NOTE: This answer is extracted from an old key. Sorry for the reference to “problem #24”—just ignore than and ask me if you need help. I also solve this problem in the key for “initial rate of reaction” rather than for “initial rate of formation” (and I reworded the problem on the handout to read). Hopefully this is helpful nonetheless.

44. Data corresponding to the chemical reaction described by \( \text{C}_2\text{H}_4(g) + \text{O}_3(g) \rightarrow 2 \text{CH}_2\text{O} + \frac{1}{2} \text{O}_2 \):

<table>
<thead>
<tr>
<th>[\text{O}_3]_0 (M)</th>
<th>[\text{C}_2\text{H}_4]_0 (M)</th>
<th>Initial Rate of formation of \text{CH}_2\text{O} (\text{M} \cdot \text{s}^{-1})</th>
<th>Initial Rate of Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50 \times 10^{-7}</td>
<td>1.0 \times 10^{-8}</td>
<td>1.0 \times 10^{-12}</td>
<td>0.50 \times 10^{-12}</td>
</tr>
<tr>
<td>1.5 \times 10^{-7}</td>
<td>1.0 \times 10^{-8}</td>
<td>3.0 \times 10^{-12}</td>
<td>1.5 \times 10^{-12}</td>
</tr>
<tr>
<td>1.0 \times 10^{-7}</td>
<td>2.0 \times 10^{-8}</td>
<td>4.0 \times 10^{-12}</td>
<td>2.0 \times 10^{-12}</td>
</tr>
</tbody>
</table>

DETAILED SOLUTION AND COMMENTARY.

(a) To determine the rate law basically means to “determine the exponents of the concentration terms in the general rate law: \( \text{Rate} = k[A]^m[B]^n \)”, which in this problem means finding “\( m \)” and “\( n \)” in:

\[
\text{Rate} = k[\text{O}_3]^m[\text{C}_2\text{H}_4]^n
\]

The easiest way to start this kind of problem is to realize that \( m \) corresponds to “how the rate of reaction depends on the concentration of \( \text{O}_3 \)” and that \( n \) corresponds to “how the rate of reaction depends on the concentration of \( \text{C}_2\text{H}_4 \)”. That means look for two trials in which only one of the concentration values has changed. Then you can compare how the rate changed with how the (single) concentration value changed.

As in my answer to #24, I will give the “verbal” (calculations in your head) way to look at this problem first, and then I will give the “brute force” algebra approach. I hope that with practice you will become familiar “seeing” how the math works so that you don’t need to do the brute force algebra approach. On the other hand, I want you to feel completely comfortable using the algebraic method as well! 😊

A. Verbal analysis. In this case, first look at trials 1 and 2 since \([\text{C}_2\text{H}_4]_0\) does not change. The concentration of \( \text{O}_3 \) *tripled* and the (initial) rate (of formation) ALSO TRIPLED. Right away that should tell you that \( m \) **must be 1**—the rate of formation is directly proportional to the concentration of \( \text{O}_3 \) (to the first power). (See the answer to #24 for more details on why this is so.) NOTE THAT THIS IS JUST THE OPPOSITE OF PROBLEMS 24 AND 26! It will be good for you to become comfortable being able to “see” these kinds of problems from “both directions”. Please ask for help if necessary!

Okay, **finding \( n \) is not as simple** in this problem! Why? You hopefully noticed that there is no pair of trials in which only the concentration of \( \text{C}_2\text{H}_4 \) changed!!!! THIS DOES NOT MEAN THAT YOU CANNOT DETERMINE \( n \)! Why? Because you already KNOW the order with respect to \( \text{O}_3 \)! Hopefully you will see how this removes the “restriction” that you have two trials with the same concentration of \( \text{O}_3 \). You must compare trials 1 and 3 or trials 2 and 3 to get information about \( n \) since those are pairs of trials in which the concentration of \( \text{C}_2\text{H}_4 \) changed. One way to reason this out (other than the “brute force” algebraic method noted below) is to first **FIGURE OUT THE FACTOR OF CHANGE IN RATE THAT SHOULD HAVE OCCURRED AS A RESULT OF THE CHANGE IN CONCENTRATION OF \( \text{O}_3 \)** since in these pairs of trials the \( \text{O}_3 \) concentration does not remain constant.

