cal.) and to 298.15°K. (−10 cal.) leads to $\Delta H_{298.15} = -394.1 \pm 0.8$ kcal./mole for the standard heat of combustion. The estimated uncertainty takes into account the impurities in the sample as well as the uncertainties involved in the combustions and calibration. Again, combining with the heat of formation of niobium pentoxide gives $\Delta H_{298.15} = -61.1 \pm 1.0$ kcal./mole as the standard heat of formation of niobium subnitride from the elements.

No previous heat of formation value of niobium subnitride exists. The present result is 4.3 kcal./mole more negative than the heat of formation of NbN (−56.8 ± 0.4 kcal./mole).[3]

Because of uncertainty regarding the composition of the sample, only a tentative value is offered for tantalum subnitride. A tentative value appears justified as no previous value exists. Four combustions gave a mean of 1124.5 ± 2.0 cal./g., after correction for incompletion of combustion (average, 36.8 cal.) and for impurities (39.5 cal.). This corresponds to $\Delta E_{303.15} = -422.7$ kcal./mole for combustion under bomb conditions. Corrections to standard conditions gives $\Delta H_{298.15} = -424.1 \pm 2.9$ kcal./mole. Combining with Humphrey's[2] heat of formation of tantalum pentoxide (−488.8 ± 0.5 kcal./mole) gives $\Delta H_{298.15} = -64.7 \pm 3.0$ kcal./mole as the tentative heat of formation from the elements. This value appears reasonable in magnitude, being 4.7 kcal./mole more netative than the heat of formation of TaN (−60.0 ± 0.6 kcal./mole).[3]

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Tracer Studies on the Mechanism of Combustion of Carbon, Sulfur and Mercuric Sulfide[1]

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The mechanisms of the reactions $C + O_2 \rightarrow CO_2$ and $S + O_2 \rightarrow SO_2$, respectively, were studied with $O^{18}O^{18}$ as tracer. It was concluded that the two oxygen atoms in each CO_2 or SO_2 molecule produced came from different O_2 molecules.

The elucidation of the mechanism of combustion of solid fuels through kinetic studies is often hampered by the difficulty of reproducing the surface conditions. However, valuable information on the mechanism of combustion can sometimes be deduced from the result of tracer studies. For example, when solid carbon, sulfur and mercuric sulfide, respectively, are burned in excess of pure oxygen, the main over-all reactions are

$$C + O_2 \longrightarrow CO_2$$
$$S + O_2 \longrightarrow SO_2$$
$$HgS + O_2 \longrightarrow Hg + SO_2$$

One may ask, "Are the two oxygen atoms in each of the CO_2 or SO_2 molecules produced in the above reactions from the same oxygen molecule or from two different oxygen molecules?" The answer was deduced from the result of the present study with $O^{18}O^{18}$ as tracer.

The principle of our method, which has already been described,[2] is very simple. Suppose oxygen gas is prepared by the thermal decomposition of O^{18}-enriched silver oxide. If the isotopic atom-fraction of O^{18} in this oxygen gas is X, the mole-fraction of $O^{18}O^{18}$ must be approximately equal to X^2. (The small isotope effect due to the difference in zero point energies of light and heavy O-atoms in O_2 may be neglected for the present purpose.) When each mole of this O^{18}-enriched oxygen gas is blended with q moles of ordinary oxygen gas, the isotopic atom fraction of O^{18} and the mole fraction of $O^{18}O^{18}$ in the mixed O_2 become $[X + q(0.0020)]/(1 + q)$ and $[X^2 + q(0.0020)^2]/(1+q)$, respectively, where 0.0020 is the atom fraction of O^{18} in ordinary oxygen gas. The isotopic distribution in this blended oxygen gas is unnatural, because according to natural probabilities if the atom fraction of O^{18} is $[X + q(0.0020)]/(1 + q)$, the mole fraction of $O^{18}O^{18}$ should be approximately $[X + q(0.0020)]^2/(1 + q)^2$. Now if this O^{18}-enriched oxygen gas with unnatural isotopic distribution is used to burn solid carbon, sulfur and mercuric sulfide, respectively, the determination of O^{18}-distribution in the combustion product (CO_2 or SO_2) could lead to the answer of the above question. Thus if both O-atoms in each CO_2 (or SO_2) molecule produced are from the same O_2 molecule, the isotopic mole fraction of $CO^{18}O^{18}$ (or $SO^{18}O^{18}$) should still be approximately equal to $[X^2 + q(0.0020)^2]/(1 + q)$. But if the two O atoms in each CO_2(or SO_2) molecule are from different O_2 molecules, the reaction would involve a reshuffling of O-atoms and yield an isotopic mole fraction of $CO^{18}O^{18}$(or $SO^{18}O^{18}$) approximately equal to $[X + q(0.0020)]^2/(1 + q)^2$ in accordance with natural probabilities.

