Ab initio molecular orbital calculations on the *Q–e* scheme for predicting reactivity in free-radical copolymerization

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Ab initio molecular orbital calculations have been performed on the reactions of unsaturated monomers with both hydrogen and methyl radicals. These calculations have utilized several basis sets, namely STO-3G, SV3-21G, SV Dunning and triple zeta valence. The correlation between the experimental *Q* and the energy of formation of the product radical was examined, whilst the electronegativity of the monomer was correlated with the *e* parameter. In addition, a *Q–e–e**-type scheme was analysed to correct for the simplification in the standard *Q–e* scheme that the monomer and the radical are identical with respect to their charge distributions. In this instance experimental *e* parameters were correlated with the average electronegativity of monomer and radical. This work shows that correlations exist between these parameters as other simpler studies (based on Huckel calculations) have reported. However, while the correlations with both *e* and the *e–e** average parameter were predictive, the relationship between *Q* and a general reactivity of the radical proved only qualitative. A statistical analysis of the data revealed a significant polar influence on this relationship; by taking this into account we were able to improve the correlation. We also rescaled the *Q–e* scheme as suggested by other authors and correlated the results of our calculations with the new numbers. This work emphasizes the difficulties in correlation analysis, which requires the separation and parameterization of polar, steric and general reactivity effects. It also stresses the requirement for accurate experimental data.

(Keywords: molecular orbital calculations; *Q–e* scheme; copolymerization)

INTRODUCTION

The aim of procedures such as the *Q–e* scheme is to predict reactivity in free-radical copolymerizations and terpolymerizations without recourse to experimental determination of kinetic rate constants. It relies on a large database of kinetic rate constants determined over the last 40 years. This is both a strength and a weakness. The strength lies in the general utility of the scheme, as proven over many years of usage. The theoretical shortcomings are well documented and we shall discuss these throughout the course of this paper. However, even if the scheme was rigorously correct there remains an implicit weakness in the kinetic rate constant database itself. Many reactivity ratios have been determined in poorly designed experiments and cannot be relied upon. An IUPAC working party has been formed[1] to make recommendations on these matters.

There have been previous attempts to justify the *Q–e* scheme in terms of molecular orbital (MO) theory which we shall review elsewhere. In addition, several authors have attempted to apply Huckel calculations to predict *Q* and *e* values, and even correlate directly stabilization energies derived from Huckel-type calculations with reactivity ratios. Some of these authors reported success in achieving predictive relationships by these simple calculations in as early as 1962[2]. The power and sophistication of modern computer technology make possible far more rigorous calculations at full *ab initio* levels so that a predictive scheme for reactivity in free-radical copolymerization may now be possible. Also, the work of Fukuda *et al.*[3] has raised interest in classical free-radical kinetics. Their work has shown that the terminal model for copolymerization is not valid and that this might be the case generally. In a recent paper[4] they invoke both implicit and explicit penultimate unit effects to explain their experimental observations. It was comments in this paper on the MO calculations of Imoto *et al.*[5] that stimulated the work reported here. Imoto *et al.* used an *ab initio* MO approach (at STO-3G level) to correlate the interaction energy of a monomeric radical and an unsaturated monomer (an analogue of the homopropagation reaction) calculated from perturbation theory with experimentally determined activation energies for homopropagation reactions. Imoto *et al.* claimed to have established a relationship between calculated parameters and experimental k_p activation data for a range of homopolymerizations.

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Copolymerizations, on the other hand, proved intractable in this aspect and they suggested that a penultimate model may be required in this instance[6].

Fukuda *et al.*[7] justified their explanation of penultimate unit effects by applying the Evans–Polanyi rule in a phenomenological approach based on a simple premise that the nature of the penultimate unit influences the radical stability. In fact it was the work of Evans, Polanyi and Eyring in establishing transition state theory that spawned the *Q–e* scheme of Alfrey and Price[8] for copolymerization back in the 1940s.

The work in this paper represents an initial foray into the important area of free-radical polymerization. Our aim is to search for an MO approach to reactivity in copolymerization and also to investigate the fundamental mechanism of the addition of radicals to monomer species. In view of the apparent success of semi-empirical MO methods reported by earlier workers, we decided to look again at the efficacy of the *Q–e* scheme, only this time using *ab initio* calculations.

Theoretical background

The Alfrey–Price *Q–e* scheme has been extensively reviewed elsewhere[9–11], so we shall not deal with it in detail. In brief, Alfrey and Price[8] suggested that a 'terminal' model for copolymerization involves four basic propagation rate constants, k_{p11}, k_{p12}, k_{p22}, and k_{p21}, which can be written as

$$k_{p11} = P_1 Q_1 \exp(-e_1^2) \tag{1}$$

$$k_{p12} = P_1 Q_2 \exp(-e_1 e_2) \tag{2}$$

$$k_{p22} = P_2 Q_2 \exp(-e_2^2) \tag{3}$$

$$k_{p21} = P_2 Q_1 \exp(-e_2 e_1) \tag{4}$$

where the P_i and Q_j are measures of the general reactivity of radical *i* and monomer *j*, respectively, while the e_i relate to their polar properties. Writing reactivity ratios r_1 and r_2 as

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

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

eliminates *P* to give r_1 and r_2 solely in terms of *Q* and *e* – the *Q–e* scheme. From the outset, the concept of fixed charged distributions on the monomers appeared to be unrealistic, as did the assignment of a single *e* value to both radicals and monomers. Nevertheless, the scheme has proved to be remarkably useful and this utility in itself suggests that the *Q* and *e* values do relate to fundamental factors affecting the transition state of propagation reactions.

Operationally, the scheme is set up by defining a reference monomer; usually, this is styrene with *Q* and *e* values of 1.0 and −0.8, respectively, to which all other monomers relate. This of course is a weakness, for if an alternative reference is chosen, e.g. ethylene[12], or if different numerical values are assigned to *Q* and *e* for styrene[13], then not only do all the other *Q* and *e* values change, but also their ranking. This is the best demonstration of the semi-empirical nature of the scheme.

Refinements have been suggested to compensate for shortcomings, most notably Wall's attempt[14] to allow for the difference in polarity between the monomer and radical by introducing an extra parameter e^*, which was defined by Wall as 'the relative charge on the radical end'.

The scheme is open to criticism in view of its undoubted empiricism; however, it is an attractive starting point for MO calculations essentially for three reasons.

