COMMUNICATIONS TO THE EDITOR

PHOTOSYNTHESIS IN VITRO

Sir:

Baly[1] originally required a pre-activated catalyst of colloidal nature for the reduction of carbon dioxide to formaldehyde and carbohydrates *in vitro*. Neither Emerson[2] nor Zscheile[3] confirms his results. Later, supporting his catalyst on an aluminated kieselguhr, Baly[4] found pre-activation unnecessary. Bell[5] does not confirm this. Baly[6] has insisted throughout that the catalyst must be alkali-free. Dhar, Rao and Ram,[7] and Rao and Dhar[8] obtain formaldehyde with nickel carbonate and colloidal ferric hydroxide as catalysts in alkaline solution (2% $NaHCO_3$).

In synthesizing formaldehyde there are two essentials: an active catalyst, and light of the proper wave length. Rao and Dhar (Ref. 8, p. 1424) used glass containers, stating that the ultraviolet under such conditions must be of limited effect. Kruyt and van der Spek[9] state that $Fe(OH)_3$ can be negatively charged in a limited range of alkaline concentrations. More alkali precipitates the sol, independently of the concentration of the catalyst. Pure $Fe(OH)_3$ sols appear unstable in 2% $NaHCO_3$. Rao and Dhar's $NiCO_3$ was apparently not colloidal.

The writer prepared catalysts as follows: (a) $Fe(OH_3)$—Krecke's method; (b) $NiCO_3$—(1) triturated $NiCO_3$ (Kahlbaum) washed free from chloride and sulfate with boiling water, (2) by precipitation from the nitrate with $NaHCO_3$, removing the nitrate by dialysis.

The following experiments were performed: (a) 500 cc. of 2% $NaHCO_3$ (Merck's c. p.) with $NiCO_3$ (quantities ranging from 0.2–10 g.); (b) 500 cc. of 2% $NaHCO_3$ with $Fe(OH)_3$ (approximately 0.5 g. added from a stable aqueous sol); (c) 500 cc. of 2% $NaHCO_3$ with $NiCO_3$, 1 g. and 25 cc. of 0.1% dimedone solution.

All were exposed for sixty hours to sunlight. The flasks were periodically shaken, as the catalyst settled out. Tests were made on all for formaldehyde (Schiff's reagent, described by Rao and Dhar) and for carbohydrates (Molisch's reagent). The sediment in experiment (c) was examined for the typical crystals that formaldehyde forms with dimedone. All results were negative.

[1] Baly, *Science*, **68**, 364–365 (1926).
[2] Emerson, *J. Gen. Physiol.*, **13**, 163 (1929).
[3] Zscheile, THIS JOURNAL, **54**, 973 (1932).
[4] Baly, *Nature*, **126**, 666 (1930).
[5] Bell, *Trans. Faraday Soc.*, **27**, 771 (1931).
[6] Baly, "Photochemical Processes," Faraday Soc. April, p. 545 (1931).
[7] Dhar, Rao and Ram, *ibid.*, p. 554.
[8] Rao and Dhar, *J. Phys. Chem.*, **35**, 1418–1432 (1931).
[9] Kruyt and van der Spek, *Kolloid-Z.*, **25**, 1–20 (1919).

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 $Fe(OH)_3$ 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*. Baly[4] 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 Schumacher[3] 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 predissociation 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 Bodenstein[2] 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).