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# A Density Functional Theory Approach to the Development of *Q*−*e* Parameters for the Prediction of Reactivity in Free-Radical Copolymerizations

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The *Q*−*e* scheme was developed for the interpretation of the reactivity of a monomer containing a double bond in free-radical copolymerizations. This empirical scheme has proven to be remarkably useful and continues to be the only general reactivity scheme in use today. To develop a reliable computational approach for the theoretical prediction of the *Q* and *e* values of molecules whose experimental *Q* and *e* values have not been established, we have analyzed the *Q*−*e* approach to develop a computational approach to their prediction. We then performed density-functional theory (DFT) calculations on molecules whose experimental *Q* and *e* values are available to develop a set of correlation parameters for monomers without experimental values. It has been demonstrated that for a general choice of the *Q* and *e* values of the reference monomer that both parameters *Q* and *e* should be dependent on the energetic properties of the free-radical reaction and the polar properties of the monomer and radical. To correlate the *Q* and *e* parameters with these properties, the overall quality of the calibrated correlation relationships should not be affected by the choice of the reference *Q* and *e* values. Satisfactory relationships have been found for the correlations of the *Q*−*e* parameters with DFT-calculated electronegativities and reaction free energies, suggesting that the electronegativity and reaction free energy determined by the DFT calculations reasonably reflect the polar and energetic properties, respectively, needed for *Q*−*e* parameter development. With the particular choice of the popularly used reference values of $Q = 1.0$ and $e = -0.8$ for styrene, the parameter *e* is dependent only on the calculated electronegativity, and the parameter *Q* is dominated by the calculated reaction free energy of the process of adding a radical to a C═C double bond. The explicit relationships obtained in this work can be used to predict unknown *Q* and *e* parameters based on DFT calculations.

## Introduction

Over 50 years ago, Alfrey and Price[1] developed an empirical model, the *Q*−*e* scheme,[2−7] for interpreting and predicting the reactivity of a monomer containing a double bond in radical copolymerizations. According to the *Q*−*e* model, each reactant, i.e., monomer or free radical, is given a parameter, *Q* for the monomer and *P* for the free radical, describing its general reactivity, and a second parameter, *e* for the monomer or free radical, related to its polar properties (in the original derivation, *e* was the permanent electric charge on the species). Assuming that the reactivity of a growing polymeric radical depends only on the nature of the terminal radical unit, for any two monomers and the corresponding two free radicals, four basic propagation rate constants, $k_{11}$, $k_{11}$, $k_{21}$, and $k_{22}$, can be derived[6]

$$k_{11} = P_1Q_1 \exp(-e_1^{\,2}) \tag{1}$$

$$k_{12} = P_1Q_2 \exp(-e_1e_2) \tag{2}$$

$$k_{21} = P_2Q_1 \exp(-e_2e_1)1 \tag{3}$$

$$k_{22} = P_2Q_2 \exp(-e_2^{\,2}) \tag{4}$$

The reactivity ratios, $r_1 \equiv k_{11}/k_{12}$ and $r_2 \equiv k_{22}/k_{21}$, are used to eliminate the parameter *P* for the free radical giving

$$r_1 = (Q_1/Q_2) \exp[-e_1(e_1 - e_2)] \tag{5}$$

$$r_2 = (Q_2/Q_1) \exp[-e_2(e_2 - e_1)] \tag{6}$$

which depend only on the monomers. Hence, the reactivity ratios $r_1$ and $r_2$ depend only on the parameters *Q* and *e*. In practice, the *Q*−*e* scheme defines a reference monomer to which all other monomers can be related; the most popularly used reference is styrene with $Q = 1.0$ and $e = -0.8$.[6,8] The *Q* and *e* values of any other monomer can be determined by using eq 5 or 6 based on the experimental reactivity ratios and the *Q* and *e* values of the reference monomer. Extensive reviews of the *Q*−*e* scheme and its strength and weakness can be found in the literature.[2−7] Despite its shortcomings, the *Q*−*e* scheme has proven to be remarkably useful and continues to be essentially the only general reactivity scheme for predicting radical copolymerizations in use today.[7] The *Q*−*e* scheme is a terminal model and, as noted previously,[9] the terminal model is sufficient for the prediction of instantaneous polymer−copolymer composition and sequence distributions for most copolymerizations. We are specifically interested in the reactivity of various monomers with each other for the development of photoresists for the 157 nm technology production of new semiconductors[10−12] so a terminal model is a reasonable first approximation. More sophisticated models such as the penultimate model have been developed by others to provide even more detail about free−radical copolymerizations.[9,13]

The aim of the *Q*−*e* scheme, which relies on a large database of kinetic rate constants determined over the last half century, is to predict the relative reactivity in free-radical copolymerizations without recourse to experimental determination of additional kinetic rate constants. An obvious limitation of the standard *Q*−*e* scheme is that one cannot predict the reactivity

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of a monomer whose $Q$ and $e$ parameters are not available empirically. Therefore, the development of a reliable approach for the computational prediction of the basic $Q$ and $e$ parameters is of real interest, particularly for new monomers for which experimental investigation would be expensive.

There have been several previous attempts to correlate the parameters $Q$ and $e$ with results from electronic structure calculations. The earliest molecular orbital (MO) calculations reported in the 1960s[5] were based on simple Hückel theory. Recent electronic structure calculations for the development of $Q-e$ parameters were based on the ab initio Hartree−Fock (HF) method.[6,14,15] However, there are serious limitations in these previous electronic structure calculations. As well-known,[16] the HF method does not account for electron correlation and, therefore, gives poor results for the reaction energies that are required in the correlation of the $Q-e$ parameters with the calculated results. In addition, most of the previous ab initio HF calculations for developing the $Q-e$ parameters were performed using the minimal STO-3G basis set, and the largest basis set used in any of the HF calculations was a triple-$\zeta$ valence (TZV) basis set. Thus, the effects of polarization and diffuse functions also have not been examined. Radom and coworkers have been using much higher level and more costly electronic structure methods to look at the details of the transition states for the addition of small radicals to small alkenes.[17,18]Although such a direct approach of calculating the kinetics of a chemical reaction based on detailed calculations on the transition state for each reaction of interest is attractive, such calculations are far too expensive computationally to use for the large substituted monomers of general interest in the development of new polymers, especially for photoresists.

There has been a rapid growth in the use of electronic structure theory in the design of molecules that have specific, required properties. One of the main reasons for this acceleration has been the development of density functional theory (DFT),[19−24] especially for molecular systems. Two important reasons that DFT is becoming so popular for such studies are its lower computational cost, formally scaling as $N^3$ (with Coulomb fitting), where $N$ is the number of basis functions, and the fact that DFT includes the effects of electron correlation at some reasonable level. The combination of lower computational cost with reasonable accuracy as compared to other approaches has led to the successful application of the DFT method to the prediction of a broad range of properties of molecules in the ground state. Thus we have chosen to use DFT as the electronic structure method for the development of a computational approach for the prediction of $Q-e$ parameters. In the current study, we have performed a series of DFT calculations with various basis sets on a variety of molecules whose experimentally derived $Q$ and $e$ values are available. The calculated results are used to develop correlations with the experimental $Q$ and $e$ values, leading to useful relationships for the prediction of the $Q$ and $e$ values of monomers whose experimental $Q$ and $e$ values are not available.

## Computational Approach

**Basic Relationships.** To predict the values of the $Q$ and $e$ parameters based on DFT calculations for molecules whose experimental $Q$ and $e$ values are not available, we first need to correlate the DFT results with available experimentally derived $Q$ and $e$ values. By definition, the parameter $e$ should reflect some polar properties of the monomer or both the monomer and the corresponding radical. Previous computational studies consistently correlated the parameter $e$ with the electronegativity. Following the correlation relationships previously described in the literature,[6] there is a linear relationship for the parameter $e$:

$$e = a_e\chi + b_e \tag{7}$$

where $a_e$ and $b_e$ are empirical constants to be determined by comparison to experimentally derived $e$ values. $\chi$ in eq 7 is the electronegativity of the monomer, denoted by $\chi_m$, or the average electronegativity of the monomer and the radical, denoted by $\chi_{av} = (\chi_m + \chi_r)/2$, in which $\chi_r$ refers to the electronegativity of the radical. Previous computational studies correlated the parameter $Q$ with different computational parameters, including the recently used expression[6]

$$\ln Q = a_Q E_y + b_Q\chi + c_Q E_y\chi + d_Q \tag{8}$$

In eq 8, $E_y$ is the energy (or free energy) of the copolymerization step

$$\text{monomer} + \text{radical} \rightarrow \text{radical chain}$$

i.e., the energy (or free energy) gained on adding the radical to the double bond of the monomer, and $a_Q$, $b_Q$, $c_Q$, and $d_Q$ are empirical constants to be determined by comparison to experimentally derived $Q$ values. A simple linear relationship,

$$\ln Q = a_Q E_y + b_Q \tag{9}$$

between the parameter $Q$ and the reaction energy $E_y$ has also been tested.[14]

To better understand the correlation relationships, we can compare the expression of the reactivity ratios in the $Q-e$ scheme with that of the well-known Arrhenius equation,[25]

$$k = A\exp(-E_a/RT) \tag{10}$$

where the reaction rate constant $k$ is determined by the activation energy $E_a$ and the preexponential factor $A$. The preexponential factor $A$ for a given temperature $T$ can be evaluated as

$$A = \kappa(k_BT/h)(Q_{TS}/Q_MQ_R) \tag{11}$$

on the basis of conventional transition state theory (CTST).[26] In eq 11, $k_B$ is Boltzmann's constant, $h$ is Planck's constant, $\kappa$ is the tunneling correction, and $Q_M$, $Q_R$, and $Q_{TS}$ represent the partition functions of the monomer, radical, and transition state of the reaction. The notation $Q_M$, $Q_R$, and $Q_{TS}$ used here for the partition functions should be distinguished from the parameter $Q$ (or $Q_1$ and $Q_2$) used in the $Q-e$ scheme. The contribution of $Q_{TS}/Q_MQ_R$ to the rate constant $k$ can also effectively be included in the Gibbs free energy of activation, $G_a$, through

$$k = \kappa(k_BT/h)\exp(-G_a/RT) \tag{12}$$

For convenience, eqs 10 and 12 are now written in the form:

$$k = B\exp(-E^{\ddagger}/RT) \tag{13}$$

where $E^{\ddagger}$ represents either the activation energy $E_a$ or the Gibbs free energy of activation $G_a$. The preexponential factor $B = \kappa(k_BT/h)(Q_{TS}/Q_MQ_R)$ when $E^{\ddagger} = E_a$ or $B = \kappa(k_BT/h)$ when $E^{\ddagger} = G_a$.

The quantity $r_1$ (or $r_2$) in eq 5 (or (6)) is the ratio of the reactivity of the first (or second) monomer with the radical corresponding to the first (or second) monomer to that of the second (or first) monomer with the same radical, remembering that the termination radical is considered to be independent of the remaining part of the growing polymeric chain. For a simple copolymerization between two monomers, the radical must be associated with one of the two monomers in eqs 5 and 6. For a more flexible choice of the radical in the development of $Q-e$ parameters, a more generalized reactivity ratio, $r_{i12}$, can be obtained:

$$k_{i1} = P_i Q_1 \exp(-e_i e_1) \tag{14}$$

$$k_{i2} = P_i Q_2 \exp(-e_i e_2) \tag{15}$$

$$r_{i12} \equiv k_{i1}/k_{i2} = (Q_1/Q_2) \exp[-e_i(e_1 - e_2)] \tag{16}$$

A comparison of eq 16 with eqs 5 and 6 indicates that $r_{i12} = r_1$ when $i = 1$ and $r_{i12} = 1/r_2$ when $i = 2$. The radical in eq 16 may not necessarily be associated with one of the two monomers, but it can be any other radical species such as the hydrogen atom, H$^\bullet$, or the methyl radical, $^\bullet$CH$_3$. In this case, $e_i$ in eq 16 does not necessarily correspond to the commonly used parameter $e$ of a monomer in the $Q-e$ scheme because the radicals, H$^\bullet$ or $^\bullet$CH$_3$, are not associated with any monomer having a double bond (they cannot be formed by adding any smaller radical to a monomer having a double bond). In a revised version of the $Q-e$ scheme, known as the $Q-e-e^*$-type scheme,[6,27] a monomer and its corresponding radical could have different parameter values, $e$ and $e^*$ referring to the monomer and radical, respectively. In terms of the $Q-e-e^*$-type scheme, $e_i$ in eqs 14−16 should be rewritten as $e_i^*$, whose value could differ from the $e_i$ value of the corresponding monomer, if the monomer exists. It is most convenient for the development of correlations of the $Q$ and $e$ parameters with results from DFT calculations to focus on the copolymerization of various monomers with the same radical to which the subscript $i$ refers, $e_i$ (or $e_i^*$) in eq 16. The value of $e_i$ (or $e_i^*$) is then always a constant to be determined by comparison with experimentally derived $Q$ and $e$ values, so long as $i \neq 1$ and $i \neq 2$, and is independent of whether one uses the standard $Q-e$ scheme or the $Q-e-e^*$-type scheme. Equation 16 is the starting point for our computational study of the $Q-e$ parameters.

