

Balancing Organic Redox Reactions

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A. Introduction

Abbreviations and conventions:

- ON = oxidation number(s).
- Equations that are incomplete or not balanced are marked with ??? in front of the Eqn number.
- The formal species “hydrogen atom” and “oxygen atom” are shown as H and O, respectively. (This point is discussed further in Notes 2 and 3.)

In general chemistry, with its usual emphasis on inorganic reactions, one learns methods for balancing redox equations by focusing on oxidation numbers (ON). However, with organic reactions, the use of ON may be unwieldy. The purpose of this document is to present an alternative approach to balancing organic reactions, avoiding direct use of ON. The approach is chemically logical, using mainstream ideas from organic chemistry. It is also consistent with the use of ON.

The general idea is that there is a “natural” way to write each half-cell reaction, somehow showing the electron transfer that is characteristic of redox reactions. With inorganic reactions, it is common to show free electrons. With organic reactions, it is common to show

species such as free hydrogen atoms or oxygen atoms. Importantly, these various ways to show electron transfer are easily related to each other.

We illustrate this first by example. Then, in the Perspective section, we return to more clearly describe the idea.

B. The reaction: oxidation of ethanol with dichromate

We focus here on one chemical reaction, the oxidation of ethanol by dichromate. We will explore various ways of balancing it -- especially the organic part.

The reaction is the oxidation of ethanol by dichromate, to yield ethanoic acid and Cr^{3+} . The reaction occurs in acidic aqueous medium.

The final, balanced equation is:



Our goal here is to show how we get that final equation.

So, how do we get it?

The first step is to break the reaction into two parts: the oxidation half cell and the reduction half cell. We understand that the dichromate is oxidizing the organic compound -- and that the Cr itself is being reduced. We thus consider the two half cells separately, and later combine them.

B.1. The reduction half cell

The inorganic half cell, the reduction of dichromate to Cr^{3+} , is straightforward, using the usual methods learned in general chemistry. The Cr starts at ON = +6, and ends at ON = +3. Thus each Cr gains 3 electrons. We then balance out the H and O by using species present in the aqueous medium. The result is:



This equation meets all the criteria for a balanced equation. It is balanced for each kind of atom, and for charge. The only thing about the equation that is "unusual" is showing the free electrons. But this is a half-cell reaction. The free electrons reflect a simple view of what happens to the Cr, and we understand that they will not appear in the final overall equation.

B.2. The oxidation half cell

The oxidation half reaction is the oxidation of ethanol to ethanoic acid.

Let's look at this half reaction more carefully, trying to use good organic chemistry. Dealing with ON for carbon often is difficult. (An alert reader may counter that the ON in this particular example are actually not difficult at all. True, but they often are difficult with complex organic compounds. For the record, I show how to balance this equation using ON in Note 1.) Thus in organic chemistry, we often deal with oxidation and reduction of C by looking at changes in the number of H and O. Oxidation is the addition of O or removal of H. That statement refers to O and H atoms, just as the symbols indicate, not to ions. It is important to understand that, because oxidation and reduction deal with electron transfers. If we are considering a C atom getting oxidized (losing electrons), showing loss of an H atom is chemically logical, but showing loss of an H⁺ ion is not.

The reaction being considered is actually the sum of two distinct reactions. I think it will be useful here to look at the two steps separately, since they are different in the H and O issues. (In practice, many people will be comfortable balancing the complete oxidation half-cell equation without considering the steps. This is addressed below, in Section B.6.)

B.3. Oxidation step 1. Alcohol to aldehyde



(Equations that are incomplete or not balanced are marked with ???.)

Inspection of Eqn 3 shows that this oxidation reaction involves loss of two hydrogen atoms. Thus we write:



This is a complete and balanced equation for this half reaction. It is also simple and chemically logical. The oxidation involves removing two H atoms, so we show 2 H atoms.

B.4. Oxidation step 2. Aldehyde to acid



In this case, the oxidation involves a gain of one oxygen atom. Thus we write:



This is a complete and balanced equation for this half reaction. Again, it is simple and chemically logical.

We can also write this equation in another form. For the moment, this is "for fun" -- just to show two equivalent equations. However, it turns out that the form below will be convenient in the next section.

Eqn 6 uses an O atom to reflect the electrons of this redox reaction. We can transform the equation to use H, instead of O. To do this, we recognize that:



Substituting Eqn 7 in Eqn 6 for O gives:



Both Eqn 6 and Eqn 8 are complete and balanced for this second oxidation step. One is no "better" than the other.

