphenylmethylsodium solution² with gaseous oxygen. As diethyl ether as used by Schlenk and Marcus in their investigations, has a very high vapor pressure and dissolves the grease of the stopcocks, it was replaced by dibutyl ether, having a vapor pressure of a few mm. only at 20°. The solution prepared and filtered in the usual way was evaporated in a stream of pure nitrogen and dibutyl ether added gradually during this process.

The solution actually used was saturated with triphenylmethylsodium and contained an excess of this substance in solid form so as to render possible the uptake of a large amount of oxygen. The solution was kept in a shaking vessel, attached to the high vacuum apparatus by a glass spiral and remained in use for many months without renewal. The diffusion of the gas into the solution can be accelerated by cooling the solution and is completed within less than one minute.

The following two experiments characterize the above solution:

A lock system of 5 cc. capacity was connected through a very narrow capillary tube to a washing bottle containing about 20 cc. of the solution. It was found that when 130 cubic mm. (at S. T. P.) of oxygen passed through the

capillary tube no measurable amount of oxygen (less than 0.005%) could be detected by a McLeod gage on the other side of the washing bottle.

In order to test whether any appreciable ortho-para conversion takes place in presence of the triphenylmethyl sodium solution, para-hydrogen was introduced into the shaking vessel (70 cc. capacity) containing the sodium compound (30 cc.). The half-life-time of the conversion under our conditions was two and one-half hours; thus, the conversion occurring during the short period of oxygen absorption is negligible. The conversion observed is most probably due to the presence of small quantities of free (paramagnetic) triphenylmethyl.

Absorption of Carbon Monoxide.—For the absorption of carbon monoxide the common cuprous oxide-ammonia solution was used. In the same arrangement as used in the case of oxygen, 500 cubic mm. (S. T. P.) of carbon monoxide (at an actual pressure of 70 mm.) were made to pass the capillary tube and again no trace (less than 0.005%) of the gas could be detected on the other side of the washing bottle.

The following experimental arrangement was used in an actual experiment, carried out at low pressure (10^{-2} mm.).³ The gas mixture was collected in a bulb of 700 cc. to which a smaller vessel was attached, containing 40 cc. of the absorbing solution cooled, in order to accelerate the diffusion of the gas, and separated from the larger bulb by a stopcock. The gas mixture (40 cubic mm. at S. T. P.) was collected in the large bulb, the stopcock opened and the absorption vessel shaken for a few hours. A control experiment, carried out with a mixture of 20 cubic mm. of normal hydrogen and 200 cubic mm. of carbon monoxide showed that no carbon monoxide could be detected in a micro-conductivity cell after the process of absorption, indicating that the amount of carbon monoxide was reduced to at least 0.1%.

Under the conditions used, the half-life-time of the ortho-para conversion was found to be one hundred hours, although no special care had been taken to exclude from the cuprous oxide-ammonia solution divalent (paramagnetic) copper compounds which certainly are responsible for the greater part of the conversion observed. In any case the conversion during the period of absorption again is negligible.

It is obvious that the methods described may be useful in experiments with other hydrogen modifications, too, such as ortho-deuterium or mixtures of light and heavy hydrogen and hydrogen deuteride.

(3) Farkas, Hirschberg and Sandler, *THIS JOURNAL*, **61**, 3393 (1939).

DANIEL SIEFF RESEARCH INSTITUTE
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Solvolytic Reactions of Organic Halides

By MICHAEL P. BALFE AND JOSEPH KENYON

While we cannot enter into the discussion of the kinetics of these reactions, which have been de-

(1) Schlenk, Houben-Weyl's "Methoden der organischen Chemie," 1924, Vol. 4, pp. 959, 974.

(2) Schlenk and Marcus, *Ber.*, **47**, 1664 (1914).