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To cite this version:

Ching Yeh Lin, Michelle L Coote, Alban Petit, Philippe Richard, Rinaldo Poli, et al.. Ab Initio Study of the Penultimate Effect for the ATRP Activation Step Using Propylene, Methyl Acrylate, and Methyl Methacrylate Monomers. Macromolecules, 2007, 40 (16), pp.5985-5994. 10.1021/ma070911u . hal-03193811

HAL Id: hal-03193811

https://hal.science/hal-03193811v1

Submitted on 9 Apr 2021

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Ab Initio Study of the Penultimate Effect for the ATRP Activation Step Using Propylene, Methyl Acrylate, and Methyl Methacrylate Monomers

Ching Yeh Lin, [a] Michelle L. Coote, [*a] Alban Petit,[b] Philippe Richard,[b] Rinaldo Poli,[*c] Krzysztof Matyjaszewski[*d]

[a] *ARC Centre of Excellence in Free-Radical Chemistry and Biotechnology, Research School of Chemistry, Australian National University, Canberra ACT 0200, Australia*

[b] *Laboratoire de Synthèse et d'Electrosynthèse Organométalliques, Faculté des Sciences "Gabriel", Université de Bourgogne, 6 Boulevard Gabriel, 21000 Dijon, France*

[c] *Laboratoire de Chimie de Coordination, UPR CNRS 8241 liée par convention à l'Université Paul Sabatier et à l'Institut National Polytechnique de Toulouse, 205 Route de Narbonne, 31077 Toulouse cedex, France*

[d] *Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, PA 15213, USA*

[*] Correspondence authors. Email: mcoote@rsc.anu.edu.au; km3b@andrew.cmu.edu; poli@lcc-toulouse.fr

Abstract

High-level ab initio molecular orbital calculations are used to study the magnitude and origin of the penultimate unit effect in atom transfer radical polymerization (ATRP) of dimers involving the co-monomers methyl acrylate (MA), methyl methacrylate (MMA) and propylene (P). The penultimate unit effects depend on the nature of the terminal unit and the halogen and can be significant, with the MMA unit in particular altering the equilibrium constant for the bond dissociation equilibrium by as much as 2 orders of magnitude. Specifically, the ratio of the equilibrium constants (K) for the bond dissociation reactions of H-M_2-M_1-Cl at 298 K, relative to the equilibrium constant (K_0) of the corresponding unimer M_1-Cl, for penultimate units M_2 = P, MA and MMA are respectively: 0.81, 1.27 and 92.46 for M_1 = P; 8.73, 2.64 and 32.69 for M_1 = MA; and 5.73, 0.78 and 1.57 for M_1 = MMA. For the bromides, H-M_2-M_1-Br, the corresponding ratios K/K_0 for M_2 = P, MA and MMA are respectively: 0.55, 0.70 and 54.79 (M_1 = P); 5.44, 0.63 and 2.38 (M_1 = MA); and 0.24, 12.18 and 43.77 (M_1 = MMA). It is shown that the penultimate unit effects arise in both the entropy and enthalpy of the equilibrium and are the result of a complex interplay of stereo-electronic effects which, for the ester linkages, are heavily influenced by intramolecular hydrogen bonding. The penultimate unit effects have important implications for initiator design; for example, they can account for the experimental observation that the isobutyrate halide is an inefficient initiator for MMA polymerization. The results also imply that penultimate unit effects need to be taken into account in the synthesis of block, gradient and random copolymers.

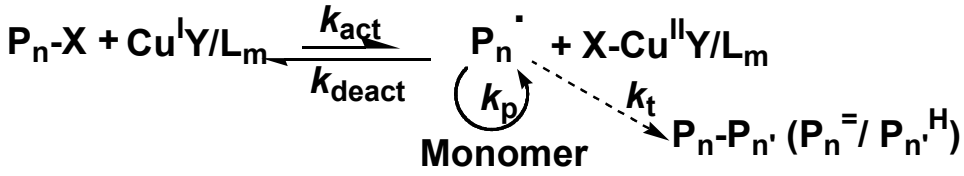
Introduction

Penultimate unit effects are well known in many types of polymerizing systems. Perhaps the most studied examples are in the propagation step of free-radical copolymerization, where, following Fukuda's seminal study in 1985,[1] it has been generally established that penultimate (rather than terminal) models are necessary for an accurate description of the copolymerization kinetics of most pairs of monomer.[2] Penultimate unit effects have also been documented in the transfer kinetics of free-radical copolymerizations,[3] and in the activation/deactivation equilibria of controlled radical polymerizations, such as nitroxide mediated polymerization[4] and in reversible addition fragmentation chain transfer (RAFT) polymerization, where penultimate unit effects of as much as 2–3 orders of magnitude have been reported.[5] It is thought that the penultimate unit can influence the rate and equilibrium constants of these reactions by a variety of different mechanisms, including steric[6] and conformational[7] effects on both the enthalpy and entropy, as well as via polar[8] and radical stabilization effects on the enthalpy.[9] Unsurprisingly, the relative importance of these various factors varies substantially with the type of reaction being studied and the substitution pattern, and also according to whether it is the rate or equilibrium constant that is being studied. For example, in the case of propagation and transfer, radical stabilization effects are generally larger in the equilibrium constants, compared with rate coefficients, due to partial cancellation from the early transition structures[8]; conversely, polar interactions are normally expected to be larger in the rate coefficients as the charge-transfer configurations are typically lowest in their relative energy in the vicinity of the transition state.[10]

Atom transfer radical polymerization (ATRP) is based on an inner sphere redox process that involves the reversible transfer of a halogen atom from a dormant species, P_n-X, and a catalyst, typically a copper(I) species complexed by multidentate amine-based ligand,

$Cu^{I}Y/L_m$.[11] This results in the formation of a radical which carries the chain growth and a metal complex in a higher oxidation state, $X\text{-}Cu^{II}Y/L_m$, which acts as spin trap. An understanding of this equilibrium is of paramount importance if one wants to fine-tune the ATRP process.

Equation 1



Experimentation has highlighted an interesting penultimate effect that plays an important role in the activation of the dormant species in ATRP.[12] For the particular case of polymerizations initiated by organohalides that are structurally derived from the monomer (*e.g.* 2-halo-isobutyrate, or H-MMA-X, for the polymerization of methyl methacrylate), the dormant species containing more than one monomeric entity (*e.g.* $H\text{-}(MMA)_n\text{-}X$ with $n \geq 2$) display a higher activation rate constant relative to the initiator ($n = 1$), for the atom transfer process in Equation 1. This seems particularly evident for 1,1-disubstituted monomers (*e.g.* MMA) but is less important for monosubstituted monomers such as styrene or methyl acrylate (MA). The enthalpy of Equation 1 (ΔH_1) can be related to the difference of two bond dissociation energies (BDEs), and since BDE(Mt-X) is obviously constant for a given halide as the chain grows, the increase in activation and/or equilibrium constants can be attributed to a decrease in the BDE(R-X) as R begins to add monomer units (Equation 2). In other words, the penultimate monomer unit can affect the homolytic strength of the carbon-halogen bond; however, contribution of entropy to the penultimate effect cannot be neglected.

