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Comparison of mechanistic models for correlation of activation energies of liquid-phase addition of carbon-centered radicals to terminal olefins[†]

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The performance of different models for the influence of enthalpy and polar effects on radical additions is compared for the extensive data set from the Fischer group, supplemented by additional data. The best correlations result from the Fischer–Radom (FR) model, but it also contains the largest number of adjustable radical-dependent parameters not based on physical observables. Updating the literature values of Δ_fH, IP, and EA that are inputs to the FR model led to some deterioration in the quality of the correlations; this is symptomatic of remaining deficiencies in the thermochemical databases. In contrast, the Lalevee–Allonas–Fouassier (LAF) model gives poorer correlation but this is in part compensated because it uses the same inputs but with no adjustable parameters. Hammett-type models based on polar and radical substituent constants rather than on molecular properties of the reactants perform even more poorly. In all cases, poorer correlation, as judged by increasing sd(ΔE), is accompanied by a systematic bias to over-predict the lower *E* values and under-predict the higher ones. The enthalpy contribution in the FR and LAF models is expressed as a linear Evans–Polanyi dependence of *E* on ΔH. Replacement by nonlinear Marcus dependences does not significantly improve performance. An attempt to significantly reduce the number of adjustable parameters in the FR model by anchoring them to a base set applicable to all radicals, which is then modulated for spin delocalization based on observable ESR hyperfine constants in the initial and adduct radicals, showed modest success.

Keywords: radical addition; mechanistic models; polar effects; enthalpy effects; thermochemical properties of radicals

INTRODUCTION

The addition of carbon-centered radicals to olefins is a common reaction step in organic synthesis, vinyl polymerization, and industrial processing, and there is obvious interest in understanding its structure-reactivity patterns in a quantitative fashion. It has been recognized since the earliest studies of radical polymerization that addition is enhanced not only by increasing reaction exothermicity (an 'enthalpy effect') but also by 'polar effects' that result from favorable charge transfer (CT) in the transition state. On the other hand, addition is decreased by steric effects, particularly from substituents at the olefinic terminus being attacked, consistent with computational evidence for an unsymmetrical approach of the radical to the double bond. A review and summary of regioselectivity and relative rate data led Tedder[1] to formulate of a set of 'rules,' of which the following are relevant to discussions herein: (a) the variation of Arrhenius *A* factors for polyatomic radicals is small and differences in reactivity are dominated by differences in the activation energies (*E*); (b) the unfavorable effect of steric compression causes addition to a terminal olefin (Eqn (1)) to occur largely at the unsubstituted

$$R^\bullet + CH_2 = CXY \rightarrow RCH_2CXY^\bullet \qquad (1)$$

terminus;[2] (c) the high exothermicity ($\Delta H \ll 0$) is associated with an early transition state and hence a muting of effects of the stability of the final adduct radical; and (d) polar effects can dramatically increase reactivity for nucleophilic radical-electrophilic olefin pairs and vice versa. In a parallel review, Giese[5] also formulated 'rules' concerning substituent effects: (a) substituents on the adduct radical center (X and Y) exert dominantly polar effects; (b) substituents on the olefinic carbon being attacked exert both polar and steric effects; and (c) substituents on the attacking radical also exert both polar and steric effects; in contrast, radical-stabilizing effects in cases (a) and

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[‡] *This paper is dedicated to the memory of Hanns Fischer and his numerous contributions to the quantification of free-radical chemistry.*

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(c) are more modest. While such 'rules' allow useful predictions of regioselectivity and of relative reactivity for a given radical reacting with a set of varied olefins or vice versa, they do not allow *a priori* quantitative predictions of *E* and rate constants (*k*).

The focus for the considerations herein is the recent comprehensive review and analysis by Fischer and Radom[6] (FR) that combined input from a particularly expansive kinetic data set from the Fischer group[7–23] and theoretical considerations from the Radom group.[24–26] Their proposed model (as described below) uses ΔH as the independent variable to quantify the enthalpy effect and IP and EA of the radical and olefin to quantify the polar effect, where ΔH, IP, and EA are the reaction enthalpy, the adiabatic ionization potentials, and the electron affinities, respectively.