B.5. Oxidation: Combining steps 1 and 2

The desired equation is the sum of Eqn 4 (first oxidation step) and Eqn 6 or 8 (second oxidation step). We choose Eqn 8 here for the second step, because the equation for the first step, Eqn 4, is in terms of H. The desired summed equation is:



Again, this is fully balanced for this double-oxidation half reaction. It is balanced for each kind of atom, and it is balanced for charge. Charge was not a difficulty, since all species were written with proper charge at the start.

Eqn 9 is chemically logical, chemically instructive, and fully balanced. It is a good chemical equation -- for a half cell. It contains an unrealistic product, the H atom -- just as equations for common inorganic half cells typically contain electrons. The H is not the final product, but we can deal with that separately, when we combine half cells (Section B.7).

B.6. Balancing the overall oxidation half-cell equation without considering the two steps separately

Although I worked through the two oxidation steps above one by one, many will find it easy enough to balance the overall reaction in one step. The oxidation of $\text{CH}_3\text{CH}_2\text{OH}$ to CH_3COOH requires one O atom and releases two H atoms. Just count the atoms. That leads to:



That equation is logical and balanced. We then put it in a more convenient form by using Eqn 7; this leads to Eqn 9, as before.

This section combines what was done above in Sections B.3, B.4 and B.5. It is fine to do it either way: going through the individual steps and then adding them, as in the earlier sections, or doing it all at once, as in this section. The purpose of presenting the individual steps earlier was to present one small step

at a time, to make the logic clear. It is fine to do multiple steps together, if you are comfortable doing so.

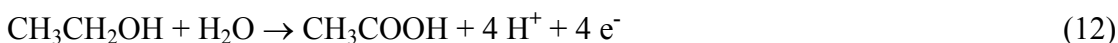
B.7. Combining the half cells

We now have equations for two half-cell reactions. The reduction half cell is described in Eqn 2. The oxidation half cell is described in Eqn 9. The former shows electron transfer in terms of free electrons; the latter shows electron transfer in terms of hydrogen atoms.

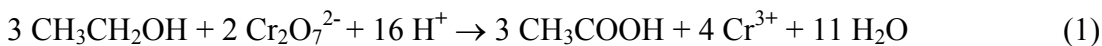
To combine these two half-cell equations, we need to get them in the same electron language. To do that, we re-write the H atom, H, as the sum of its parts:



Substituting Eqn 11 in Eqn 9 gives



To obtain the final equation for the overall reaction, we combine the reduction half cell and the oxidation half cell, as usual with redox equations. The reduction half cell is Eqn 2, and shows 6e^- . The form of the oxidation half cell that is convenient here is Eqn 12; it shows 4e^- . To get the electrons to balance out when the two are combined, we take 2 times Eqn 2, and add 3 times Eqn 12. The result is Eqn 1 -- the final desired equation.



This final equation includes the H^+ ion. That is fine here, since the reaction occurs in acidic aqueous medium. The choice of which species are acceptable depends on the specifics of the case at hand. However, free electrons and free hydrogen atoms generally do not belong in final equations for real processes.

C. Perspective

Redox reactions involve electron transfer.

To help us visualize and balance redox reactions, we commonly divide them into two parts: one for oxidation and one for reduction. We recognize an oxidation half cell because there is a loss of electrons; equivalently, there may be a loss of hydrogen or gain of oxygen. We recognize a reduction half cell because there is a gain of electrons -- or a gain of hydrogen or loss of oxygen. These "half-cell reactions" are hypothetical, and we often write them with unrealistic species, such as free electrons or hydrogen atoms. These unrealistic species must disappear when we combine the two half cells into an equation for the complete redox reaction. However, the half-cell reactions are instructive to us, as well as useful in working out the complete equation.

For simple chemicals, we may write the redox half cell with free electrons, making use of the oxidation numbers. For example:



For more complex chemicals, and particularly for organic chemicals, we may write the redox half cell with free hydrogen or oxygen atoms. For example:



That is, redox half cells may show the formal species e^- , H or O. In combining the half cells, we need to eliminate these formal intermediates. To do that, we recognize various relationships between them, all of which follow good chemical logic.

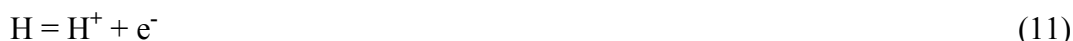
We used two such relationships above.

- Eqn 7 is a relationship between H and O atoms:



We used this relationship in Section B.4. In that case, we had two partial reactions, one showing H and one showing O. Eqn 7 allowed us to combine those into an equation showing only one electron form.

- Eqn 11 is a relationship between H and e^- .