By using eq 13 for the rate constants $k_{i1}$ and $k_{i2}$, we obtain an alternative expression of the reactivity ratio $r_{i12}$,

$$r_{i12} = (B_{i1}/B_{i2}) \exp[-(E^{\ddagger}_{i1} - E^{\ddagger}_{i2})/RT] \tag{17}$$

Equations 16 and 17 give

$$\ln Q_2 = \ln Q_1 + e_i(e_1 - e_2) + \ln(B_{i1}/B_{i2}) - (E^{\ddagger}_{i1} - E^{\ddagger}_{i2})/RT \tag{18}$$

For convenience, here subscript 1 refers to the reference monomer and subscript 2 refers to the monomer whose $Q$ and $e$ values are to be determined on the basis of the reference values. For the copolymerization of various monomers with the same radical to which subscript $i$ refers, the parameter $e_i$ and activation energy $E^{\ddagger}_{i1}$, along with the parameters $Q_1$ and $e_1$, all become constants. Furthermore, if the change of the preexponential factor for different monomers is neglected, $\ln(B_{i1}/B_{i2})$ is zero, particularly when $E^{\ddagger} = G_a$. When $E^{\ddagger} = G_a$, $\ln(B_{i1}/B_{i2})$ is zero, if we assume that the $\kappa$ values are the same. Thus, eq 18 reduces to

$$\ln Q_2 = E^{\ddagger}_{i2}/RT - e_i e_2 + C \tag{19}$$

with $C$ a constant. In the formulation with $E^{\ddagger} = E_a$, previous studies have shown that the presence of a different substituent in the position $\gamma$ to the radical center can affect both the entropy of activation through steric effects as well as the activation energy,[9] which means that there may be variations in the constant $C$. However, such a dependence only occurs in more detailed models than the terminal model that we are using. Equation 19 shows that in addition to the constant contributions from the $e$ value of the radical $i$ and from the $Q$ and $e$ values of the reference monomer 1, the $Q$ value of monomer 2 is dependent on both its own $e$ value and the activation energy for the radical-monomer reaction. This implies that the polar properties affecting the parameter $e$ could also affect the parameter $Q$.

To use eq 19 to calculate the $Q$ value of a monomer, one needs to determine the activation energy for the reaction of the monomer with a radical. However, the reliable computational determination of an activation energy or Gibbs free energy of activation is significantly more expensive than that of a reaction energy[28] and, therefore, achieving a reliable theoretical prediction by directly using eq 19 is computationally very time-consuming. Fortunately, the computation can be simplified by using previously found correlations between the activation energy and reaction energy.[29,30] The results calculated by Fueno and Kamachi for the reaction of methyl radical with a number of vinyl compounds suggest that the correlation between the activation energies and heats of reaction calculated at the HF/3-21G level is very close to being linear.[29] In addition, "an extremely good linear relationship" between the activation energy and reaction energy ($\Delta E$) was found by Davis and Rogers,[6] whose ab initio calculations were also performed using the Hartree−Fock (HF) theory. Recent theoretical studies[17,18] on the addition of radicals to alkenes show that reliable energy barriers can only be obtained at very sophisticated levels of ab initio theory, such as the QCISD(T)/6-311+G(3df,2p) level, or by using DFT. In most cases, approximate linear relationships between the experimental activation energies and the experimental reaction enthalpies are found, as shown in the review by Fischer and Radom.[18] We can then assume

$$E^{\ddagger} = wE_y + l \tag{20}$$

where $w$ and $l$ are empirical constants; substitution of eqs 7 and 20 into eq 19 with removal of the subscript 2 gives

$$\ln Q = a_Q E_y + b_Q \chi + c_Q \tag{21}$$

yielding three independent constants to be calibrated: $a_Q = w/RT$, $b_Q = -e_i a_e$, and $c_Q = C + l/RT - e_i b_e$. The difference between eq 21 and eq 8 is that the cross term, $E_y\chi$, disappears in eq 21. Based on eqs 7 and 19, eq 8 is mathematically equivalent to be the one derived from using eq 22 or 23, instead of eq 20:

$$E^{\ddagger} = wE_y + uE_y\chi + l \tag{22}$$

$$E^{\ddagger} = wE_y + uE_y\chi + v\chi + l \tag{23}$$

These equations reveal that the cross term, $E_y\chi$, is unnecessary if the linear relationship between the activation energy and reaction energy found by Davis and Rogers is generally applicable. A more complicated correlation relationship, such as eq 22 or 23, would be required if the cross term, $E_y\chi$, cannot be ignored. This analysis indicates that the linear correlation relationship, i.e., eq 20, is not a necessary condition for the existence of eq 8. Equation 8 is reasonable so long as eq 23 is satisfied. Because the experimental activation energies ($E_a$) and reaction enthalpies ($\Delta H$) are available[18] for 10 of the monomers

**TABLE 1: Representative Monomers with Experimental *Q* and *e* Values**

| | Laurier et al.[a] | | Greenley[b] | |
|---|---|---|---|---|
| monomer | *Q* | *e* | *Q* | *e* |
| 1. acrylic acid | 0.68 | 1.33 | 0.83 | 0.88 |
| 2. acrylonitrile | 0.51 | 1.19 | 0.48 | 1.23 |
| 3. 1,3-butadiene | 2.36 | −1.17 | 1.70 | −0.50 |
| 4. butyl acrylate | 0.41 | 1.06 | 0.38 | 0.85 |
| 5. methacrylonitrile | 0.85 | 0.69 | 0.86 | 0.68 |
| 6. methyl acrylate | 0.38 | 0.75 | 0.45 | 0.64 |
| 7. methyl methacrylate | 0.76 | 0.38 | 0.78 | 0.40 |
| 8. styrene (reference) | 1.00 | −0.80 | 1.00 | −0.80 |
| 9. vinyl acetate | 0.024 | −0.02 | 0.026 | −0.88 |
| 10. vinyl chloride | 0.033 | −0.10 | 0.056 | 0.16 |
| 11. vinylidene chloride | 0.29 | 0.26 | 0.31 | 0.34 |
| 12. ethene | | | 0.016 | 0.05 |
| 13. propene | | | 0.009 | −1.69 |
| 14. isobutene | | | 0.023 | −1.20 |
| 15. isoprene | | | 1.99 | −0.55 |
| 16. acrolein | | | 0.80 | 1.31 |
| 17. methacrolein | | | 1.83 | 0.71 |
| 18. vinylidene cyanide | | | 14.22 | 1.92 |
| 19. methyl vinyl ketone | | | 0.66 | 1.05 |
| 20. vinyl ethyl ether | | | 0.018 | −1.81 |
| 21. acrylamide | | | 0.23 | 0.54 |
| 22. allyl alcohol | | | 0.005 | −1.48 |
| 23. 2-vinylpyridine | | | 1.41 | −0.42 |
| 24. methacrylic acid | | | 0.98 | 0.62 |
| 25. vinyl methyl ether | | | 0.029 | −1.16 |
| 26. vinyl fluoride | | | 0.008 | 0.72 |
| 27. tetrafluoroethylene | | | 0.032 | 1.63 |

[a] Data from ref 8. [b] Data from ref 43.

(i.e., molecules 2, 5, 6, 10−14, 16, and 22 listed in Table 1) considered in the present study, we tested both eqs 20 and 23 for these 10 monomers and found that eq 23 showed an improved correlation.[31]

**Electronegativity from DFT Calculations.** Mulliken's electronegativity, $\chi$, of a molecule is defined as the average of its (first) ionization potential (IP) and its electron affinity (EA), i.e., $\chi = (\mathrm{IP} + \mathrm{EA})/2$. By using Koopmans' theorem (KT), we obtain[6,21]

$$\chi_{\mathrm{m}} = -(\epsilon_{\mathrm{HOMO}} + \epsilon_{\mathrm{LUMO}})/2 \tag{24}$$

$$\chi_{\mathrm{r}} = -\epsilon_{\mathrm{SOMO}} \tag{25}$$

and

$$\chi_{\mathrm{av}} \equiv (\chi_{\mathrm{m}} + \chi_{\mathrm{r}})/2 = -(\epsilon_{\mathrm{HOMO}} + \epsilon_{\mathrm{LUMO}})/4 - \epsilon_{\mathrm{SOMO}}/2 \tag{26}$$

Here, $\epsilon_{\mathrm{HOMO}}$ is the eigenvalue of the highest occupied molecular orbital (the negative of the ionization potential), $\epsilon_{\mathrm{LUMO}}$ the eigenvalue of the lowest unoccupied molecular orbital (electron affinity), and $\epsilon_{\mathrm{SOMO}}$ the eigenvalue of the singly occupied molecular orbital (either the ionization potential or the electron affinity in terms of KT). Koopmans' theorem is valid for the first ionization potential of the HF wave function in a complete basis set. An issue with the expression for $\chi$ at the DFT level is that the energies of the Kohn−Sham (KS) orbitals can be quite different from the energies of the HF molecular orbitals depending on which exchange-correlation functional is used. KT rigorously applies to the HF method and approximate versions are available for DFT.[21] A problem with DFT is that the IP given by the DFT HOMO energy with typical exchange-correlation functionals is usually too small and it may not be appropriate to use the LUMO energy from DFT to estimate the EA because the DFT LUMO may be more indicative of the energy of the first excited state.[32] Even though the DFT KS orbital energies for most exchange-correlation functionals may not be good approximations for the IP and EA, a linear dependency of $|\epsilon_i^{\mathrm{KS}} - \epsilon_i^{\mathrm{HF}}|$ vs $\epsilon_i^{\mathrm{HF}}$ has been previously established.[33,34] Another approach is to directly evaluate IP and EA without using Koopman's theorem but with additional energy calculations on the corresponding ionic states: $\mathrm{IP} = E(\mathrm{M}^+) - E(\mathrm{M})$ and $\mathrm{EA} = E(\mathrm{M}) - E(\mathrm{M}^-)$ where $E(\mathrm{M})$, $E(\mathrm{M}^+)$, and $E(\mathrm{M}^-)$ are total energies of the neutral, cationic, and anionic systems, respectively. However, the use of eqs 7−9, 20, and 21 requires only that a satisfactory linear correlation relationship between the calculated $\chi$ values exists independent of how the IP and EA values are calculated; i.e., it does not matter if Koopmans' theorem is valid for the absolute values as long as the linear correlation exists. We thus examined the possible linear relationships between the $\chi_{\mathrm{m}}$ values calculated with and without the use of Koopmans' theorem.

Another issue to be addressed is the use of restricted or unrestricted open-shell DFT calculations for the radical. In principle, with the use of Koopmans' theorem, Mulliken's electronegativity of a radical, $\chi_{\mathrm{r}} = -\epsilon_{\mathrm{SOMO}}$, should be obtained from a restricted open-shell DFT calculation.[21] The $-\epsilon_{\mathrm{SOMO}}$ values obtained from unrestricted open-shell DFT calculations are generally larger than those from the corresponding restricted open-shell DFT calculation using the same exchange-correlation functional and the same basis set. We also examined whether a possible linear correlation relationship between these two kinds of $-\epsilon_{\mathrm{SOMO}}$ values exists.

