THE PHOTOCHEMICAL FORMATION OF ETHYLENE IODIDE IN SOLUTIONS OF CARBON TETRACHLORIDE

Sir:

Ethylene iodide, which decomposes photochemically when exposed to the 303 and 313 $m\mu$ mercury lines [THIS JOURNAL, **57**, 2411 (1935)] and undergoes an iodine sensitized decomposition at wave lengths of 436 to 579 $m\mu$ [Dickinson and Nies, *ibid.*, **57**, 2382 (1935)], has been found to be formed rapidly when solutions of ethylene and iodine in carbon tetrachloride are exposed to red light. A tungsten lamp with a Corning Filter No. 241 having maximum transmission at a wave length of *ca.* 700 $m\mu$ was used. Solutions containing iodine were thoroughly shaken in an all-glass apparatus at 25° under a constant pressure of ethylene. All air was removed from the system by evacuation while the solution was frozen with a carbon dioxide–alcohol mixture. The rate of disappearance of iodine was determined by light absorption. No measurable dark reaction occurred over periods of thirty-six hours. The rate of the reaction was dependent on the pressure of ethylene and fell off with decreasing concentrations of iodine. Since the efficiency of formation of iodine atoms from excited iodine molecules may be small at λ 700 $m\mu$ (although the falling off in this efficiency with increase in wave length is not as great (Dickinson and Nies, *loc. cit.*) as was formerly thought) the observed photoiodination at 700 $m\mu$ may possibly proceed through the action of excited iodine molecules, whereas the photo-decomposition yields iodine atoms and the sensitized decomposition proceeds through the action of iodine atoms. This mechanism may obtain in the photoiodination of butene-1 by incandescent lamps as reported recently by Forbes and Nelson [THIS JOURNAL, **58**, 182 (1936)].

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AN EXPLANATION OF THE RELATIVELY LARGE CONCENTRATION OF O^{18} IN THE ATMOSPHERE

Sir:

Dole [THIS JOURNAL, **57**, 2731 (1935)] finds in preliminary experiments that water made by combining atmospheric oxygen with hydrogen is 4.6 p. p. m. heavier than water made by combining oxygen from Lake Michigan water with the same hydrogen. This difference in density Dole (private communication) has since revised to 6.0 p. p. m. Morita and Titani [*Bull. Chem. Soc. Japan*, **11**, 36 (1936)] comparing waters made from essentially pure, protium report a difference of 8.0 p. p. m. due to the difference between atmospheric oxygen and water oxygen. We have found in this Laboratory differences of 5.8 and 6.2 p. p. m. in two experiments in which we have compared the densities of protium oxide from atmospheric oxygen with protium oxide from water oxygen. Urey and Greiff [THIS JOURNAL, **57**, 325 (1935)] calculate for the reaction

$$O_2^{16} + 2H_2O^{18} \text{ (1)} = O_2^{18} + 2H_2O^{16} \text{ (1)}$$
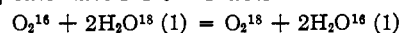
an enrichment factor 1.01 at 0°. This corresponds to a water density difference of not more than 2.0 p. p. m. since the enrichment factor diminishes with increasing temperature.

Part of the difference between these figures may be explained if one assumes that the atmosphere is in equilibrium with the ocean in respect to oxygen isotope concentrations. We find that Lake Michigan water is heavier than Cambridge tap water by 0.4 ± 0.3 p. p. m.—a negligible difference. Gilfillan [*ibid.*, **56**, 406 (1934)] reports that ocean water is 2.3 p. p. m. heavier than Cambridge tap water. We have found a difference of 1.8 p. p. m. [*ibid.*, **56**, 1650 (1934)]. Thomson, Wirth and Utterbeck's results [*ibid.*, **57**, 400 (1935)] indicate that ocean water in general is not more than 1.7 p. p. m. heavier than their fresh water.

Fresh water, being essentially a distillate from the ocean, is presumably lighter because of the greater volatility of water containing the lighter isotopes of hydrogen and oxygen. Although the vapor pressures given by Wahl and Urey [*J. Chem. Phys.*, **3**, 411 (1935)] indicate that more than half of the change in density occurring when normal water is evaporated is due to separation of the oxygen isotopes, yet it is improbable that more than 1 p. p. m. of the density difference between ocean water and fresh water is due to the oxygen isotopes.

It seems improbable that either the density measurements of the theoretical calculations are sufficiently in error to account for the remaining difference of 3 p. p. m. The conclusion to which this leads, namely, that the atmosphere is not in equilibrium with the waters of the globe with respect to its content of oxygen isotopes, is less sur-