



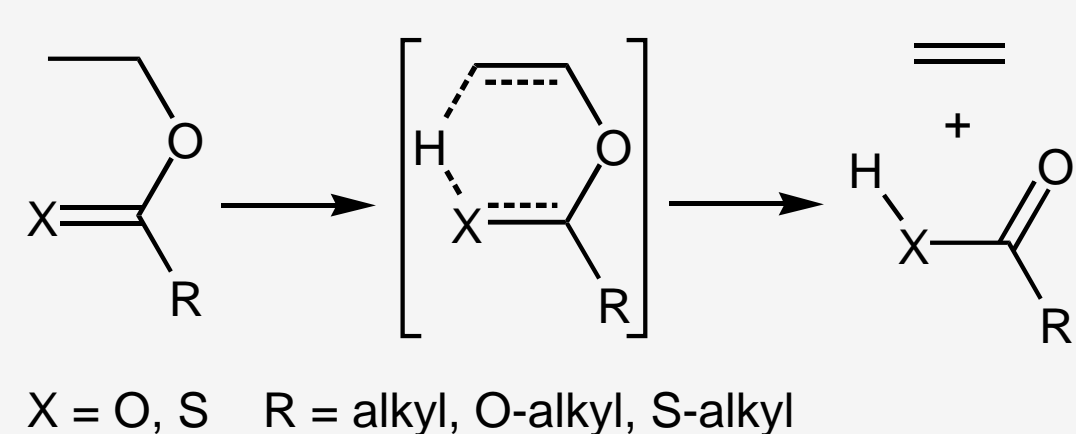
Quantum-Mechanical Calculations of Thermal Elimination Reactions: Carboxylic Acid Derivatives and Xanthates (*Tschugaef*-Reaction)

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Introduction:

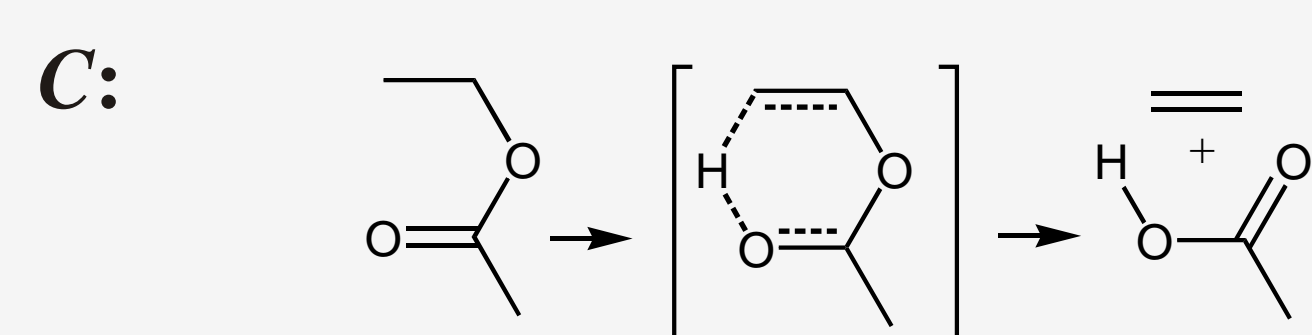
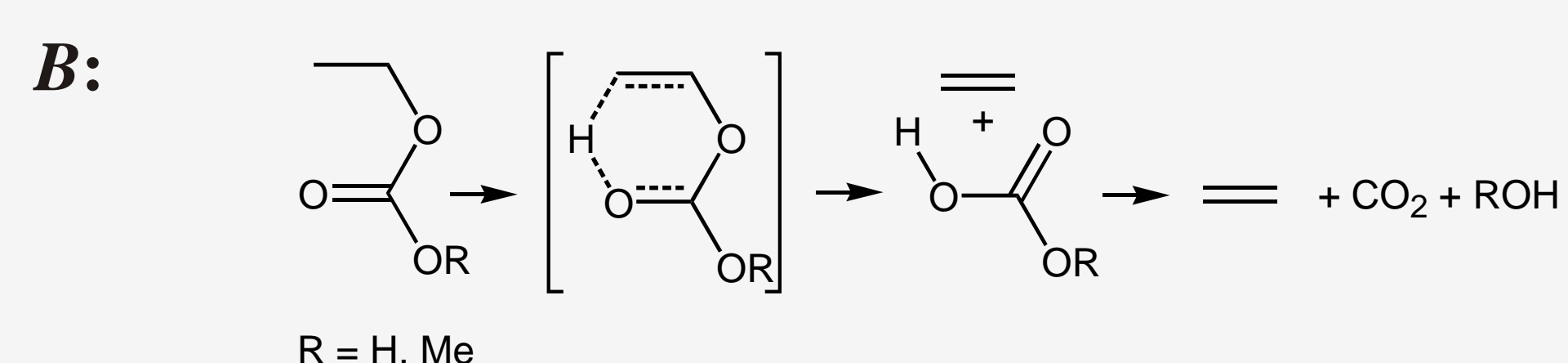
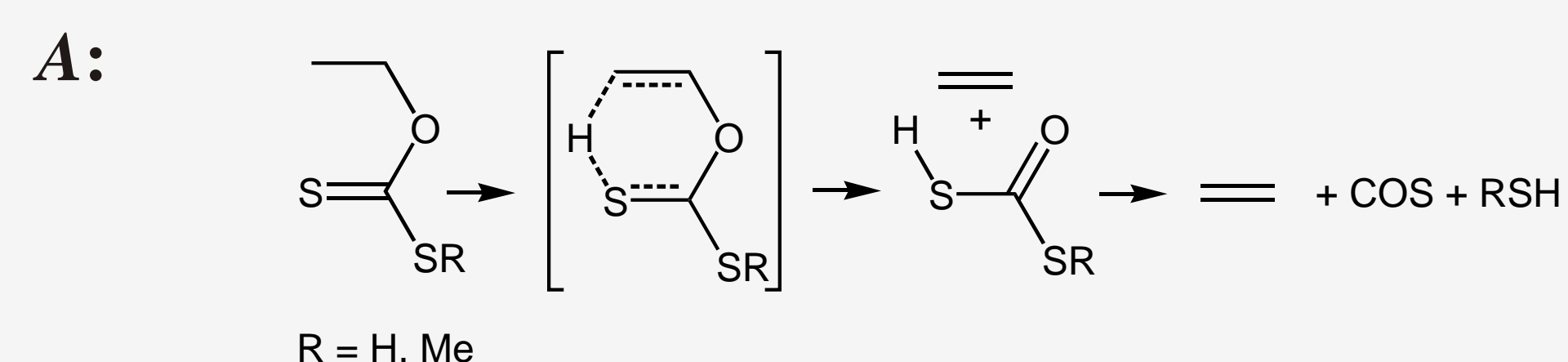
The *Tschugaef*-reaction and related thermal elimination reactions of carboxylic acid derivatives are formally known as *retro-ene* reactions.^[1] For this kind of reactions a concerted mechanism with a six membered ring transition state is postulated.^[2]



This mechanism should be confirmed by using quantum-mechanical calculations (*ab initio* methods). An alternative reaction pathway with a radical transition state should be investigated, too. *Retro-ene* reactions are well known since many years. The *Tschugaef*-reaction for example has been first described in 1898.^[3] For this type of reaction kinetic investigations have been published,^[4] but up to now, there are no quantum-mechanical calculations known for the thermodynamics and kinetics of these elimination reactions. Unfortunately, in organic synthesis ester eliminations are of limited importance, only. The reasons are high reaction temperatures and, therefore high energy barriers. Current kinetic investigations show that the substituents have a distinct influence on the energy of activation.^[5] The quantum-mechanical calculations should allow to investigate the influence of different substituents on the energy of activation including sterical and electronical effects.

Reactions of Interest:

The following reactions **A** - **C** will be discussed.