Equation 2

$$\Delta H_1 = \text{BDE(R-X)} - \text{BDE(Mt-X)}$$

Understanding the energetic effect of the penultimate unit in ATRP is also relevant for the re-initiation by macromonomers for the generation of block co-polymers, as well as for controlling the microstructure for statistical and gradient copolymers.[11g,13] Moreover, it would be interesting to determine whether bulky penultimate units such as MMA or MA could be exploited to enhance activation rate constant of the relatively inactive terminal alkyl halide derived from α-olefin, e.g. propylene (P).[14] In an analogous manner, TEMPO has been shown to control the copolymerization of styrene with acrylonitrile, even though it is unable to control the homopolymerization of the latter monomer,[4a] and a similar situation was recently reported for methyl methacrylate copolymerization with styrene.[15]

In the present work, we use computational chemistry to study the magnitude and origin of the penultimate unit effect in the ATRP of dimers involving the co-monomers MA, MMA and P. We have recently carried out a computational study of the BDEs (Equation 3) of a variety of commonly used ATRP initiators, including several ones that contain a single monomer unit, in order to evaluate their relative activities in ATRP.[16] The results of this study were found to be in excellent agreement with the available thermochemical data and could be qualitatively related to the experimentally known initiator activities. These computational results can therefore be used as a valuable guide for the selection of an appropriate initiator for any given monomer. A more rigorous approach, however, must take into account the penultimate effect. In this contribution, we present a computational analysis of the effect of the penultimate monomer unit on the carbon-halogen homolytic bond strength. Since the relevant effect is believed to be limited to the penultimate monomer unit (namely the activities should be similar for H-$(M)_n$-X , where M is the monomer, for $n \geq 2$), and because of computational complexity as n increases, our study was limited to molecules that contain two monomer units (both homo and heteroleptic). We have selected dormant species that contain propylene (P), methyl acrylate (MA) and methyl methacrylate (MMA), in all possible

combinations, and either chlorine or bromine chain ends. The bond strengths and thermodynamic parameters will be compared with those of the initiators that contain only a single monomer unit, *i.e.* H-P-X, H-MA-X and H-MMA-X, and also with the C-H and C-F BDEs of the corresponding H-$(M)_n$-H and H-$(M)_n$-F systems. The latter comparison will help us in assessing the relative importance of radical stabilization, polar and steric effects.

Equation 3

$$\text{R-X} \rightleftharpoons \text{R}^{\bullet} + \text{X}^{\bullet}$$

Computational Methods

Bond dissociation energies (BDEs) were computed using standard density functional theory (DFT) and ab initio molecular orbital theory calculations. Initially all conformations of the R and R-X molecules were generated by a molecular mechanics force field (MMFF) conformational search by use of the Spartan 04 Macintosh (v.1.0.1) program. The MMFF force field does not include parameters for hydrocarbon radicals, so these were treated as sp^2-centers. All conformers were then re-optimized at the B3-LYP/6-31G(d) level of theory in Gaussian 03,[17] and the global minimum structure was selected on the basis of these more-accurate results. Frequencies were also calculated at this level of theory on the global minimum energy structures, and scaled by the appropriate scale factors.[18] For the systems containing two chiral centers (H-M_2-M_1-X; M_2 = MA; M_1 = P, MA, MMA; X = Cl, Br), full conformational searches were performed on *both* diastereomers and the lowest energy species overall was selected for the study. For both the H-MA-M_1-Cl and H-MA-M_1-Br species, these lowest energy diastereomers were *RR*, *RS* and *RS* for M_1 = P, MA, MMA, respectively. For H-MA-M_1-Cl, the energy differences between the lowest energy conformations of each diastereomer were 1.35, 0.29 and 0.30 kcal mol^{-1} for M_1 = P, MA and MMA, respectively; for H-MA-M_1-Br, the corresponding values were 1.24, 0.72 and 0.30 kcal mol^{-1}.

Improved energies were calculated using a modified version of the G3(MP2)-RAD level of theory using a combination of Molpro 2002.6[19] and Gaussian 03,[17] as described below. To assist in the qualitative rationalization of the results, the charge distributions (within the closed-shell species) and spin density distributions (within the radicals) were calculated using a Natural Bond Orbital (NBO) population analysis, carried out at the ROHF/cc-pVTZ level of theory. It should be noted that all DFT calculations on radicals were performed using the spin-unrestricted formalism; all ab initio calculations were performed using restricted open-shell wavefunctions.

In standard G3(MP2)-RAD,[20] coupled cluster calculations [URCCSD(T)] with a large triple zeta basis set (called G3MP2large) are approximated as the sum of calculations at the lower-cost URCCSD(T)/6-31G(d) level of theory, and a basis set correction term, calculated as the difference in the corresponding ROMP2/G3MP2large and ROMP2/6-31G(d) energies. A higher-level correction term and spin orbit corrections[21] for atoms are also included. This method has been shown to reproduce the heats of formation of a large test of open- and closed-shell species to within approximately 1 kcal mol^{-1},[20] and provide excellent absolute and relative values of R–X bond dissociation energies (R= Me, Et, *i*Pr, *t*Bu; X = H, CH_3, OCH_3, OH and F).[22] In our modified version of this method, we simply replace calculations with the double-zeta Pople basis set (6-31G(d)) with equivalent calculations using the double-zeta Dunning basis set, cc-pVDZ, and calculations with the triple-zeta Pople basis set (G3MP2large) with equivalent calculations using the triple-zeta Dunning basis set, cc-pVTZ. This modification is made necessary because there is no G3MP2large basis set defined for the Br atom. The higher-level correction term has not been reoptimized for our modified method; however, it constitutes only a small contribution to the absolute BDEs (<2.23 kcal mol^{-1}), and always cancels entirely from the relative BDEs (and hence penultimate unit effects), and we therefore do not expect it to influence the present results.