1. As stated above, the success of the scheme indicates that the *P*, *Q* and *e* parameters do relate to factors affecting the transition state.
2. There is a large body of experimental data with which calculated parameters can be correlated.
3. Previous attempts to develop predictive schemes based on both Huckel theory and minimal basis set *ab initio* calculations had seen some success. Hence our interest relates to the factor, or factors, that limit the degree of correlation found, i.e. is it the level of calculation or the *Q–e* scheme itself?

The initial *Q* and *e* values used in this study were taken from Greenley's listing in the 'Polymer Handbook'[15]. This categorizes monomer *Q* and *e* values into different groupings. The six primary monomers acrylic acid, acrylonitrile, butadiene, methyl acrylate, methacrylonitrile and methyl methacrylate were selected as group one as their reactivity ratios with styrene were said to be 'narrowly defined' by a number of investigators. The *Q* and *e* values of a secondary group of 10 common vinyl monomers, Q_2 and e_2, were determined using equation (7), with the primary monomer group supplying the Q_1 and e_1 values

$$\ln(Q_1/r_1) - e_1^2 = -e_2 e_1 + \ln Q_2 \tag{7}$$

Laurier *et al.*[16] have pointed out the deficiencies in the calculation and listing procedure used by Greenley, and reported a methodology for determining *Q* and *e* values using a statistically correct process. Consequently, we concentrated the majority of our effort on the monomer *Q* and *e* values calculated by Laurier *et al.*[16]. These are given as the top 11 monomers in *Table 1*. All the *Q* and *e* values used are listed in *Table 1*, which also functions as a key to the points plotted in the graphs given in the results section.

The next step is to relate the *P*, *Q* and *e* values with quantities that can be calculated. Despite the rapid rise in computer power, it is still a lengthy process to calculate activation energies directly. The algorithms for finding the saddle point corresponding to the transition state are complex and fraught with convergence difficulties. However, successful transition state calculations have been carried out for methyl radical addition to monomers in a paper by Fueno and Kamachi[17]. Larger calculations for monomeric radical addition may be possible and we are currently attempting these. A simpler approach is to invoke the Evans–Polanyi rule, which is based on the observation that lower activation energies generally lead to more exothermic reactions. In other words, the calculated heat or energy of reaction ΔE is a measure of the activation energy $E^{\#}$ and therefore the rate.

Evans *et al.*[18] point out that for a propagation-type reaction the heat of polymerization can be expressed as

$$\Delta E = \Delta E_0 - R_a - R_m + R_f \tag{8}$$

in which ΔE_0 is the heat (or energy) of reaction for a propagation step in ethylene polymerization. R_a, R_m and R_f are the resonance energies of the specific attacking radical, the monomer and the product radical, respectively. By invoking the Evans–Polanyi rule, as discussed above, a simple expression for activation energy

Table 1 Q and e experimental values from the literature

	Values from Greenley[15]		Values from Laurier *et al.*[16]	
Monomer key	Q	e	Q	e
1. Styrene	1.00	−0.80	1.00	−0.80
2. Methyl acrylate	0.45	0.64	0.38	0.75
3. Acrylonitrile	0.48	1.23	0.51	1.20
4. Methyl methacrylate	0.78	0.40	0.76	0.38
5. Methacrylonitrile	0.86	0.68	0.85	0.69
6. Acrylic acid	0.83	0.88	0.68	1.33
7. Vinyl acetate	0.026	−0.88	0.024	−0.02
8. Vinylidene chloride	0.31	0.34	0.289	0.26
9. n-Butyl acrylate	0.38	0.85	0.41	1.06
10. Vinyl chloride	0.056	0.16	0.033	−0.10
11. 1,3-Butadiene	1.70	−0.50	2.36	−1.17
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 fluoride	0.008	0.72		
21. Vinyl ethyl ether	0.018	−1.80		
22. Acrylamide	0.23	0.54		
23. Allyl alcohol	0.005	−1.48		
24. 2-Chlorobutadiene	10.52	1.20		
25. 2-Vinylpyridine	1.41	−0.42		
26. Tetrachloroethylene	0.001	1.24		
27. Methacrylic acid	0.98	0.62		
28. Tetrafluoroethylene	0.032	1.63		
29. Vinyl methyl ether	0.029	−1.16		
30. 2,5-Dichlorostyrene	1.50	0.94		
31. *N*-Vinylpyrrolidone	0.088	−1.62		
32. *p*-Methoxystyrene	1.53	−1.40		
33. *p*-Methylstyrene	1.100	−0.63		
34. 2-Hydroxyethyl methacrylate	1.78	−0.39		

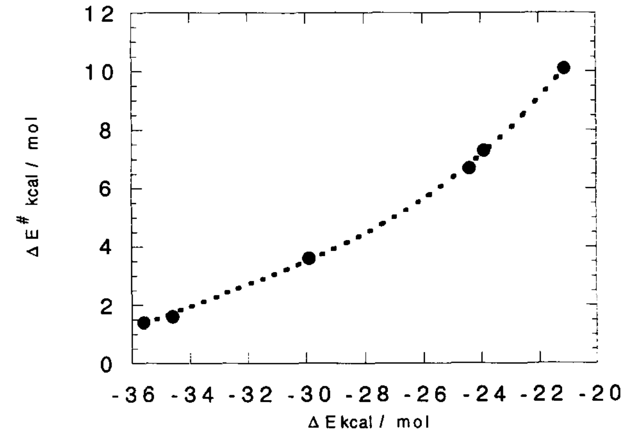


Figure 1 Relationship between the calculated heat of reaction and the activation energy for the reaction of a methyl radical with a number of vinyl compounds (taken from ref. 17)

can be stated

$$\Delta E^{\#} = \Delta E_0 - k(R_f - R_a - R_m) \qquad (9)$$

where k is a proportionality factor. The simplification here is that a straightforward linear relationship between activation energy and heat of reaction is assumed. There is no fundamental reason for this and the data of Fueno and Kamachi[17] suggest a more complex association. This can be demonstrated using data from the aforementioned paper for methyl radical addition to different monomers (*Figure 1*).

These Fueno and Kamachi data were obtained from transition state calculations. More recent work on a larger group of vinyl monomers suggests that this non-linear relationship may be the result of coincidental scatter, and in fact an extremely good linear relationship is predicted between energy of activation and energy of reaction[19].

Evans and Polanyi suggested that the Alfrey–Price Q parameter can be written as

$$Q = \exp[(R_a - R_m)/RT] \qquad (10)$$

and that e can be obtained from the electronic charge on the substituted carbon of the monomer. Similarly, e^* values can be obtained for the radical as we shall discuss later.

