JOURNAL OF CHEMICAL EDUCATION

Article

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Why Combustions Are Always Exothermic, Yielding About 418 kJ per Mole of O_2

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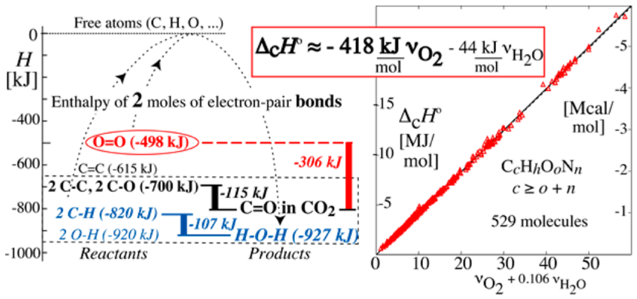
S *Supporting Information*



ABSTRACT: The strongly exothermic nature of reactions between molecular oxygen and all organic molecules as well as many other substances is explained in simple, general terms. The double bond in O_2 is much weaker than other double bonds or pairs of single bonds, and therefore the formation of the stronger bonds in CO_2 and H_2O results in the release of energy, which is given off as heat or increases thermal motion. This explains why fire is hot regardless of fuel composition. The bond energies in the fuel play only a minor role; for example, the total bond energy of CH_4 is nearly the same as that of CO_2. A careful analysis in terms of bond enthalpies, counting double bonds as two bonds to keep the total number of bonds unchanged, gives the heat of combustion close to −418 kJ/mol (i.e., −100 kcal/mol) for each mole of O_2, in good agreement (±3.1%) with data for >500 organic compounds; the heat of condensation of H_2O, −44 kJ/mol, is also included in the analysis. For 268 molecules with ≥ 8 carbon atoms, the standard deviation from the predicted value is even smaller, 2.1%. This enables an instant estimate of the heat of combustion simply from the elemental composition of the fuel, even for a complex mixture or unknown molecular structure, and explains principles of biofuels production. The analysis indicates that O_2, rather than fuels like octane, H_2, ethanol, or glucose, is the crucial "energy-rich" molecule; we briefly explain why O_2 is abundant in air despite its high enthalpy.

KEYWORDS: *First-Year Undergraduate/General, Upper-Division Undergraduate, Physical Chemistry, Misconceptions/Discrepant Events, Thermodynamics, Textbooks/Reference Books*

■ INTRODUCTION

Fire has fascinated humans since time immemorial, and it was one of the four Greek classical elements. In our daily lives, reactions of organic molecules with oxygen from the air are crucial to provide useful energy, via combustion in furnaces and heat engines, while in our bodies, the cellular respiration of O_2 is an indispensable energy source. Why these important reactions are always exothermic, or in lay terms, why fire is hot regardless of the fuel, is a fundamental chemistry question that should be explained in general- and physical-chemistry textbooks. Surprisingly, a simple, valid explanation of the exothermicity of combustion reactions has apparently not been provided,[1−5] not even in textbooks on combustion[6−9] or in the technical literature on heats of combustion.[10−12]

While calculations of heats of combustion to four significant figures for specific combustions reactions, based on tabulated heats of formation, are part of most chemical thermodynamics courses,[1−5] they do not represent any insight since most tabulated heats of formation were in turn determined from measured heats of combustion,[10] which means that the reasoning is cyclical. Empirical multiparameter fits of experimental data to produce an equation predicting the heat of combustion (per gram) from the elemental composition[11,12] also do not provide much understanding. We show below that a straightforward, general explanation of what makes fire hot can be provided in conceptual general-chemistry terms and results in a simple, predictive formula for heats of combustion.

