SPECIAL ARTICLES

ISOTOPIC COMPOSITION OF PHOTOSYNTHETIC OXYGEN

RECENT interest in the isotopic composition of photosynthetic oxygen[1] has prompted us to submit for publication the results of an investigation begun in 1942, but interrupted by factors related to the war. We believe, however, that the research was carried to the point where the conclusions given here may be considered to be reliable.

Although it has been known since 1935 that atmospheric oxygen contains a greater abundance of O^{18} than the oxygen combined in water,[2] there has as yet been no convincing explanation of the phenomenon. The most attractive theory is that of Greene and Voskuyl[3] in which it is postulated that the isotopic composition of oxygen evolved in the photosynthetic reaction is an average of that in atmospheric carbon dioxide and water. As carbon dioxide which is in equilibrium with water has an enhanced O^{18} content[4] this theory could explain quantitatively the observed enrichment of O^{18} in atmospheric oxygen.

Ruben, Randall, Kamen and Hyde[5] showed by means of mass spectrometric studies of water, oxygen and carbon dioxide involved in the photosynthesis reaction that none of the oxygen atoms in the oxygen came from the carbon dioxide, but entirely from the water present. The validity of this conclusion is discussed by Kamen and Barker.[6] Assuming for the moment its correctness, the theory of Greene and Voskuyl for the greater ratio of O^{18} in air-oxygen than in water-oxygen will have to be abandoned.

However, as the experimental differences are small we decided to repeat the work of Ruben, Randall, Kamen and Hyde using the density method[7] of isotopic analysis because of the greater sensitivity of this method, and using carbon dioxide which had previously been brought into equilibrium with the water of culture medium. We found it necessary to separate the CO_2 from the reaction products as there appeared to be an oxygen isotopic exchange between the carbon dioxide and the water formed in the combination of the photosynthetic oxygen and tank hydrogen. Table 1 gives the final results of the measurements after corrections had been applied for the water used in diluting the sample to give a large enough bulk for accurate measurement and for the isotopic composition of the hydrogen used in reducing the photosynthetic oxygen to water.

As the carbon dioxide contained oxygen from which water having an excess density of 8.2 parts per million could be made, it is evident that the oxygen evolved in photosynthesis more nearly resembles the water oxygen in its isotopic composition than it does the carbon dioxide oxygen.

It is interesting to note that the excess density observed is almost exactly equal to that (1.3 parts per million) predicted by Urey and Greiff[8] for the isotopic exchange equilibrium at 25° C,

$$O_2^{16} + 2\,H_2O^{18}\,(l) \rightleftarrows O_2^{18} + 2\,H_2O^{16}\,(l) \qquad (1).$$

The data of Table 1 verify the conclusion of Ruben, Randall, Kamen and Hyde, while at the same time they disprove the tentative theory of Greene and Voskuyl. However, if there are other mechanisms by which oxygen atoms could exchange randomly and irreversibly between carbon dioxide and oxygen of the atmosphere, the enrichment of O^{18} in the atmosphere could then be accounted for.

TABLE 1

EXCESS DENSITY IN PARTS PER MILLION OF WATER OBTAINED IN THE COMBINATION OF PHOTOSYNTHETIC OXYGEN

Name of plant	Extent of dilution of water sample	Excess density parts per million
Water Plants		
Chlorella Pyrenoidosa	None	0.6
Chlorella Pyrenoidosa	1.5 × original volume	1.3
Chlorella Pyrenoidosa	1.5 × original volume	1.8
Chlorella Pyrenoidosa	1.5 × original volume	1.5
Chlorella Pyrenoidosa	None	0.6
	Average	1.16
Air Plants		
Sunflower	3 × original volume	1.0
Sunflower	7 × original volume	1.1
Coleus	3 × original volume	1.4
	Average	1.17

This work is a contribution from the Chemical Laboratory of Northwestern University.

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[1] See the accompanying paper by M. Kamen and H. A. Barker.

[2] M. Dole, *Jour. Am. Chem. Soc.*, 57: 2731, 1935; *Jour. Chem. Phys.*, 4: 268, 1936; Swartout and Dole, *Jour. Am. Chem. Soc.*, 61: 2025, 1939.

[3] C. H. Greene and R. J. Voskuyl, *Jour. Am. Chem. Soc.*, 58: 693, 1936.

[4] L. A. Webster, M. H. Wahl and H. C. Urey, *Jour. Chem. Phys.*, 3: 129, 1935.

[5] S. Ruben, M. Randall, M. Kamen and J. L. Hyde, *Jour. Am. Chem. Soc.*, 63: 877, 1941.

[6] M. Kamen and H. A. Barker, *loc. cit.*

[7] For experimental details see M. Dole and R. L. Slobod, *Jour. Am. Chem. Soc.*, 62: 471, 1940.

[8] H. C. Urey and L. J. Greiff, *Jour. Am. Chem. Soc.*, 57: 325, 1935.