Molecular orbital calculations

Early attempts at correlating reactivity with molecular orbital calculations were based on Huckel theory. This is a very approximate method for describing the electronic structure of a system in that it only considers the π electrons. Furthermore, gross assumptions are made as to the form of the Hamiltonian and the values of the diagonal and off-diagonal elements which are obtained empirically. In spite of this, good correlations have apparently been obtained between resonance stabilization energies calculated by Huckel theory and Alfrey–Price Q parameters.

During the 1960s and 1970s more refined 'semi-empirical' methods such as CNDO, INDO and MINDO were developed and these are now incorporated in computer packages such as MOPAC[20] and AMPAC[21]. These methods include the σ electrons and hence account for chemical reactivity more fully, but they still rely on drastic approximations to the Hamiltonian and the use of experimental quantities such as the atomic ionization potentials and electron affinities. Despite recent increases in computer power, these methods are still widely used, both as a quick route to approximate data for small molecules and in some cases as the only feasible route for molecular orbital calculations for very large systems of atoms.

The development of mini supercomputers and, more recently, powerful workstations together with accessible programs has made full-blown *ab initio* molecular orbital calculations on small systems (up to, say, 15 atoms) relatively routine over the past couple of years. Approximations are still made, even at this level. In particular, the atomic orbitals are represented by a limited 'basis set' of mathematical functions, most often Gaussian functions. The number of these functions and the way in which they are combined determine the level of calculation and ultimately the accuracy of the result. A further approximation is that calculations are usually carried out at the Hartree–Fock level, although electron correlation can now be included in a number of ways.

The *ab initio* calculations in the literature[22] pertaining to monomer reactivities have all been made using a minimal basis set (STO-3G, meaning three Gaussian functions are used to represent one Slater-type atomic orbital. For an explanation of the terms used to describe basis sets we refer the reader to the book by Clark[23]). Energies and geometries calculated at this level are often in poor agreement with experiment. For example, a carbon radical centre is predicted to be pyramidal rather than planar. The work by Fueno and Kamachi[17] on methyl addition to monomers used an SV3-21G basis set, which is the minimum required to get approximately correct geometries for radicals. The use of extended basis sets such as this also improves the agreement between calculated and experimental energies.

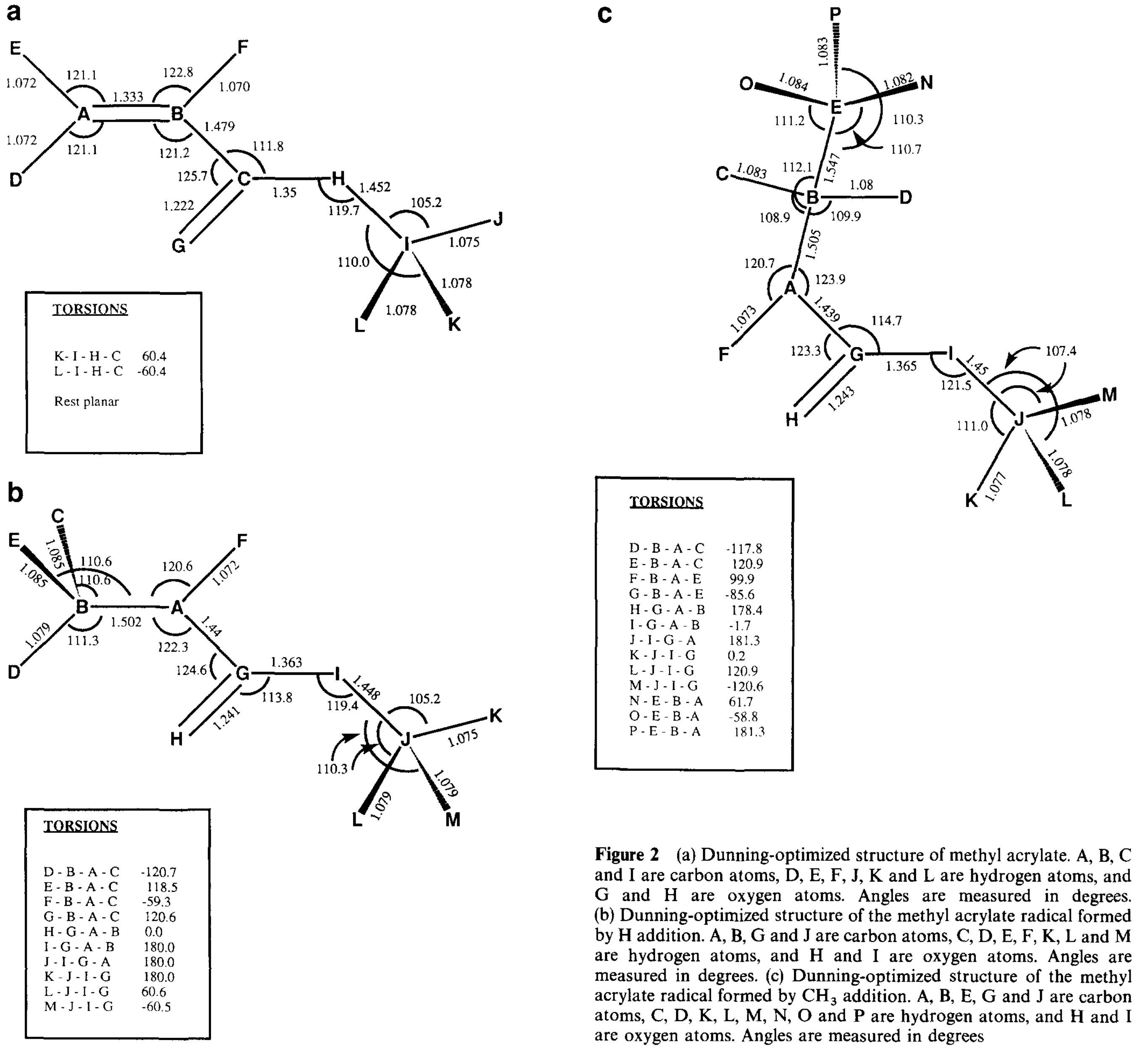
Our own work on reactions of small molecules (unpublished results) has led us to the view that even more flexible basis sets such as the SV Dunning[24] or the triple zeta valence (TZV)[25,26] sets are required to obtain geometries and energy changes approaching experimental accuracy. Thus, the TZV basis set predicts energies to within 3 kcal mol^{-1} (1 cal = 4.2 J) of the experimental enthalpies of reaction for small molecules. We therefore believe that calculations at this level should provide a critical test of both the models proposed to represent the *Q–e* parameters and the *Q–e* scheme itself.