**Reaction Free Energy from DFT Calculations.** Because of the inclusion of correlation energy effects in DFT calculations, the enthalpic contribution to the free energy of the reaction of a monomer (M) with a radical ($\mathrm{R}^\bullet$), $\mathrm{M} + \mathrm{R}^\bullet \rightarrow \mathrm{MR}^\bullet$, is expected to be significantly more accurate at the DFT level than those obtained at the HF level. This expectation is confirmed by the excellent agreement of our calculated results with available experimental data for the addition of H to simple olefins.[35−37] Previous computational studies have shown that the use of isodesmic reactions with some level of correlation energy treatment are a good way to predict heats of formation of molecules or in the case that we are interested in, relative C−H or C−C bond energies.[38,39]A potentially better approach for us to predict $E_y(\mathrm{M} + \mathrm{R}^\bullet \rightarrow \mathrm{MR}^\bullet)$ is to evaluate the free energy of the following isodesmic reaction:

$$\mathrm{M} + \mathrm{AR}^\bullet \rightarrow \mathrm{MR}^\bullet + \mathrm{A}$$

in which A represents a monomer whose experimental reaction free energy, $E_y(\mathrm{A} + \mathrm{R}^\bullet \rightarrow \mathrm{AR}^\bullet)$, is available or for which we know the heats of formation of A and $\mathrm{AR}^\bullet$. Given the reaction enthalpy, the free energy of the isodesmic reaction can be evaluated by adding the entropy contribution based on standard statistical mechanical calculations. This allows us to eliminate systematic errors in the calculation of the bond energy by relating it back to an established standard. Note that all $E_y$ values used in the present study refer to the Gibbs free energy of reaction. Thus, a notation $\Delta G_y$, instead of $E_y$, may be more reasonable to represent this quantity but we have kept the traditional notation $E_y$ for comparison with previous studies on the *Q*−*e* scheme.[6] Because the isodesmic reaction free energy $E_y(\mathrm{M} + \mathrm{AR}^\bullet \rightarrow \mathrm{MR}^\bullet + \mathrm{A})$ is $E_y(\mathrm{M} + \mathrm{R}^\bullet \rightarrow \mathrm{MR}^\bullet) - E_y(\mathrm{A} + \mathrm{R}^\bullet \rightarrow \mathrm{AR}^\bullet)$, we have $E_y(\mathrm{M} + \mathrm{R}^\bullet \rightarrow \mathrm{MR}^\bullet) = E_y(\mathrm{M} + \mathrm{AR}^\bullet \rightarrow \mathrm{MR}^\bullet + \mathrm{A}) + E_y(\mathrm{A} + \mathrm{R}^\bullet \rightarrow \mathrm{AR}^\bullet)$. This suggests that the more reliable $E_y(\mathrm{M} + \mathrm{R}^\bullet \rightarrow \mathrm{MR}^\bullet)$ value, denoted by $E_y^{\mathrm{estimate}}(\mathrm{M} + \mathrm{R}^\bullet \rightarrow \mathrm{MR}^\bullet)$, is the calculated $E_y(\mathrm{M} + \mathrm{AR}^\bullet \rightarrow \mathrm{MR}^\bullet + \mathrm{A})$ value, denoted by $E_y^{\mathrm{calc}}(\mathrm{M} + \mathrm{AR}^\bullet \rightarrow \mathrm{MR}^\bullet + \mathrm{A}) = E_y^{\mathrm{calc}}(\mathrm{M} + \mathrm{R}^\bullet \rightarrow \mathrm{MR}^\bullet) - E_y^{\mathrm{calc}}(\mathrm{A} + \mathrm{R}^\bullet \rightarrow \mathrm{AR}^\bullet)$, plus the experimental $E_y(\mathrm{A} + \mathrm{R}^\bullet \rightarrow \mathrm{AR}^\bullet)$

value, denoted by $E_y^{\mathrm{expt}}(\mathrm{A} + \mathrm{R}^\bullet \rightarrow \mathrm{AR}^\bullet)$. Thus, we have $E_y^{\mathrm{estimate}}(\mathrm{M} + \mathrm{R}^\bullet \rightarrow \mathrm{MR}^\bullet) = E_y^{\mathrm{calc}}(\mathrm{M} + \mathrm{R}^\bullet \rightarrow \mathrm{MR}^\bullet) + E_y^{\mathrm{expt}}(\mathrm{A} + \mathrm{R}^\bullet \rightarrow \mathrm{AR}^\bullet) - E_y^{\mathrm{calc}}(\mathrm{A} + \mathrm{R}^\bullet \rightarrow \mathrm{AR}^\bullet)$. When we use the same A and $\mathrm{R}^\bullet$ for a series of monomers (M), $E_y^{\mathrm{expt}}(\mathrm{A} + \mathrm{R}^\bullet \rightarrow \mathrm{AR}^\bullet) - E_y^{\mathrm{calc}}(\mathrm{A} + \mathrm{R}^\bullet \rightarrow \mathrm{AR}^\bullet)$ is a constant correcting for possible systematic errors in the calculation of the reaction free energies. Obviously, the $Q$ values given by the calibrated eqs 8 and 9 are independent of the $E_y^{\mathrm{expt}}(\mathrm{A} + \mathrm{R}^\bullet \rightarrow \mathrm{AR}^\bullet) - E_y^{\mathrm{calc}}(\mathrm{A} + \mathrm{R}^\bullet \rightarrow \mathrm{AR}^\bullet)$ value and independent of whether the directly calculated $E_y(\mathrm{M} + \mathrm{R}^\bullet \rightarrow \mathrm{MR}^\bullet)$, i.e., $E_y^{\mathrm{calc}}(\mathrm{M} + \mathrm{R}^\bullet \rightarrow \mathrm{MR}^\bullet)$, values or the more reliable $E_y^{\mathrm{estimate}}(\mathrm{M} + \mathrm{R}^\bullet \rightarrow \mathrm{MR}^\bullet)$ values are used as $E_y$ to calibrate eqs 8 and 9. Thus the directly calculated $E_y(\mathrm{M} + \mathrm{R}^\bullet \rightarrow \mathrm{MR}^\bullet)$ values can be used in the present calibration study.

**Computational Details.** Geometries of all monomers and the corresponding radicals formed from the addition of the $\mathrm{H}^\bullet$ and $^\bullet\mathrm{CH}_3$ radicals to the monomers considered in this study were fully optimized by using gradient-corrected DFT with Becke's three-parameter hybrid exchange functional and the Lee−Yang−Parr correlation functional (B3LYP)[40] and with the 6−31G* basis set.[16] Analytic second derivative calculations, which yield the harmonic vibrational frequencies, were performed at the optimized geometries to ensure that the optimized geometries are minima on the potential energy hypersurface (all real frequencies) and to evaluate the thermal correction (including zero-point vibration correction) to the Gibbs free energy of reaction. The geometries optimized at the B3LYP/6-31G* level were further refined at the B3LYP/6-31+G* level of theory. When there is more than one possible radical structure formed from the reaction of a monomer with $\mathrm{H}^\bullet$ or $^\bullet\mathrm{CH}_3$, the results calculated for the lowest energy structure are used in the calibration. The lowest energy geometries optimized at the B3LYP/6-31+G* level were also used to perform single-point energy calculations with larger basis sets, i.e., the 6-311+G* and 6-311++G** basis sets.[16] The correlation consistent basis sets aug-cc-pVDZ and aug-cc-pVTZ were also used in some energy calculations.[41] The energies, $E(\mathrm{M}^+)$ and $E(\mathrm{M}^-)$, of the ionic states of each monomer M were calculated at the B3LYP/6-31+G* level by using the geometry of the neutral monomer optimized at the B3LYP/6-31+G* level. Hence, the $\mathrm{IP} = E(\mathrm{M}^+) - E(\mathrm{M})$ and $\mathrm{EA} = E(\mathrm{M}) - E(\mathrm{M}^-)$ values determined by these DFT energy calculations are the vertical ionization potential and vertical electron affinity, respectively.

All of the B3LYP DFT calculations on the open-shell systems, i.e., radicals and ionic states of monomers, described above were performed by using the unrestricted open-shell Kohn−Sham formalism. For comparison, we also performed B3LYP/6-31+G* DFT energy calculations using the restricted open-shell Kohn−Sham equation (ROB3LYP/6-31+G*) on radicals by using the geometries optimized with the unrestricted open-shell Kohn−Sham equation at the B3LYP/6-31+G* level. All the calculations were performed by using the *Gaussian98* program[42] on a 16-processor SGI Origin 2000 computer.

## Results and Discussion

To predict $Q-e$ parameters using eqs 7−9, 20, and 21, we need to determine the empirical constants in these equations. The reliability of the parameters is dependent not only on the theory used to obtain these relationships and the computational approach but also on the reliability of the experimental values of the $Q-e$ parameters used in the calibration. The most popular experimental $Q$ and $e$ values in use are those listed by Greenley in the "Polymer Handbook".[43] Laurier et al.[8] have pointed out the deficiencies in the calculation and listing procedure used by Greenley and proposed an approach to determine $Q$ and $e$ values by using a statistically correct process. However, they determined the $Q$ and $e$ values for only 11 monomers including the reference monomer, styrene; these are the first 11 molecules listed in Table 1. We will discuss the calibration using both the Greenley and Laurier et al. sets of the $Q$ and $e$ values; all the $Q$ and $e$ values used are listed in Table 1.

**Calibration of the *e* Parameter.** Before discussing the relationship between the experimental $e$ and calculated electronegativity ($\chi_{\mathrm{av}}$ or $\chi_{\mathrm{m}}$) values, we first compared the $\chi_{\mathrm{av}}$ and $\chi_{\mathrm{m}}$ values calculated using different computational approaches. It has been demonstrated[32] that DFT calculations can reliably predict vertical molecular ionization potentials (IP) and electron affinities (EA) by total energy calculations. Thus, the (IP + EA)/2 values of the 27 monomers calculated without using Koopmans' theorem at the B3LYP/6-31+G*//B3LYP/6-31+G* level can be used to benchmark the $\chi_{\mathrm{m}}$ values calculated using Koopmans' theorem at the same level. A least-squares fitting process gives an excellent relationship (in hartrees),

$$(\mathrm{IP} + \mathrm{EA})/2 = 0.8341[-(\epsilon_{\mathrm{HOMO}} + \epsilon_{\mathrm{LUMO}})/2] + 0.03735 \tag{27}$$

with a correlation coefficient ($R$) of 0.952 and a root-mean-square deviations (RMSD) of 0.006 518 hartree (∼0.177 eV). This demonstrates that the use of Koopmans' theorem in our DFT calculations of the electronegativity is satisfactory for the purpose of this study in that all we need is to have a linear relationship. A more detailed theoretical study on linear correlation relationships for the IP, EA, electronegativity, etc. between the DFT results calculated with and without using Koopmans' theorem is currently in progress in our laboratory.

We also found an excellent linear relationship between the $-\epsilon_{\mathrm{SOMO}}$ values (used in calculating the radical's electronegativity, $\chi_{\mathrm{r}}$) calculated for the 27 radicals (formed from the monomer + $\mathrm{H}^\bullet$) using the unrestricted and restricted Kohn−Sham equations at the B3LYP/6-31+G*//B3LYP/6-31+G* level,

$$-\epsilon_{\mathrm{SOMO}}(\mathrm{unrestricted}) = 1.398[-\epsilon_{\mathrm{SOMO}}(\mathrm{restricted})] + 0.07429\ (\mathrm{hartree}) \tag{28}$$

with $R = 0.970$ and RMSD = 0.007 70 hartree (∼0.209 eV). This demonstrates that it does not matter in the calculation of $\chi_{\mathrm{r}} = -\epsilon_{\mathrm{SOMO}}$ whether the unrestricted or restricted open-shell Kohn−Sham equations are used for the open-shell DFT calculations on radicals, as again, all we need is a linear relationship. Unless indicated, all $\chi_{\mathrm{av}}$ and $\chi_{\mathrm{m}}$ values in the discussion below are based on the use of Koopmans' theorem and the $\epsilon_{\mathrm{SOMO}}$ from the unrestricted Kohn−Sham equations.

We first discuss possible linear relationships between the $e$ values determined by Laurier et al.[8] and the $\chi_{\mathrm{av}}$ and $\chi_{\mathrm{m}}$ values calculated for the reactions of monomers with the H radical. The results are summarized in Table 2, and some of the calculated results are depicted in Figures 1 and 2 in comparison with the corresponding experimental $e$ values. As shown in Table 2 for the DFT calculations at each level of theory, the linear correlation relationship between the $e$ and $\chi_{\mathrm{m}}$ values is as good as the linear relationship between the $e$ and $\chi_{\mathrm{av}}$ values. The correlation based on the DFT calculations using the restricted Kohn−Sham equation (at the ROB3LYP/6-31+G*//B3LYP/6-31+G* level) is slightly worse than that using the unrestricted Kohn−Sham equation (at the B3LYP/6-31+G*//B3LYP/6-31+G* level). The largest $R$ value (best fit) is associated with the linear correlation relationship between the experimental $e$ values and the (IP + EA)/2 values calculated by

**TABLE 2: Linear Correlation between the Calculated Electronegativities and the Experimental *e* Values Determined by Laurier et al.[8]**

| method[a] | results | | |
|---|---|---|---|
| | linear equation[b] | $R^c$ | RMSD[d] |
| reaction of monomer with H$^\bullet$ | $\chi_m = -(\epsilon_{HOMO} + \epsilon_{LUMO})/2$ | | |
| | $\chi_r = -\epsilon_{SOMO}$ | | |
| B3LYP/6-31G*//B3LYP/6-31G* | $e = 35.06\chi_{av} - 5.922$ | 0.921(11) | 0.297 |
| B3LYP/6-31+G*//B3LYP/6-31G* | $e = 34.72\chi_{av} - 6.285$ | 0.930(11) | 0.281 |
| B3LYP/6-31+G*//B3LYP/6-31+G* | $e = 34.77\chi_{av} - 6.295$ | 0.930(11) | 0.281 |
| ROB3LYP/6-31+G*//B3LYP/6-31+G* | $e = 43.53\chi_{av} - 5.481$ | 0.909(11) | 0.319 |
| B3LYP/6-311+G*//B3LYP/6-31+G* | $e = 34.78\chi_{av} - 6.366$ | 0.933(11) | 0.276 |
| B3LYP/6-311++G**//B3LYP/6-31+G* | $e = 35.05\chi_{av} - 6.437$ | 0.930(11) | 0.280 |
| B3LYP/6-31G*//B3LYP/6-31G* | $e = 43.33\chi_m - 6.061$ | 0.919(11) | 0.302 |
| B3LYP/6-31+G*//B3LYP/6-31G* | $e = 42.75\chi_m - 6.598$ | 0.932(11) | 0.277 |
| B3LYP/6-31+G*//B3LYP/6-31+G* | $e = 42.88\chi_m - 6.622$ | 0.932(11) | 0.277 |
| B3LYP/6-311+G*//B3LYP/6-31+G* | $e = 42.64\chi_m - 6.672$ | 0.932(11) | 0.278 |
| B3LYP/6-311++G**//B3LYP/6-31+G* | $e = 43.11\chi_m - 6.787$ | 0.929(11) | 0.284 |
| reaction of monomer with H$^\bullet$ | $\chi_m = -(IP + EA)/2$ | | |
| B3LYP/6-31+G*//B3LYP/6-31+G* | $e = 43.54\chi_m - 7.054$ | 0.959(11) | 0.218 |
| reaction of monomer with $^\bullet CH_3$ | $\chi_m = -(\epsilon_{HOMO} + \epsilon_{LUMO})/2$ | | |
| | $\chi_r = -\epsilon_{SOMO}$ | | |
| B3LYP/6-31G*//B3LYP/6-31G* | $e = 36.95\chi_{av} - 6.248$ | 0.935(11) | 0.271 |
| B3LYP/6-31+G*//B3LYP/6-31G* | $e = 36.34\chi_{av} - 6.582$ | 0.941(11) | 0.259 |

[a] Unless indicated by ROB3LYP, all DFT calculations on open-shell systems were performed using the unrestricted open-shell Kohn−Sham equations. ROB3LYP refers to the DFT calculations on radicals using restricted open-shell Kohn−Sham equations. [b] Fit to the *e* values of Laurier et al.[8] $\chi_{av} = (\chi_m + \chi_r)/2$. The calculated $\chi_m$, $\chi_r$, and $\chi_{av}$ values are all given in au (i.e., hartrees). [c] Linear correlation coefficient. Values in parentheses are the number of data points used for the least-squares fitting. [d] Root-mean-square deviation of the calculated *e* values from the experimental *e* values.