Having obtained the geometries, frequencies and improved energies, partition functions and corresponding thermodynamic functions (i.e. enthalpy H, entropy S, and Gibb's free energy G) were calculated at 298 K using the standard textbook formulae, based on the statistical thermodynamics of an ideal gas under the harmonic oscillator / rigid rotor approximation.[23] The equilibrium constant for each dissociation reaction was then calculated using the standard formula,

Equation 4

$$K(T) = (c^{\circ})^{\Delta n} e^{(-\Delta G/RT)} = (c^{\circ})^{\Delta n} \left(\frac{\prod_{\text{products}} Q_j}{\prod_{\text{reactants}} Q_i} \right) e^{(-\Delta E/RT)}$$

where: T is the absolute temperature (298 K), c° is the standard unit of concentration (c° = 0.040897 mol L^{-1}), R is the universal gas constant (8.3143 J mol^{-1} K^{-1}), Δn is the change in moles upon reaction, Q_i and Q_j are the molecular partition functions of reactant i and product j respectively, ΔG is the Gibb's free energy of reaction, and ΔE is the zero-point vibrational energy corrected energy change for the reaction.

In order to improve the accuracy of the calculations all relevant low frequency torsional modes in the C–Br and C–Cl dissociations were treated separately as hindered internal rotations using a standard procedure, described previously.[24] Full rotational barriers for these modes were calculated at the B3-LYP/6-31G(d) level of theory as relaxed scans in steps of 10° and are provided in the Supporting Information. Since the C–H and C–F bond dissociation reactions were used merely to assist in the interpretation of the reaction enthalpies, the less computationally intensive harmonic oscillator approximation was used for these systems.

It should be noted that in the present work, all BDEs were calculated using the global minimum energy conformations (and, where relevant, the lowest energy stereoisomer) of each species. However, in some cases, the second lowest energy conformation obtained from the

calculations was found to be very close to the most stable one, and could be thermally populated at the temperature of the ATRP. Thus, to be rigorous, one should consider a Boltzmann weighted-averaged energy for the purpose of calculating the thermodynamic parameters. However, we consider that the simple BDE estimation by using only the most stable conformation (and stereoisomer) for the halide and for the free radical provides a relevant value for the purpose of the present investigation. In essence, we expect that conformers that are close enough in energy to the global minimum to be significantly populated are likely to have very similar BDEs, and hence averaging their values is unlikely to affect the results. One might argue that the population of higher energy conformations could have an important effect on the atom transfer kinetics (k_{act} and k_{deact} in Equation 1), because the conformational equilibrium is attained much more rapidly than the time scale for the atom transfer process. Therefore, there is the possibility that a less populated, higher energy conformation is more reactive than the lower energy one if its atom transfer barrier is lower. This issue, however, is beyond the scope of the present investigation. In any case, the apparent polymerization rate constant depends on rate coefficients of propagation step but only on the thermodynamics of the atom transfer process in Equation 1 (namely k_{act}/k_{deact}), and not on the individual values of the transfer rate constants.

Results and Discussion

The enthalpies, entropies and free-energies of the bond homolysis reactions ($H–M_2–M_1–X \rightarrow H–M_2-M_1\bullet + \bullet X$) were calculated at the G3(MP2)-RAD level of theory for all combinations of M_1, M_2 = P, MA and MMA and X = Cl and Br (see Table 1). Figure 1 shows the optimized conformations of the $H–M_2–M_1–Cl$, $H–M_2–M_1–Br$ and $H–M_2–M_1\bullet$ species; full geometries of all species are provided in the Supporting Information.

INSERT TABLE 1 AND FIGURE 1

Optimized Conformations. From the comparison of the various geometries in Figure 1, it can be appreciated that the best conformation for a pair of related chloride and bromide compounds is always the same. However, a change is often observed on going from the halogenated compounds to the free radical. In particular, whenever two carboxylate moieties are present and one monomer unit is MMA, the carboxylate moieties tend to stack with each other for the halogenated compounds to form a sort of incomplete boat conformation, whereas they are part of a more open chain in the corresponding free radicals (see the H-MA-MMA-X and H-MMA-MA-X series in Figure 1). The transformation of an sp^3 to sp^2 C atom is certainly responsible for this variation. On the other hand, the H–MA-MA-X molecules form an open structure unlike those containing one MMA unit. Thus, the additional CH_3 group is also playing a role, probably disfavoring the open structure by way of an additional 1,3 *gauche* interaction. Interestingly, the H–MMA-MMA-X molecules also prefer a more open conformation (possibly due to increased steric crowding), and in these cases it is the radical that forms the stacked conformation.

Reaction Entropies. The bond breaking process entails an entropy increase, which can essentially be related to the additional translational component associated to the release of the X free atom, and also a small and constant electronic contribution of 2.754 cal mol^{-1} K^{-1}, due to the unpairing of two electrons and to the availability of the two degenerate α and β states. However, it is interesting to examine all contributions to the reaction entropy (translational, rotational, vibrational and electronic) individually, see Table 2. The translational contribution to the reaction entropy is restricted to a relatively narrow range, 34.8–36.1 (for X = Cl) and 35.9–38.0 (X = Br) cal mol^{-1} K^{-1}. As a reference, the calculated translational S_{298} values for

free Cl and Br are 36.59 and 39.01 cal mol^{-1} K^{-1}, respectively. The increase of ΔS_{298}(transl) is less than the free halogen atom values, because R-X has more translational entropy than the free radical R. The entropy of R-Br is slightly greater than that of the related R-Cl.

INSERT TABLE 2

The rotational contribution is always negative and small, *i.e.* the saturated R-X has slightly more rotational entropy than the R radical. The range is between -0.26 cal mol^{-1} K^{-1} (H–MA-MMA-Cl) for the heavier systems and -3.80 cal mol^{-1} K^{-1} (H-P-Br) for the smaller ones. This parameter generally increases with the size of R; in particular, there is a drastic increase on going from the one-monomer to the two-monomer molecules. However, some minor deviations to this trend occur due to conformational differences. For example, when the terminal unit (i.e. M_1 in H–M_2–M_1–X) is MMA, the contribution of the rotational entropy decreases when the MA penultimate unit (M_2) is replaced with the larger MMA unit as the conformation of the radical product becomes less extended and the closed shell species becomes more extended. However, the opposite occurs when the terminal unit is MA, as in this case it is the conformation of the reactant closed shell species that becomes less extended when the MMA penultimate unit replaces an MA unit.

The largest effect on the spread of ΔS_{298}(total) is due to the vibrational contribution, ΔS_{298}(vibr), which includes both the contribution from the true vibrational modes and also those low frequency torsional modes treated as hindered internal rotations. The corresponding value, ΔS_{298}(vibr'), in which all modes are treated under the harmonic oscillator approximation is also shown in Table 2 for purposes of comparison. Comparing these values, it is seen that the harmonic oscillator approximation introduces a large error (as much as 3 kcal mol^{-1} in some cases), and these errors are typically largest in the dimer species (i.e. in the

presence of a penultimate unit). This highlights the important contribution of hindered internal rotations to penultimate unit effect, a feature originally discussed in the context of propagation reactions by Heuts et al.[25] These results also further reinforce the importance of treating low frequency torsional modes of oligomeric radicals as hindered internal rotations in accurate thermochemical studies, a result also seen in computational studies of RAFT polymerization[26] and propagation.[25,27,28] For the remainder of this section, we will focus on the more accurate hindered rotor values.