The heats of reaction of a few specific combustion reactions have been explained in terms of bond energies,[5,7] but this has not revealed why all combustions of organic molecules are exothermic. Most bond-energy analyses have remained opaque since double bonds were treated on par with single bonds. We count double bonds as two bonds since the total number of electron-pair bonds is the same in reactants and products; only when the number of bonds remains unchanged is a general analysis per bond meaningful. On this basis, it becomes apparent that combustions are exothermic because of the unusually small bond-dissociation energy of O_2 (per pair of electron-pair bonds). This fact is not obvious in the conventional analyses. The energy of "the O═O bond" in O_2, 498 kJ/mol at 298 K,[13] is even somewhat larger than that of H−H (436 kJ/mol),[13] C−H (ca. 410 kJ/mol),[14−16] or C−C (ca. 350 kJ/mol)[16,17] bonds, while the calculation in terms of enthalpies of formation[1−5] sets the enthalpy of O_2 to zero and thus completely hides the molecule's bond energy. An attempted explanation of the exothermicity of combustions in terms of changes in electronegativity differences of bonded atoms[3] does not stand up to closer scrutiny, as shown below.

DOI: 10.1021/acs.jchemed.5b00333
J. Chem. Educ. XXXX, XXX, XXX−XXX

Our semiquantitative bond-energy analysis indicates, and a rigorous calculation confirms, that the heat of combustion is close to −418 kJ/mol for each mole of O_2 in the combustion reaction, most of which can be attributed to the relatively weak double bond of O_2. We validate our result on >500 heats of combustion reported in the literature[10] and show that our simple formula predicts the heat of combustion accurately to a few percent for molecules without an excess of heteroatoms or for any larger molecules.

As a timely application, we show how insights from this analysis can explain principles of biofuels production. Our analysis strongly suggests that O_2, rather than fuels like H_2, octane, ethanol, or glucose, is the crucial "energy-rich" molecule that makes combustion reactions highly exothermic. Finally, we briefly explain why in spite of its high bond enthalpy, O_2 is abundantly present in our atmosphere.

■ ANALYSIS AND DISCUSSION

Examples of Reactions Involving Fuels of "High Energy Density"

The reactions of octane and ethanol with molecular oxygen

$$C_8H_{18} + 12.5O_2 \rightarrow 8CO_2 + 9H_2O(l) \qquad \Delta_c H^o = -5470.1\ \text{kJ/mol}$$

$$CH_3CH_2OH + 3O_2 \rightarrow 2CO_2 + 3H_2O(l) \qquad \Delta_c H^o = -1366.7\ \text{kJ/mol}$$

are typical examples of strongly exothermic combustions, with heats of reaction exceeding 1 MJ/mol. (In general-chemistry textbooks, "/mol" is usually omitted;[16,18,19] see the discussion in the Supporting Information.) The concept of a "high energy density" of fuels such as H_2, octane, etc. might suggest that the chemical energy of combustion resides in these fuels. However, the reaction of solid carbon ("anthracite coal") and hydrogen ("rocket fuel")

$$C(s) + 2H_2 \rightarrow CH_4 \qquad \Delta_r H^o = -74.8\ \text{kJ/mol}$$

is only weakly exothermic. However, when we add O_2 to these reactants,

$$C(s) + 2H_2 + \mathbf{2O_2} \rightarrow CO_2 + 2H_2O(l) \qquad \Delta_r H^o = -965\ \text{kJ/mol}$$

the reaction is much more exothermic, which indicates that the underlying reason for the exothermicity of combustions must be sought with O_2, which we will confirm below. It is also instructive to consider

$$Si(s) + \mathbf{O_2} \rightarrow SiO_2 \qquad \Delta_r H^o = -911\ \text{kJ/mol}$$

which is strongly exothermic without traditional fuels and without formation of CO_2 or H_2O. This again underlines the crucial role of O_2, as does the comparison of the combustion

$$C_6H_{12}O_6 + \mathbf{6O_2} \rightarrow 6\mathbf{CO_2} + 6H_2O(l) \qquad \Delta_r H^o = -2805\ \text{kJ/mol}$$

with the analogous, less exothermic reaction with H_2

$$C_6H_{12}O_6 + \mathbf{12H_2} \rightarrow 6\mathbf{CH_4} + 6H_2O(l) \qquad \Delta_r H^o = -889\ \text{kJ/mol}$$

The exothermic character of all combustions has occasionally been attributed to the formation of CO_2,[18] maybe based on its negative heat of formation (−393.5 kJ/mol) or its large C=O bond energy of 804 kJ/mol. This explanation is not valid since reactions producing CO_2 without O_2 as a reactant are not particularly exothermic (see the Supporting Information) and since the total bond energies of CO_2 and CH_4 (1608 and 1660 kJ/mol, respectively) are almost the same.