There have often been differences of opinion in the literature whether to classify a given radical as nucleophilic (electron donating) or electrophilic (electron accepting). These are partly semantic because 'philicity' is not an absolute property of a radical but depends also on the 'philicity' of the olefin, that is, a radical may behave in a nucleophilic manner toward an olefin with strongly electron-accepting substituents but in an electrophilic manner toward an olefin with strongly electron-donating substituents. The use of the term 'ambiphilic' for such borderline cases[6] is therefore useful.

THE DATA SET

We restrict considerations herein to experimental data that give absolute *k* and/or *E* values for a given radical with a significant range of olefin structures.[27,28] The bulk of the data set consists of over 200 values of activation energies *E*(R,X,Y) determined by Fischer and coworkers[7–23] for most of the combinations involving 13 radicals with varying polarity and 20 terminal olefins with varying polarity. The radicals include methyl (Me), *t*-butyl (tBu), benzyl (Bn), hydroxymethyl (MOH), 2-hydroxy-2-propyl (POH), *t*-butoxycarbonylmethyl (MEst), 1-*t*-butoxycarbonylethyl (EEst), 2-*t*-butoxycarbonyl-2-propyl (PEst), cyanomethyl (MCN), 2-cyano-2-propyl (PCN), 2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-yl (cMal, the cyclic malonyl radical from Meldrum's acid), 3,3,3-trifluoroacetonyl (FAc), and, for a smaller range of olefins, cumyl (Cum). The olefins, labeled as 'X,Y' to indicate the substituents in Eqn (1), include H,H, H,Me, H,Et, Me,Me, H,Ph, Me,Ph, Ph,Ph, H,SiMe$_3$, H,C(=O)H, H,C(=O)OMe, Me,C(=O)OMe, H,CN, Me,CN, H,OEt, Me,OMe, H,OC(=O)Me, Me,OC(=O)Me, H,Cl, Me,Cl, and Cl,Cl. Values of *k* in solution near ambient temperature were obtained directly from kinetic ESR measurements; *k* was determined from the enhanced real-time decay of the radical in the presence of added olefin compared with its unperturbed second-order decay.[29]

Two approximations were made by FR[6] to obtain and model the *E* values. First, for the cases where temperature dependence was explicitly studied, small variations in the *A* factors for a given radical with a set of varied olefins were attributed to *A*–*E* compensation associated with experimental error. Therefore, based on entropy considerations and losses of internal rotations, a single *A* factor was assigned for each radical which generally decreased from *prim* ($\approx 10^{8.5}$ M^{-1} s^{-1}) to *tert* radicals ($\approx 10^{7.5}$ M^{-1} s^{-1}). This radical-specific *A* factor was then used to convert *k* values near ambient temperature to *E* values.[30,31] There are occasional modest differences between the *k* values in the original papers[7–23] and the final compilation;[6] we take the latter to be the definitive set. We then 're-calculated' the *E* values from the *A* value assigned to each radical and the temperature specified in the original paper. This process resulted in a few minor differences from the parallel *E* values presented in the compilation,[6] a few minor systematic offsets for certain radicals that suggest that a slightly different *A* value was used from that specified (particularly for MOH and cMal), and a few outliers with significant differences that probably resulted from typographical errors (and have been 'corrected'). These 're-calculated' *E* values are shown in Table 1 and are the dependent variables in all correlations considered below. Second, the kinetic data were obtained in (differing) solvents, whereas the ΔH, IP, and EA variables considered in the model are gas-phase values. Although specific solvent effects were typically small,[32] comparison of liquid-phase and gas-phase data suggested a systematic offset of $(E_{\text{liq}} - E_{\text{gas}}) \approx -1.5$ kcal mol^{-1}, without any obvious structural dependence.

We supplemented the FR data set with additional sources that report absolute *k* values for selected radicals with a fairly wide range of olefins in the liquid phase and for which values of the correlating variables are available.[33] Studies by Giese and coworkers[5] on cyclohexyl radical (cHx) played an important role in highlighting the polar effect. Radicals are generated by reaction of alkylmercuric salts (RHgX) with sodium borohydride through the intermediacy of an alkylmercuric hydride (RHgH). In the presence of an olefin at ambient temperature, formal addition of R—H occurs, most efficiently for a nucleophilic R with an electrophilic olefin.[34] We converted relative *k* values for several olefins at 20 °C[5] to absolute *k* values by anchoring them to $k = 10^{8.3}\exp(-2440/RT)$ M^{-1} s^{-1} for H,CO$_2$Me,[35] this value in turn having been anchored to known rate constants for combination with a persistent nitroxide. We then made a small adjustment to $A = 10^{8.5}$ M^{-1} s^{-1}, the value used by FR[6] for the *sec* radical cMal, to obtain the *E* values in Table 1.[36] This data set includes an additional olefin, H,C(=O)Me.