The contribution of ΔS_{298}(vibr) to the total entropy change can be either positive or negative, and can vary by as much as 8 kcal mol^{-1} as the penultimate unit is altered. In general one might have expected the vibrational entropy to decrease upon dissociation, as the free radical contains one less vibrational degree of freedom. However, this small effect can be enhanced (or countered) by a decrease (or increase) in the flexibility of the oligomeric chain, associated with, for example, changes in the intramolecular hydrogen bonds and/or the alignment of various functional groups with the unpaired electron in the radical. Unsurprisingly, therefore, the most significant penultimate unit effects occur when the terminal unit contains a carboxylic acid group (i.e. MA or MMA). In the case of the methyl acrylate unimers, the vibrational contribution to the BDEs is large and negative, presumably due to the vibrational restrictions imposed by the need for the π-accepting carboxylic acid group to align with the unpaired electron in the product radical. This contribution becomes much less negative when penultimate units are added, as other factors (such as increased steric pressure in the closed shell species and reduced flexibility due to intramolecular hydrogen bonding) take over. In contrast, the vibrational contribution for the methyl methacrylate terminated species shows opposite effect: the vibrational contribution for the unimers is relatively small (though still negative), and (with one exception) becomes much more negative with the introduction of penultimate units. It would appear that the steric

pressure from the additional α-methyl group reduces the vibrational flexibility of the closed shell unimeric species, while differing hydrogen bonding interactions in the closed- and open-shell species lead to the differing penultimate unit effects. In that regard, we note that the combinations of methyl acrylate with methyl methacrylate units (in either order) lead to higher than expected vibrational contributions, presumably due to the increased hydrogen bonding (and hence reduced vibrational entropy) in the stacked conformations of the closed shell species. In a similar manner, the species containing two methyl methacrylate units possess a lower than expected vibrational contribution as in those cases it is the open-shell species that forms the stacked conformation (see Scheme 1).

INSERT SCHEME 1

In summary, the main conclusions that can be drawn from these data is that the entropic component of the penultimate unit effect is significant (as much as 10.83 kcal mol^{-1} K^{-1}), it arises predominantly in the vibrational (and internal rotational) partition functions, it depends on a complex interplay of stereo-electronic effects and, in the case of acrylate and methacrylate units, it is heavily influenced by intramolecular hydrogen bonding.

Reaction Enthalpies A close inspection of Table 1 reveals that the penultimate unit effect on the enthalpy can be very significant in these systems, ranging from –3.29 kcal mol^{-1} (for H-MMA-MMA-Br, relative to H-MMA-Br) to 1.82 kcal mol^{-1} (for H-MA-MA-Cl, relative to H-MA-Cl). Although the penultimate unit effects depend on the nature of the terminal unit (and, to a lesser extent, the halogen), some generalizations may be made. In particular, it is seen that the MA penultimate unit strengthens the breaking bond, relative to hydrogen, with the strengthening effect being largest for the MA terminal unit. The MMA penultimate unit usually weakens the breaking bond relative to hydrogen, except when the terminal unit is MA. The propyl penultimate unit shows a relatively weak effect on bond dissociation enthalpy

(typically less than 1 kcal mol^{-1}) and can either strengthen or weaken the bond, depending upon the nature of the terminal unit and the halogen.

Previously, it has been found that both the polarity and radical stabilization ability of a substituent can affect the R-X bond dissociation energy of small molecules (R-X; R = Me, Et, iPr and t-Bu; X = H, CH_3, OCH_3, OH and F), with the radical stabilization effect of R being most dominant for the (relatively non-polar) R–H compounds and the polar effect of R being dominant for the (more polar) R–F compounds.[29] One might expect the larger R–Cl and R–Br compounds of the present work to have intermediate polarities to these extremes and thus display intermediate behavior, though their BDEs are likely to be further complicated by steric effects. To help de-convolute these factors, the corresponding C–H and C–F bond dissociation energies were calculated (see Table 3), together with the charges on the halogen in the closed-shell species and the spin densities on the nominal radical carbon in the open-shell species (see Table 4). The penultimate unit effects on the bond dissociation enthalpies for all systems are also plotted in Figure 2.

INSERT TABLE 3, TABLE 4 and FIGURE 2

Polar Effect Considering first polar factors, it is seen in Table 4 that the breaking alkyl-halogen bond shows some degree of polarity in all cases and thus resonance between the covalent and ionic (i.e. $alkyl^+ X^-$) forms is likely to affect the strength of the breaking bond. Not unexpectedly, the fluorides show the largest degree of charge separation and have the strongest bonds, followed by the chlorides and then the bromides. Within each series, the degree of charge separation depends upon the nature of the terminal unit, with the propyl unit affording the most polar bonds and the acrylate and methacrylate units the least. This is readily understood in terms of the electron donating properties of an alkyl substituent versus

the electron accepting properties of an ester substituent. However, importantly, the polarity of the breaking bonds appears to be relatively unaffected by the nature of the penultimate unit. This is because the methyl and ester groups donate or accept electrons principally via hyperconjugation and resonance, respectively, and in these systems there is no possibility for conjugation between the chain end and the gamma-carbon. Although the ester groups could in principle interact with the chain end inductively as well, they are relatively weak sigma acceptors (compared with, for example, a cyano group) and this weak effect diminishes rapidly with distance from the chain end. Thus, for these substituents at least, polar factors do not contribute significantly to the origin of the penultimate unit effect.

Radical Stabilization Effect The contribution of radical stabilization effects can be assessed through an examination of the alkyl–H BDEs (Table 3) as in these systems the polar effects are minimal and the steric effects, though present, are expected to be smaller than in the halogenated systems. Although the BDEs depend strongly on the nature of the terminal unit, the penultimate unit effects are relatively small (< 1 kcal mol^{-1}). This is also evident in the spin densities on the nominal radical carbon, which provide an indication of how well the substituents can delocalize the unpaired electron. It is seen from Table 4 that, not unexpectedly, the spin densities depend strongly on the nature of the terminal unit, with the propyl unit affording the least delocalization and the methyl methacrylate unit the most. However, they are relatively independent of the nature of the penultimate unit. As in the case of the polar effect, this stems from the fact that, for the specific substituents considered in the present work (ester and alkyl groups), their principal mode of interaction with an unpaired electron occurs via resonance or hyperconjugation and, in the present systems, there is no possibility for conjugation between the gamma carbon and the unpaired electron.