Let’s work with trials 1 and 3 since the rate ratio there is a whole number (4:1) rather than a fraction (3:4 or 4:3). In going from trial 1 to trial 3, the concentration of \( \text{O}_3 \) doubled. From our analysis above, we know that the rate should **double** as a result of the change in \( \text{O}_3 \) concentration, because we determined that the exponent \( m \) is just “one”. But we notice that the rate did NOT double, it became FOUR TIMES as great. That is, there is an “extra factor of two” present, so that **must be a result of the change in concentration of \( \text{C}_2\text{H}_4 \)**. We are sort of calculating what the factor of change **would have been** if the concentration of \( \text{O}_3 \) had **not** changed! That is, it would have been a factor of 2. And by what factor did the concentration of \( \text{C}_2\text{H}_4 \) change? A factor of two as well (it doubled, from \( 1.0 \times 10^{-8} \) M to \( 2.0 \times 10^{-8} \) M). So that means that the **exponent of \([\text{C}_2\text{H}_4]_0\) must also be a “one”.**
Is this result consistent with the changes from trial 2 to trial 3? Yes! The concentration of O₃ became 2/3 of what it was (1.0 is 2/3 of 1.5) and the concentration of C₂H₄ became 2 times what it was, so if both of the exponents are "one", the rate should just become 2/3 x 2 = 4/3 times the original rate, which it does! (Again, see answer to #24 to follow this "factor" logic.) Another way to reason this out without doing the "brute force" calculation below was discussed with a few students in lab on Wednesday and also in the email I sent out on this problem last week. I will not discuss that method here.

B. Brute force approach. The basic idea is to use the general rate law relation to generate a pair of equations corresponding to a pair of trials and then use algebra (divide one whole equation by the other) to solve for the unknown exponent (if you pick two trials in which only one concentration value changes, then you will only have one "unknown" exponent to solve for).

To solve for "m" in this problem. Pick trials 1 and 2 as above ([C₂H₄] doesn't change) and substitute values into the general rate equation:  
\[ \text{rate} = k[O₃]^m[C₂H₄]^n \]

Trial 1:  \[ 1.0 \times 10^{-12} \text{ M s}^{-1} = k(0.50 \times 10^{-7} \text{ M})^m(1.0 \times 10^{-8} \text{ M})^n \]

Trial 2:  \[ 3.0 \times 10^{-12} \text{ M s}^{-1} = k(1.5 \times 10^{-7} \text{ M})^m(1.0 \times 10^{-8} \text{ M})^n \]

There are multiple ways to use algebra to solve this "system of two equations". The most straightforward way is to divide the equation having the larger rate in it by the one with the smaller rate (I find it easier to work with values greater than one rather than fractions!). (Note that this works simply because if \( a = b \) and \( c = d \), then it follows that \( a/c = b/d \).) So, dividing Trial 2's equation by Trial 1's, you get (after canceling out a bunch of identical terms and units in the numerator and denominator of both sides):

\[
\frac{3.0}{1.0} = \frac{(1.5 \times 10^{-7} \text{ M})^m}{(0.50 \times 10^{-7} \text{ M})^m}
\]

Recall that \( (xy)^a = x^ay^a \), and \( \frac{x^a}{y^a} = \left( \frac{x}{y} \right)^a \) so the above simplifies to:

\[
\frac{3.0}{1.0} = \frac{(1.5)^m(10^{-7} \text{ M})^m}{(0.50)^m(10^{-7} \text{ M})^m} \Rightarrow 3.0 = \left( \frac{1.5}{0.50} \right)^m = 3.0 = 3.0^m
\]

from which it is clear that \( m \) must be 1.

To solve for "n" in this problem. Pick Trials 1 and 3 (or 2 and 3) and substitute into the rate equation as above except that now you know that \( m = 1 \! \). You see, once you know the value of \( m \), you don't have to worry about whether or not the concentration of O₃ changes!