Heat of Reaction in Terms of Bond Energies

Combustions are exothermic if the products have a lower total enthalpy than the reactants. Reactants and products contain the same atoms, and only the bonding is different, so the heat of combustion,[3,19] also known as the enthalpy (change) of combustion,[1] can be calculated from bond-dissociation energies $D_{i,m}$ and stoichiometric coefficients ν_i according to[5]

$$\Delta_c H^o \approx \sum_{i(\text{reactants})} \nu_i \sum_m D_{i,m} - \sum_{i(\text{products})} \nu_i \sum_m D_{i,m} \tag{1}$$

The sum over i in eq 1 includes all reactants and products, while the sum over m takes into account all bonds within reactant or product i. Note that in this bond-energy approach, the separated atoms (rather than the most stable forms of the elements[1−5]) define the zero point of the enthalpy scale. This zero point is shared by reactants and products since they contain the same atoms.

Instead of the bond-dissociation energy, we will consider the closely related bond-*formation* enthalpy of bond m in substance i, per mole, which we define as

$$\bar{H}_{B,i,m} = -D_{i,m} \tag{2}$$

While bond-*dissociation* energies are more positive for stronger bonds, the enthalpy is reduced by bonding, so the bond-*formation* enthalpies used in the following are more negative for stronger bonds. Other details of bond energies and enthalpies are discussed in the Supporting Information.

Most important in our analysis of combustion reactions are the total bond-formation enthalpies of O_2 (−498 kJ/mol), CO_2 [2 × (−804 kJ/mol)], and H_2O (−927 kJ/mol) at 298 K, which have been determined with high accuracy.[13] Enthalpies of C−H, C−C, C−O, and other bonds in the organic fuel[13,17] are necessarily averages with greater uncertainties, but this does not significantly affect our analysis since the well-defined −306 kJ/mol difference between the double-bond enthalpies of O_2 and of C=O in CO_2 is dominant.

Unchanged Number of Electron-Pair Bonds in Combustion Reactions

Our analysis of the enthalpy per bond or pair of bonds will be based on the observation that the total number of bonds does not change during a combustion reaction if double bonds are counted as two bonds and triple bonds as three. Examples are shown in Figure SI1. To confirm this result more generally, we consider the main elements in organic fuels, where C usually has four electron-pair bonds, O has two bonds, and H one bond; this holds before and after the reaction. In this atom-based analysis, every bond is counted exactly twice, so the total number of bonds in reactants containing n_C carbon, n_O oxygen, and n_H hydrogen atoms is given by

$$n_{\text{bonds}} = 4n_C/2 + 2n_O/2 + n_H/2 = 2n_C + n_O + n_H/2 \tag{3}$$

Since the numbers of C, O, and H atoms, n_C, n_O, and n_H, are the same in the reactants and products, according to eq 3, the total numbers of bonds in reactants and products are also the same. This applies even for special cases like C≡O and ionic groups (see the Supporting Information).

Bond Enthalpy Changes for Model Combustion Reactions

According to eqs 1 and 2, we can estimate the heat of reaction in terms of bond-formation enthalpies. To provide some simple examples, Figure 1, panel a shows the enthalpies of a few molecules relevant in combustions in terms of four bonds. Specifically,

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O(l) \quad \Delta_c H^o = -890\ \mathrm{kJ/mol}$$

