

Later, in a letter, Professor Dhar emphasized the necessity of incident light of wave lengths 2900–3000 Å. and preferred Schryver's test to Schiff's. The writer then irradiated an uncovered beaker containing 300 cc. of 2% NaHCO_3 and colloidal $\text{Fe}(\text{OH})_3$ with a mercury arc lamp. Schryver's and Molisch's tests were negative.

The status of this problem is extraordinarily involved, though it can hardly be doubted that some workers have succeeded in obtaining formaldehyde *in vitro*. Baly⁴ claims that small amounts of thorium oxide markedly affect yields. Accurate quantitative data are required, particularly with varying amounts of impurities which promote or inhibit the reaction. The writer cannot claim, either with sunlight or with the arc lamp, to have duplicated exactly the illumination used by Rao and Dhar. The Indian sunlight may be sufficiently intense in the ultraviolet region that glass containers do not filter out all these rays. With the arc lamp, secondary reactions may occur, *e. g.*, polymerization of formaldehyde to sugars, though the writer found none.

One concludes that no procedure has yet been published whereby conditions for obtaining formaldehyde and carbohydrates *in vitro* can be duplicated in other laboratories.

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GASEOUS PHOTO DECOMPOSITION OF CHLORINE DIOXIDE

Sir:

Qualitative investigations of the photo formation of Cl_2O_6 from ClO_2 have already been made.^{1,2} Bodenstein and Schumacher³ discuss this reaction and arrive at one molecule of Cl_2O_6 per two quanta absorbed, their equations leading to a maximum decrease in volume of one mole per einstein. The absorption spectrum of ClO_2 ⁴ indicates a region of pre-dissociation below 3750 Å. The schemes given by Schumacher for decomposition in this region and the Band region lead to the same decrease in volume per einstein as before.

Preliminary quantitative experiments on the gaseous photo ClO_2 decomposition point to a chain reaction. ClO_2 was prepared by the method used by Bodenstein² and no attempt was made to remove Cl_2 . The gas was contained in a Suprax cell 10 cm. long, fitted with plane ends 5 cm. in diameter. The cell was filled by streaming a small percentage of the

¹ Booth and Bowen, *J. Chem. Soc.*, 510 (1925).

² Bodenstein, Harteck and Padelt, *Z. anorg. Chem.*, **147**, 233 (1925).

³ Bodenstein and Schumacher, *Z. physik. Chem.*, **5B**, 233 (1929).

⁴ Schumacher, *Z. physik. Chem.*, Bodenstein Band, 704 (1931).

gas through in the presence of oxygen, at a total pressure of one atmosphere and at 15°. The reaction was followed by the pressure changes on a sulfuric acid manometer.

The light absorbed was measured with a thermopile-galvanometer system which was calibrated using a filament lamp from the Bureau of Standards and checked by experiments on $\text{Cl}_2\text{-O}_3$ mixtures. On insolation with light of 3650 Å. there was a sharp decrease in pressure which was eventually followed by an almost equally sharp increase in pressure. The decrease in pressure in the first part of the experiment appears to be due to the formation of Cl_2O_6 and its deposition on the walls. It is suggested that the increase in pressure which follows is due to the sensitized decomposition of Cl_2O_6 by Cl atoms.⁵ Using higher concentrations of ClO_2 , larger amounts of Cl_2O_6 accumulate and after-effects of insolation indicate that it may start to decompose at an appreciable rate before all the ClO_2 has decomposed, and furthermore it does not all decompose to $\text{Cl}_2 + \text{O}_2$. One would expect the state of the surface to be an important factor.

The final rise in pressure shows a close resemblance to that obtained with $\text{Cl}_2\text{-O}_3$.⁶ A similar rise is recorded in one experiment⁷ with Cl_2O and since the formation of ClO_2 has been shown to occur in this reaction it is possible that it can also be explained by the final decomposition of Cl_2O_6 , which only occurs when Cl atoms are no longer used up by ClO_2 , Cl_2O and O_3 in the different experiments. Quantitative experiments with 3650 Å. showed an over-all decrease in volume varying between 5 and 23 moles per einstein in the first part of different experiments on the photo decomposition of gaseous ClO_2 , while the end gave increases in volume up to 10 moles per einstein absorbed, indicating that we are probably dealing with a chain reaction.

⁵ Allmand and Spinks, *Chem. News*, **142**, 333 (1931).

⁶ Allmand and Spinks, *J. Chem. Soc.*, 1652 (1931).

⁷ Finkelnburg, Schumacher and Stieger, *Z. physik. Chem.*, **15B**, 153 (1931).

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ALKYLATIONS OF NITRILES IN LIQUID AMMONIA

Sir:

The reaction of phenylacetonitrile which has been communicated by J. A. Nieuwland and L. H. Baldinger [*THIS JOURNAL*, **54**, 828 (1932)] has also been observed by the writer and E. C. Knowles [Knowles, M. S. Dissertation, R. P. I., 1929]. Similar alkylations of nitriles in liquid ammonia have also been reported [Cloke, Anderson, Lachmann and Smith, *THIS JOURNAL*, **53**, 2791 (1931); Knowles and Cloke, "Substituted Phenyl-