Stereoelectronic Effects For the present substituents, it seems likely that the penultimate unit effects arise predominantly in steric interactions, complicated by the

associated conformational changes in the open- and closed-shell species and the potential for intramolecular H-bonding. The steric effects can either lead to an increase or decrease in the bond dissociation enthalpy (relative to the H penultimate unit) depending upon whether the relief of steric strain in the breaking bond outweighs the potential increase in steric strain as the radical conformation reorganizes so as to, for example, accommodate the sp^2 hybridized radical center.

If we focus first on the bromide and chloride systems, we find that with a terminal MMA unit, the inclusion of bulky penultimate units decrease the BDE (with respect to that with a hydrogen penultimate unit) implying that the relief of steric strain in the breaking bond outweighs any increases to steric strain in the radicals. The only exception to this trend occurs when the penultimate unit is MA. As noted above, combinations of MA and MMA units form a stacked conformation in the closed shell species, stabilized by hydrogen bonding. These hydrogen bonds, which are absent in the open conformation of the radical product, help to stabilize the closed shell system, leading to a higher than expected BDE. In contrast to the MMA terminated species, the propyl and MA terminated species have one less bulky substituent in the α-position, and are consequently less crowded in the closed-shell system. As a result, penultimate unit effects are generally much smaller and the increase in steric strain in the radical species becomes relatively more important. In these cases, only the bulkiest penultimate unit (MMA) leads to a lowering of the BDE (compared with the corresponding MA penultimate unit). Even here, the MMA penultimate unit remains stabilizing (compared with H) for the MA terminated radicals, due to the formation of the H-bonded stacked conformation in the closed shell species (see Scheme 1).

In the case of the fluorides and alkanes, the departing atom is much smaller and the steric effects are generally much less significant, with the resultant penultimate unit effects falling into a much narrower range (up to 1 kcal mol^{-1}). The majority of the chemical trends

are similar to those for the chlorides and bromides, though some minor deviations arise due to conformational differences. For example, the MMA penultimate unit is much less destabilizing in the MMA terminated closed shell species as (unlike the corresponding chloride and bromide) these now can form the stacked conformation, and are thus stabilized by H-bonding.

In summary, the penultimate unit effect on the bond dissociation enthalpies of the chlorides and bromides is significant (up to 3.29 kcal mol^{-1}), and, like the corresponding entropic component, heavily influenced by steric effects and, in the case of the acrylate and methacrylate units, intramolecular hydrogen-bonding. For these systems at least, the polar and radical stabilization effects appear to be relatively minor; however, the possibility that these play a role in other systems (containing for example strong sigma accepting groups) cannot as yet be ruled out.

Reaction Free Energies Unsurprisingly, the penultimate unit effects on the free energies are also significant, depending upon whether the penultimate unit effects on the entropy and enthalpy reinforce one another or oppose one another. Interestingly, the effect of intramolecular hydrogen bonding on the free energies is much smaller than might have been expected as the effects on the enthalpies and entropies tend to counteract one another. In essence, the formation of intramolecular hydrogen-bonded conformations (in either the closed-shell or open-shell species) tends to lower the energy but at the same time reduce the vibrational flexibility (see Scheme 1). Nonetheless, penultimate unit effects of more than 2 kcal mol^{-1} are observed due to incomplete cancellation of the entropic and enthalpic components.

The activation rate constants have been determined for some of the monomeric and dimeric species studied in this paper.[12] Thus, the relative values of the activation rate constant

for H-MMA-Br is 8 times smaller than for H-MMA-MMA-Br and 1.6 times smaller than for H-MA-MMA-Br. These values could be compared with the 44 and 12 times smaller equilibrium constants, respectively. In a similar manner, H-MA-Br is activated in ATRP 4 times slower than H-MMA-MA-Br and 1.1 times slower than H-MA-MA-Br. These values can be compared with 2.38 and 0.63 ratios of the equilibrium constants presented in Table 1. In making these comparisons it should be noted that the ATRP equilibrium constant is the ratio of the activation and deactivation rates constants (cf. Equation 1), and the latter should also be influenced by penultimate effects.

Practical Aspects. It therefore appears that significant penultimate unit effects, as much as 2 orders of magnitude in the systems studied, can occur in ATRP. Such effects would therefore have to be taken into account when modeling the kinetics of ATRP, particularly in the synthesis of block, gradient and statistical copolymers. One would also expect that penultimate unit effects could have important consequences for initiator design in ATRP. Indeed, experimentation confirms the importance of penultimate effect in the ATRP of acrylates and methacrylates.[13a-b,30] Thus, 2-bromoisobutyrate is a less efficient initiator for MMA polymerization than the corresponding dimer, unless a halogen exchange process is employed. In contrast, 2-halopropionates are quite efficient initiators for the polymerization of acrylates.

Similar observations have been made in other controlled radical polymerization systems. For example, monomeric alkoxyamines derived from isobutyrate (H-MMA-Y) are relatively stable but not efficient for MMA polymerization, whereas dimeric and polymeric species are much more active but impossible to isolate. In a similar way, RAFT reagents based on isobutyrates are relatively poor transfer agents for MMA, and indeed calculations have shown that the inclusion of the (penultimate) cyanoisopropyl initiator fragment (in

$S{=}C(CH_3)SC(CH_3)(COOCH_3)CH_2C(CH_3)_2CN$) increases the chain transfer efficiency by approximately 3.4 kcal mol^{-1}.[31]

The penultimate effects are also important in carbocationic systems. Tert-butyl halides are poor initiators for isobutylene whereas the dimeric species, namely the 2,4,4-trimethylpentyl halides, are very efficient. Early studies on the hydrolysis of the corresponding halides revealed that the latter are >100 times more reactive, due to a so-called B-strain (back strain effect).[32] The bulky neopentyl group forces the tertiary halide from sp^3 to an sp^2 carbocationic configuration. An analogous situation occurs in ATRP systems in which sp^3 hybridization of a dormant alkyl halide is converted to sp^2 hybridization of a propagating radical. In a similar way, the deactivation rate constants of radicals to dormant alkyl halides is reduced by bulky penultimate units, resulting in an overall increase of ATRP equilibrium constants.

In principle, penultimate unit effects might also be exploited to enhance activation rate constant of the relatively inactive terminal alkyl halide derived from α-olefin, e.g. propylene (P).[14] Indeed, as noted earlier, similar strategies have been successfully adopted in nitroxide mediated polymerization whereby the control of both acrylonitrile[4a] and methyl methacrylate[15] has been effected through copolymerization of these monomers with styrene. Certainly, the penultimate effects in systems based on propylene terminal unit, as shown in Table 1, are quite significant. However, the activity of the propylene dormant species is 10^7 times smaller than the acrylate dormant species.[12] Thus, even a 100 fold increase in activity is not sufficient to reactivate propylene dormant species with (meth)acrylate penultimate unit. Consequently, the ATRP copolymerization of α-olefins with (meth)acrylates is accompanied by the irreversible formation of dormant species derived from α-olefins.[33] For successful control of α-olefins via this strategy, co-monomers displaying stronger penultimate unit effects are required.

