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DFT characterization of the first step of methyl acrylate polymerization: Performance of modern functionals in the complete basis limit

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ABSTRACT

We obtain values of the reaction barrier for the reaction of methyl acrylate CH_2=$CHCOOCH_3$ (MA) with the radical $CH_3CHCOOCH_3$ (HMA·) by density functional theory (DFT) using a variety of functionals and basis sets. Structures for the reactants and the transition state are optimized in B3LYP/cc-pVTZ. We extrapolate energies for these structures to the complete basis set (CBS) limit for each of the functionals B3LYP, PBE, TPSS, BMK, HSE2PBE, mPW1PW91, B97-1, wB97-XD, and M06-2X. The extrapolation follows the energies obtained by the basis sets cc-pVnZ with n = 2, 3, and 4. The estimate of the barrier height is sensitive to the basis and the choice of functional.

In order to recover the rate constant for the radical addition we require partition functions as well as the barrier height. To obtain the partition functions for internal rotation in MA, the radical HMA·, and the transition state for their addition HMAMA·(TS), we trace one-dimensional torsional potentials in B3LYP/cc-pVTZ. Using this data we employ a range of approximations to the partition function ranging from the harmonic oscillator limit, interpolation schemes linking the harmonic oscillator and free rotor limits, and semi-classical expressions. Comparison with the partition functions obtained by direct sum of Boltzmann factors with energy eigenvalues obtained by solution of the Schrödinger equations (total eigenvalue sum or TES) for the one-dimensional torsional potentials show that Mielke and Truhlar's TDPPI-HS approximation is very accurate.

Estimates of activation energies and rate constants for the addition reaction based on the modern functionals wB97-XD and M06-2X in the CBS limit and the TES partition functions reproduce the best experimental measurement.

1. Introduction

Free radical addition has generally been described within the absolute rate theory [1], which represents the rate according to

$$k(T) = \frac{k_B T}{h} \frac{Q^{\ddagger}}{Q_M Q_R} e^{-\Delta E_0^{\ddagger}/RT} \quad (1)$$

The reaction barrier $\Delta E_0^{\ddagger}$ and partition functions for the activated complex $Q^{\ddagger}$, the monomer Q_M, and the radical Q_R are required to evaluate this expression. Quantum chemical methods can give all the information necessary for evaluation of the rate constant under the assumptions that: (1) energy is separable into terms dealing with rotation, vibration, and electronic contributions; (2) vibrations are separable into normal modes of motion; and (3) nuclear motion takes place on a single potential surface defined by the electronic energy of a single state.

The model for radical polymerization is that (1) an initiator I_2 is decomposed by heat or light to radicals I·. (2) The radical adds to a monomer M to form the first of a sequence of larger radicals IM_1·. (3) Propagation extends the chain length according to $M + IM_j \cdot \rightarrow IM_{j+1}\cdot$. These addition reactions are called ADj in the work we describe below. Finally (4) termination ends the growth of the polymer, either by a coupling reaction or by disproportionation.

Most attention has been given to the first few propagation steps. For methyl acrylate the minimal model of the first propagation step AD1 involves the species shown in Fig. 1, in which MA is the monomer, HMA· represents the radical and the transition state geometry is represented by HMAMA·(TS).

The initiation step has not been overlooked. Dossi et al. [2] studied the addition of initiating radicals methyl (Me·), phenyl (Ph·), benzoyl (BzO·), *tert*-butoxy (tBuO·), and 2-cyanoprop-2-yl (CNP·, derived from 2,2′-azoisobutyronitrile, called AIBN) to the monomers methyl acrylate (MA), methyl methacrylate (MMA), acrylonitrile, and styrene. They find reasonable agreement with experimental enthalpies and activation energies for the addition

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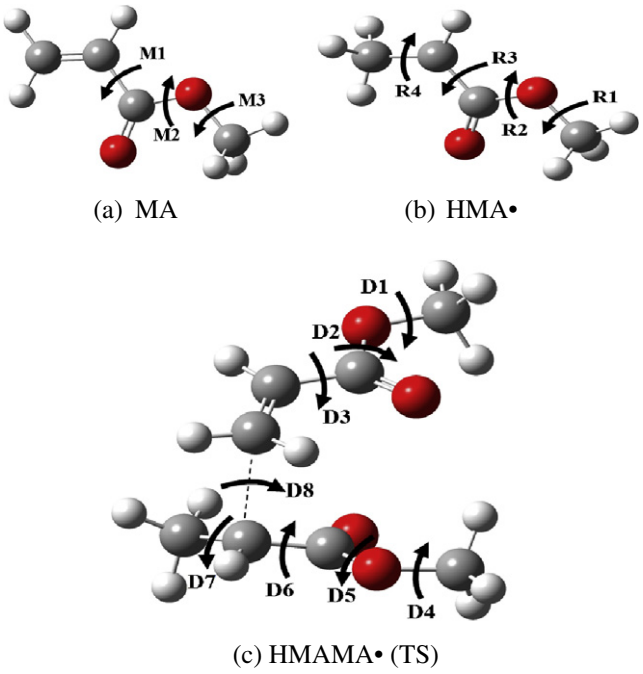