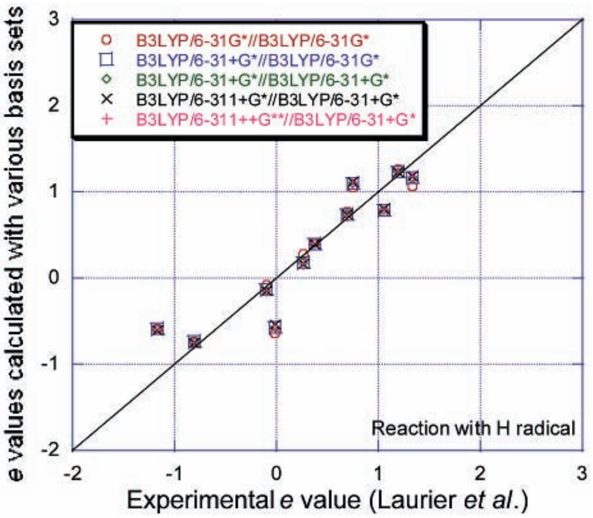

**Figure 1.** Plot of the various calculated versus experimental *e* values. The calculated *e* values are evaluated by use of the relationship $e = a_e\chi_{av} + b_e$, in which $\chi_{av} = -(\epsilon_{HOMO} + \epsilon_{LUMO})/4 - \epsilon_{SOMO}/2$, for the reactions with the H radical based on the experimental *e* values determined by Laurier et al.[8]

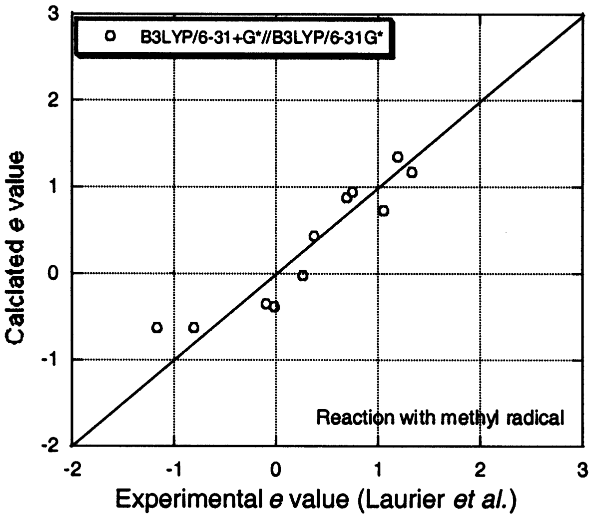

**Figure 2.** Plot of the calculated versus experimental *e* values. The calculated *e* values are evaluated by use of the relationship $e = a_e\chi_{av} + b_e$, in which $\chi_{av} = -(\epsilon_{HOMO} + \epsilon_{LUMO})/4 - \epsilon_{SOMO}/2$, for the reactions with the methyl radical based on the experimental *e* values determined by Laurier et al.[8]

directly calculating the total energies. The fact, as shown by eq 24, that there is a linear relationship between the directly calculated electronegativities and those from KT, is consistent with the act that the correlation relationships based on the DFT calculations using Koopmans' theorem are also adequate.

The basis set dependence of the results can be seen from the changes in the *R* values and the corresponding RMSD values for the reaction of the monomer with the H radical. As shown in Table 2, no matter whether $\chi_{av}$ or $\chi_m$ is used, from B3LYP/6-31G*//B3LYP/6-31G* to B3LYP/6-31+G*//B3LYP/6-31G*, *R* changes by only ∼0.01. Improving the quality of the basis set does not further improve the results; *R* is always ∼0.93, as shown in Table 2 and Figure 1. These results demonstrate that DFT calculations at the B3LYP/6-31+G*//B3LYP/6-31G* level and $\chi$ values determined by KT are sufficient. Hence, we only performed DFT calculations on the reactions with the methyl radical at the B3LYP/6-31+G*//B3LYP/6-31G* level. The results based on the calculations at the B3LYP/6-31G*//B3LYP/6-31G* level are also listed in Table 2 for comparison. The linear relationship based on the DFT calculations on the reactions of the monomer with the methyl radical at the B3LYP/6-31+G*//B3LYP/6-31G* level is slightly better than the corresponding linear relationship based on the DFT calculations on the reactions of the monomer with the H radical at the same level.

The quality of the linear correlation between the 27 experimental *e* values listed by Greenley and the $\chi_{av}$ values calculated at various levels for the reaction with H radical is shown in Figure 3. Figure 3a reveals that the results calculated at the B3LYP/6-31G*//B3LYP/6-31G* level are only slightly worse than those calculated with larger basis sets, and that the results

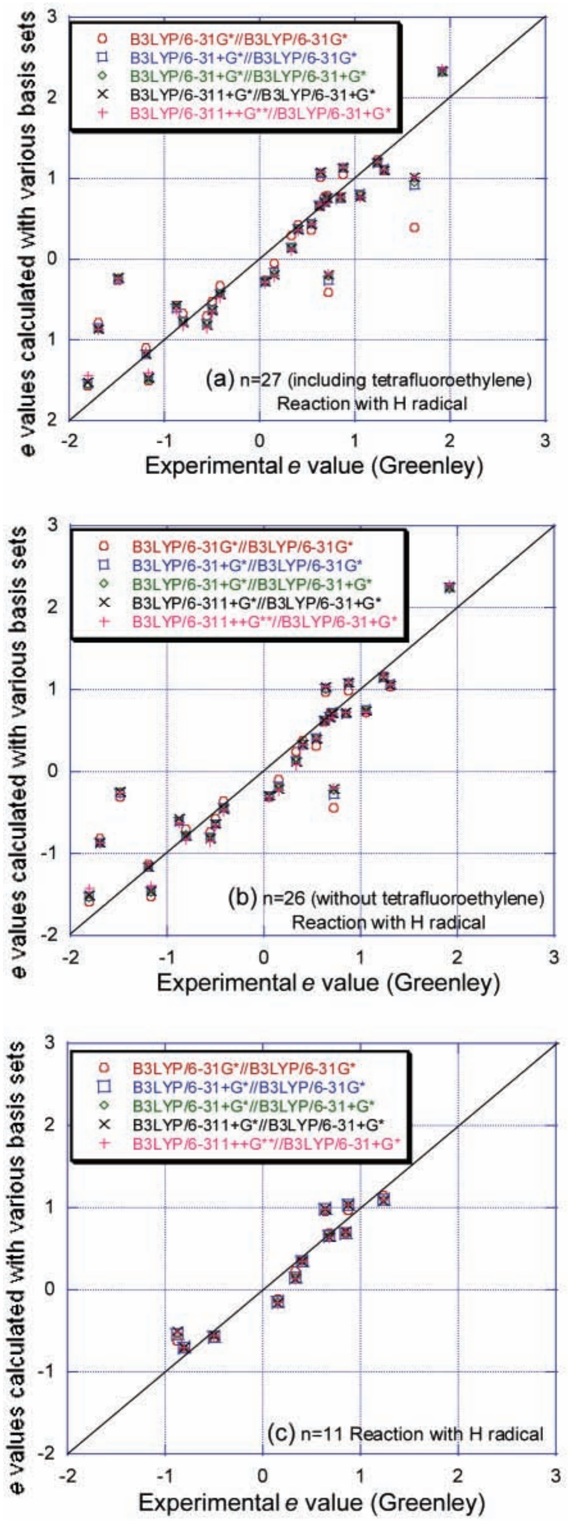

**Figure 3.** Plots of the calculated versus experimental $e$ values for all of the 27 monomers (a), the 26 monomers without tetrafluoroethylene (b), and the first 11 monomers (c). The calculated $e$ values are evaluated by use of the relationship $e = a_e\chi_{av} + b_e$, in which $\chi_{av} = -(\epsilon_{HOMO} + \epsilon_{LUMO})/4 - \epsilon_{SOMO}/2$, for the reactions with the H radical based on the experimental $e$ values listed by Greenley.[43]

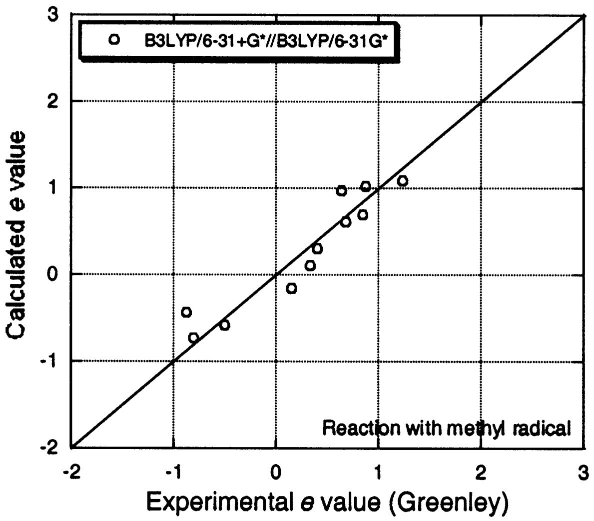

**Figure 4.** Plot of the calculated versus experimental $e$ values. The calculated $e$ values are evaluated by use of the relationship $e = a_e\chi_{av} + b_e$, in which $\chi_{av} = -(\epsilon_{HOMO} + \epsilon_{LUMO})/4 - \epsilon_{SOMO}/2$, for the reactions with the methyl radical based on the experimental $e$ values listed by Greenley.[43]

calculated with the larger basis sets are nearly identical. As shown in Figure 3a, the calculated $e$ values are, on the whole, in good agreement with the corresponding experimental $e$ values, although the deviations are a little larger for a few monomers including tetrafluoroethylene, which will be discussed below as an exception. The linear correlation relationships for the other 26 monomers excluding tetrafluoroethylene and for the first 11 monomers in Table 1 are shown in Figures 3b,c and 4 and summarized in Table 3. The three additional monomers showing significant deviations (see Figure 3b) are allyl alcohol, propene, and vinyl fluoride. As shown in Table 3, most of the observations for the correlation between the experimental $e$ values determined by Laurier et al. and the calculated electronegativities are also correct for the correlation between the experimental $e$ values listed by Greenley and the calculated results. Two minor but noticeable changes are that the correlation of the $e$ values with the $\chi_m$ values is slightly worse than that with the $\chi_{av}$ values, and that the correlation with the (IP + EA)/2 values calculated without using Koopmans' theorem is not any better for the 26 monomers.

We also examined whether there is a linear relationship between the $e$ values determined by Laurier et al.[8] and those by Greenley[24] for the 11 monomers listed in Table 1 and found a linear relationship with $R = 0.876$ and RMSD = 0.326. This implies a significant experimental error, at least for the $e$ values listed by Greenley if the $e$ values determined by Laurier et al. are believed to be more accurate. It also suggests that as long as the correlation coefficient $R$ between the experimental $e$ values and calculated electronegativities is greater than 0.876, then a good fit has been achieved. As shown in Tables 2 and 3, the correlation coefficients of all of the linear relationships between the experimental $e$ and calculated $\chi_{av}$ values are larger than 0.876, illustrating that the calibrated relationships are satisfactory. The differences between the two sets of experimental $e$ values most likely come primarily from the errors of the $e$ values listed by Greenley. Thus, it is not difficult to understand why we observe some "abnormal" changes (although negligible) of the correlations in Table 3, e.g., the "best" correlation is accidently associated with the smallest basis set. Actually, because of the likely errors in the $e$ values listed by Greenley, we cannot really distinguish between any of the DFT calculations.

