1. The fact that "crossover" products are not observed in the ozonolysis of 3-heptene does not rule out the proposed mechanism. It would suggest the recombination of the fragments could be occurring within a solvent cage. A solvent cage is somewhat analogous to a contact ion pair (aka tight ion or intimate ion pair) from our discussion of substitution reactions. One way to check for the possibility of crossover products would be to increase the concentration of the starting 3-heptene.


Both reactions are consistent with the mechanism where OH attacks the oxirane preferentially at the least hindered carbon by an S_n2 pathway.

\[ \text{e.g.,} \]

\[ \begin{align*}
R' \quad \text{O} \quad \text{N} \\
R \\
\end{align*} \]

(R = CH_3, R' = H or CH_3)

4. This is a bit of a vague problem! For an example, see this reference: Bartlett, Trachtenberg, J. Am. Chem. Soc. 1958, 80, p5808.)
What seems clear is that the rate differences have to be due to differences in the $\Delta N^*$ and $\Delta S^*$ values. It would seem likely that the runs at 0°C are probably dominated by $\Delta N^*$, and the rates of the runs at 103°C are significantly affected by both $\Delta N^*$ and $\Delta S^*$. At 0°C, the $\Delta S^*$ term will likely be negligible compared to $\Delta N^*$, so if $A$ reads much faster than $B$, the $\Delta N^*$ term for $A$ is smaller than the $\Delta N^*$ for $B$ (with both being positive). For the rate of the run of $B$ to be equivalent to $A$ at 103°C means the $\Delta S^*$ for $B$ is much larger than the $\Delta S^*$ for $A$. Here are some sample numbers that would give the data supplied in the problem:

$$ \begin{align*}
\text{A:} & \quad \Delta H^* = +10.2 \text{ kcal/mol} \\
& \quad \Delta S^* = -30 \text{ e.u.}
\end{align*} $$

$$ \begin{align*}
\text{B:} & \quad \Delta H^* = +3.3 \text{ kcal/mol} \\
& \quad \Delta S^* = +25.4 \text{ kcal/mol}
\end{align*} $$


The large negative $\Delta S^*$ for the dimerization of Cp seems easy to rationalize as it indicates a high degree of order in the TS since this is concerted vsm (Diels-Alder). For the pyrrole dimer of the dimer the $\Delta S^*$ would not be expected to be nearly as "ordered" as the D-A run so $\Delta S^*$ could be close to zero or even positive. This is be
the dimer is pretty much locked in the conformation needed for the retro Diels-Alder run.


There are two ways to approach this problem to obtain $\Delta N^\pm$:

1. Using Arrhenius theory says plot $\ln k$ vs $1/T$ (temperature in Kelvin) and the slope of the line $= -\Delta H^\pm / R$. This leads to an $\Delta H^\pm = +22.3$ kJ/mol. From this, the $\Delta N^\pm$ can be calculated since $\Delta N^\pm = \Delta H^\pm - RT$, thus $\Delta N^\pm = 22.3$ kJ/mol at 25°C. Another method to estimate $\Delta N^\pm$ uses transition state theory. In this method, $\Delta N^\pm$ can be calculated from the slope of a plot of $\log (k/T)$ versus $1/T$ by the relationship:

$$\Delta H^\pm = -4.576 \times \text{slope} \quad \text{(eqn 6.34)}$$

The slope using this method is $-4871.6$, so $\Delta H^\pm = -4871.6 \times \left(-4.576/1000\right) = 22.3$ kJ/mol. The value of $\Delta S^\pm$ can be calculated using eqn 6.36 (p. 342), using our value of +22.3 for $\Delta N^\pm$ and using the value of $k_B$ at 25°C (converted to Kelvin). This results in a $\Delta S^\pm$ at 25°C of -4.05 e.u.

Another way to estimate the $\Delta S^\pm$ comes from eqn 6.37, which shows there is a close relationship between $\Delta S^\pm$ and the Arrhenius A value (A values in units of sec$^{-1}$ and temp around 300 K):

$$\Delta S^\pm = 4.575 \log A - 60.53$$

Remember from the Arrhenius plot the y-intercept $= \ln A$, and since the y-intercept is 0.87, the A value $= 2.4$. Then using the
The equation above gives an estimate of $\Delta S^\ddagger$ at -3.9 R.u.
So both methods give slightly negative $\Delta S^\ddagger$ values which suggests a more ordered transition state compared to the starting p-keto acid. This supports a concerted mechanism as follows:

\[
\begin{align*}
\text{Ph-C-} & \text{C-} \text{C-ON} \equiv \\
\text{Ph-C=O} & \rightarrow \text{Ph-C=C-CH}_3 + \text{CO}_2 \\
& \downarrow \text{tautomerization} \\
\text{Ph-C-} & \text{C-CH}_3
\end{align*}
\]

Carry out the Arrhenius plot by plotting $ln K$ vs $1/T$ (in Kelvin) and the slope of the line is $-E_a/R$. From this the $E_a$ is calculated to be $+12.6$ kcal/mol (the literature value uses more data and comes out $40.9 \pm 1.7$ kcal/mol). This $E_a$ is ~22 kcal/mol less than that for 2-butenone which suggests the 2-tert-butyl groups lower the barrier to rotation about the C=C. This can be understood to be relieving steric strain (van der Waals) present between these 2-tert-butyl groups in the starting alkene.