CALCULATION METHODS

The calculations reported in this paper are all at the Hartree–Fock level and were performed using the GAMESS suite of programs[27], which provides a state-of-the-art package for *ab initio* calculations. Our procedure was as follows. Preliminary monomer structures were obtained by direct minimization of the STO-3G total energies with respect to all geometric variables, i.e. bond lengths and angles. Where necessary several starting structures were used to achieve convergence. These structures were then refined by successive reoptimization of the geometry using SV3-21G and TZV basis sets, except where intractable convergence difficulties were encountered or the system was too large for our computational resources.

The final structures are not reported here owing to space restrictions, but they are available (in Z-matrix format) from the authors on request. Examples of such data for methyl acrylate are given in *Figure 2*, where the bond lengths are given in angstroms.

Calculations were performed on each monomer and the corresponding radicals formed by addition of a hydrogen or a methyl radical to the α carbon. We were restricted to these 'model' reactions by the limitations of our computational resources and the inherent n^4 scaling of the time for Hartree–Fock calculations, where n is the number of electrons in the system. The output



TORSIONS

K - I - H - C	60.4
L - I - H - C	-60.4

Rest planar

TORSIONS

D - B - A - C	-120.7
E - B - A - C	118.5
F - B - A - C	-59.3
G - B - A - C	120.6
H - G - A - B	0.0
I - G - A - B	180.0
J - I - G - A	180.0
K - J - I - G	180.0
L - J - I - G	60.6
M - J - I - G	-60.5

TORSIONS

D - B - A - C	-117.8
E - B - A - C	120.9
F - B - A - E	99.9
G - B - A - E	-85.6
H - G - A - B	178.4
I - G - A - B	-1.7
J - I - G - A	181.3
K - J - I - G	0.2
L - J - I - G	120.9
M - J - I - G	-120.6
N - E - B - A	61.7
O - E - B - A	-58.8
P - E - B - A	181.3

Figure 2 (a) Dunning-optimized structure of methyl acrylate. A, B, C and I are carbon atoms, D, E, F, J, K and L are hydrogen atoms, and G and H are oxygen atoms. Angles are measured in degrees. (b) Dunning-optimized structure of the methyl acrylate radical formed by H addition. A, B, G and J are carbon atoms, C, D, E, F, K, L and M are hydrogen atoms, and H and I are oxygen atoms. Angles are measured in degrees. (c) Dunning-optimized structure of the methyl acrylate radical formed by CH_3 addition. A, B, E, G and J are carbon atoms, C, D, K, L, M, N, O and P are hydrogen atoms, and H and I are oxygen atoms. Angles are measured in degrees

includes the optimized geometry, molecular orbital energies (eigenvalues) and total electronic energy as well as orbital population – this output is tabulated elsewhere[28]. All calculations were performed on UNIX workstations made by Sun, Silicon Graphics and IBM. Typical calculation times were of the order of 1–3 days of CPU per species at the TZV level.

RESULTS AND DISCUSSION

The e *parameter*

Previously, Colthup[22] considered a linear correlation between the *e* parameter and the charge on the β carbon, which we examined at all levels of calculation. We found a poor correlation based on STO-3G calculations, owing possibly to differences in the structures used. The correlation deteriorated with more flexible basis sets. We took this as a manifestation of the inadequacies of representing experimental *e* values in this way. As an alternative, we examined a procedure proposed by Hoyland[29]. He found a good correlation between the average electronegativity of monomer and radical and the *e* parameter and proposed using Mulliken's method[30] for defining electronegativity but without doing any calculations. We have, therefore, used his proposed relationship to examine the correlation between calculated electronegativity and the *e* parameter.

The electronegativity χ, as defined by Mulliken, is given by

$$\chi = (I + A)/2 \qquad (11)$$

where I is the ionization potential and A is the electron affinity. Assuming Koopman's theorem to be applicable, then

$$\chi_{\text{monomer}} = -(\varepsilon_n + \varepsilon_{n+1})/2 \qquad (12)$$

where ε_n is the energy of the highest occupied molecular orbital (HOMO) and ε_{n+1} is the energy of the lowest unoccupied molecular orbital (LUMO). For the radical the electron affinity equals the ionization potential and

$$\chi_{\text{radical}} = -\varepsilon_n \qquad (13)$$

where ε_n is the energy of the singly occupied molecular orbital (SOMO). We examined the correlation between the experimentally determined values of *e* and the average electronegativity of radical and monomer

$$\chi_{\text{av}} = (\chi_{\text{monomer}} + \chi_{\text{radical}})/2 \qquad (14)$$

The units we use for χ are Hartrees (1 Hartree = 627.7 kcal mol^{-1}). We examined the correlation at all levels of calculation and on both the Greenley and Laurier data. Let us consider the relationship between *e* and monomer electronegativity for the Greenley data first. The best correlation we obtained was for the most sophisticated calculation level (TZV): this is shown in *Figure 3*, where several of the outlying points are labelled.

The two points above the line refer to tetrafluoroethylene (28) and 2-chlorobutadiene (24), and the two below the line are propene (13) and allyl alcohol (23). The difficulties in obtaining precise experimental *Q* and *e* values for unconjugated monomers were addressed by Laurier *et al.* It may be that these outlying points are a manifestation of poor experimental data. However, the fact that the fit improves with the size of the basis set suggests that the model is reasonable, and that the residual scatter might result from the use of Koopman's theorem for calculating χ and errors in the experimental *e* values. In addition, there is the dubious assignment of a single *e* value for monomers and radicals. An attempt to allow for this is our use of the average electronegativity values, and Greenley's *e* data are plotted against these χ_{av} data in *Figure 4*. Reference to the correlation coefficients listed in *Tables 2* and *3* indicates an improved correlation with the average electronegativity, particularly with respect to the previously wayward points.