**Calibration of the $Q$ Parameter.** The differences between the two sets of experimental ln $Q$ values are much smaller than the differences between the two sets of experimental $e$ values. Between the two sets of ln $Q$ values, there is an excellent linear correlation relationship with $R = 0.993$ and RMSD = 0.162 in

**TABLE 3: Linear Correlation between the Calculated Electronegativities and the Experimental *e* Values Listed by Greenley[43]**

| method[a] | results | | |
|---|---|---|---|
| | linear equation[b] | $R^c$ | RMSD[d] |
| reaction of monomer with H$^\bullet$ | $\chi_m = -(\epsilon_{HOMO} + \epsilon_{LUMO})/2$ | | |
| | $\chi_r = -\epsilon_{SOMO}$ | | |
| B3LYP/6-31G*//B3LYP/6-31G* | $e = 32.65\chi_{av} - 5.545$ | 0.970(11) | 0.165 |
| B3LYP/6-31+G*//B3LYP/6-31G* | $e = 31.56\chi_{av} - 5.734$ | 0.955(11) | 0.201 |
| B3LYP/6-31+G*//B3LYP/6-31+G* | $e = 31.58\chi_{av} - 5.740$ | 0.954(11) | 0.202 |
| ROB3LYP/6-31+G*//B3LYP/6-31+G* | $e = 39.75\chi_{av} - 5.029$ | 0.937(11) | 0.235 |
| B3LYP/6-311+G*//B3LYP/6-31+G* | $e = 31.37\chi_{av} - 5.762$ | 0.950(11) | 0.210 |
| B3LYP/6-311++G**//B3LYP/6-31+G* | $e = 31.72\chi_{av} - 5.846$ | 0.951(11) | 0.208 |
| B3LYP/6-31G*//B3LYP/6-31G* | $e = 38.60\chi_m - 5.415$ | 0.925(11) | 0.257 |
| B3LYP/6-31+G*//B3LYP/6-31G* | $e = 37.12\chi_m - 5.738$ | 0.914(11) | 0.274 |
| B3LYP/6-31+G*//B3LYP/6-31+G* | $e = 37.22\chi_m - 5.757$ | 0.914(11) | 0.274 |
| B3LYP/6-311+G*//B3LYP/6-31+G* | $e = 36.84\chi_m - 5.772$ | 0.909(11) | 0.281 |
| B3LYP/6-311++G**//B3LYP/6-31+G* | $e = 37.45\chi_m - 5.904$ | 0.911(11) | 0.279 |
| B3LYP/6-31G*//B3LYP/6-31G* | $e = 32.71\chi_{av} - 5.538$ | 0.908(26) | 0.416 |
| B3LYP/6-31+G*//B3LYP/6-31G* | $e = 33.76\chi_{av} - 6.164$ | 0.913(26) | 0.404 |
| B3LYP/6-31+G*//B3LYP/6-31+G* | $e = 33.70\chi_{av} - 6.156$ | 0.914(26) | 0.401 |
| ROB3LYP/6-31+G*//B3LYP/6-31+G* | $e = 39.06\chi_{av} - 4.929$ | 0.903(26) | 0.426 |
| B3LYP/6-311+G*//B3LYP/6-31+G* | $e = 33.88\chi_{av} - 6.256$ | 0.913(26) | 0.405 |
| B3LYP/6-311++G**//B3LYP/6-31+G* | $e = 35.04\chi_{av} - 6.511$ | 0.913(26) | 0.405 |
| B3LYP/6-31G*//B3LYP/6-31G* | $e = 32.96\chi_m - 4.525$ | 0.873(26) | 0.483 |
| B3LYP/6-31+G*//B3LYP/6-31G* | $e = 35.64\chi_m - 5.467$ | 0.885(26) | 0.462 |
| B3LYP/6-31+G*//B3LYP/6-31+G* | $e = 35.68\chi_m - 5.479$ | 0.886(26) | 0.459 |
| B3LYP/6-311+G*//B3LYP/6-31+G* | $e = 35.90\chi_m - 5.590$ | 0.884(26) | 0.463 |
| B3LYP/6-311++G**//B3LYP/6-31+G* | $e = 38.11\chi_m - 6.004$ | 0.881(26) | 0.469 |
| reaction of monomer with H$^\bullet$ | $\chi_m = -(IP+EA)/2$ | | |
| B3LYP/6-31+G*//B3LYP/6-31+G* | $e = 37.09\chi_m - 6.012$ | 0.923(11) | 0.261 |
| B3LYP/6-31+G*//B3LYP/6-31+G* | $e = 39.97\chi_m - 6.585$ | 0.872(26) | 0.485 |
| reaction of monomer with $^\bullet CH_3$ | $\chi_m = -(\epsilon_{HOMO} + \epsilon_{LUMO})/2$ | | |
| | $\chi_r = -\epsilon_{SOMO}$ | | |
| B3LYP/6-31G*//B3LYP/6-31G* | $e = 33.61\chi_{av} - 5.705$ | 0.961(11) | 0.188 |
| B3LYP/6-31+G*//B3LYP/6-31G* | $e = 32.22\chi_{av} - 5.852$ | 0.943(11) | 0.226 |

[a] Unless indicated by ROB3LYP, all DFT calculations on open-shell systems were performed using the unrestricted open-shell Kohn–Sham equations. ROB3LYP refers to the DFT calculations on radicals using restricted open-shell Kohn–Sham equations. [b] Fit to the *e* values determined by Greenley.[43] $\chi_{av} = (\chi_m + \chi_r)/2$. The calculated $\chi_m$, $\chi_r$, and $\chi_{av}$ values are all given in au (i.e., hartrees). [c] Linear correlation coefficient. Values (*n*) in parentheses are the numbers of data used for the least-squares fitting. Fitting with $n = 11$ refers to the same 11 monomers for which the *e* values determined by Laurier et al.[8] are available. [d] Root-mean-square deviation of the calculated *e* values from the experimental *e* values.

contrast to the values discussed above for the *e* values. The two sets of experimental *Q* values are consistent with each other at least for the 11 monomers. Hence, the correlations of the calculated results with the two sets of ln *Q* values for the first 11 monomers are very similar as shown in Tables 4 and 5 and Figures 5 –12.

As shown in Table 4 for the calibration of eq 8 with the *Q* values determined by Laurier et al., the calibrated results are nearly identical, independent of whether $\chi_{av}$ or $\chi_m$ is used as $\chi$ in eq 8. Thus we only listed the calibration results with $\chi_m$ in Table 5 for the calibration with the *Q* values listed by Greenley. As shown in Figure 9a, the calculated ln *Q* values based on the reaction with the H radical are, on the whole, in good agreement with the corresponding experimental data listed by Greenley. The major exception is tetrafluoroethylene ($C_2F_4$) whose ln *Q* value of ~0.52 calculated at the B3LYP/6-31+G* level leads to a *Q* value that is ~4.0 larger than the corresponding experimental $Q = 0.032$ ($\ln Q = -3.44$). This unexpected deviation could be due to an error in our DFT calculations, or the simplified model used in the correlation analysis, or problems in the experimental interpretation of the data. It is distinctly possible that $C_2F_4$ with its very different total $\sigma$ and $\pi$ bond energies as compared to a normal olefin does not fit on the same set of curves as those of other hydrocarbon-type olefins.

To determine whether the DFT calculations are responsible for the large deviation for the ln *Q* value of $C_2F_4$, we also used eq 9, i.e., the simple linear relationship between ln *Q* and $E_y$ (the Gibbs free energy of reaction), in the calibration with the same 27 monomers at the same level of theory. The ln *Q* values determined by using the eq 9 are compared with the corresponding experimental data in Figure 10a. As shown by comparison between Figures 9a and 10a, the ln *Q* values determined by eq 9 do not dramatically differ from the corresponding ln *Q* values determined by eq 8, showing that the ln *Q* value is dominated by the reaction free energy. The calculated reaction free energy ($E_y$) for $C_2F_4 + H^\bullet \rightarrow CHF_2\text{-}CF_2^\bullet$ is not sensitive to the basis set used in the DFT calculations. The $E_y$ value of −45.94 kcal/mol calculated with the 6-31+G* basis set is very close to the $E_y$ values of −46.15 kcal/mol with the aug-cc-pVDZ basis set and −45.87 kcal/mol with the aug-cc-pVTZ basis set. The calculated $E_y$ value of ~−46 kcal/mol is only ~3 kcal/mol larger than the free energy of reaction, −49 kcal/mol, derived from available thermodynamic data. A similar error of ~3 kcal/mol is found in the addition of H to $C_2H_4$ to form $C_2H_5^\bullet$.[44] Assuming for tetrafluoroethylene that the deviation of the calculated ln *Q* value from the experimental value is completely attributed to the error in the DFT calculation of $E_y$, an ideal $E_y$ value for a perfect fit to the experimental *Q* value of 0.032 ($\ln Q = -3.44$) would be ~−35 kcal/mol. The $E_y$ value expected from the experimental *Q* value of 0.032 differs by ~11 kcal/mol, as compared to our calculated $E_y$ value of ~−46 kcal/mol, and by ~14 kcal/mol, as compared to the experimental $E_y$ value ~−49 kcal/mol. Thus, the dramatic deviation of the calculated ln *Q* value from the experimental ln *Q* value for tetrafluoroethylene is possibly due to the simplified model itself, although possible experimental uncertainty for this particular system has been pointed out by other authors.[6] Further

**TABLE 4: Correlation of the Calculated Reaction Free Energies and Electronegativities with the Experimental $Q$ Values Determined by Laurier et al.[8]**

| | results[b] | | |
|---|---|---|---|
| method[a] | ln $Q$ | $R$[c] | RMSD[d] |
| reaction of monomer with H$^\bullet$ | use $\chi_m = -(\epsilon_{HOMO} + \epsilon_{LUMO})/2$; $\chi_r = -\epsilon_{SOMO}$ | | |
| B3LYP/6-31G*//B3LYP/6-31G* | $-1128E_y + 459.2\chi_{av} + 5314E_y\chi_{av} - 98.176$ | 0.964(11) | 0.356 |
| B3LYP/6-31+G*//B3LYP/6-31G* | $-1336E_y + 521.0\chi_{av} + 6074E_y\chi_{av} - 115.334$ | 0.973(11) | 0.307 |
| B3LYP/6-31+G*//B3LYP/6-31+G* | $-1343E_y + 523.8\chi_{av} + 6106E_y\chi_{av} - 115.861$ | 0.973(11) | 0.305 |
| ROB3LYP/6-31+G*//B3LYP/6-31+G* | $-1395E_y + 743.5\chi_{av} + 8973E_y\chi_{av} - 116.305$ | 0.974(11) | 0.300 |
| B3LYP/6-311+G*//B3LYP/6-31+G* | $-1415E_y + 537.6\chi_{av} + 6432E_y\chi_{av} - 118.983$ | 0.979(11) | 0.269 |
| B3LYP/6-311++G**//B3LYP/6-31 + G* | $-1424E_y + 542.3\chi_{av} + 6460E_y\chi_{av} - 120.207$ | 0.979(11) | 0.273 |
| B3LYP/6-31G*//B3LYP/6-31G* | $-1319E_y + 507.9\chi_m + 7772E_y\chi_m - 86.747$ | 0.982(11) | 0.255 |
| B3LYP/6-31+G*//B3LYP/6-31G* | $-1515E_y + 532.0\chi_m + 8249E_y\chi_m - 98.274$ | 0.987(11) | 0.217 |
| B3LYP/6-31+G*//B3LYP/6-31+G* | $-1523E_y + 535.1\chi_m + 8298E_y\chi_m - 98.826$ | 0.986(11) | 0.218 |
| B3LYP/6-311+G*//B3LYP/6-31+G* | $-1569E_y + 527.1\chi_m + 8471E_y\chi_m - 98.215$ | 0.990(11) | 0.188 |
| B3LYP/6-311++G**//B3LYP/6-31+G* | $-1595E_y + 537.6\chi_m + 8591E_y\chi_m - 100.427$ | 0.989(11) | 0.194 |
| B3LYP/6-31G*//B3LYP/6-31G* | $-252.1E_y - 22.501$ | 0.905(11) | 0.565 |
| B3LYP/6-31+G*//B3LYP/6-31G* | $-257.7E_y - 22.818$ | 0.905(11) | 0.566 |
| B3LYP/6-31+G*//B3LYP/6-31+G* | $-257.8E_y - 22.831$ | 0.905(11) | 0.566 |
| ROB3LYP/6-31+G*//B3LYP/6-31+G* | $-288.4E_y - 24.802$ | 0.902(11) | 0.575 |
| B3LYP/6-311+G*//B3LYP/6-31+G* | $-258.2E_y - 22.256$ | 0.905(11) | 0.565 |
| B3LYP/6-311++G**//B3LYP/6-31+G* | $-257.8E_y - 22.354$ | 0.909(11) | 0.556 |
| reaction of monomer with H$^\bullet$ | use $\chi_m = -(IP + EA)/2$ | | |
| B3LYP/6-31+G*//B3LYP/6-31+G* | $-1653E_y + 746.7\chi_m + 8660E_y\chi_m - 143.177$ | 0.984(11) | 0.240 |
| reaction of monomer with $^\bullet CH_3$ | use $\chi_m = -(\epsilon_{HOMO} + \epsilon_{LUMO})/2$ | | |
| B3LYP/6-31G*//B3LYP/6-31G* | $-1225E_y + 209.9\chi_{av} + 5829E_y\chi_{av} - 44.654$ | 0.969(11) | 0.328 |
| B3LYP/6-31+G*//B3LYP/6-31G* | $-1399E_y + 202.6\chi_{av} + 6342E_y\chi_{av} - 45.233$ | 0.980(11) | 0.267 |
| B3LYP/6-31G*//B3LYP/6-31G* | $-1330E_y + 284.3\chi_m + 7826E_y\chi_m - 48.745$ | 0.983(11) | 0.243 |
| B3LYP/6-31+G*//B3LYP/6-31G* | $-1479E_y + 256.7\chi_m + 7989E_y\chi_m - 48.002$ | 0.989(11) | 0.200 |
| B3LYP/6-31G*//B3LYP/6-31G* | $-265.4E_y - 9.967$ | 0.908(11) | 0.559 |
| B3LYP/6-31+G*//B3LYP/6-31G* | $-273.0E_y - 9.125$ | 0.911(11) | 0.548 |