This can be done like problem 7. Plot $\log k/T$ versus $1/T$ (in Kelvin).
Take the slope of that line and $\Delta N^\#$ is calculated with this:  

\[(\text{eqn 6.34}) \quad \Delta N^\# = -4.576 \times \text{slope} \quad \frac{1000}{\text{to have answer in kкал/mol}}\]

Then using this $\Delta N^\#$ the $\Delta S^\#$ is calculated using eqn 6.36:

$$\Delta S^\# = \left[ R \times 2.303 \times \log(\frac{k}{T}) \right] - \frac{\Delta N^\#}{T} - \left[ R \times 2.303 \times \log(kJ/mol) \right]$$

The $E_a$ can be calculated at a particular temperature using eqn 6.35:

$$E_a = \Delta N^\# + RT$$

And the $A$ value can be calculated using eqn 6.37:

$$\Delta S^\# = 4.575 \log A - 60.53$$

The literature values for this problem are: $\Delta N^\# = 45.0 \pm 1.1 \text{kкал/mol}$, $\Delta S^\# = 2.2 \text{ e.u.}$, $E_a = 46.3 \pm 1.3 \text{kкал/mol}$, and $\log A = 14.0$.

10 Remember from p. 343: "The value of $\Delta S^\#$ for a rxn provides an estimate of the change in the order of the system on going from reactants to activated complex." The key in the problem is the $\Delta S^\#$ of -11.3 e.u., which is an increase in the order in the transition state compared to the starting material. This would suggest a non-dissociative mechanism.

11 For an excellent description of this problem, or at least parts of it, see p. 344 of "Organic Chemistry" by Paula Bruice (4th ed). Most C-H bonds are worth about 100 kкал/mol, while an N-C bond is worth 103 kкал/mol and H-Br worth 87 kкал/mol. Thus, the rxn
of a C-H bond w/ a C\(^+\) is slightly exoergic, while the
run of a C-H bond w/ a Br\(^+\) is fairly endoergic. The run coordinate
diagrams for each run class leading to say 1\(^+\), 2\(^+\), or 3\(^+\) radicals
are as follows:

\[ \text{alkane} + C\(^+\) \]
\[ \longrightarrow \text{alkane} + \text{Br}\(^+\) \]
\[ \text{1}^+ R^+ \]
\[ \text{2}^+ R^+ \]
\[ \text{3}^+ R^+ \]

a) The selectivity for bromination is much higher b/c it has a late
TS, since endoergic, hence the TS has significant radical character,
so the differences in radical stability are more important in
determining differences in the E_o's.

b) Note: this question is referring to an intramolecular run. The
explanation is basically given on page 358 of the text. ... "The TS
lies further to the right for Br abstraction, so that more radical
character is developed at the TS and there is a greater difference
between the energies of the benzylic radical w/ D and the radical
w/o D substitution (Figure 6.41)."

have not yet waded through this paper, but the answers are 4.86,
2.67, and 1.81 for toluene, ethylbenzene, and cumene (isopropylbenzene),
respectively.
Ref: Jones and Bender, J. Am. Chem. Soc. 1960, 82, p.6322. Ps. 7

This is a secondary isotope effect of the $\beta$ variety (one bond away from the reacting site, the ketone carbon). Predicting the magnitude of this run is difficult. The reference indicates that $K_A/K_B = 1.411$ and "At each concentration, the deuterium compound is less dissociated than the hydrogen compound."


This should be an inverse 1st isotope effect (decrease in $\sigma$ character going from starting material to the TS), thus $K_A/K_B < 1$. The 1st value is in fact just slightly less than one (0.98).

Ethanol has a lower dipole moment than water so ethanol does not effectively solvate the carboxylate anion as well as water. Hence, the effect of the substituent on the benzene ring is more prominent.


To carry out this Hammett analysis requires plotting $\log k$ (for each substituent given in Table 6.12) versus the $\sigma$ constant for each substituent (given in Table 6.8). The slope of the line is the $k_0$ constant $p$. Doing this yields $p = 1.76$. Since $p$ is positive, a negative charge develops in the TS of the substituent-carrying molecule. To make this fit well the proposed TS, (Figure 6.69b) requires that "negative charge is developed on both sulfur atoms in the transition state as bond making is somewhat advanced over bond breaking."
Plotting the log \( \frac{A}{A_0} \) (where \( A_0 = 1 \)) versus \( \sigma \) yields a linear correlation with slope = -0.91. Hence \( \rho = -0.91 \), suggesting a positive change is developing in the TS. From the author's answer book: "The addition is strongly electrophilic. That is, the reaction is facilitated by electron-donating substituents on the carbon-carbon double bond."


This is an inverse 2° C isotope effect since \( k_D / k_H < 1 \). This is consistent with a decrease in \( \sigma \) character going from starting material to the TS (\( sp^2 \rightarrow sp^3 \)). Since the \( k_D / k_H \) for propene-1-d and propene-2-d are the same, this suggests about the same amount of bonding to each olefinic carbon in the TS, leading to the equilibrium.