Conclusions

In the present work we have identified significant penultimate effects in the equilibrium constants between active and dormant species of atom transfer radical systems. They occur in both the entropy and enthalpy of the equilibrium and are the result of a complex interplay of stereo-electronic effects and, for the acrylic and methacrylic ester linkages, heavily influenced by intramolecular hydrogen bonding. They show most dramatic effects in MMA based systems where penultimate unit effects of as much as 2 orders of magnitude are observed. As a result, H-MMA-X initiators are not efficient for MMA but dimeric species are much more efficient. Such significant penultimate unit effects are important in initiator design, and should also be taken into account when modeling the kinetics of controlled radical polymerization, particularly for the synthesis of block, gradient and statistical copolymers.

Acknowledgments

RP thanks CINES and CICT (program CALMIP) for granting free CPU time. PR thanks the Conseil Régional de Bourgogne for funding to upgrade the University's computing facilities. KM appreciates support from the National Science Foundation (CHE-04-05627). MLC acknowledges support from the Australian Research Council under their Centres of Excellence program, and generous allocations of computing time on the National Facility of the Australian Partnership for Advanced Computing.

Supporting Information Available. B3-LYP/6-31G(d) optimized geometries of all species, associated total energies and entropies, and the rotational potentials obtained for the

hindered rotor calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Scheme 1. The hydrogen-bonding contribution to the penultimate unit effect of MMA versus MA.

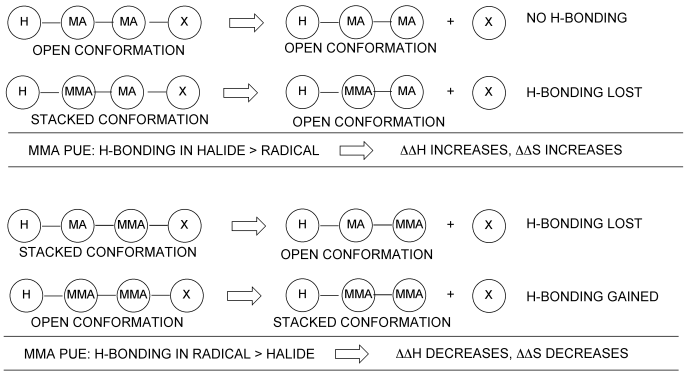


Table 1. Thermodynamic parameters for the homolytic bond rupture of the M_1–X bond in H–M_2-M_1-X (M_1, M_2 = P, MA, MMA; X = Cl, Br, F and H) and H-M_1-X.[a]

R		X	ΔH_{298}/	ΔS_{298}/	ΔG_{298}/	$\Delta\Delta H_{298}$[b]/	$\Delta\Delta S_{298}$[c]/	K/K_0 [d]
M_2	M_1		kcal mol^{-1}	cal mol^{-1} K^{-1}	kcal mol^{-1}	kcal mol^{-1}	kcal mol^{-1} K^{-1}	
-	P	Cl	84.61	35.44	74.04	0	0	1
P	P	Cl	85.18	36.95	74.17	0.57	1.50	0.81
MA	P	Cl	85.80	39.90	73.90	1.19	4.46	1.27
MMA	P	Cl	83.24	39.85	71.36	-1.37	4.40	92.46
-	MA	Cl	74.66	28.39	66.19	0	0	1
P	MA	Cl	75.09	34.14	64.91	0.43	5.75	8.73
MA	MA	Cl	76.48	36.42	65.62	1.82	8.02	2.64
MMA	MA	Cl	75.82	39.22	64.13	1.16	10.83	32.69
-	MMA	Cl	74.36	36.73	63.40	0	0	1
P	MMA	Cl	72.91	35.36	62.37	-1.44	-1.37	5.73
MA	MMA	Cl	74.64	37.17	63.55	0.28	0.44	0.78
MMA	MMA	Cl	72.21	30.44	63.14	-2.14	-6.29	1.57
-	P	Br	74.44	35.23	63.93	0	0	1
P	P	Br	75.29	36.91	64.28	0.85	1.69	0.55
MA	P	Br	75.67	38.68	64.14	1.24	3.46	0.70
MMA	P	Br	73.47	39.95	61.56	-0.96	4.73	54.79
-	MA	Br	65.37	30.01	56.43	0	0	1
P	MA	Br	66.07	35.71	55.42	0.70	5.70	5.44
MA	MA	Br	67.17	35.12	56.70	1.80	5.11	0.63
MMA	MA	Br	67.18	37.79	55.91	1.81	7.78	2.38
-	MMA	Br	64.49	35.91	53.78	0	0	1
P	MMA	Br	63.84	30.88	54.63	-0.65	-5.04	0.24
MA	MMA	Br	64.90	42.27	52.30	0.41	6.36	12.18
MMA	MMA	Br	61.20	32.40	51.54	-3.29	-3.51	43.77

[a]Calculated at the G3(MP2)-RAD level of theory using the hindered rotor model to treat all low frequency torsional modes. [b]$\Delta\Delta H_{298} = \Delta H_{298}$(H–$M_2$-$M_1$-X) - ΔH_{298}(H-M_1-X). [c]$\Delta\Delta S_{298} = \Delta S_{298}$(H–$M_2$-$M_1$-X) - ΔS_{298}(H-M_1-X). [d]$K/K_0 = \exp(-\Delta\Delta G_{298}/RT)$

Table 2. Contributions to the homolytic carbon-halogen bond rupture entropy for all H-M_2-M_1-X (M_1, M_2 = P, MA, MMA; X = Cl, Br) molecules.[a]