[a] Unless indicated by ROB3LYP, all DFT calculations on open-shell systems were performed using the unrestricted open-shell Kohn−Sham equations. ROB3LYP refers to the DFT calculations on radicals using restricted open-shell Kohn−Sham equations. [b] Fitting to the ln $Q$ values determined by Laurier et al.[8] $\chi_{av} = (\chi_m + \chi_r)/2$. $E_y$ is the Gibbs free energy of reaction, i.e., the reaction energy plus thermal correction (including zero-point vibration correction) to the Gibbs free energy of reaction. The calculated $\chi_m$, $\chi_r$, $\chi_{av}$, and $E_y$ values are all given in au. [c] Correlation coefficient. Values in parentheses are the numbers of data used for the least-squares fitting. [d] Root-mean-square deviation of the calculated ln $Q$ values from the corresponding experimental ln $Q$ values.

ab initio and experimental studies on the free-radical reactions of this monomer are desired. For this reason, tetrafluoroethylene should be excluded from our calibration to obtain more reliable explicit relationships for predicting the $Q$ and $e$ values of monomers whose experimental $Q$ and $e$ values are not available, although the inclusion of tetrafluoroethylene in the calibrations does not dramatically change the calculated $Q$ and $e$ values for other monomers as Figures 3, 9, and 10 show.

The data in Tables 4 and 5 indicate that the calibration of eq 8 always gives a correlation coefficient $R$ value of ∼0.98 for the 11 monomers or ∼0.97 for the 26 monomers, regardless of the size of the basis set, independent of whether the H radical or the methyl radical is considered, and independent of whether Koopmans' theorem is used or not. The linear correlation of the experimental ln $Q$ values with the calculated $E_y$ values, i.e., eq 9, is also good, with $R = \sim 0.89-0.91$ for the first 11 monomers and $R = \sim 0.96$ for the 26 monomers. In addition, we also used eq 21 and found no significant changes of the $R$ and RMSD values going from eq 9 to eq 21. These results confirm that these $Q$ values in the $Q-e$ scheme are mainly determined by the reaction free energies.

**Comparison with Previous Computational Results.** On the basis of ab initio HF/STO-3G calculations on some substituted ethylenes, Colthup tested a linear correlation relationship between the previously used experimental $e$ values and the total electron densities on the $=CH_2$ carbon and a linear correlation relationship between the previously used experimental ln $Q$ values and the calculated reaction energies.[14] In a later study, which is the latest and most extensive computational study prior to the present one,[6] Rogers et al. found that the two linear relationships proposed by Colthup do not work with the more recently established experimental $Q$ and $e$ values. Rogers et al.'s computational studies are based on ab initio HF calculations (in some cases with larger basis sets than STO-3G), and also used eqs 7−9. The results of our calibration study can directly be compared with those reported by Rogers et al. because both Rogers et al.'s and ours are based on the same resources of experimental $Q$ and $e$ values (i.e., those determined by Greenley and Laurier et al.). In particular, the 11 molecules from Laurier et al.'s experimental data set are exactly the same. Compared to our explicit linear relationships between the parameter $e$ and the DFT-calculated $\chi_{av}$ values, Rogers et al.'s explicit linear relationships[6] between the parameter $e$ and the $\chi_{av}$ values calculated at the HF/STO-3G level have smaller correlation coefficient $R$ values, 0.828 with Greenley's data and 0.813 with Laurier et al.'s data. Rogers et al.'s explicit linear relationships[6] based on the HF calculations using larger than minimal basis sets can be considered to be equally good because the correlation coefficient $R$ values (0.889−0.969) are close to ours and are always larger than the correlation coefficient (0.876) of the linear relationship between the experimental $e$ values listed by Greenley and the experimental $e$ values determined by Laurier et al. This shows that the electronegativities based on both DFT and HF theory are equally good for the purpose of the correlation analysis. However, the situation is quite different for the calculated energetic properties. Rogers et al.'s calibration study on the parameter $Q$ used eqs 8 and 9 (in which $\chi = \chi_m$) for the 11 monomers for which the Laurier et al. data are available. For the reaction of these 11 monomers with the H radical, the correlation coefficient $R^2$ of their calibrated eq 8 is 0.77−0.85 compared to the $R^2$ values of 0.964−0.980 (corresponding to $R = 0.982-0.990$) of our calibrated eq 8, and the correlation

**TABLE 5: Correlation of the Calculated Reaction Free Energies and Electronegativities with the Experimental *Q* Values Listed by Greenley[43]**

| method[a] | results[b] | | |
|---|---|---|---|
| | ln *Q* | *R*[c] | RMSD[d] |
| reaction of monomer with H$^\bullet$ | use $\chi_m = -(\epsilon_{HOMO} + \epsilon_{LUMO})/2$ | | |
| B3LYP/6-31G*//B3LYP/6-31G* | $-1211E_y + 472.9\chi_m + 7197E_y\chi_m - 80.066$ | 0.977(11) | 0.258 |
| B3LYP/6-31+G*//B3LYP/6-31G* | $-1374E_y + 487.4\chi_m + 7519E_y\chi_m - 89.608$ | 0.980(11) | 0.238 |
| B3LYP/6-31+G*//B3LYP/6-31+G* | $-1382E_y + 490.3\chi_m + 7562E_y\chi_m - 90.104$ | 0.980(11) | 0.238 |
| B3LYP/6-311+G*//B3LYP/6-31+G* | $-1416E_y + 479.7\chi_m + 7669E_y\chi_m - 89.067$ | 0.982(11) | 0.225 |
| B3LYP/6-311++G**//B3LYP/6-31+G* | $-1440E_y + 489.6\chi_m + 7784E_y\chi_m - 91.137$ | 0.982(11) | 0.228 |
| B3LYP/6-31G*//B3LYP/6-31G* | $-225.4E_y - 15.280$ | 0.895(11) | 0.539 |
| B3LYP/6-31+G*//B3LYP/6-31G* | $-230.4E_y - 15.457$ | 0.895(11) | 0.537 |
| B3LYP/6-31+G*//B3LYP/6-31+G* | $-230.5E_y - 15.467$ | 0.895(11) | 0.537 |
| ROB3LYP/6-31+G*//B3LYP/6-31+G* | $-259.8E_y - 22.387$ | 0.899(11) | 0.528 |
| B3LYP/6-311+G*//B3LYP/6-31+G* | $-230.7E_y - 14.932$ | 0.894(11) | 0.538 |
| B3LYP/6-311++G**//B3LYP/6-31+G* | $-230.5E_y - 15.042$ | 0.898(11) | 0.529 |
| B3LYP/6-31G*//B3LYP/6-31G* | $-417.6E_y + 73.35\chi_m + 1034E_y\chi_m - 28.583$ | 0.970(26) | 0.508 |
| B3LYP/6-31+G*//B3LYP/6-31G* | $-460.7E_y + 82.11\chi_m + 1176E_y\chi_m - 31.232$ | 0.970(26) | 0.505 |
| B3LYP/6-31+G*//B3LYP/6-31+G* | $-460.0E_y + 81.38\chi_m + 1167E_y\chi_m - 31.167$ | 0.970(26) | 0.506 |
| B3LYP/6-311+G*//B3LYP/6-31+G* | $-469.2E_y + 82.47\chi_m + 1213E_y\chi_m - 30.827$ | 0.970(26) | 0.506 |
| B3LYP/6-311++G**//B3LYP/6-31+G* | $-477.4E_y + 86.64\chi_m + 1265E_y\chi_m - 31.637$ | 0.970(26) | 0.502 |
| B3LYP/6-31G*//B3LYP/6-31G* | $-295.2E_y - 19.846$ | 0.962(26) | 0.569 |
| B3LYP/6-31+G*//B3LYP/6-31G* | $-297.6E_y - 19.816$ | 0.962(26) | 0.570 |
| B3LYP/6-31+G*//B3LYP/6-31+G* | $-297.7E_y - 19.822$ | 0.962(26) | 0.570 |
| ROB3LYP/6-31+G*//B3LYP/6-31+G* | $-324.3E_y - 20.790$ | 0.961(26) | 0.577 |
| B3LYP/6-311+G*//B3LYP/6-31+G* | $-298.9E_y - 19.199$ | 0.961(26) | 0.577 |
| B3LYP/6-311++G**//B3LYP/6-31+G* | $-296.0E_y - 19.168$ | 0.962(26) | 0.566 |
| reaction of monomer with H$^\bullet$ | use $\chi_m = -(\mathrm{IP} + \mathrm{EA})/2$ | | |
| B3LYP/6-31+G*//B3LYP/6-31+G* | $-1366E_y + 428.5\chi_m + 7112E_y\chi_m - 82.774$ | 0.983(11) | 0.220 |
| B3LYP/6-31+G*//B3LYP/6-31+G* | $-520.4E_y + 97.86\chi_m + 1415E_y\chi_m - 35.199$ | 0.969(26) | 0.514 |
| reaction of monomer with $^\bullet CH_3$ | use $\chi_m = -(\epsilon_{HOMO} + \epsilon_{LUMO})/2$ | | |
| B3LYP/6-31G*//B3LYP/6-31G* | $-1242E_y + 271.6\chi_m + 7412E_y\chi_m - 45.900$ | 0.977(11) | 0.259 |
| B3LYP/6-31+G*//B3LYP/6-31G* | $-1366E_y + 241.8\chi_m + 7453E_y\chi_m - 44.744$ | 0.980(11) | 0.240 |
| B3LYP/6-31G*//B3LYP/6-31G* | $-235.2E_y - 3.791$ | 0.890(11) | 0.550 |
| B3LYP/6-31+G*//B3LYP/6-31G* | $-241.8E_y - 2.895$ | 0.892(11) | 0.544 |

[a] Unless indicated by ROB3LYP, all DFT calculations on open-shell systems were performed using the unrestricted open-shell Kohn–Sham equations. ROB3LYP refers to the DFT calculations on radicals using restricted open-shell Kohn–Sham equations. [b] Fitting to the ln *Q* values determined by Greenley.[43] $E_y$ is the Gibbs free energy of reaction, i.e., the reaction energy plus thermal correction (including zero-point vibration correction) to the Gibbs free energy of reaction. The calculated $\chi_m$ and $E_y$ values are all given in au. [c] Correlation coefficient. Values (*n*) in parentheses are the numbers of data used for the least-squares fitting. Fitting with $n = 11$ refers to the same 11 monomers for which the *Q* values determined by Laurier et al.[8] are available. [d] Root-mean-square deviation of the calculated ln *Q* values from the corresponding experimental ln *Q* values.