$$4H_2 + 2O_2 \rightarrow 4H_2O(l) \quad \Delta_c H^o = -1143\ \mathrm{kJ/mol}$$

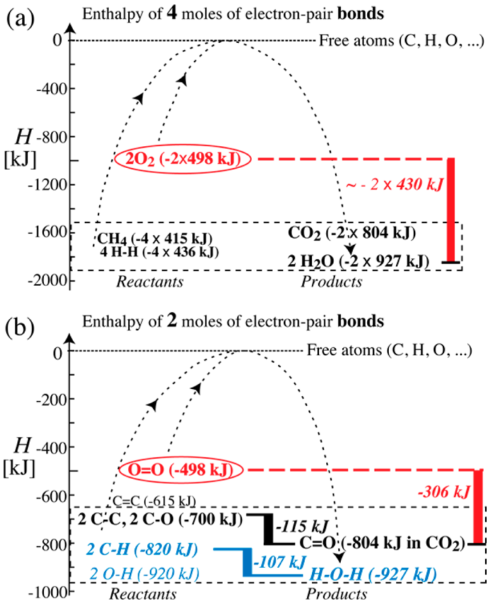


Figure 1. Bond-formation enthalpies of (a) four and (b) two moles of electron-pair bonds in reactants (left) and products (right) relevant for (a) combustion of hydrogen and of methane; (b) combustion of a general C-, H-, and O-containing organic fuel. Note that the bond-formation enthalpy of the double bond in O_2 is distinctly higher (less negative) than that of other pairs of bonds.

There are eight bonds in the reactants and eight in the products, so if the average enthalpy per bond is higher in the reactants, the reaction is exothermic. More conveniently, an analysis of the enthalpy per four bonds shows that CH_4, CO_2, 4 H_2, and 2 H_2O (four bonds each) have similar bond enthalpies, while the enthalpy of 2 O_2 is ~2 × 430 kJ/mol higher than that of H_2O. This excess enthalpy of O_2 is the main reason for consistently negative heats of combustion and their large magnitudes.

Electronegativities and Exothermicity of Combustion?

The bond-enthalpy diagram in Figure 1, panel b reveals that an explanation of combustion exothermicity in terms of Pauling electronegativities[3] is not convincing. According to this theory, the reactant molecules with atoms of similar electronegativities and therefore weak bonds are converted into compounds (CO_2, H_2O) that have strong bonds between atoms of very different electronegativities, and the energy difference is released as heat.[3] In reality, however, C−C and C−O bonds have similar strengths, see Figure 1, panel b, as do the bonds in CH_4 and CO_2, see Figure 1, panel a, in spite of the different electronegativities of C, H, and O. In addition, given that the electronegativity of N is also fairly different from those of C and H,[3] this theory would also predict reactions of the type 6 CH_4 + 7 N_2 → 8 NH_3 + 2 C_3N_3 to be exothermic, while in reality they are endothermic ($\Delta_r H^o$ = +426 kJ/mol for the given reaction: natural gas does not react with the nitrogen in air; also see Figure SI2 for relevant bond enthalpies).

General Heat of Combustion Analysis

By applying our bond-enthalpy analysis to the combustion of a general organic compound containing C, H, and O,

$$C_cH_hO_o + \nu_{O_2}O_2 \rightarrow \nu_{CO_2}CO_2 + \nu_{H_2O}H_2O \tag{4}$$

we can derive a simple relation between $\Delta_c H^o$ and the stoichiometric coefficient ν_{O_2}, as shown in eqs S1−S10 in the Supporting Information. The gist of the calculation can be understood based on Figure 1, panel b, which shows bond-formation enthalpies of double bonds in O_2 and C═O of CO_2 as well as of two single bonds in H_2O and in organic fuels.

First, we note that for every two C−H bonds, one molecule of H_2O (with two O−H bonds) is formed, with ΔH^o of about −107 kJ/mol, see Figure 1, panel b. Thus, we can account for the number of bonds in H_2O without involving bonds in O_2. As a result, each bond in O_2 can be matched by a bond in CO_2 (see eq S4 in the Supporting Information); the conversion of O═O to a C═O bond in CO_2 is accompanied by an enthalpy change of −306 kJ/mol, which is the dominant contribution to the heat of combustion. In addition, one C═C, two C−C, or two C−O bonds of the fuel are also converted to a double bond in CO_2, with ΔH^o of about −115 kJ/mol.

