An inspection of Table I shows that the deuterium content of the ethane fraction in mixtures of acetone and deutero-biacetyl at room temperatures is less than the amount which might be anticipated from the direct decomposition of the deutero-biacetyl.[18] A plausible explanation of this fact can be found in the homogeneous recombination of methyl and acetyl radicals which is of importance at the lower temperatures but not at the higher. In the presence of acetone, which is also being photochemically decomposed, the concentrations of methyl and acetyl radicals are increased and diffusion to the walls hindered. Since no reaction, such as (3), occurs, there are relatively few deutero-radicals in the presence of a large number of light radicals. Under these conditions radicals containing deuterium (which probably lead to ethane formation at the walls in the case of biacetyl alone at low pressures) may be used up according to reaction (2), and consequently less deutero-ethane would be formed. Reaction (6) may take place to some extent homogeneously, and this may also be of some significance as the acetyl radical concentration is increased.

In connection with the photolysis of biacetyl at room temperature it has been reported previously,[19] and it was observed again in this investigation with deutero-biacetyl that the ratio of the carbon monoxide fraction to the ethane fraction exceeds two. Assuming that methyl and acetyl radicals are present in the photolysis of biacetyl, one of the possible causes of this result might also be the formation of acetone from methyl and acetyl radicals. In this case, the disappearance of some of the molecules of biacetyl would result in the formation of carbon monoxide, but no ethane. Moreover, at the higher temperatures reaction (8) will become increasingly important.

Summary

The near ultraviolet photochemical decomposition of acetone in the presence of about 1% deutero-biacetyl was investigated in the temperature range 25 to 99°. At room temperature practically no deuterium was found in the ethane formed, and no change either in the ethane to carbon monoxide ratio or in the quantum yield of ethane formation was observed when deutero-biacetyl was present. Likewise, the addition of light biacetyl did not alter the quantum yield of carbon monoxide formation.

At a temperature of 80° or above the ethane fraction contains appreciable amounts of deuterium, indicating that at higher temperatures methyl radicals probably attack the deutero-biacetyl molecules.

It was concluded that the reaction $CH_3 + CH_3COCOCH_3 = CH_3COCH_3 + CH_3CO$ is not of importance in accounting for the low quantum yield of the photolysis of acetone.

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[18] As already mentioned, the direct decomposition in the presence of acetone should be less than in the blank. Also, some light biacetyl is formed during the photolysis of acetone at room temperature. However, it is estimated that the average deuterium content of the biacetyl present during a run will be approximately 83%. On this basis about 1.5–2% D might be expected in the ethane.

[19] Kirkbride and Norrish, *Trans. Faraday Soc.*, **27**, 404 (1931).

[CONTRIBUTION FROM THE AVERY LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF NEBRASKA]

The Removal of Oxygen Impurity from Tank Nitrogen by Means of Cobaltous Oxide

BY H. ARMIN PAGEL AND ELDON D. FRANK

LeBlanc and Möbius[1] have shown that pure oxygen at atmospheric pressure and room temperature is rapidly absorbed by cobaltous oxide if the oxide is prepared in high vacuum at comparatively low decomposition temperatures. We have found that the oxygen impurity in tank nitrogen can be removed by passing the latter through a column of cobaltous oxide prepared according to the above conditions.

Preparation of the Oxide.—The Pyrex glass absorption tower, which was used in a vertical position, was made as follows. The bulb containing the cobaltous oxide was 18 cm. long by 2 cm. inside diameter. A 5-mm. inside diameter tube sealed to the lower end of the bulb extended downward about 6 cm. where it was bent at 90 degrees and connected to a three-way stopcock by means of heavy pressure tubing. A plug of Pyrex glass wool just below the seal served to hold the oxide in place. A section of tubing 8 cm. long by 8 mm. inside diameter was sealed to the upper end of the bulb. Twenty-five grams of Baker and Adamson reagent quality, cobaltous carbonate was then introduced through this opening after which a two-way stopcock was sealed on. (In order to recharge the tower it was then merely necessary to break the 8 mm. section to remove the contents. Any adhering oxide was dissolved

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[1] M. LeBlanc and E. Möbius, *Z. physik. Chem.*, **142**, 175 (1929).

with concentrated hydrochloric acid, after which the apparatus was thoroughly rinsed with distilled water and dried.)