The thermal elimination of xanthates (**A**) is well known as *Tschugaef*-reaction. This reaction starts with reaction temperatures of about 100 °C,^[6] already. In contrast to the elimination reactions of xanthates (**A**) the elimination of organic carbonates (**B**) and carboxylic acid esters (**C**) needs reaction temperatures of 200 to 300 °C.^[7]

Theoretical approach:

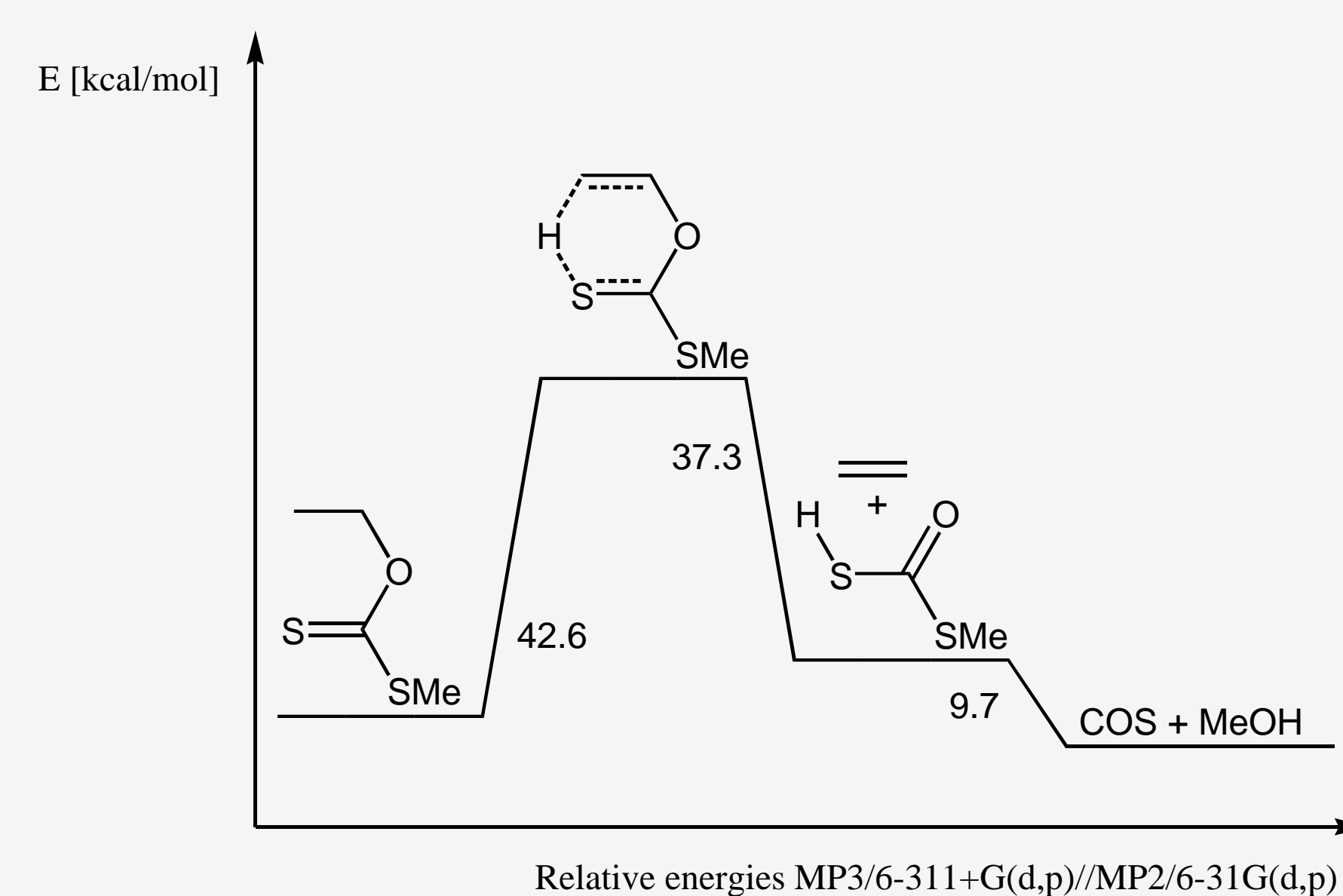
The geometries of the starting compounds, the transition state geometries and the geometries of the products were optimized using the MP2-method and the 6-31G(d,p) basis set. Frequency calculations were made and single point energies were fixed using MP3/6-311+G(d,p)/MP2/6-31G(d,p). The transition states of subsequent decomposition reactions to COS/RSH and CO₂/ROH from the primary products were not investigated assuming that the activation energies should be very low. In all cases entropy effects were not considered.