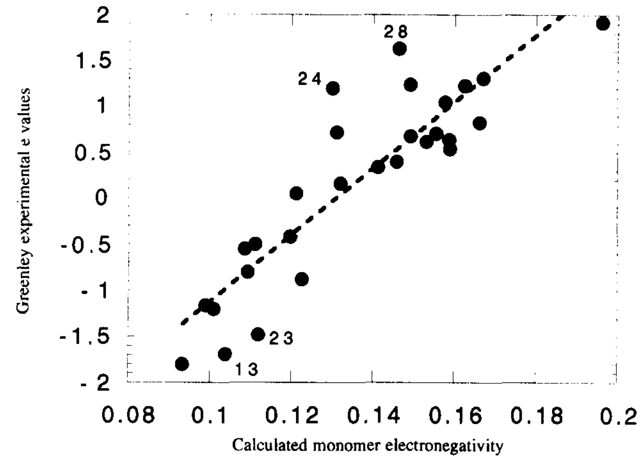


Figure 3 Linear, least-squares fit to the plot of monomer electronegativity χ_m (Hartrees) and experimental *e* values (Greenley data). Electronegativity was calculated using the TZV basis set

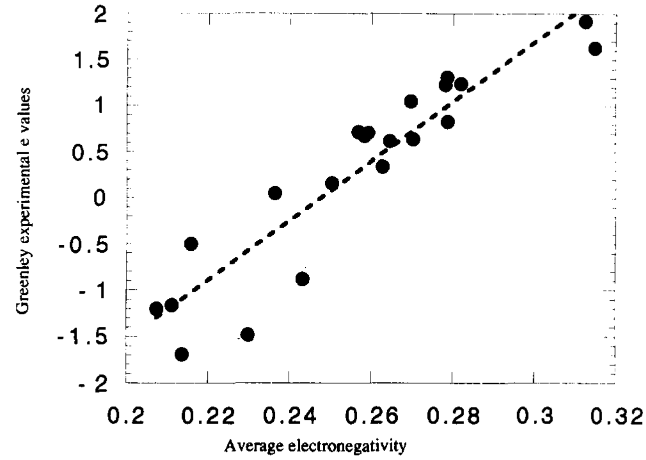


Figure 4 Linear, least-squares fit to the plot of average electronegativity χ_{av} (Hartrees) and experimental *e* values (Greenley data). Electronegativity was calculated using the TZV basis set

Table 2 Correlation coefficients for the linear, least-squares fit to the relationship between calculated monomer electronegativity and the experimental *e* parameter

Data	Level	Correlation coefficient *R*	
	STO-3G	0.800	
Greenley	SV3-21G	0.881	
	TZV	0.887	(*Figure 3*)
	STO-3G	0.849	(*Figure 5b*)
Laurier	SV3-21G	0.948	
	Dunning	0.973	
	TZV	0.970	(*Figure 6b*)

Table 3 Correlation coefficients for the linear, least-squares fit to the relationship between calculated average electronegativity and the experimental *e* parameter

Data	Level	Correlation coefficient *R*	
Greenley	STO-3G	0.828	
	SV3-21G	0.889	
	TZV	0.924	(*Figure 4*)
Laurier	STO-3G	0.813	(*Figure 5a*)
	SV3-21G	0.914	
	Dunning	0.956	
	TZV	0.969	(*Figure 6a*)

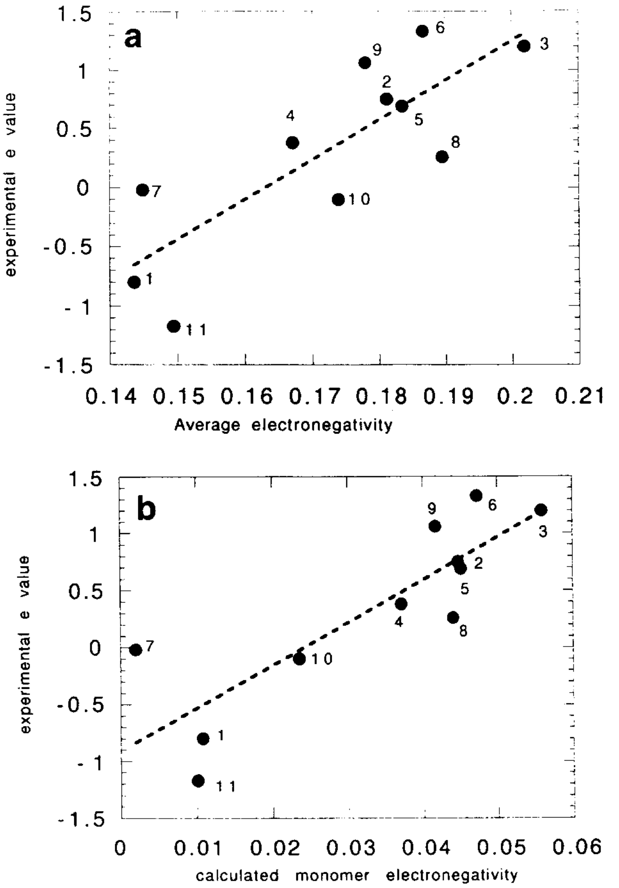


Figure 5 Linear, least-squares fits to the plots of (a) average electronegativity χ_{av} (Hartrees) and (b) monomer electronegativity χ_m (Hartrees) with the Laurier experimental *e* values. Electronegativities were calculated using the STO-3G basis set

Turning now to correlations with the experimental *e* values given by Laurier *et al.*[16], these are plotted in *Figures 5* and *6* for the STO-3G and TZV basis sets, respectively; the correlation coefficients are listed in *Tables 2* and *3*.

As can be seen, the correlations based on extended basis sets can be considered predictive. An interesting point is that for these well-determined experimental values there is no improvement in adopting the χ_{av} parameter. Therefore, it may be that the assumption made by Price and Alfrey that allows the use of a single *e* parameter is valid except for one or two unusual monomers (for which the *Q*–*e* scheme was never intended), e.g. tetrafluoroethylene, and even these can be accommodated by the use of the average electronegativity parameter.

The Q parameter

As we have not been able to perform calculations on the actual reaction between a monomeric radical and a monomer (because of the size of the system), we have relied on model reactions. Initially, we followed the model of Colthup[22], whereby the polymer radical is represented by a monomer unit to which a hydrogen atom has been added. Colthup related the *Q* parameter to the energy of formation (E_Y) of this H–monomer radical

$$H^{\bullet} + CH_2{=}CXY \rightarrow CH_3{-}CXY^{\bullet}$$

$$\Delta E_{H\ reaction} = E_{CH_3CXY} - E_{CH_2CXY} - E_H = E_Y$$

We cannot propose a more suitable (practical) model at present. However, we are aware from some of our other work that the energetics of reactions involving bare hydrogen atoms are poorly reproduced at even a high *ab initio*/Hartree–Fock level because of electron correlation. We therefore sought to overcome this known problem by replacing the H radical with a methyl radical

$$CH_3^{\bullet} + CH_2{=}CXY \rightarrow CH_3CH_2{-}CXY^{\bullet}$$

$$\Delta E_{CH_3\ reaction} = E_{CH_3CH_2CXY} - E_{CH_2CXY} - E_{CH_3} = E_Y$$

Our results at SV3-21G level agreed in most cases with those of Fueno and Kamachi[17]. The difference between H and CH_3 radical addition can be seen from *Figure 7*. This means that our attempt to represent general monomer reactivity by H or CH_3 radical addition may yet be improved as an even larger radical will be different