Fig. 1. Structures for species in the addition reaction AD1: (a) MA, (b) HMA· and (c) HMAMA· (TS). Torsions are M1 = ethenyl-ester; M2 = carbonyl-methoxy; M3 = methoxy methyl; R1 methoxy-methyl; R2 = carbonyl-methoxy; R3 = C_2H_4 radical-ester; R4 = Methyl-CH radical site. The transition state has corresponding torsions, D1 ↔ M3; D2 ↔ M2; D3 ↔ M1; D4 ↔ R3; D5 ↔ R2; D6 ↔ R1; D7 ↔ R4; D8 is the torsion about the bond forming in the transition state. We found and confirmed B3LYP/6-31G(d) coordinates reported by Coote [11], and computed corresponding coordinates in B3LYP/cc-pVTZ. Notice that the ester groups are stacked in the optimized structure; the carbonyls are reversed in orientation in this case, but alternatively the carbonyls could be aligned. The reversed form shown is favored by about 3 kJ mol^{-1}.

reactions of methyl radical and the monomers within the model B3LYP/6-31G(d) (see Table 1 for a guide to density functionals mentioned in this report). A substantial improvement is effected by enhancing the basis to 6-311+G(d,p). Harmonic approximations were used for partition functions for all vibrations. Computed activation energies for the reactions of the several initiator radicals and monomers range from about 40 kJ mol^{-1} for CNP· to about 4 kJ mol^{-1} or Ph·; log(k_I) ranges from 3 to 11. The activation energies for this reaction vary more weakly with the choice of monomer; for methyl radical, log(k_I) ranges from 9 to 10. For the first propagation step computations predict a range of log(k_P) from 4.4 (acrylonitrile) to 5.5 (MMA). Corresponding experimental values are 4.7 and 6.3 so the model seems to underestimate rates somewhat.

Table 1
Density functionals mentioned in this work.

Abbreviation	References
B3LYP	Becke [24] and Lee et al. [25]
B1B95	Zhao et al. [26] and Becke [27]
MPWB1K	Zhao and Truhlar [28]
BMK	Boese and Martin [29]
BB1K	Zhao et al. [30]
MPW1K	Zhao and Truhlar [25]
MPW1B95	Zhao and Truhlar [25]
M06-2X	Zhao and Truhlar [31]
wB97-XD	Chai and Head-Gordon [32]
HSE2PBE	Heyd and Scuseria [33]
MPW1PW91	Zhao and Truhlar [25]
B97-1	Becke [34]
TPSS	Tao et al. [35]
PBE	Perdew et al. [36]

Perhaps the most through study specific to the MA system is the work of Yu et al. [3]. These authors pursued the following steps for AD1, AD2, and AD3:

1. Optimization of the structures of the monomer, radical, and their transition state by UB3LYP/6-31G(d).
2. Exploration of the effect of basis set choice with single point calculations with UB3LYP, using Pople basis sets ranging from 6-31G(d) to 6-311G(3df,2p).
3. Exploration of the effect of functional choice with the 6-31G(d,p) basis, using B1B95 and MPWB1K, the latter parametrized to treat barriers.
4. Treatment of low frequency internal motions either as harmonic oscillations or as hindered internal rotation.

These authors explored chain length effects and solvent effects as well, which we do not discuss here. They observed that B3LYP barrier heights for the addition of HMA· radical with monomer MA (corrected for zero-point vibrational energy) varied with basis, from 22.7 kJ mol^{-1} with 6-31G(d) to 28.0 kJ mol^{-1} with 6-311+G(d,p). The barrier heights for MPWB1K/6-31G(d,p) and B1B95/6-31G(d,p) were 18.3 and 20.4 kJ mol^{-1} respectively.

Results of modeling may be compared with the Arrhenius parameters from pulsed laser studies by Beuermann and Buback [4], $A = 1.66 \times 10^4$ L mol^{-1} s^{-1} and E_a = 17.7 kJ mol^{-1}. The activation energy, recovered from regression of ln(k_P) vs 1/T, depends not only on the reaction energy barrier but also on the treatment of the low-frequency internal motions and the associated vibrational partition functions. When these were described in the harmonic approximation, B3LYP values increased from 30 to 35 kJ mol^{-1}, the MPWB1 K value rose to 25.5 kJ mol^{-1}, and the B1B95 value became 27.9 kJ mol^{-1}. Treating the motions as hindered rotations required tracing the potentials and evaluating partition functions for the torsional states by summing Boltzmann factors referring to the computed eigenvalues. This correction increased barrier heights by 0.9 kJ mol^{-1} in reaction AD1. Effects are more significant for later propagation steps AD2 and AD3, and in those cases tend to reduce barrier heights.

Değirmenci et al. [5] pursued the following steps:

1. Optimization of the structures of the monomer, radical, and their transition state by B3LYP/6-31+G(d);
2. Exploration of the effect of functional choice by single point calculations with the 6-311+G(3df,2p) basis, using BMK, MPW1 K, BB1 K, MPWB1 K, and MPW1B95;
3. Treatment of low frequency internal motions as harmonic oscillations.

These authors added methyl radical to MA to produce the reactant CH_3MA· for their AD1 propagation step CH_3MA·+MA → CH_3MAMA· (see Fig. 4 in their report). Computed values of log(k_P) at 303.15 K show that use of the MPW1 functional improves rate constant estimates substantially over use of the B3LYP functional. Regression of log(k_P) computed with the model MPWB1K/6-311+G(3df,2p)//B3LYP/6-31+G(d) vs. 1/T over the range 250–350 K produced estimates of Arrhenius parameters A and E_a of

Table 2
ln(k_P) at 303.15 K for reaction AD1 computed with various DFT functionals and the 6-311+G(2df,2p) basis set (see Ref. [5]).

Exp [5]	B3LYP	BMK	MPW1K	BB1K	MPWB1K	MPW1B95
9.60	1.45	3.13	3.80	2.86	4.70	5.46