Thermal decomposition of the cobaltous carbonate was carried out by placing the charged absorption tower into a "split" type, horizontal bore electric furnace having heating elements 30.5 cm. long by 3.2 cm. bore. The open ends of the furnace were plugged with rock wool to eliminate heat loss. A Cenco-Hyvac pump was connected to the upper stopcock by means of heavy pressure tubing. All rubber connections were wired and painted with varnish to prevent leakage. Before evacuating, it was found necessary to have the charge so distributed that there be some clearance over the entire surface, and that the stopcock be opened very cautiously, otherwise a considerable portion of the charge may be carried into the vacuum line. The evacuation was started at room temperature with the furnace rheostat set in advance to provide a gradual temperature rise from room temperature to 330 to 340° in approximately two and one-half hours. After this temperature was reached the evacuation was continued three and one-half to four hours more to complete the decomposition. The absorption tower was then removed from the furnace and the oxide allowed to cool *in vacuo*. By holding the tower in a horizontal position and slowly rotating about twenty times, the very finely powdered oxide was found to form small round granules ranging from about 0.5 to 1.5 mm. in diameter. The tower was then mounted in a vertical position and cautiously filled with tank nitrogen through the lower stopcock which also served first to sweep any air from the nitrogen line. It was then ready for use. A Hoke-Phoenix pressure regulator in conjunction with a mercury trap was used to control the nitrogen pressure.

Purification of Nitrogen.—The nitrogen was purified at room temperature by passing it up through the absorption tower mounted in the vertical position.

The light olive green color of cobaltous oxide changes to chocolate-brown when oxygen is absorbed; therefore the progressive vertical rise of brown coloration of the cobaltous oxide column was observed as the practical measure of the absorbing capacity of the various lots of oxide prepared. In each case equal volumes of tank nitrogen (known to contain 0.08% oxygen) were passed through the absorption tower at the rate of two liters per hour, and in some cases also at one liter per hour. It was thus shown that the purifying capacity of cobaltous oxide prepared at 330 and 340° was essentially the same, namely, thirty liters of that particular tank nitrogen at the rate of two liters per hour and over sixty liters at the rate of one liter per hour. Decidedly less absorbing capacity was found with the oxide prepared at 320 and 355°. Regardless of the rate of nitrogen flow the charge was considered depleted when the brown coloration had advanced to a position not less than 1 cm. from the top of the charge.

The decreased capacity at the increased rate of nitrogen flow would indicate that under such conditions there was insufficient time for diffusion into the granules and that the coloration was largely on the surface. In two cases air was passed through the absorption tower at the rate of 100 ml. per hour, merely as a test of total absorbing capacity. A capacity of about 1.8 liters of air was found. This indicates that in terms of the tank nitrogen a purifying capacity of over 350 liters might be realized if the nitrogen were passed through very slowly. In all cases the junction between the green and brown areas continued to be extremely sharp and well defined as the coloration ascended. Moisture appeared to have no effect on the absorbing capacity. The reaction color, however, was gray instead of brown.

The complete absorption of the oxygen impurities was shown by the well-known alkaline manganous hydroxide method. All solutions were prepared according to Hand.[2] In these tests the purified nitrogen was bubbled through a column of solution 1.5 cm. in diameter by 8 cm. high, in a specially constructed apparatus which provided air-free conditions. One test was carried out on each of four different lots of cobaltous oxide, as follows: two and one-half liters of nitrogen at the rate of 2.5 liters per hour; 2.5 liters at 6 liters per hour; two runs, 7 liters at 2 liters per hour. A negative test for oxygen was obtained in all cases.

After a three-month interval between observations, it was found that a partially depleted absorption tower had apparently lost none of its absorbing capacity.

Summary

The highly reactive form of cobaltous oxide prepared by the method of LeBlanc and Möbius has been shown to be very effective in removing the oxygen impurity in tank nitrogen. Experimental details and a discussion of the observations and results have been included.

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[2] P. Hand, *J. Chem. Soc.*, **123**, 2573 (1923).