References:

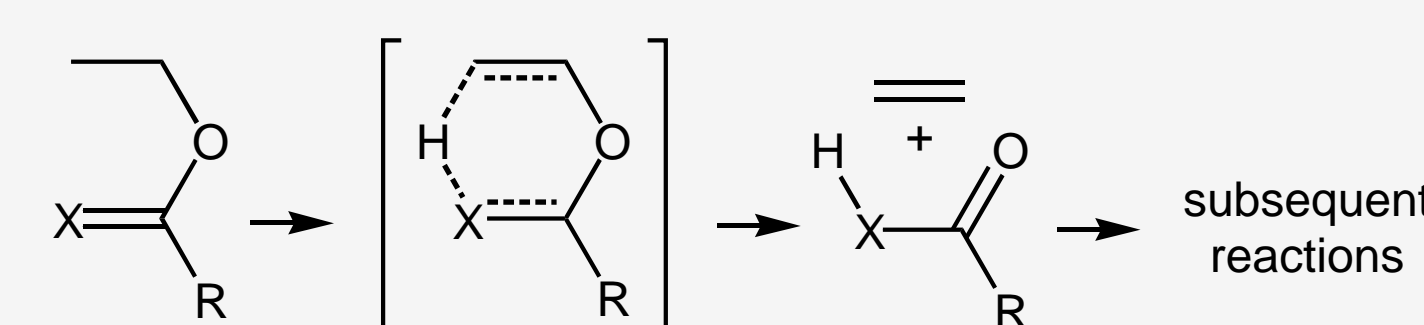
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Results:

The *Tschugaef*-reaction (**A**) is synthetically important due to low reaction temperatures and a simple preparation of the xanthates. For the elimination of the xanthates the lowest activation energy was calculated to 42.6 kcal/mol. Without considering entropic effects the reaction was exothermic.



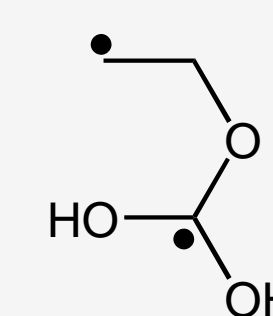
The activation barrier of the decomposition reaction of ethyl acetate under formation of ethylene and acetic acid (**C**) is given in the literature (kinetic studies) with 48.0 (±2.0) kcal/mol.^[8] 47.4 kcal/mol were calculated for the activation barrier under consideration of the zero-point energy. Without consideration of entropic effects the reaction was slightly exothermic. Resembling good results were calculated for the thermal decomposition of the investigated carbonates (**B**). An activation energy of 52.9 kcal/mol was calculated for the monoethylcarbonate. For the ethylmethylcarbonate an activation energy of about 53.9 kcal/mol was calculated. In kinetic studies an activation energy of 49.0 kcal/mol was found.^[9] This activation energy is in good agreement with the calculated energies. The activation energies and the reaction energies without consideration of entropic effects are shown in the following scheme.



R	X	E _a [kcal/mol]	Reaction energies [kcal/mol]
OMe	O	53.9	+12.4
OH	O	52.9	+8.8
Me	O	47.4	+5.8
SMe	S	42.6	-4.4

Calculated activation- and reaction energies

For the thermal decomposition of carboxylic acid esters a radical (triplet) transition state was assumed.



An activation energy of 95.3 kcal/mol was calculated. In the case of the radical-reaction pathway the energy was higher than the energy of a concerted mechanism. Therefore, a radical mechanism is probably not possible. The geometries of the xanthates have shown to have the same properties as the oxygen derivatives. Interaction could be predicted and we can predict a late transition state, too. It is remarkable that the geometries of the starting compounds were very different, but the geometries of the transition states were all almost planar six membered rings.

Conclusions:

Quantum-mechanical calculations confirm that thermal elimination reactions have a

- concerted six-membered ring transition state,
- a late transition state and
- do not proceed via a radical mechanism.

The calculated activation energies have shown to be in good agreement with the literature known.

The *Tschugaef*-reaction shows the lowest energy of activation of the calculated carboxylic acid derivatives.

The challenge is now to investigate elimination reactions with activation barriers which are lower than about 40.0 kcal/mol. By this way, sensitive organic substrates could be used in thermal elimination reactions, too.