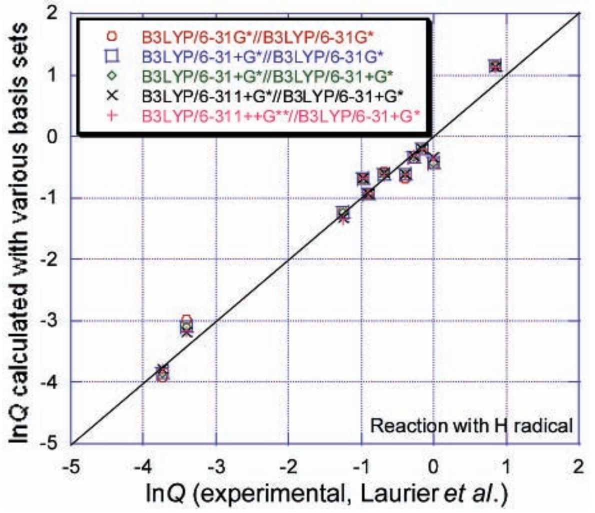

**Figure 5.** Plot of the calculated versus experimental ln *Q* values. The calculated ln *Q* values are evaluated by use of the relationship $\ln Q = a_Q E_y + b_Q \chi_m + c_Q E_y \chi_m + d_Q$, in which $\chi_m = -(\epsilon_{HOMO} + \epsilon_{LUMO})/2$, for the reactions with the H radical based on the experimental *Q* values determined by Laurier et al.[8]

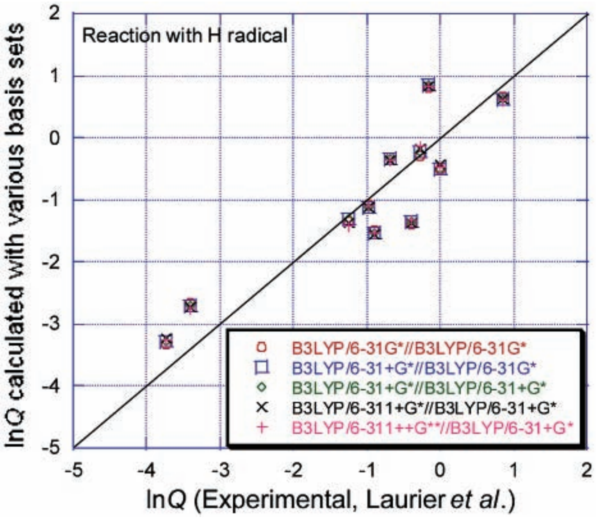

**Figure 6.** Plot of the calculated versus experimental ln *Q* values. The calculated ln *Q* values are evaluated by use of the relationship $\ln Q = a_Q E_y + b_Q$ for the reactions with the H radical based on the experimental *Q* values determined by Laurier et al.[8]

coefficient $R^2$ of their calibrated eq 9 is 0.69–0.71 compared to the $R^2$ values of 0.814–0.826 (corresponding to $R = 0.902$–$0.909$) of our calibrated eq 9. For the reaction of these 11 monomers with the methyl radical, the correlation coefficient of their eq 8 is 0.86–0.89 compared to the $R^2$ values of 0.966–0.978 (corresponding to $R = 0.983$–$0.989$) of our eq 8, and the correlation coefficient of their eq 9 is 0.667–0.75 compared to the $R^2$ values of 0.824–0.830 (corresponding to $R = 0.908$–$0.911$) of our eq 9. The DFT calculations lead to significantly better correlation

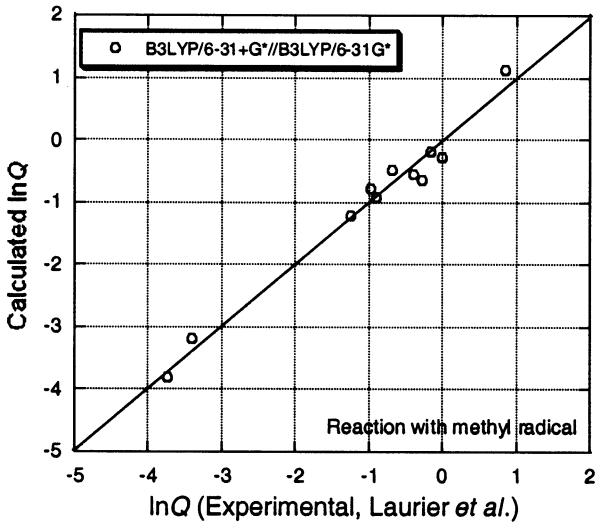

**Figure 7.** Plot of the calculated versus experimental ln $Q$ values. The calculated ln $Q$ values are evaluated by use of the relationship ln $Q = a_QE_y + b_Q\chi_m + c_QE_y\chi_m + d_Q$, in which $\chi_m = -(\epsilon_{HOMO} + \epsilon_{LUMO})/2$, for the reactions with the methyl radical based on the experimental $Q$ values determined by Laurier et al.[8]

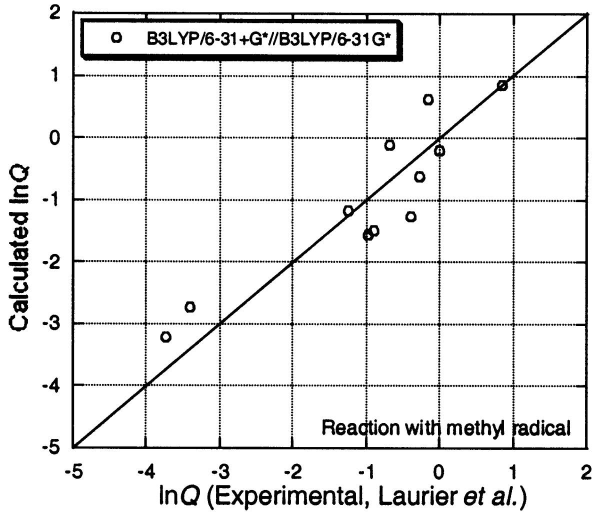

**Figure 8.** Plot of the calculated versus experimental ln $Q$ values. The calculated ln $Q$ values are evaluated by use of the relationship ln $Q = a_QE_y + b_Q$ for the reactions with the methyl radical based on the experimental $Q$ values determined by Laurier et al.[8]

relationships between the parameter $Q$ and the calculated results than do the HF results.

**Alternative Reference Monomer.** Despite the advantages of the $Q$−$e$ scheme in the practical application, many researchers have addressed its theoretical weakness.[2−7,45] A critical issue addressed recently[6] concerns the arbitrariness of the reference values for $Q$ and $e$. If an alternative reference is chosen, e.g., ethylene, or if different numerical values are assigned to the $Q$ and $e$ for styrene, then not only do all the other $Q$ and $e$ change, but so do their relative orderings.[6] While pointing out that the choice of styrene as a reference with $Q = 1.0$ and $e = -0.8$ was somewhat arbitrary, Kawabata et al.[45] proposed to redefine the $e$ value for styrene to be zero. This simplifies eq 5 to give a very simple form: $r_1 = 1/Q_2$. Based on this equation and the experimental reactivity ratios reported by Laurier et al.,[8] the revised $Q$ values, denoted by $Q'$ here for convenience, for the monomers 1 to 11 in Table 1 are 3.70, 2.5, 1.75, 1.82, 2.78, 1.3, 1.96, 1.0, 0.04, 0.06, and 0.67, respectively.[6,45] The relative order of this set of $Q$ values is quite different from that of the $Q$ values derived by Laurier et al. using the same experimental reactivity ratios but using different reference $Q$ and $e$ values for styrene. This observation is one of criticisms of the semiempirical nature of the scheme.[6]

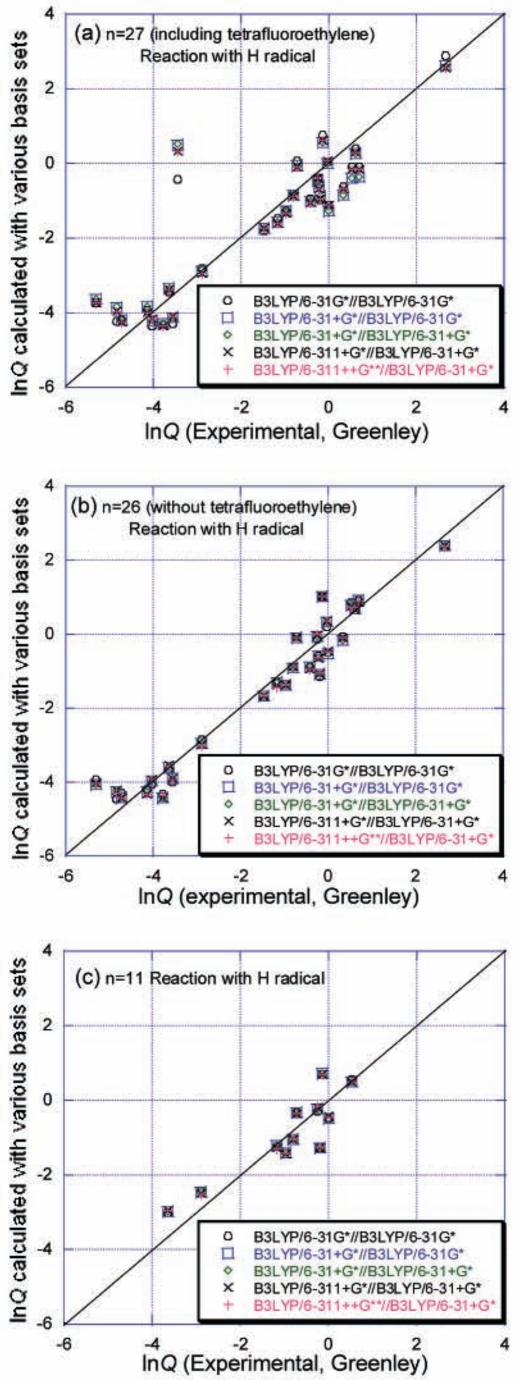

**Figure 9.** Plots of the calculated versus experimental ln $Q$ values for all of the 27 monomers (a), the 26 monomers without tetrafluoroethylene (b), and the first 11 monomers (c). The calculated ln $Q$ values are evaluated by use of the relationship ln $Q = a_QE_y + b_Q\chi_m + c_QE_y\chi_m + d_Q$, in which $\chi_m = -(\epsilon_{HOMO} + \epsilon_{LUMO})/2$, for the reactions with the H radical based on the experimental $Q$ values listed by Greenley.[43]

To better understand this critical issue, we also used eq 8 with this set of $Q'$ values and found excellent explicit relationships. For example, using the DFT results calculated at the B3LYP/6-31+G*//B3LYP/6-31G* level, we have

$$\ln Q' = -1448E_y + 557.0\chi_m + 8065E_y\chi_m - 99.130 \quad (29)$$

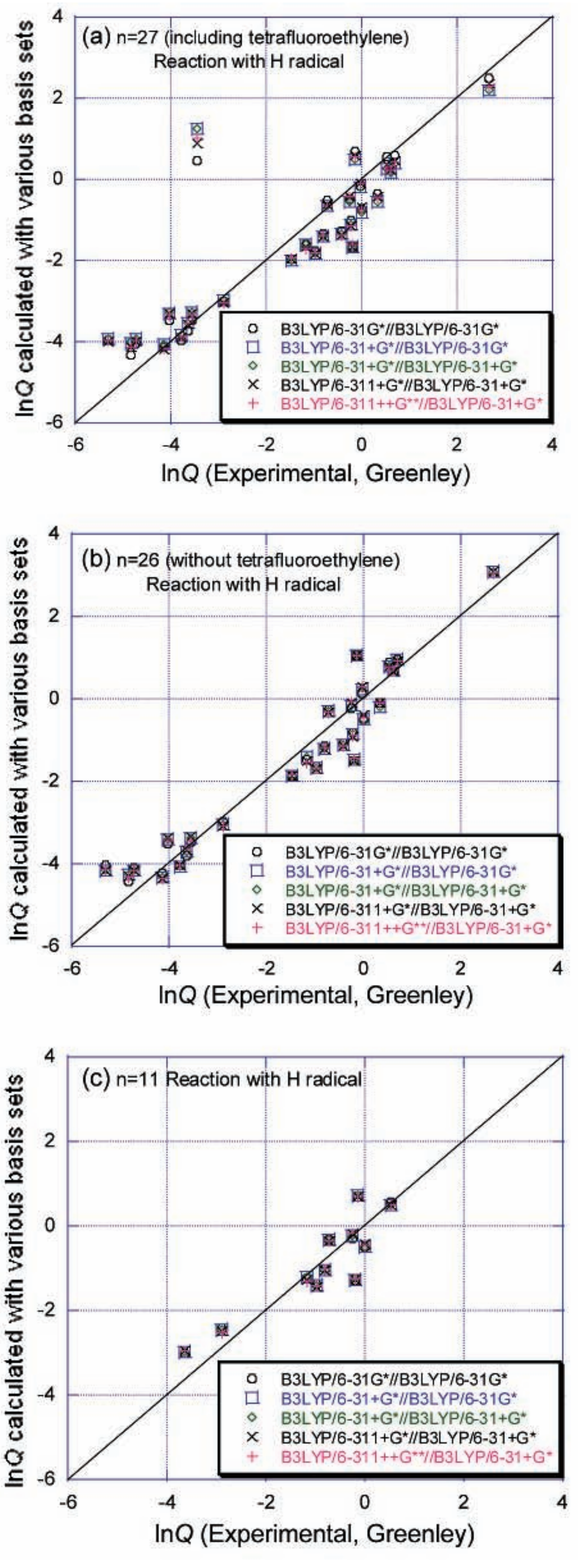

**Figure 10.** Plots of the calculated versus experimental ln $Q$ values for all of the 27 monomers (a), the 26 monomers without tetrafluoroethylene (b), and the first 11 monomers (c). The calculated ln $Q$ values are evaluated by use of the relationship $\ln Q = a_Q E_y + b_Q$ for the reactions with the H radical based on the experimental $Q$ values listed by Greenley.[43]

with $R = 0.981$ and RMSD $= 0.284$. The agreement between the calculated and experimental results is depicted in Figure 13.

The remaining question now is whether eq 8 could always work no matter how we change the reference $Q$ and $e$ values.