We used this relationship in Section B.7. In that case, we had two partial reactions, one written with e^- and one written with H. Eqn 11 allowed us to combine those into a single equation -- in this case, one with all electron forms canceling out.

Another relationship we might have used is:



Overall, Equations 7, 11 and 15 allow us to interconvert among three formal ways of representing electron intermediates: free electrons or hydrogen or oxygen atoms. Thus, we are free to write whichever of them seems most chemically appropriate for a particular half-cell; we can then combine half-cell equations no matter which electron form they show by using these relationships.

Some additional relationships that might come up are briefly noted in Section F.

D. Shortcuts -- a general comment

From time to time the question comes up of whether we should teach -- or encourage -- a "shortcut". This is a gray area, and needs to be considered in each particular case. However, as a general philosophical point, I prefer that we start by teaching things that are correct and logical. If shortcuts follow, that may be fine. Certainly, when students discover a shortcut on their own, they deserve a good explanation of why it works. And there may be times when we teach a shortcut or simplified method because it is not practical to be more rigorous.

Examples here where this might be relevant include the breakdown of the oxidation to two steps vs one, and considering the half cells separately, rather than trying to balance the whole equation at once. Whether these are good examples is a matter of taste.

As noted, this section is gray. The main point is to encourage the use of good chemical logic as much as possible. Shortcuts should be identified as such.

E. A possible shortcut for balancing the organic half cell

Here is a possible alternative approach that was offered to me for balancing the organic half cell; the approach might be considered a shortcut.

The presentation of this shortcut here is loosely based on a real discussion. The purpose here is to discuss the merits of one or another approach. Discussing alternative approaches should serve to highlight their strengths and weaknesses.

For simplicity, let's consider step 1 of the oxidation reaction discussed above: Eqn 3.



The suggested approach starts by noting that H^+ is a likely product. Since 2 H are removed, we start by writing the following as our "trial equation":



That achieves balance for H, but it is unbalanced for charge. To solve that problem, we now add electrons as needed to achieve charge balance:



This is a complete and balanced equation for this half reaction. It is fully equivalent to Eqn 4 -- because $2 \text{H} = 2 \text{H}^+ + 2 \text{e}^-$ (by Eqn 11).

Thus the first point is that this approach works; it gives a correct answer. The purpose of discussing it further, comparing it to what was done in Section B.3, is to explore the logic of the two approaches.

Both approaches ultimately make use of electrons, in some form. In the approach of Section B.3, presented earlier, the electrons are considered from the start -- because this is a redox

equation, fundamentally involving electron transfer. The first equation written, Eqn 4, is chemically logical and balanced. Further manipulation of the equation may be done for convenience. In contrast, in the shortcut approach, the electrons that are so fundamental are ignored in the initial step, and added back only later to get the equation to work out. The first equation written, Eqn 16, is neither chemically logical nor balanced; further manipulation is required simply to get a meaningful equation.

In the end, this comes out fine, but why not just do the chemistry logically in the first place? It is not obvious that the “shortcut” is any shorter, and it is certainly less logical. What, then, is its merit?

In discussing the shortcut with one person, they seemed unsure how to explain what they had done, and unsure what to do in a case that did not ultimately produce H^+ . That discussion suggested that the shortcut was being used as a blind mechanical trick, with poor understanding of the chemistry. In contrast, the approach in Section B.3 is chemically logical right from the start. Then, it is meshed with whatever specific constraints are relevant to the problem at hand, such as relating H atoms to free electrons, using Eqn 11. Further, the approach is easily generalized to other cases -- simply by looking at what the electrons are doing.

If anyone has an example where they think the proposed shortcut is particularly appropriate, please contribute. Discussing such examples could be instructive.

F. Other relationships

We briefly note some additional cases. These were not relevant in our example above, but are relevant to some reactions. They can be seen as simple extensions to the story above. The first two reflect simple chemistry, and the final group considers biochemical cofactors that carry electrons (hydrogen).

F.1. Hydrogen gas



F.2. Hydride ion

The hydride ion is H^- -- and a good source of electrons, as a reducing agent. For example, the reducing agent $LiAlH_4$ can be thought of as formally containing $Li^+ + Al^{3+} + 4 H^-$. The hydride ion is easily related to other hydrogen species, as desired. One such relationship is:



F.3. Biochemical cofactors

In biochemistry, electrons are carried by cofactors, such as flavin adenine dinucleotide (FAD)

or nicotinamide adenine dinucleotide (NAD). (The details of these cofactors are not of concern here.) We often show the electrons in the form of hydrogen atoms. Thus we commonly write simply FADH_2 and FAD for the two forms of FAD -- with and without the two electrons (two hydrogen atoms).