Next, we exploit that the number of all bonds in a hydrocarbon fuel equals the number of O_2 molecules (eq S9). In the products, every bond of O is half shared with C (in CO_2) or H (in H_2O). Thus, the reductions in enthalpy from two C−H bonds to H_2O (−107 kJ/mol) and from two bonds not involving H to C═O in CO_2 (−115 kJ/mol), see Figure 1, panel b, average to about −111 kJ/mol for each mole of O_2, which adds to the −306 kJ/mol for each mole of O_2 resulting from the conversion to CO_2. Together, this gives −417 kJ/mol for each mole of O_2, that is,

$$\Delta_c H^o \approx (-417\ \mathrm{kJ/mol})\nu_{O_2} \tag{5}$$

This is derived more rigorously in the Supporting Information. The analysis indicates that of the numerical factor in eq 5, one can attribute −306 kJ/mol, that is, about $^3/_4$ of the heat of combustion, to the unusually high bond-formation enthalpy (i.e., weak bonds) of O_2, see Figure 1, panel b, while about −111 kJ/mol is due to the lower bond-formation enthalpies of H_2O and CO_2 relative to H- and C-containing reactants, respectively. Eq 5 implies that about 417 kJ of heat is released per mole of O_2 consumed in a combustion reaction, as indicated in the title of the paper.

Heat of Condensation of H_2O

In physical chemistry, the heat of combustion value is usually based on reaction to $H_2O(l)$, the state of H_2O at standard conditions (298 K and 1 bar).[1−5] The conversion from $H_2O(g)$ to $H_2O(l)$ results in an enthalpy change of −44 kJ/mol, the heat of condensation, due to H-bond formation between H_2O molecules. Thus, the prediction of the heat of combustion should include a simple second term from H_2O condensation:

$$\Delta_c H^o \approx (-417\nu_{O_2} - 44\nu_{H_2O(l)})\ \mathrm{kJ/mol} \tag{6}$$

This corresponds to the "higher heating value" of the fuel, while eq 5 gives the "lower heating value".[7]

Heat of Combustion from Elemental Composition

The stoichiometric coefficients in the combustion reaction 4 are related to the elemental composition numbers c, h, o, and n of the fuel, $C_cH_hO_oN_n$, according to[10]

$$\nu_{CO_2} = c = n_C, \qquad \nu_{H_2O} = h/2 = n_H/2 \tag{7}$$

$$\nu_{O_2} = (c + h/4 - o/2) = \nu_{CO_2} + \nu_{H_2O}/2 - o/2 \tag{8}$$

Thus, we can rewrite eq 6 purely in terms of fuel composition as

$$\begin{aligned}\Delta_c H^o &\approx -417\ \text{kJ/mol} \times (\nu_{O_2} + 0.106\nu_{H_2O(l)}) \\ &= -417\ \text{kJ/mol} \times (c + 0.3h - 0.5o)\end{aligned} \tag{9}$$

The corresponding lower heating value, eq 5, is −417 kJ/mol ($c + h/4 - o/2$). In the following, we will show that eq 9 predicts most heats of combustion with an error of only a few percent. Note that eq 9 enables the prediction of the heat of combustion of complex fuel mixtures, such as gasoline, C_8H_{15}, simply from their elemental composition, while previous approaches for calculating heats of combustion require knowledge of the molecular structures.[6−9]

Comparison with Experimental Data

Figure 2, panel a compares our simple predictions of $\Delta_c H^o$ according to eq 9 (dashed line) with experimental heats of combustion compiled by Domalski,[10] plotted as a function of (ν_{O_2} + 0.106 $\nu_{H_2O(l)}$), for over 500 compounds whose heteroatoms do not exceed the carbon atoms in number (i.e., $c \geq n + o$). The data[10] include linear and cyclic aliphatic hydrocarbons, aromatics, alcohols, carbohydrates, linear and cyclic ethers, aldehydes, ketones, aliphatic, unsaturated, and aromatic acids, esters, steroids, lactones, amines, amides, amino acids, N-containing heterocycles, and porphyrines. The plot shows the predicted linear relation between $\Delta_c H^o$ and (ν_{O_2} + 0.106 $\nu_{H_2O(l)}$) with a slope of −418 kJ/mol (solid line), that is,

$$\begin{aligned}\Delta_c H^o &\approx -418\ \text{kJ/mol} \times (\nu_{O_2} + 0.106\nu_{H_2O(l)}) \\ &= -418\ \text{kJ/mol} \times (c + 0.3h - 0.5o)\end{aligned} \tag{10}$$

which agrees within 0.3% with the predicted −417 kJ/mol (dashed line) of eq 9.