R		X	ΔS_{298} (trans)	ΔS_{298} (rot)	ΔS_{298} (vibr')[b]	ΔS_{298} (vibr)[c]
M_2	M_1		cal mol^{-1} K^{-1}	cal mol^{-1} K^{-1}	cal mol^{-1} K^{-1}	cal mol^{-1} K^{-1}
-	P	Cl	34.81	-3.00	0.99	0.87
P	P	Cl	35.56	-1.56	-1.33	0.19
MA	P	Cl	35.87	-1.12	-0.49	2.40
MMA	P	Cl	35.93	-1.10	0.23	2.25
-	MA	Cl	35.58	-1.91	-4.45	-8.03
P	MA	Cl	35.87	-1.22	-4.55	-3.26
MA	MA	Cl	36.04	-0.66	-4.62	-1.72
MMA	MA	Cl	36.08	-0.32	-2.96	0.71
-	MMA	Cl	35.70	-1.31	-0.52	-0.42
P	MMA	Cl	35.93	-0.84	1.40	-2.50
MA	MMA	Cl	36.08	-0.26	0.71	-1.40
MMA	MMA	Cl	36.11	-0.83	-2.46	-7.59
-	P	Br	35.91	-3.78	0.33	0.35
P	P	Br	37.06	-2.24	-2.16	-0.65
MA	P	Br	37.59	-1.78	-2.12	0.12
MMA	P	Br	37.70	-1.88	-1.16	1.38
-	MA	Br	37.09	-2.70	-5.05	-7.13
P	MA	Br	37.59	-1.91	-5.29	-2.72
MA	MA	Br	37.89	-1.12	-6.31	-4.41
MMA	MA	Br	37.96	-1.02	-5.76	-1.91
-	MMA	Br	37.29	-2.02	-1.39	-2.11
P	MMA	Br	37.70	-1.33	-0.64	-8.26
MA	MMA	Br	37.96	-0.96	-1.05	2.51
MMA	MMA	Br	38.03	-1.40	-4.03	-6.98

[a]Each reaction has a ΔS_{298} (electr) contribution of 2.754 cal mol^{-1} K^{-1}. [b]Includes contribution from low frequency torsional modes, treated under the harmonic oscillator approximation. [c]Includes contribution from low frequency torsional modes treated as hindered internal rotations.

Table 3. Thermodynamic parameters for the homolytic bond rupture of the M_1–X bond in H-M_2-M_1-X and H-M_1-X (M_1, M_2 = P, MA, MMA; X = F and H).[a]

R		X	ΔH_{298}/	ΔS_{298}/	ΔG_{298}/	$\Delta\Delta H_{298}$[b]/	$\Delta\Delta S_{298}$[c]/	K/K_0[d]
M_2	M_1		kcal mol^{-1}	cal mol^{-1} K^{-1}	kcal mol^{-1}	kcal mol^{-1}	kcal mol^{-1} K^{-1}	
-	P	F	115.29	36.25	104.48	0	0	1
P	P	F	115.04	35.16	104.55	-0.25	-1.08	0.89
MA	P	F	115.99	37.37	104.84	0.70	1.13	0.54
MMA	P	F	114.79	37.04	103.75	-0.50	0.79	3.45
-	MA	F	104.06	32.05	94.50	0	0	1
P	MA	F	104.31	33.11	94.44	0.25	1.06	1.12
MA	MA	F	104.91	33.51	94.91	0.85	1.47	0.50
MMA	MA	F	104.78	37.30	93.66	0.72	5.26	4.17
-	MMA	F	105.64	35.45	95.07	0	0	1
P	MMA	F	104.85	37.28	93.73	-0.79	1.83	9.62
MA	MMA	F	106.30	36.71	95.36	0.66	1.26	0.62
MMA	MMA	F	105.79	38.15	94.42	0.15	2.69	3.02
-	P	H	99.83	31.75	90.36	0	0	1
P	P	H	99.26	31.55	89.86	-0.56	-0.20	2.34
MA	P	H	99.98	31.89	90.47	0.15	0.13	0.83
MMA	P	H	99.84	30.80	90.66	0.02	-0.95	0.60
-	MA	H	95.54	27.64	87.30	0	0	1
P	MA	H	94.48	27.17	86.38	-1.06	-0.47	4.74
MA	MA	H	95.91	29.65	87.07	0.37	2.01	1.48
MMA	MA	H	95.95	30.78	86.77	0.41	3.14	2.44
-	MMA	H	92.05	30.51	82.95	0	0	1
P	MMA	H	91.61	29.84	82.72	-0.44	-0.67	1.49
MA	MMA	H	92.13	27.94	83.80	0.08	-2.57	0.24
MMA	MMA	H	92.83	31.72	83.37	0.78	1.21	0.49

[a]Calculated at the G3(MP2)-RAD level of theory in conjunction with the harmonic oscillator approximation. [b]$\Delta\Delta H_{298} = \Delta H_{298}$(H-$M_2$-$M_1$-X) - ΔH_{298}(H-M_1-X). [c]$\Delta\Delta S_{298} = \Delta S_{298}$(H-$M_2$-$M_1$-X) - ΔS_{298}(H-M_1-X). [d]$K/K_0 = \exp(-\Delta\Delta G_{298}/RT)$

Table 4. Charge on X in H–M_2–M_1–X and Spin Density on the Nominal Radical Carbon in H-M_2-M_1• [a]

M_2	M_1	Charge on X in H–M_2–M_1–X			Spin density
		X = Br	X = Cl	X = F	
H	P	-0.112	-0.162	-0.439	0.900
P	P	-0.115	-0.169	-0.445	0.899
MA	P	-0.130	-0.177	-0.448	0.906
MMA	P	-0.103	-0.156	-0.449	0.899
H	MA	-0.040	-0.107	-0.405	0.825
P	MA	-0.038	-0.103	-0.411	0.827
MA	MA	-0.059	-0.121	-0.409	0.831
MMA	MA	-0.026	-0.093	-0.410	0.829
H	MMA	-0.060	-0.122	-0.422	0.768
P	MMA	-0.058	-0.121	-0.427	0.776
MA	MMA	-0.054	-0.109	-0.426	0.773
MMA	MMA	-0.054	-0.118	-0.424	0.782

[a]Charges calculated at the ROHF/cc-pVTZ level of theory on the basis of an NBO population analysis.