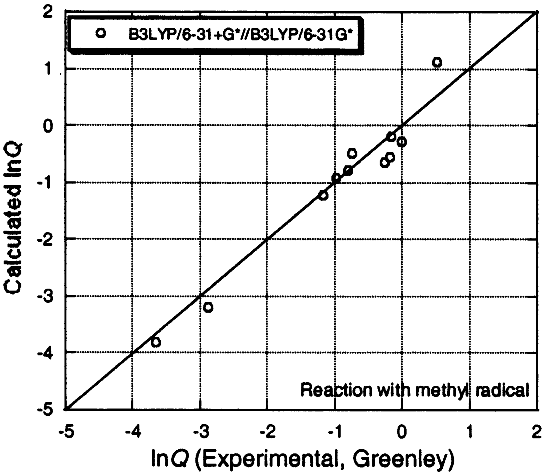

**Figure 11.** Plot of the calculated versus experimental ln $Q$ values. The calculated ln $Q$ values are evaluated by use of the relationship $\ln Q = a_Q E_y + b_Q \chi_m + c_Q E_y \chi_m + d_Q$, in which $\chi_m = -(\epsilon_{\mathrm{HOMO}} + \epsilon_{\mathrm{LUMO}})/2$, for the reactions with the methyl radical based on the experimental $Q$ values listed by Greenley.[43]

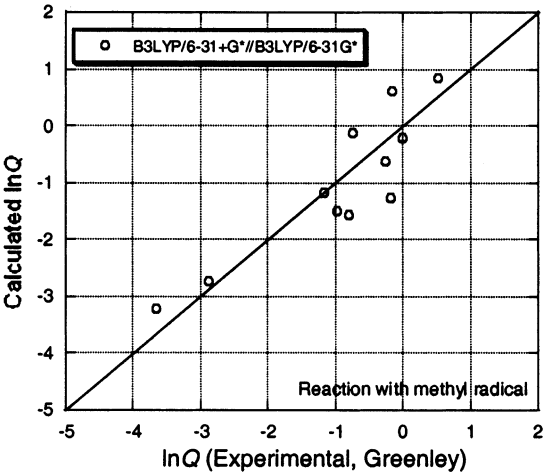

**Figure 12.** Plot of the calculated versus experimental ln $Q$ values. The calculated ln $Q$ values are evaluated by use of the relationship $\ln Q = a_Q E_y + b_Q$ for the reactions with the methyl radical using the experimental $Q$ values listed by Greenley.[43]

To answer this question, we further explore the nature of the $Q-e$ scheme starting from eq 16. Remember that the subscripts 1, 2, and $i$ refer to the reference monomer, the monomer under consideration, and the radical designed to react with all of the monomers, respectively. When the reference values $Q_1$ and $e_1$ are changed into $Q_1'$ and $e_1'$, the values $Q_2$ and $e_2$ are changed into $Q_2'$ and $e_2'$, respectively, so that eq 16 is satisfied, i.e.

$$r_{i12} = (Q_1'/Q_2') \exp[-e_i'(e_1' - e_2')] \qquad (16a)$$

Equations 16 and 16a lead to

$$(Q_1/Q_2) \exp[-e_i(e_1 - e_2)] = (Q_1'/Q_2') \exp[-e_i'(e_1' - e_2')] \qquad (30)$$

which gives

$$\begin{aligned} \ln Q_2' = {} & \\ & \ln Q_2 + e_i'e_2' - e_ie_2 + \ln Q_1' - \ln Q_1 + e_ie_1 - e_i'e_1' \\ & = \ln Q_2 + e_i'e_2' - e_ie_2 + (\text{a constant}) \qquad (31) \end{aligned}$$

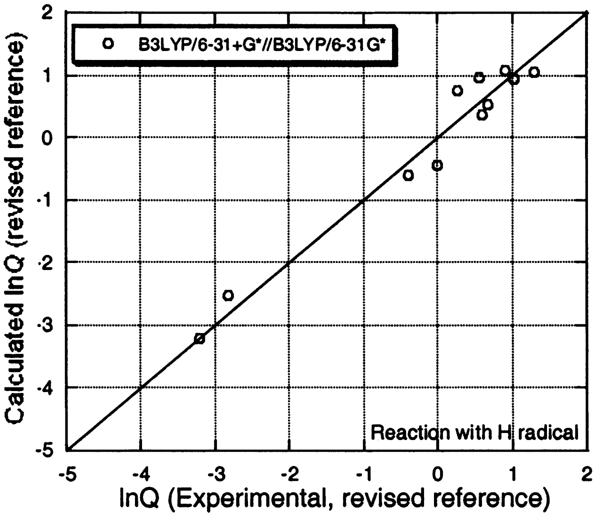

**Figure 13.** Plot of the calculated versus revised experimental ln $Q$ values. The calculated ln $Q$ values are evaluated by use of the relationship $\ln Q = a_Q E_y + b_Q \chi_m + c_Q E_y \chi_m + d_Q$, in which $\chi_m = -(\epsilon_{HOMO} + \epsilon_{LUMO})/2$, for the reactions with the H radical based on the revised experimental $Q$ values based on the revised reference values (i.e., $Q = 1.0$ and $e = -0.8$) for styrene.

and, when $e_i' \neq 0$,

$$e_2' = (e_i e_2 + \ln Q_2' - \ln Q_2 - \ln Q_1' + \ln Q_1 - e_i e_1 + e_i' e_1')/e_i' = (e_i e_2 + \ln Q_2' - \ln Q_2)/e_i' + (\text{a constant}) \qquad (32)$$

The parameter $e$ in the $Q-e$ scheme was designed to reflect the effect of molecular polar properties on the reactivity ratio, and the parameter $Q$ was designed to reflect the effect of the remaining properties (particularly the energetic properties and, as shown above, is dominated by the free energy of the radical addition reaction). However, eq 31 indicates that the factors affecting the $e$ value (i.e., $e_2$ or $e_2'$ here) could also affect the $Q$ value (i.e., $Q_2'$ here), even if they have no effect on the $Q_2$ value. Similarly, eq 32 suggests that the factors affecting the $Q$ value (i.e., $Q_2$ or $Q_2'$ here) could also affect the $e$ value (i.e., $e_2'$ here), even if they have no effect on the $e_2$ value. So eqs 31 and 32 clearly show that for an arbitrary choice of the reference values, the $Q$ and $e$ values of other monomers should actually be affected by all of the same factors, i.e., the energetic and polar properties. Therefore, eq 8 should always work well for the parameter $Q$ no matter how the reference $Q$ and $e$ values are changed, whereas eq 7 should not always be expected to work satisfactorily for the parameter $e$ when the reference $Q$ and $e$ values are changed. Nevertheless, an extended relationship similar to eq 8, i.e.

$$e = a_e E_y + b_e \chi + c_e E_y \chi + d_e \qquad (33)$$

should always work well for the parameter $e$ for whatever reference $Q$ and $e$ values are chosen. In eq 33, $a_e$, $b_e$, $c_e$, and $d_e$ are empirical constants to be determined by a least-squares fitting process. However, even though eqs 8 and 33 should always work well for the parameters $Q$ and $e$, an ideal choice of the reference $Q$ and $e$ values would be to completely separate the effects of the energetic and polar properties on the parameters $Q$ and $e$ such that the parameter $Q$ is only determined by the energetic properties and the parameter $e$ is only determined by the polar properties. In this respect, the popularly used reference values of $Q = 1.0$ and $e = -0.8$ for styrene are likely close to this ideal choice, as we have demonstrated an excellent linear relationship between the experimental $e$ values and the calculated electronegativities and a reasonable linear relationship between the experimental ln $Q$ values and the calculated reaction free energies.

**Prescription for Prediction of the $Q$ and $e$ Values.** Theoretically, a variety of reference monomers and computational approaches may be used to calculate the $Q$ and $e$ values of a monomer (M) whose experimental $Q$ and $e$ values are not available. On the basis of the present theoretical study, a reliable and computationally efficient prescription can be recommended. This prescription requires the evaluation of $E_y$ (i.e., the free energy of the reaction $M + H^\bullet \rightarrow MH^\bullet$), $\chi_m$ (i.e., the electronegativity of M calculated using eq 24), and $\chi_{av}$ (i.e., the average electronegativity calculated using eq 26) at the B3LYP/6-31+G*//B3LYP/6-31G* level. The calculated $\chi_{av}$, $E_y$, and $\chi_m$ values (all in atomic units, i.e., hartrees)[46] are then used in the relationships derived from comparing to Laurier et al.'s data,

$$e = 34.72\chi_{av} - 6.285$$

$$\ln Q = -1515E_y + 532.0\chi_m + 8249E_y\chi_m - 98.274$$

to determine the $Q$ and $e$ values. The calculated $\chi_{av}$, $E_y$, and $\chi_m$ values (all in atomic units, i.e., hartrees)[47] can also be used in the relationships derived from comparison to Greenley's data, resulting in the following equations for $e$ and $Q$

$$e = 31.56\chi_{av} - 5.734$$

$$\ln Q = -460.7E_y + 82.11\chi_m + 1176E_y\chi_m - 31.232$$

We suggest that these values be used with some care when highly fluorinated double bonds are involved due to the above discussion on a particular monomer, i.e., tetrafluoroethylene ($C_2F_4$).

## Conclusion

The development of a means for predicting parameters for the $Q-e$ scheme for the prediction of monomer reactivity in free-radical copolymerizations has been investigated by performing a theoretical analysis based on a formal comparison with the Arrhenius equation and by carrying out various density functional theory calculations on various molecules whose experimental $Q$ and $e$ values are available. The theoretical analysis has demonstrated that for a general choice of the $Q$ and $e$ values of the reference monomer, the parameters $Q$ and $e$ are dependent on both the energetic properties of the free-radical reaction and the polar properties of the monomer and radical. Thus an ideal choice of the reference values would be such that the parameter $Q$ is only determined by the energetic properties and the parameter $e$ is only determined by the polar properties. Our calculated results suggest that the most popularly used reference values of $Q = 1.0$ and $e = -0.8$ for styrene are likely close to this ideal choice. In general, for correlation of both parameters $Q$ and $e$ with all these properties, the overall reliability of the calibrated correlation relationships should not be affected by changing the reference $Q$ and $e$ values. The computational results demonstrate satisfactory correlations of the $Q-e$ parameters with the DFT-calculated electronegativities and reaction free energies, illustrating that the electronegativity and reaction free energy determined by the density functional theory calculations reasonably reflect the polar and energetic properties, respectively, for the purpose of these correlations.

The calibrated correlation relationships are satisfactory and, therefore, can be used in future computational predictions of the *Q* and *e* values whose experimental *Q* and *e* values have not been established. Finally, we provide a recommended prescription for calculating the *Q* and *e* values of an unknown monomer (M) containing a C═C bond.

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**Supporting Information Available:** Two figures showing the correlations described by eqs 27 and 28: Plot of the calculated (IP + EA)/2 versus the calculated $-(\epsilon_{\mathrm{HOMO}} + \epsilon_{\mathrm{LUMO}})/2$ and plot of $-\epsilon_{\mathrm{SOMO}}$ determined by the unrestricted open-shell DFT calculation versus $-\epsilon_{\mathrm{HOMO}}$ determined by the restricted open-shell DFT calculation for the 27 radicals. Two tables showing the calculated *Q*, ln *Q*, and *e* values obtained from the prescription given above in comparison with the corresponding experimental data.

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(31) For the 10 monomers, by performing a least-squares fit, we obtain

$$E_{\mathrm{a}} = 0.3840\bullet(\Delta H) + 15.238\ \text{(kcal/mol)}$$

with a correlation coefficient (*R*) of 0.932 and a root-mean-square deviation (RMSD) of 0.509 kcal/mol and

$$E_{\mathrm{a}} = 1.557\bullet(\Delta H) - 0.1945\bullet\chi - 0.00837\bullet(\Delta H)\chi + 42.541\ \text{(kcal/mol)}$$

with $R = 0.962$ and RMSD = 0.386 kcal/mol. Here, $E_{\mathrm{a}}$ and $\Delta H$ refer to the experimental values, and $\chi = -(\epsilon_{\mathrm{HOMO}} + \epsilon_{\mathrm{LUMO}})/2$ calculated for the monomer at the B3LYP/6-31+G*//B3LYP/6-31G* level.

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(37) On the basis of the available experimental heats of formation ($\Delta_{\mathrm{f}}H°$), the enthalpy changes of reaction $\mathrm{M} + \mathrm{H}^{\bullet} \rightarrow \mathrm{MH}^{\bullet}$ can be determined to be −38.75, −38.79, and −38.45 kcal/mol for M = $C_2H_4$, $CH_3CH{=}CH_2$, and $(CH_3)_2C{=}CH_2$, respectively. The respective enthalpy changes calculated at the B3LYP/6-31+G* level are −39.12, −39.10, and −39.29 kcal/mol.

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(46) If the $\chi_{av}$, $E_y$, and $\chi_m$ values are in electronvolts, the corresponding explicit relationships are $e = 1.276\chi_{av} - 6.285$ and $\ln Q = -55.67E_y + 19.55\chi_m + 11.14E_y\chi_m - 98.274$.

(47) If the $\chi_{av}$, $E_y$, and $\chi_m$ values are in electronvolts, the corresponding explicit relationships are $e = 1.160\chi_{av} - 5.734$ and $\ln Q = -16.93E_y + 3.017\chi_m + 1.588E_y\chi_m - 31.232$.