The quality of the predictions can be further quantified in terms of the ratios of the measured and predicted (from eq 9) heats of combustion, $(\Delta_c H^o)/(\Delta_c H^o)_{pred}$. Figure 2, panel b displays the histogram of the distribution of that ratio for all 663 molecules[10] (except those containing nitrates), shown as open bars, and for 529 molecules not dominated by heteroatoms, that is, with $c \geq n + o$, plotted as filled bars. The ratios for the latter in particular are narrowly clustered, with an average at around 1.002, corresponding to the prefactor of −418 kJ/mol in eq 10, and a standard deviation from the mean of 3.1%. For larger molecules, the uncertainty is even smaller, for example, 2.1% for molecules with eight or more carbon atoms, based on 268 entries in Domalski's database,[10] with an average prefactor of −416 kJ/mol, again close to the predicted −417 kJ/mol of eq 9. This validates our analysis and makes it attractive for practical applications to complex molecules where experimental data may not be available or to fuels where only the elemental composition is known.

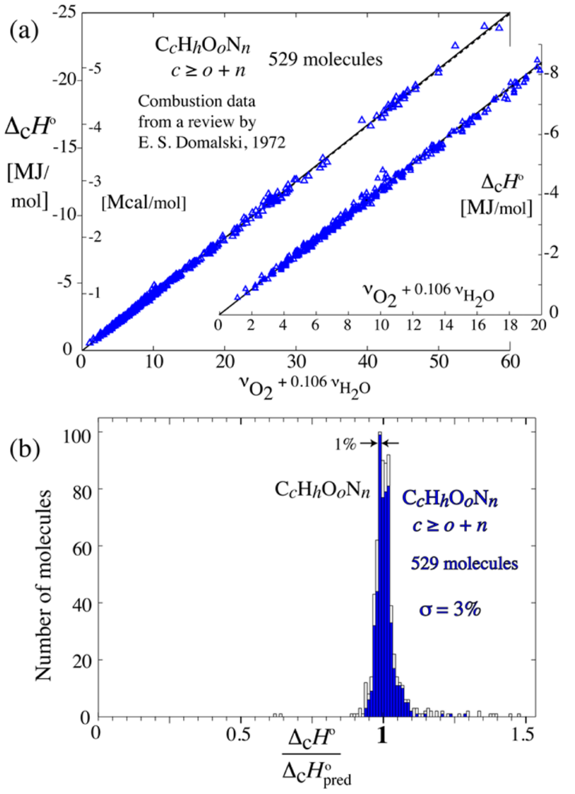


Figure 2. (a) Heats of combustion plotted versus (ν_{O_2} + 0.106 $\nu_{H_2O(l)}$) for 529 molecules[10] not dominated by heteroatoms ($c \geq o + n$). Dashed line, theoretical prediction; solid line, best linear fit (see text). Five data points with larger heats of combustion are not shown but are also close to the theoretical prediction. The inset on the right shows data for smaller molecules with higher resolution. (b) Distribution of the ratio of measured and predicted heats of combustion. Open bars, all uncharged molecules in ref 10; filled bars, molecules not dominated by heteroatoms. A corresponding analysis only in terms of the number of carbon atoms in the fuel, shown in Figure S13, gives less good agreement with the experimental values.

Most of the outliers with >10% deviation in Figure 2, panel b are low-molar-mass compounds with small heats of combustion affected by special features such a triple bonds or ionic interactions. These are discussed in the Supporting Information together with the effects of nitrogen and sulfur. For the combustion of ammonia, the prediction by eq 10 is accurate within 1%. Aromatic stabilization actually improves the agreement with our prediction since it moves C═C bonds to lower enthalpy, closer to pairs of C−C bonds (see Figure 1b); for benzene, the prediction by eq 10 is accurate to within 0.2% (−3273 vs −3268 kJ/mol).