Experimental

Preparation of the Labeled Oxygen Gas.—Labeled oxygen gas was prepared by thermal decomposition of O^{18}-labeled silver oxide. The labeled silver oxide was precipitated from its saturated solution in O^{18}-enriched water (10.7 atom % in O^{18}) with a concentrated solution of KOH in O^{18}-enriched water. The precipitate, about 1.4 g., was washed with 20 ml. of ordinary water ten times, vacuum dried and then left in a drying oven at 105° for three days. It was stored in a desiccator before use. The oxygen gas so prepared contained 5.8 atom % O^{18} and 0.336 mole % of $O^{18}O^{18}$.

Combustion Experiments.—The combustion was carried out in an enclosed Pyrex tube which was approximately 25 cm. long and had a total inside volume of about 12.5 ml. In each experiment about 120 to 140 mg. of labeled silver oxide prepared above was weighed out and placed at one

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[2] R. C. Jarnagin and J. H. Wang, THIS JOURNAL, 80, 786 (1958).

end of the combustion tube. At the other end of the tube was placed a weighed amount of ordinary silver oxide which is equal to 1.05 times the weight of the labeled silver oxide. The fuel, 12 to 15 mg. of carbon, sulfur or mercuric sulfide, was placed near the center of the tube. The combustion tube then was evacuated slowly. The silver oxides were then decomposed in turn by heating with a micro Bunsen burner. The blended oxygen gas so produced had an unnatural O^{18} distribution as explained above. The combustion was started by gently heating the center portion of the tube, where the fuel was placed, with the micro burner. This caused the fuel to spark, and the combustion was usually finished in a few seconds. The fuels used were: charcoal, Fisher, activated, pulverized; graphite, Fisher, Acheson No. 38, pulverized; mercuric sulfide, Fisher M-195, powder.

In the burning of powdered charcoal or graphite, considerable amount of solid carbon was left unoxidized after each combustion was finished. The gas mixture left after combustion was found by mass spectrometric analysis to contain 1 part of CO, 1 to 8 parts of O_2 and 2 to 16 parts of CO_2. Even in some blank experiments in which powdered charcoal was burnt in 100 to 1000 times excess of ordinary oxygen, 1 mole of CO was produced for every 2 or 3 mole of CO_2 formed. Presumably because of the elongated shape of the combustion tube, the CO molecules formed could rapidly diffuse to colder parts of the tube and thus escape further oxidation by O_2. However, this finding itself cannot prove that the CO_2 molecules were formed through the stepwise oxidation of carbon by molecular oxygen.

Mass-spectrometric Analysis.—The gaseous mixture left after each combustion was analyzed by means of a Consolidated-401 mass-spectrometer for all the isotopic species of O_2, CO and CO_2 (or SO_2). In some experiments the CO_2 was frozen out of the gaseous mixture by means of liquid nitrogen and analyzed separately. The results are consistent with those analyses without this separation step. The calculation of the isotopic mole fractions in the case of O_2 and CO_2 from the mass-spectra was simple because $O^{18}O^{18}$ and $C^{12}O^{18}O^{18}$ were the only molecular species in the mixture which contributed to the $m/e = 36$ and 48 peaks, respectively. (The contribution of $C^{13}O^{17}O^{18}$ to the $m/e = 48$ peak was negligible as compared to that of $C^{12}O^{18}O^{18}$.)

The evaluation of the isotopic mole fraction of $SO^{18}O^{18}$ was more complex because of the presence of 4.2% of S^{34}. Thus the $m/e = 68$ peak was contributed by both $S^{32}O^{18}O^{18}$ and $S^{34}O^{16}O^{18}$. If we use $(\overline{64})$, $(\overline{66})$, $(\overline{68})$ to denote the heights of the peaks for $m/e = 64$, 66, 68, respectively, we have

$$(\overline{66}) = (S^{32}O^{18}O^{16}) + (S^{34}O^{16}O^{16})$$

$$(\overline{68}) = (S^{32}O^{18}O^{18}) + (S^{34}O^{18}O^{16})$$

$$\frac{(\overline{64})}{(S^{34}O^{16}O^{16})} = \frac{95.1}{4.2}$$

$$\frac{(S^{32}O^{18}O^{16})}{(S^{34}O^{18}O^{16})} = \frac{95.1}{4.2}$$

where 95.1 is the % abundance of S^{32} in nature. Solving these equations simultaneously and assuming that $(S^{33}O^{17}O^{18})$ is negligible, we get

$$(S^{32}O^{18}O^{18}) = (\overline{68}) - \frac{4.2}{95.1}\left[(\overline{66}) - \frac{4.2}{95.1}(\overline{64})\right]$$

Thus the mole fraction of $SO^{18}O^{18}$, which includes both $S^{32}O^{18}O^{18}$ and $S^{34}O^{18}O^{18}$, can be computed readily by the usual procedure.

