Appreciating Oxygen

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In recent years, there has been a popular interest in oxygen as it has become the name of a Broadway play, a new health magazine, a television network, a computer project at MIT, and at least one new book. In spite of this, and because of its availability, its importance as an energy source is commonly overlooked. It is more common to speak of fossil fuels, hydrogen, or carbohydrates as the major energy sources in chemistry and biology but these compounds are some of the most stable organic molecules found in nature. These compounds are made of strong bonds and have little tendency to combine with any other molecules. Indeed, hydrocarbons were known as paraffins because of their low affinity for reaction. However, oxygen is a diradical held together with a bond energy of just 496 kJ mol^{-1} *(1)*. By contrast, the oxygen atom forms two *strong* bonds in each of the combustion products; carbon dioxide (799 kJ mol^{-1}) and water (926 kJ mol^{-1}). As a result, every mole of oxygen that reacts releases, on average, 460 kJ.[1] It is the uniquely weak bonding in the oxygen molecule that makes combustion one of the most exothermic reactions in chemistry. By contrast, the bond strengths of the organic molecules are very similar to the bond strengths of the combustion products. Thus, in a chemical sense, the oxygen molecule is the energy source and the other "fuels" are merely vehicles to allow each oxygen atom to form strong bonds in the combustion products. It is the relative scarcity of compounds to react with the plentiful oxygen that leads to an underestimation of the importance of oxygen.

A striking result of this fact is that the heat of combustion of any organic molecule can be calculated approximately by merely balancing the reaction and determining how many moles of oxygen are reacted when the organic molecule is burned. For example, the oxidation of methane uses two moles of oxygen per mole of methane releasing approximately $2 \times 460 = 920$ kJ mol^{-1} *of methane*. The experimental heat of combustion of methane is 890 kJ mol^{-1} *(2)*. For a mole of glucose, which combines with 6 moles of oxygen to form CO_2 and water, the calculated value is 2760 kJ whereas the experimental value is 2801 kJ mol^{-1} of glucose *(3)*. Therefore the approximate heat of combustion (or partial oxidation) of any organic molecule may be calculated with reasonable accuracy simply by balancing the equation. Of course, one can also calculate the caloric value (Calories per gram) of sucrose or other common foods from this approach. The breadth of these calculations can be seen in Table 1. While these values are not exact, the conceptual value of these calculations should be clear.

The role of oxygen as the energy source is even more obvious in biological systems. The majority of ATP bonds generated in glucose metabolism derive from the oxidation of the hydrogen atoms that are removed from the organic substrates. The aerobic metabolism of a glucose molecule consumes six oxygen molecules and can generate 38 ATP bonds. This should raise the question about the origin of the energy produced in anaerobic processes. With no available oxygen, the anaerobic metabolism of glucose can generate only two molecules of ATP per glucose molecule. The small quantity of energy required for these two ATP bonds comes from rearranging the oxygen atoms of the carbohydrate molecule to generate products with improved resonance structures. Note that no oxygen is consumed in these two *balanced* reactions (Scheme I). The intuition gained from this approach can be very valuable for students.

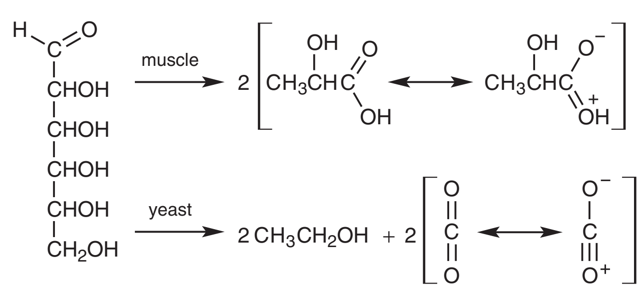
Many textbooks point out that our fossil fuels and carbohydrates derive their chemical energy from the sun. It should be noted that methane is abundant on many planets and moons far from the sun but that free oxygen is found on none of them. There are plenty of oxygen atoms out there but they are all bound up with carbon, hydrogen, metals, silicon, and so forth. While the earthly "fuels" may result from the sun's energy, it is really the oxygen molecules generated during photosynthesis that are trapping the energy of the sun and facilitating life on earth.

Given the great exothermicity of these oxygen reactions, it is surprising that so many organic compounds can survive their

Table 1. Enthalpy Calculated from the Amount of Oxygen Used

Compound	Moles of O_2	$\Delta H°$/(kJ mol^{-1})		Error (%)
		Calc	Exp	
Methane	2.0	–920	–890	3.4
Octane	12.5	–5750	–5452	5.5
Methanol	1.5	–690	–726	5.0
Ethanol	3.0	–1380	–1367	1.0
Benzoic Acid	7.5	–3450	–3227	6.9
Sucrose	12.0	–5520	–5644	2.2
Thiophene	6.0	–2760	–2805	1.6

NOTE: The experimental data is from ref *2*.



Scheme I. Balanced equations of the anaerobic metabolism of glucose.

constant exposure to oxygen. Why don't we experience "spontaneous human combustion"? Put another way, if oxygen is so thermodynamically reactive, why is it so kinetically unreactive? This is the second great property of oxygen. Because its two unpaired electrons have the same spin, the first step of its reaction with any diamagnetic molecule (having paired spins) must generate two radical products with the same spin. These initial radical products are usually high energy reactive intermediates and their formation will be slow. Once the reaction is initiated however, subsequent reactions can easily continue the chain of further reactions that lead to carbon dioxide and water. Antioxidants are compounds that can stop these chains by forming stable radical products.

Thus, oxygen is the unique molecule that stores the energy coming from the sun and provides the energy for life on earth.

Note

1. The value of 460 kJ mol^{-1} is an approximate value averaged from calculations using experimental data of numerous organic compounds. For example, using the data in Table 1, the experimental $\Delta H°$ for octane is −5452 kJ mol^{-1}. Balancing the equation for the combustion of octane requires 12.5 moles of oxygen. Therefore this reaction evolves −5452/12.5 = −436 kJ per mole of oxygen reacted. Methanol needs 1.5 moles of oxygen and evolves 720 kJ of heat, which gives −720/1.5 = −484 kJ per mole of oxygen. The average value is (436 + 484)/2 = 460 kJ per mol of oxygen. Other examples give values closer to 460 kJ but an average value is in this neighborhood.

Literature Cited

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