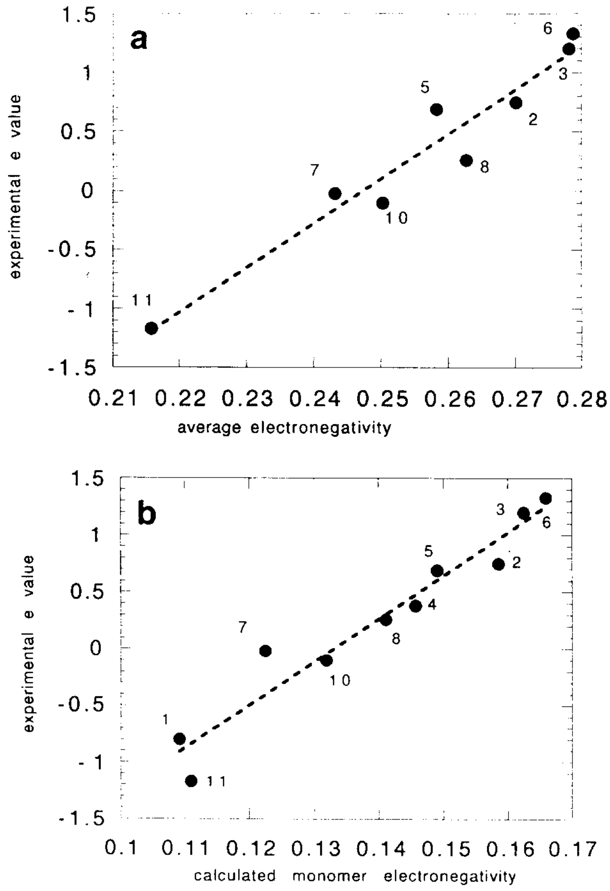


Figure 6 Linear, least-squares fits to the plots of (a) average electronegativity χ_{av} (Hartrees) and (b) monomer electronegativity χ_m (Hartrees) with the Laurier experimental *e* values. Electronegativities were calculated using the TZV basis set

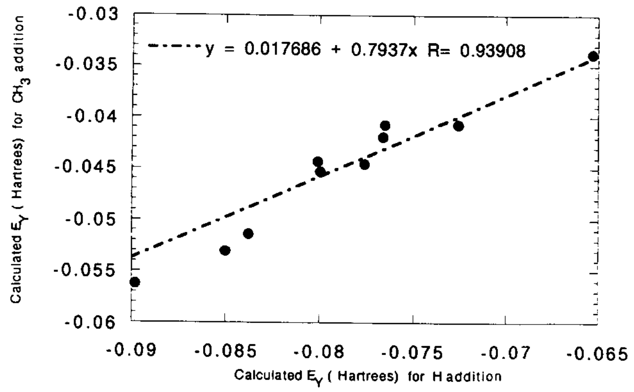


Figure 7 Linear, least-squares fit to the plot of E_Y (Hartrees) for H addition *versus* E_Y (Hartrees) for CH_3 addition. Calculations were made using the SV Dunning basis set on the Laurier monomer set. R is the correlation coefficient

again. The selection criteria for adopting a model reaction are practicality and the need for a reaction which enables the designation of a 'general reactivity' of the monomer. For this we needed a reaction that all the monomers would undergo and one which would be free of a large polar influence.

Model analysis

Colthup directly correlated E_Y with $\ln Q$. When we also did this for the Greenley data, we observed considerable scatter for both the E_Y H data and the E_Y CH_3 data. These plots are shown in *Figure 8*. It is intuitively clear that there is some correlation, though a high-order/polynomial fit would be required and any form of predictive relationship appears unlikely.

Therefore, we decided to take the best data set available, i.e. the Laurier experimental data coupled with the SV Dunning level calculated data*, and performed a statistical analysis to determine the best model available. The plots for this data set are shown in *Figure 9* together with a simple linear, least-squares fit of the data.

The model we selected as a starting point is

$$\ln Q = \beta_0 + \beta_1 E_Y + \beta_2 \chi_m + \beta_{12} E_Y \chi_m \qquad (15)$$

where χ_m is the electronegativity of the monomer. This was shown earlier to be linearly correlated with the experimental e value. We performed a Box–Cox transformation using this model and the data set and confirmed that the use of a log transformation for Q gives a near-optimum fit and a normal distribution of the residuals.

If the Q–e scheme is successful in truly isolating the general reactivity and polarity contributions into two parameters then we would expect the last two terms in equation (15) to be insignificant.

Let us consider first the CH_3 addition data. Whilst the term in χ_m was found to be barely significant, the interaction $E_Y \chi_m$ is highly significant (at the 99% confidence level). This can be demonstrated from the coefficients given in *Table 4*. The coefficient of determination R^2 is the proportion of variability in the data explained by the model. $R^2_{(adj)}$ is a rescaling of R^2 which removes the impact of changing degrees of freedom and gives a quantity that is more comparable than R^2 for models involving different numbers of parameters. The closer $R^2_{(adj)}$ is to unity then the better the fit to the model. For a detailed explanation of $R^2_{(adj)}$ readers are referred to a standard statistics text[31]. The improvement