Trial 1:  \[ 1.0 \times 10^{-12} \text{ M s}^{-1} = k(0.50 \times 10^{-7} \text{ M})^1(1.0 \times 10^{-8} \text{ M})^n \]

Trial 3:  \[ 4.0 \times 10^{-12} \text{ M s}^{-1} = k(1.0 \times 10^{-7} \text{ M})^1(2.0 \times 10^{-8} \text{ M})^n \]

Dividing Trial 3's equation by Trial 1's, you get (recalling that \( \frac{ab}{cd} = \frac{a}{c} \cdot \frac{b}{d} \)):  

\[
\frac{4.0}{1.0} = \frac{(1.0 \times 10^{-7} \text{ M})^1}{(0.50 \times 10^{-7} \text{ M})^m} \cdot \frac{(2.0 \times 10^{-8} \text{ M})^n}{(1.0 \times 10^{-8} \text{ M})^n}
\]

\[ \Rightarrow 4.0 = 2 \times 2^n \]

Rate became 4 times what it was (in going from Trial 1 to Trial 4).  
Factor of 2 came from the change in concentration of O₃.
So clearly, \( n = 1 \). \( (2 = 2^n) \) and thus the rate law is:

\[
\text{rate} = k[O_3][C_2H_4]
\]

(**NOTE: In lab (and possibly on an exam), you will need to know how to solve for \( n \) if it is not "obvious" or an integer value (due to experimental error or uncertainty). For example, to solve for \( n \) in

\[
2.13 = 2.00^n,
\]

you need to "take the log (or ln) of both sides" to obtain:

\[
\log(2.13) = \log(2.00)^n
\]

which, using the property of logs that \( \log(x)^n = n\log(x) \) becomes

\[
\log(2.13) = n\log(2.00)
\]

so that you can solve for \( n \):

\[
\frac{\log(2.13)}{\log(2.00)} = \frac{0.328}{0.301} = 1.09 = 1.1
\]

(b) The term "order" refers to the value of the exponent. Since the exponents here are "one" for both reactants, the order is 1 for both reactants (or "first order" with respect to \( O_3 \) and \( C_2H_4 \)).

(c) Solving for \( k \) in the rate law expression gives:

\[
k = \text{initial rate of reaction (for a given trial)} \div \frac{[O_3][C_2H_4]}{\text{for that trial}}
\]

Using trial 1:

\[
k = \frac{0.50 \times 10^{-12} \text{ M} \cdot \text{s}^{-1}}{0.50 \times 10^{-11} \text{ M} \cdot (1.0 \times 10^{-6} \text{ M})} = 1000 \text{ M}^{-1} \cdot \text{s}^{-1} 
\]

**Normally you would calculate the \( k \) value for all trials and average them since they may not be identical to the number of digits that are justified. Here all values turned out to be the same so I will not show the calculations. Note that the units of \( k \) are not always the same; you need to figure those out by analyzing the units in each calculation of a "\( k \)". Note also that you should be careful to indicate precision properly (write the number of digits that indicate properly where the uncertainty lies**.

(d) Once the rate law and "\( k \)" are known, you can calculate (i.e., "predict") what the rate of reaction ought to be for a given set of concentrations (as long as the \( T \) is kept the same, of course)! Just substitute the concentration values into the rate law!

\[
\text{Rate (of rxn)} = (1.0 \times 10^3 \text{ M}^{-1} \cdot \text{s}^{-1})[O_3][C_2H_4] = (1.0 \times 10^3 \text{ M}^{-1} \cdot \text{s}^{-1})(2.0 \times 10^{-7} \text{ M})(2.0 \times 10^{-7} \text{ M}) = 4.0 \times 10^{-11} \text{ M} \cdot \text{s}^{-1}
\]

Reminder (again): The rate just calculated is actually the rate of reaction (asked for in the problem), which is not the same as the "rate of formation of \( C_2H_2O \)" (which is what many of you may have calculated). The rate of formation of \( C_2H_2O \) is twice the rate of reaction in this case because the coefficient of \( C_2H_2O \) is 2 in the balanced equation. So many of you probably ended up with 8.0 \( x \) 10^{-11} M \cdot s^{-1}. 