Evidences for the Absence of O^{18}-Exchange between the Gaseous Species.—Since the present method of tracing reaction mechanisms is based on the assumption of the absence of O-atom exchange, it is imperative to verify this assumption experimentally before definite conclusions can be drawn. This was done by analyzing the unreacted oxygen gas left after each combustion experiment for the relative amounts of $O^{15}O^{16}$, $O^{16}O^{18}$ and $O^{18}O^{18}$, respectively. In every case it was found that the mole fraction of $O^{18}O^{18}$ in the unreacted oxygen gas was, within experimental error, equal to that of the original blended oxygen gas of unnatural isotopic distribution. This shows that there was no O-atom exchange between the pairs O_2–O_2, O_2–CO_2, O_2–CO and O_2–SO_2, respectively, under the present experimental conditions.

There was no experimental proof for the absence of O-atom exchange between the pairs SO_2–SO_2 or CO_2–CO_2 under the present experimental conditions. However, by diluting the doubly O^{18}-labeled SO_2 and CO_2 samples with ordinary SO_2 and CO_2 gas, respectively, it was shown that there was no O-atom exchange between the above said pairs in 4 hours at room temperature. It seems unlikely that such O-atom exchange had taken place in the combustion experiments since only a small spot of the combustion tube was heated to a higher temperature for a few seconds in each experiment. Brandner and Urey[3] found no detectable O-atom exchange between CO and CO_2 below 900°. The rate of O-atom exchange between two CO_2 molecules in the absence of water should be even slower from structural considerations.

Results and Discussion

The results of mass spectrometric analysis of the combustion products are listed in Tables I and II.

TABLE I

COMBUSTION OF SOLID CARBON IN OXYGEN GAS

Atom % of O^{18} in the oxygen gas used = 2.93%; mole % of $O^{18}O^{18}$ in the oxygen gas used = 0.164%

	Isotopic mole % of $CO^{18}O^{18}$ produced		
	Calcd.		
Sample	O-atoms in each CO_2 molecule from the same O_2 molecule	O-atoms in each CO_2 molecule from different O_2 molecules	Found by mass-spectrometric analysis
Powdered charcoal	0.164	0.086	0.080
Powdered charcoal	.164	.086	.075
Powdered charcoal	.164	.086	.081
Powdered graphite	.164	.086	.084
Powdered graphite	.164	.086	.087
Powdered graphite	.164	.086	.081

TABLE II

COMBUSTION OF SULFUR AND MERCURIC SULFIDE IN OXYGEN GAS

Atom % of O^{18} in the oxygen gas used = 2.93%; mole % of $O^{18}O^{18}$ in the oxygen gas used = 0.164%

	Isotopic mole % of $SO^{18}O^{18}$ produced		
	Calcd.		
Sample	O-atoms in each SO_2 molecule from the same O_2 molecule	O-atoms in each SO_2 molecule from different O_2 molecules	Found by mass-spectrometric analysis
Powdered sulfur	0.164	0.086	0.086
Powdered sulfur	.164	.086	.089
Powdered sulfur	.164	.086	.083
Powdered sulfur	.164	.086	.081
Powdered HgS	.164	.086	.105
Powdered HgS	.164	.086	.102
Powdered HgS	.164	.086	.097
Powdered HgS	.22[a]	.15	.18
Powdered HgS	.22[a]	.15	.14

[a] The oxygen gas used to burn this sample contained 3.86 atom % of O^{18} and 0.22 mole % of $O^{18}O^{18}$.

The data in Tables I and II show that when powdered charcoal, graphite and sulfur, respectively, are burnt in an atmosphere of pure oxygen, the two O-atoms in each CO_2 or SO_2 molecule are from different O_2 molecules. In the case of the combustion of mercuric sulfide, the present results are inconclusive because of the larger experimental uncertainties.

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(3) J. D. Brandner and H. C. Urey, *J. Chem. Phys.*, **13**, 351 (1945).