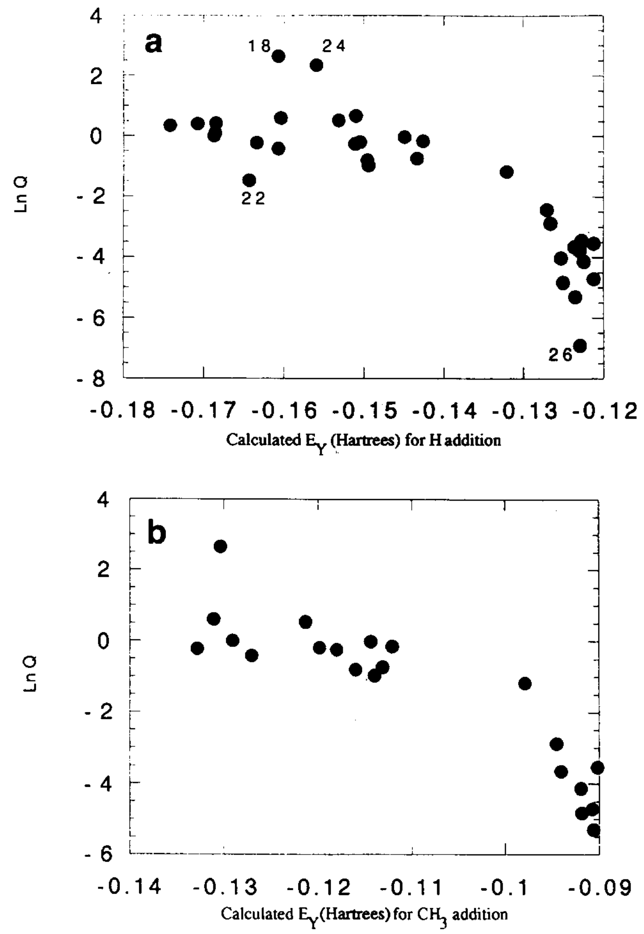


Figure 8 Plots of E_Y (Hartrees) (a) for H addition and (b) for CH_3 addition *versus* $\ln Q$. Data are from the Greenley monomer set and calculations were made using the STO-3G basis set

Table 4 Comparison of models for fitting the calculated data to the Laurier Q data using equation (15)

			Coefficient of determination	
		Model	R^2	$R^2_{(adj)}$
Dunning	CH_3 addition	β_0, β_1 only	0.667	0.630
		β_0, β_1, β_2, β_{12}	0.892	0.846
	H addition	β_0, β_1 only	0.697	0.664
		β_0, β_1, β_2 only	0.800	0.750
		β_0, β_1, β_2, β_{12}	0.832	0.760
SV3-21G	CH_3 addition	β_0, β_1 only	0.67	0.63
		β_0, β_1, β_2 only	0.75	0.69
		β_0, β_1, β_2, β_{12}	0.89	0.85
	H addition	β_0, β_1 only	0.71	0.67
		β_0, β_1, β_2 only	0.83	0.79
		β_0, β_1, β_2, β_{12}	0.85	0.79
STO-3G	CH_3 addition	β_0, β_1 only	0.75	0.72
		β_0, β_1, β_2 only	0.79	0.73
		β_0, β_1, β_2, β_{12}	0.86	0.80
	H addition	β_0, β_1 only	0.68	0.65
		β_0, β_1, β_2 only	0.74	0.68
		β_0, β_1, β_2, β_{12}	0.77	0.67

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*The SV Dunning data were selected despite the fact that the TZV basis set is more flexible. Unfortunately, we could not complete all the TZV calculations as butyl acrylate was too large for our resources, and so the SV Dunning set represents our best complete set of data

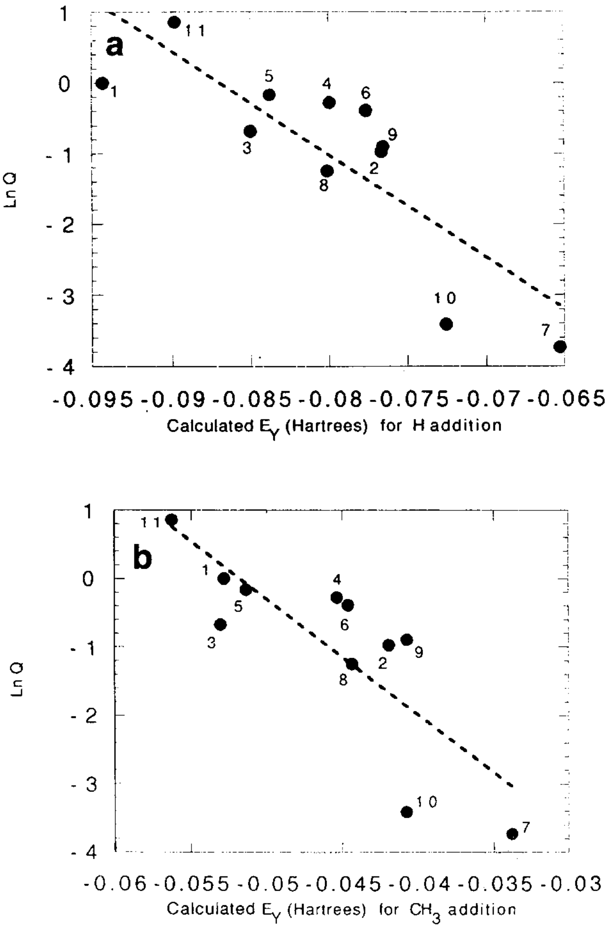

Figure 9 Linear, least-squares fits to the plots of E_Y (Hartrees) (a) for H addition and (b) for CH_3 addition *versus* ln Q. Data are from the Laurier monomer set and calculations were made using the SV Dunning basis set

in $R^2_{(\mathrm{adj})}$ confirms that a polar influence on either or both of Q and E_Y cannot be ignored.

A similar treatment of the H addition data was slightly complicated by the fact that χ_m and $E_Y\chi_m$ are highly correlated owing to the structure of the particular data set. Despite this, model equation (15) was again found to provide a significantly better fit than the model excluding polar factors.

Figure 10 shows the plots of observed *versus* predicted values for these two data sets. It is noticeable that vinyl chloride (10) is an outlier in the CH_3 data set (the standard residual is $>3\sigma$). This may be expected as the experimental Q value for vinyl chloride is subject to considerable error.

Subsequently, we applied this model to the STO-3G and SV3-21G calculations in conjunction with the Laurier data. The results of the correlations are given in *Table 4*. It is noteworthy that the CH_3 addition data give a better fit than the H addition data in all cases. There is no improvement on changing the basis set from SV3-21G to SV Dunning, which suggests that the nature of the basis set is not the limiting factor preventing a better correlation. The evidence points to the model reactions we adopted as the limiting factor. As methyl addition appears to be a considerable improvement over hydrogen addition, this indicates that an even larger radical might give a better correlation.

Rescaling the Q–e scheme

Kawabata *et al.*[13] pointed out that the choice of styrene as a reference with Q and e values of 1.0 and -0.8, respectively, was somewhat arbitrary. They opted to redefine the e value for styrene to zero. This simplifies equation (5), which reduces to the form (M_1 = styrene)

$$r_1 = 1/Q_2 \qquad (16)$$

Revised Q values based on the reactivity ratios given in the Laurier paper and equation (16) are given in *Table 5*.