Removal of Oxygen Atoms in Biofuel Production

Oxygen or nitrogen atoms in a fuel reduce the energy density of the fuel since unlike C or H, they do not react with O_2 and thus do not increase the number of O_2 molecules in the combustion reaction. While N is only "dead weight" since the coefficient n of nitrogen does not show up in our eq 10, the presence of oxygen in the fuel actually *reduces* the magnitude of the heat of combustion by (418 kJ/mol) o/2 in eq 10. For instance, glucose, $C_6H_{12}O_6$, has only 72% of the molar heat of combustion of cyclohexane, C_6H_{12}.[10] Since glucose has a 2.14-times larger molar mass than cyclohexane, the heat of combustion per mass of glucose is only $^1/_3$ of that of cyclohexane. This doubly undesirable effect of oxygen in the fuel on the combustion energy density is an important impetus for the removal of oxygen atoms in the production of biofuels such as ethanol or butanol from sugars such as glucose. Because of its oxygen atom, even ethanol still has a 15% smaller heat of combustion than ethane (−1366.7 vs −1558.3 kJ/mol,[10] respectively); per mass, its heat of combustion is only 62% of that of octane/gasoline (−29.7 vs −48 MJ/kg, respectively).

Further, our analysis reveals why oxygen atoms cannot be removed from sugars as O_2: the high enthalpy of O_2, see Figure 1, would require an excessive energy input. Instead, in anaerobic fermentation or pyrolysis processes, some feedstock carbon or hydrogen is sacrificed as CO_2 or H_2O,[20] which is energetically favorable according to Figure 1, panel b.

"Energy-Rich" Molecules

Combustion fuels such as octane, ethanol, or hydrogen are commonly regarded as molecules of high energy, which is sometimes summarized as the concept that a more reduced molecule or carbon atom has a higher energy.[21] However, this is misleading since the total bond enthalpy of CH_4 is actually slightly lower than that of CO_2, see Figure 1, panel a, and the listed fuels cannot give off significant energy in the absence of O_2 or F_2. Therefore, instead of referring to the "energy density" of such fuels, one should use the term "combustion-energy density". Similarly, it is inconsistent for biochemistry textbooks to define the energy content of molecules in terms of bond energies and then refer to "energy-rich products such as starch and sucrose"[20] without mentioning the more energy-rich O_2 molecule. The analysis in Figure 1 clearly identifies O_2 as a particularly "energy-rich" molecule, crucial for making combustions strongly exothermic regardless of the composition of the organic fuel.

Our treatment based on bond enthalpies provides simple, general explanations for various experimental observations. For instance, the diagram in Figure 1, panel b shows that molecules with C−C, H−H, and C−H bonds have rather similar enthalpies and thus readily explains why reactions between "fuels of high energy density" such as C and H_2 are in fact not strongly exothermic without O_2. It also demonstrates that anaerobic fermentation of glucose to CO_2 and lactic acid or ethanol is only moderately exothermic because the enthalpy of a C=O double bond of CO_2 is only about −104 kJ/mol lower than that of two C−O or C−C bonds in glucose.

O_2 in the Atmosphere

Why is O_2 abundant in air despite its high enthalpy? Our analysis has shown that O_2 is unusually energy-rich, so the free energy of the atmosphere would be reduced if O_2 reacted away. Indeed, for the first 2 billion years of the earth's history, atmospheric levels of O_2 were low, less than 10% of today's value.[22] All the O_2 in the earth's atmosphere has been produced by photosynthesis in cyanobacteria, algae, and higher plants. It is interesting to note that O_2 is a by- or waste-product of photosynthetic H^+- and e^--production from H_2O.[22] The disadvantage of the production of O_2, which is energetically so unfavorable, is overcompensated by the ubiquitous availability of H_2O as a proton and electron source for photosynthesizing organisms. It is the price that photosynthetic organisms have to pay (with "cheap" energy from the sun) to be able to live wherever H_2O is present. In addition, they can later recover the energy of O_2 by cellular respiration.[22]

These considerations show that atmospheric O_2 stores energy originating from the sun, and that the heat of combustion in air can be regarded as fossil solar energy, even when abiotically generated methane is involved. Finally, given the high bond enthalpy of O_2, one may wonder why N_2 in the atmosphere does not combust exothermically. An explanation mostly in terms of the high enthalpies of nitrogen−oxygen bonds is given in the Supporting Information.

