

2E07: AN EXPERIMENTAL AND COMPUTATIONAL STUDY OF METHYL ESTER DECOMPOSITION PATHWAYS USING SHOCK TUBES.

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In our paper ([15] in the paper), we determined a different branching ratio for the production of CO₂ and CO from the radical CH₃OCO. We expect that the predicted CO₂ mole fraction would be too high compared to the measured CO₂ in our previous work, if the branching ratio that you propose is used. The rates that we calculated from *ab initio* are: $k_3 = 2.3 \times 10^{11} T^{0.546} \exp(-13600 \text{cal}/RT)$ $k_4 = 2.5 \times 10^{12} T^{0.55} \exp(-21600 \text{cal}/RT)$. Our branching ratio of R3/R4 is 1.6 compared to 6.0 from your rate constants at 1400 K. The reaction barriers that we calculate are similar to those that you report, so that the difference should be in the pre-exponential factors. If the 3 parameter fits are linearized 2 parameter fits, the main difference seems to be R3 which has A-factor of 1.0×10^{14} [1/s] in your rate constant compared to our value of 2.1×10^{13} [1/s]. Your value is quite high for a beta scission reaction. We carefully calculated our A-factors by computing and integrating the torsional potential energy of the internal rotors.”

Reply by David Davidson

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The calculated reaction barriers for reaction R3 and R4 in our study are actually different from those obtained in Glaude et al. paper ([15] in the paper). Glaude et al. use the CBS-Q method; while G3//B3LYP, a higher level of theory, is used in our study. In addition, Glaude et al. use transition state theory (TST) to calculate rate constants for the reverse reactions, namely R-3 and R-4; and rate constants for reactions R3 and R4 are obtained from those of R-3 and R-4 using the thermodynamic properties of the involved species; while we calculate the rate constants for R3 and R4 explicitly using RRKM theory. For that reason, the rate constant (or branching ratio) comparison is affected by both barrier heights and thermodynamic properties.

Table 1 presents forward, reverse barriers calculated at the two levels of theory for reaction R3 (CH₃OCO = CH₃ + CO₂). The CBS-Q barrier height for reaction R-3 (denoted as $\Delta V_{\text{reverse}}^\ddagger$ in Table 1) is about 2 kcal/mol lower than that derived from G3//B3LYP. Such a difference in barrier height will cause both the forward and reverse rate constants to differ by a factor of 3 at 1000 K and a factor of 2 at 1400 K. The difference in the energetics for R4 is less than 1 kcal/mol; this introduces insignificant difference in rate constants at high temperatures, e.g. 1400K.

Table 1: Energetic information for the reaction CH₃OCO = CH₃ + CO₂ (R3) at different levels of theory. Numbers are in kcal/mol

Level of theory	ΔV^\ddagger	$\Delta V_{\text{reverse}}^\ddagger$	Reference
CBS-Q	12.8	35.5	This study
G3//B3LYP	13.7	37.4	this study (also ref.15)

In addition to the difference in the potential energy surface, the difference in the optimized geometries and frequencies between the two electronic structure methods might contribute to the difference in the rate constants. Moreover, the potential energy surface for the $\text{CH}_3\text{OCO} = \text{CH}_3\text{O} + \text{CO}$ channel in the transition state vicinity is rather “flat” (cf. Fig. 1), an variational effects should be taken into account. Such a treatment will lower the TST rate constants. As a result, our rate constants for reaction R4 are lower than that those introduced by Glaude et al., leading to the higher CO_2/CO ratio.

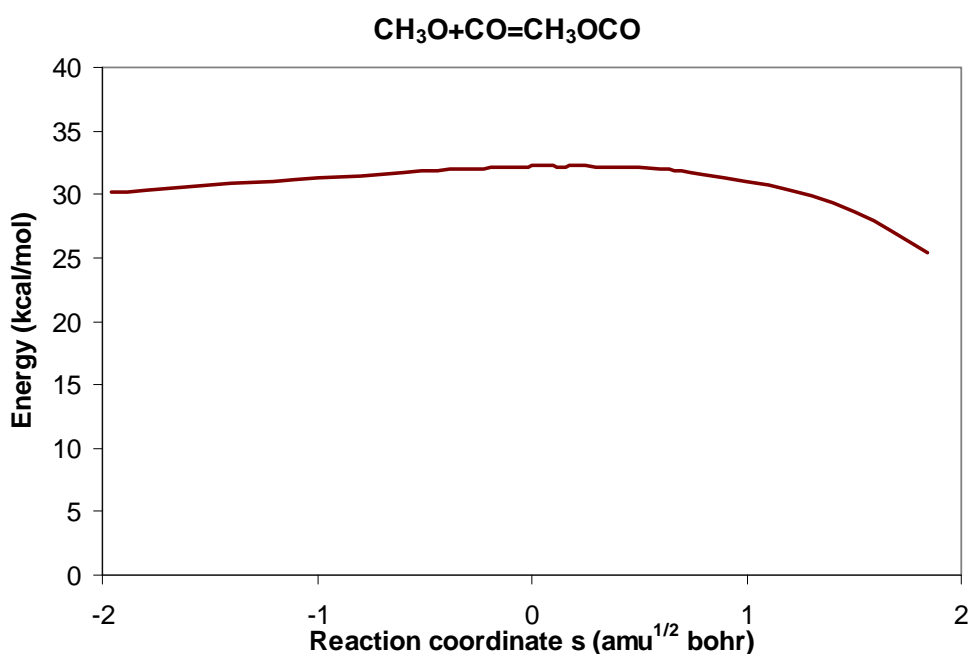


Figure 1: Potential energy surface at the vicinity of the transition state ($s = 0$) for the $\text{CH}_3\text{OCO} = \text{CH}_3\text{O} + \text{CO}$ channel. The energy is relative to the classical energy (no zero-point energy correction included) of the reactant, CH_3OCO .

Because different dynamic methods and correction methods are used to calculate explicitly the rate constant for the both forward and reverse reactions (e.g. R3 and R-3); such rate constants are not inconsistent in terms of thermodynamic data. For that reason, we use the calculated rate constants for R3 and R4 as presented in the paper and thermodynamic properties of related species calculated at the G3//B3LYP level to obtain the rate constants for reverse reactions R-3 and R-4, respectively. Such a rate constant update does not affect the result in this study since the decomposition of CH_3OCO dominates in the pyrolysis condition. The updated rate constant expressions for reaction R-3 and R-4 are:

$$k_{-3} = 6.89 \times 10^6 T^{1.774} \exp(-36678/RT) \text{ [cm}^3 \text{ mole}^{-1} \text{ s}^{-1}]$$

$$k_{-4} = 7.10 \times 10^5 T^{1.897} \exp(-6669 / RT) \quad [\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}]$$