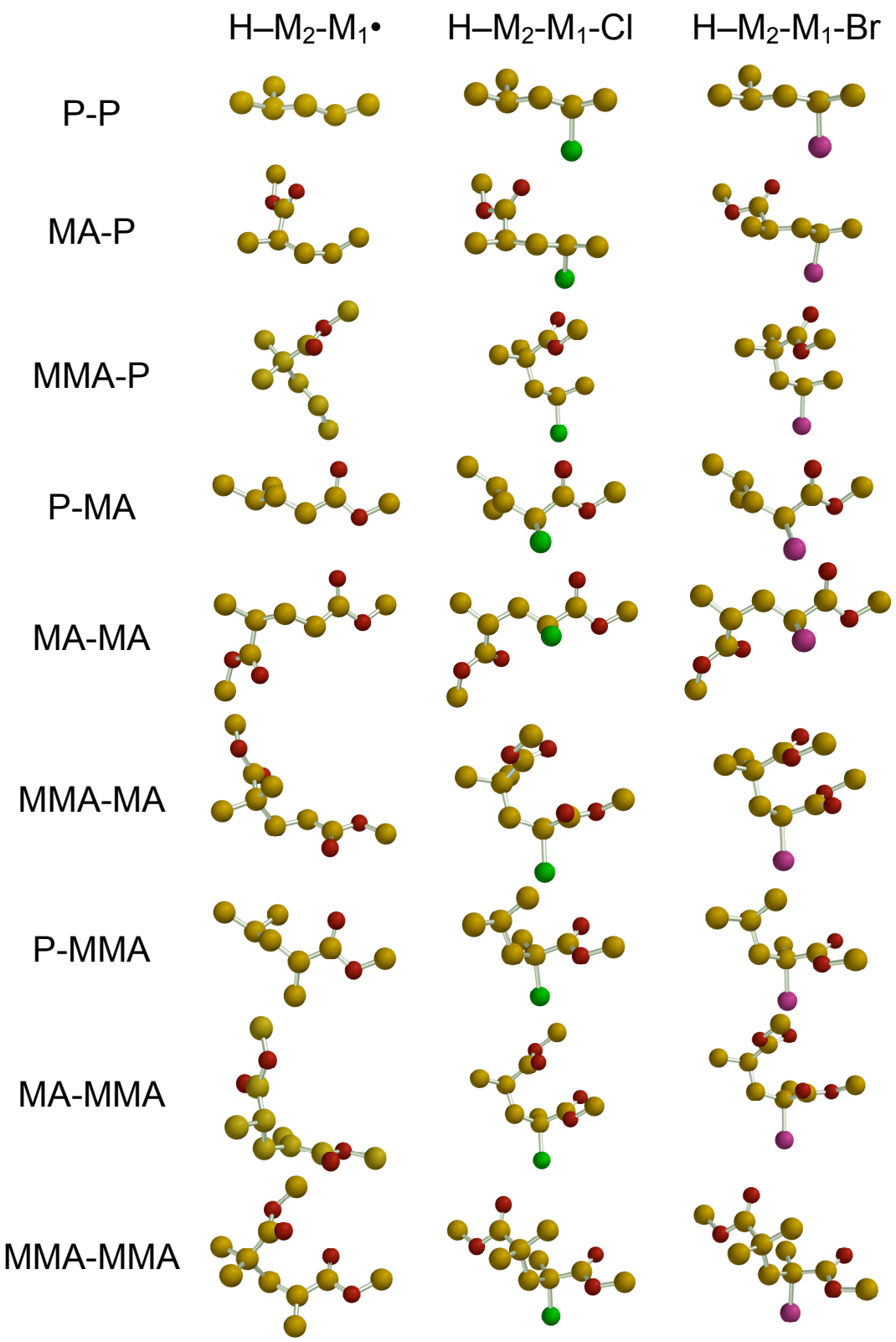


Figure 1. Views of the lowest energy optimized geometries for all H–M_2-M_1•, H–M_2-M_1-Cl and H–M_2-M_1-Br molecules.

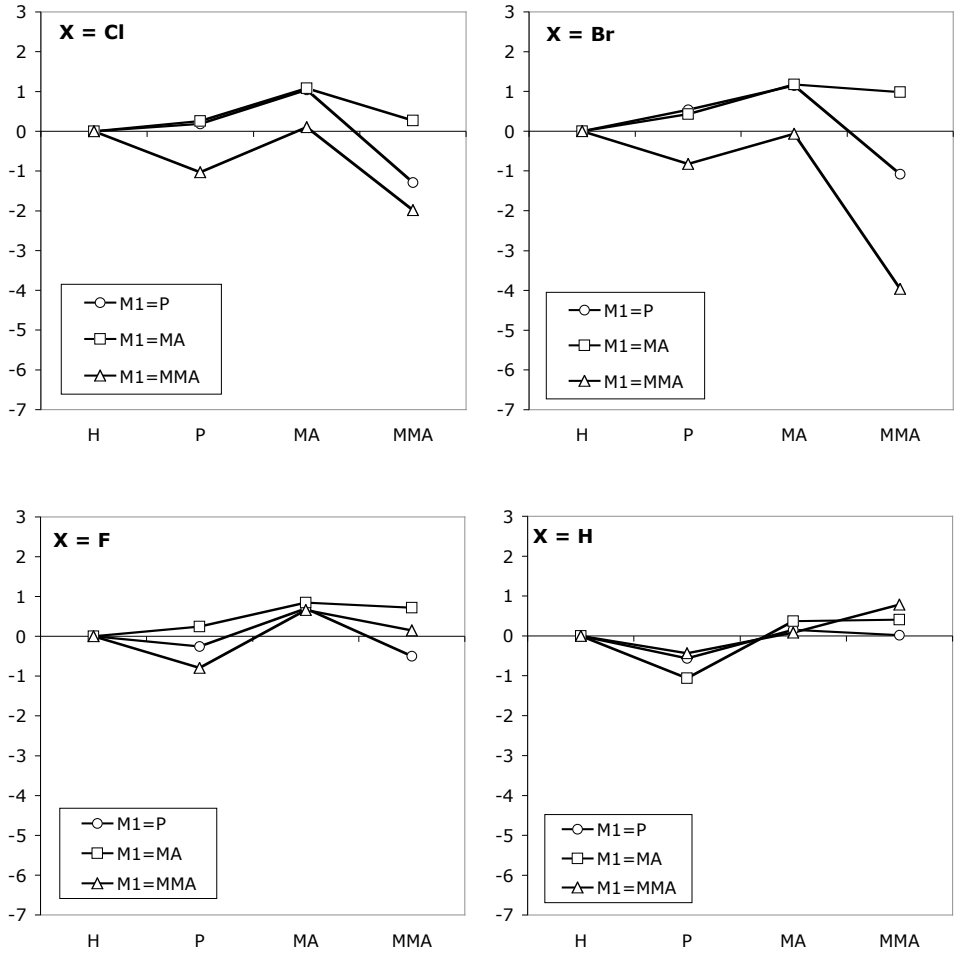
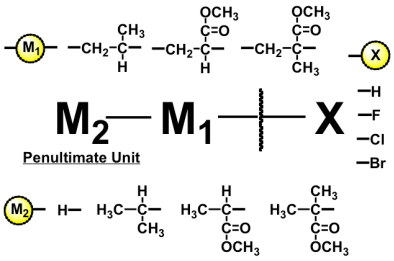


Figure 2. Effect of the penultimate unit (M_2, relative to M_2 = H) on the bond dissociation enthalpy (kcal/mol) of H-M_2–M_1–X, for M_2, M_1 = propyl (P), methyl acrylate (MA) and methyl methacrylate (MMA) and X = Cl, Br, F and H.

TOC Entry


M1
CH3
CH2
C
H
OCH3
C=O
X
M2
M1
X
H
F
Cl
Br
Penultimate Unit
M2
H
H3C
CH3
OCH3