Teaching "What Makes Fire Hot"

The insights and results presented here can be easily incorporated into chemistry courses at different levels. In a survey course, the questions "Why is fire hot?" or "What makes fire hot?" can now be answered by simply stating that the double bond in O_2 is unusually weak, compared to other double bonds or pairs of bonds, and that formation of the stronger bonds in H_2O and CO_2 reduces the potential energy of the molecules, which results in the release of heat or an increase in the thermal motion of the gas molecules; this results in flame propagation under suitable heat- and mass-transfer conditions.[6]

In a general chemistry course for chemistry majors, a more quantitative analysis in terms of bond energies or enthalpies can be included along the lines of Figure 1. In other words, here an additional question, "How much heat can be produced from combustion of a certain fuel?" can be answered. The heat of combustion per mole of O_2 used in the analysis can be rounded to −400 kJ/mol to keep the number simple, or it can be increased to −430 kJ/mol to get fairly good agreement with experimental data even without mentioning the effect of H_2O condensation. The topic is attractive because it connects the areas of bond energies and thermochemistry in a context that students can relate to such as the combustion of gasoline or ethanol.

In a thermodynamics course, one can quickly justify the formula for the heat of combustion, eq 6, based on the enthalpy differences between reactants and products as highlighted in Figure 1, panel b, plus the heat of condensation of H_2O. In this fashion, I have successfully included the topic in my junior-level thermodynamics course. The excellent agreement with the large set of experimental data in Figure 2, which validates the simple formula, could be shared with physical chemistry students. In homework problems, one can ask students to quickly predict heats of combustion even of complex mixed fuels such as gasoline, C_8H_{15}, simply from the elemental composition, or to explain why ethanol produces less combustion heat than the corresponding volume of gasoline (−23.2 MJ/L and ca. −33 MJ/L, respectively).

■ CONCLUSIONS

Our analysis provides simple answers to two related, important questions: "What makes fire hot?" and "How much heat is produced?" in the combustion of a certain fuel. One can now explain that the double bond in O_2 is unusually weak, and therefore the formation of the stronger bonds in CO_2 and H_2O results in the release of heat or an increase in thermal motion. We have pointed out that in a general analysis of bond enthalpies, it is crucial to count electron-pair bonds so that the total number of bonds remains unchanged. This enables a general analysis of the enthalpy in the reactants and products per bond (or more conveniently per two bonds so that O_2 and H_2O can be treated per molecule). We have confirmed by rigorous calculation and by analysis of an extensive database that the heat of combustion is close to −418 kJ/mol for each mole of O_2, of which −306 kJ/mol can be attributed to the weak double bond (less negative bond-formation enthalpy) of O_2 and the rest to the stronger bonds in H_2O compared to two C−H bonds, and in CO_2 compared to two C−C or C−O bonds in the reactants. By taking into account the heat of condensation of H_2O, −44 kJ/mol, our simple equation predicts heats of combustion with good precision, for example, $\pm$ 2.1% for molecules with $\geq$ 8 carbons. It can even be applied to complex mixed fuels for which only the elemental composition is known. The analysis reveals a doubly undesirable effect of oxygen atoms in a fuel and the prohibitive energetic cost of removing them as O_2, which is relevant in the context of biofuels. Generally, our analysis indicates that it is not the organic fuel but rather O_2 that is "energy-rich". The presence of large quantities of O_2 in the earth's atmosphere in spite of its high enthalpy is explained by photosynthesis from H_2O, a ubiquitous proton and electron source for plants and algae.

■ ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.5b00333.

> Derivation of eq 5; discussions of terminology and units for $\Delta_c H^o$, limited importance of CO_2 in making combustions exothermic, bond energies and bond-formation enthalpies, outliers and deviations from predicted behavior due to unusual structural features, analysis for nitrogen- and sulfur-containing compounds, and why the atmosphere does not combust spontaneously (PDF)

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Notes

The author declares no competing financial interest.

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