NAD is a bit more complicated, because NAD itself actually is an ion. The idea is the same, however:



There is also a phosphorylated form of NAD, called NADP. However, the phosphate group has no direct role in carrying H, and the relationship is quite the same as for NAD:



This approach is easily extended to other electron (hydrogen) carriers, such as pyrroloquinoline quinone (PQQ):



G. Acknowledgment

The discussion here started with M. Farooq Wahab, then of the Chemistry Dept, University of Karachi, noting the difficulty of using ON with organic reactions. He also emphasized the importance of balancing such reactions in analytical chemistry, even though organic chemists are often rather casual about balancing equations.

H. Notes

1. Using oxidation numbers (ON)

The particular equation at hand is actually easy enough to balance by the usual procedures using ON, as taught in general chemistry. For the record, we do that here.

The basic description of the reaction is

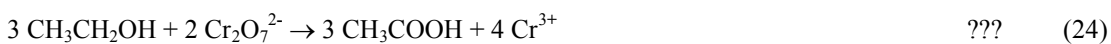


I have included a coefficient 2 for the Cr^{3+} , since there must be 2 Cr^{3+} for a single $\text{Cr}_2\text{O}_7^{2-}$.

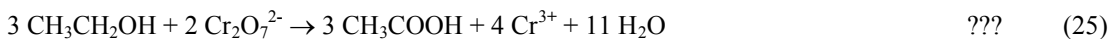
For Cr: The Cr is reduced from +6 to +3, and there are 2 Cr; therefore, the equation as written above involves a 6 electron gain, total, for the two Cr atoms.

For C: We assign the usual +1 for H and -2 for O. For $\text{CH}_3\text{CH}_2\text{OH}$, there are 6 H = 6+ and 1 O = 2-. Total of H and O is 4+, therefore the total ON for the two C atoms is 4-. Similarly, for CH_3COOH , the total ON for the two C atoms is 0. Thus the C atoms, together, lose 4 electrons.

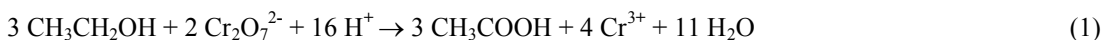
To balance the 6 e^- gain of the Cr and the 4 e^- loss of the C, we multiply the former by 2 and the latter by 3:



That takes care of the redox (electron transfer) part of the balancing. We now complete the balancing, using water and its common ions. There are 17 O on the left, 6 on the right. So we add 11 H₂O to the right to achieve O balance:



There are now 18 H on the left and 34 on the right. So we add 16 H⁺ to the left to achieve H balance:



The usual checking shows that the equation is fully balanced, for each element and for charge. In fact, it is the correct final equation, Eqn 1.

On my web page of practice quizzes for intro organic/biochem is one called "Quiz: Oxidation and reduction". This is an exercise to help students see the equivalence of the two methods for dealing with redox of carbon compounds: assigning ON and counting H and O. Both methods focus on counting the electrons, the heart of the redox reaction.

2. The hydrogen atom: how to show it in an equation.

There are various ways to show the hydrogen atom. These include H, as I have done, or H· or [H]. It does not matter, so long as we understand what is meant -- in particular, that it is the neutral species, with one electron. (The dot on H· serves to remind us of that one electron. It also relates to the common electron dot formula for hydrogen gas, H:H.) The H atom is not a stable final product (or reactant) in such equations, and will not appear in the final equation for a complete real process (under ordinary conditions). However, it lets us focus on one step of a complex reaction, without worrying about the detail of where the hydrogen comes from or goes.

Sometimes we use [H] to denote "reducing power". The term may be used qualitatively or quantitatively. For example, the symbol [H] over the reaction arrow means to use a reducing agent, typically some source of H.

In biochemistry, 2 H may well end up reducing NAD⁺ to NADH + H⁺. This was introduced in Section F.3. But it is also common that we simply want to be able to count the amount of reducing power, without worrying about its form.

My Metabolism handout, posted at the website for Intro Organic/Biochem, has a section on "Electron carriers (H carriers)". It includes a discussion of how we show hydrogen atoms, with an emphasis on the biochemical usage.

Similarly, the hydride ion, H⁻, might be shown as H:·. (The hydride ion was introduced in Section F.2.)

3. The oxygen atom: how to show it in an equation.

This note follows from the preceding note, on the hydrogen atom. We might show the oxygen atom as O or [O]. I choose to show it simply as O. I suppose we might show it with dots, but that seems unwieldy in this case.