We took these revised ln Q values and plotted them against E_Y for CH_3 addition (SV Dunning basis set). The

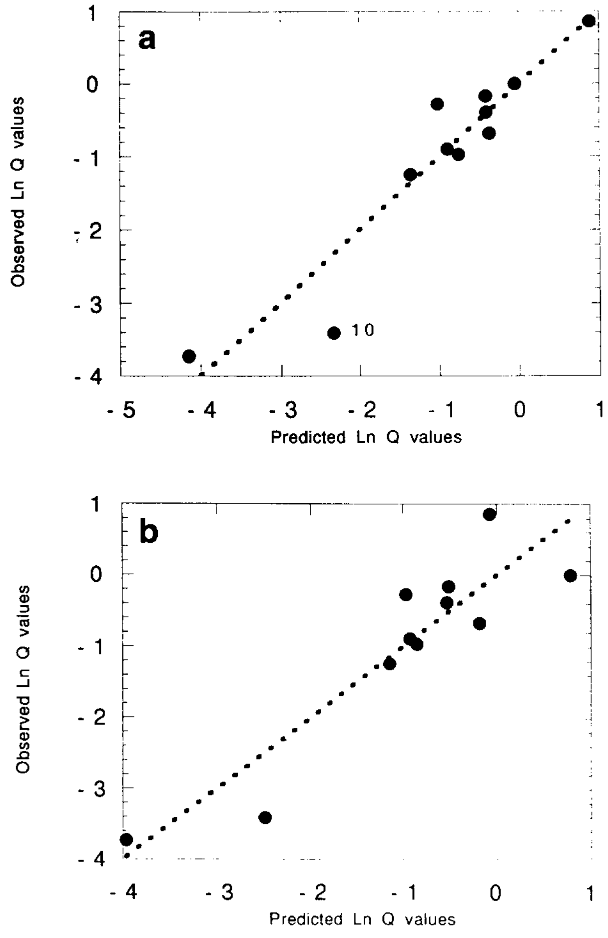

Figure 10 Plots of observed *versus* predicted ln Q values using a multiple regression fit to equation (15) with the Laurier experimental data set and data calculated from the SV Dunning basis set for (a) CH_3 addition and (b) H addition

Table 5 Revised Q values based on the reference values for styrene of $Q=1$ and $e=0$

Monomer	New ln Q
1. Styrene	1.0
2. Methyl acrylate	1.3
3. Acrylonitrile	2.5
4. Methyl methacrylate	1.96
5. Methacrylonitrile	2.78
6. Acrylic acid	3.70
7. Vinyl acetate	0.04
8. Vinylidene chloride	0.67
9. n-Butyl acrylate	1.82
10. Vinyl chloride	0.06
11. 1,3-Butadiene	1.75

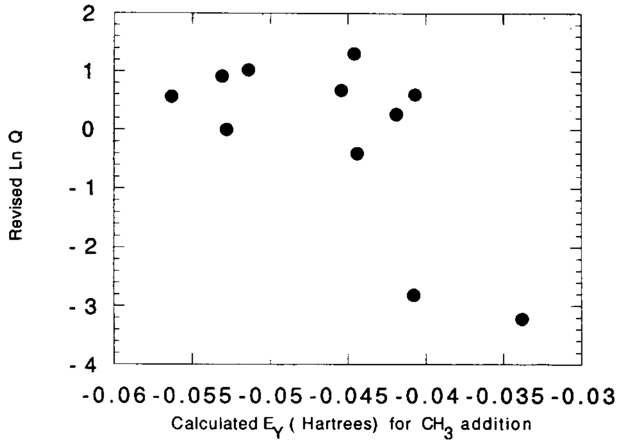

Figure 11 Plot of revised $\ln Q$ values *versus* E_Y (Hartrees) for CH_3 addition for the Laurier monomer set using the SV Dunning basis set for calculation

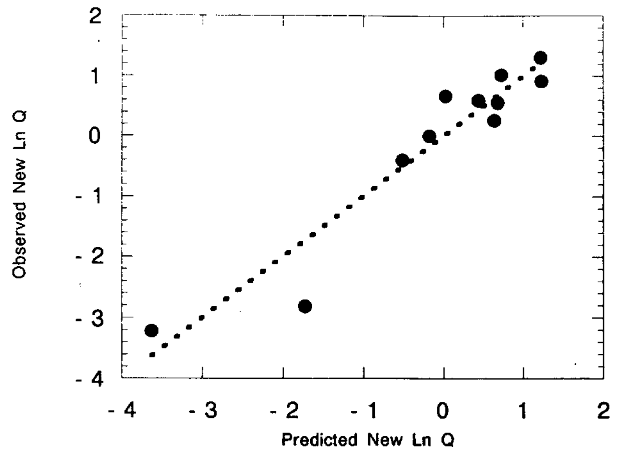

Figure 12 Plot of observed *versus* predicted revised ln Q values using a multiple regression fit to equation (15) with the Laurier experimental data set and data calculated from the SV Dunning basis set

Table 6 Comparison of models for fitting the Dunning CH_3 addition values and the revised Q values (equation (15))

			Coefficient of determination	
		Model	R^2	$R^2_{(adj)}$
Dunning	CH_3 addition	β_0, β_1 only	0.40	0.35
		β_0, β_1, β_2 only	0.79	0.74
		β_0, β_1, β_2, β_{12}	0.91	0.87

resulting graph in *Figure 11* shows a significant deterioration in any linear correlation (cf. *Figure 9b*). However, when we analysed for the influence of polar effects on the relationship, as we did before, we got a significant improvement on including both χ_m and $E_Y\chi_m$ factors. The coefficients of determination are given in *Table 6*. In fact, we get the best fit yet with these revised values in conjunction with the full equation (15). The plot of observed ln Q *versus* predicted ln Q is given in *Figure 12*.

CONCLUSIONS

The experimental e parameter can be directly correlated with the electronegativity of the monomer in most cases. The linear relationship between them can be considered to be predictive. No predictive relationship exists between Q and a general reactivity of the monomer, although a significant correlation exists. This work shows that the Q and e factors do not succeed in completely separating polar and general reactivity effects. The degree to which they are separated is dependent to some extent on the arbitrary choice of reference monomer. If this is taken into account then we can obtain an improved correlation between Q and computed parameters which includes contributions from the electronegativity of the monomer.

The use of flexible basis sets, e.g. TZV and SV Dunning, does improve the correlations as does the adoption of well-determined Q and e values. One of the major restrictions in this type of study is selecting good quality experimental data, and in this respect the Q and e values of Laurier *et al.*[16] have proved invaluable to our work.

One limiting factor in this work was the use of methyl and hydrogen addition to the monomer as a model propagation reaction. A better correlation for Q may well be obtained if a more realistic propagation reaction could be studied. Undoubtedly this will be possible in the near future as computer power continues to increase rapidly.

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