Relative rate constants for addition of 5-hexen-1-yl radical (Hx), also expected to be nucleophilic and considered herein as identical to a *n*-hexyl radical for the addition process in which the double bond should be a spectator group, were determined[37] at 69 °C in competition with its cyclization, for which *k* is known. We adjusted the reported *k* values upward by a factor of 2.1 based on a re-evaluation of *k* for cyclization[38,39] and converted them to the *E* values in Table 1 by use of $A = 10^{8.5}$ M^{-1} s^{-1} as recommended by FR[6] for *prim* radicals.[40]

Rate constants for the highly electrophilic CF$_3^{\bullet}$ (FMe) and CF$_3$CF$_2$CF$_2^{\bullet}$ (FPr) radicals, which also provide the most exothermic additions, were determined by real-time optical detection of radical adduct formation after pulsed-laser generation of FMe or FPr.[41,42] They were converted to the *E* values in Table 1 by the use of $A = 10^{8.2}$ M^{-1} s^{-1} as recommended by FR.[6]

THE CORRELATING VARIABLES

Addressing the 'enthalpy effect' requires values of ΔH(R,X,Y),[44] defined in terms of enthalpies of formation in Eqn (2), for the 247 individual reactions:

$$\Delta H(\text{R},\text{X},\text{Y}) = \Delta_f H(\text{RCH}_2\text{CXY}^{\bullet}) - \Delta_f H(\text{R}^{\bullet}) - \Delta_f H(\text{CH}_2 = \text{CXY}) \quad (2)$$

Table 1. E(R,X,Y) values (kcal mol^{-1}) for liquid-phase addition of radicals to terminal olefins[a]

Olefin[b]/radical	Me	Bn	tBu	POH	MOH	PEst	MEst	PCN	MCN	cMal	FAc	EEst	Cum	cHx[c]	Hx[d]	FMe/FPr[e]
H,H	6.74		6.04		7.62		6.04		6.34		5.69					
H,Me	6.61		6.23		7.87		4.91		5.62	4.46	4.36					
H,Et	6.28	9.46	6.12		7.80		5.10	8.60	5.67	4.31	4.14	7.06		7.11[f]		1.92[fg]
Me,Me	6.21		6.36		7.94		4.40		5.67	3.98	2.57	6.69				
H,Ph	4.19	7.39	3.28	2.22	5.23	5.06	3.01	5.94	3.71	3.30	2.30	3.96	5.98	3.84	4.70	0.65[h],0.77[g]
Me,Ph	4.09	7.55	3.75	2.98	5.12	5.00	2.59	5.96	3.41	3.25	2.19	3.77	5.28	3.87	5.05	0.36[h],0.42[g]
Ph,Ph	3.54	6.62	2.06	2.23	4.16	4.71	2.03	5.27	2.70	2.89	2.25	3.40		3.11		
H,SiMe$_3$	5.61	9.46	4.83	4.20	6.66	7.57	4.81	8.11	5.58	4.31	4.30	6.34				
H,CHO	3.58	6.91	1.45	0.0[i]	2.56	5.71	3.96	6.37	5.22	4.72	5.00	4.40		1.75		
H,CO$_2$Me	4.03	7.95	2.00	0.0[i]	3.20	5.97	3.81	7.11	4.40	4.72	4.59	5.03	6.21	2.71	3.85	
	4.0[j]		1.3[j]	0.4[k]								4.4[j]				
Me,CO$_2$Me	3.82	7.01	2.31	0.40	3.30	5.29	3.23	6.20	3.97	3.35	3.28	4.21	5.50	2.88		1.26[g]
				1.0[k]												
H,CN	3.69	6.99	1.08	0.0[i]	2.94	5.49	3.75	6.05	4.40	4.53	5.36	4.45	5.62	1.95	3.33	2.12[h],2.53[g]
Me,CN	3.54	6.34	1.74	0.0[i]	3.24	5.18	3.44	6.45	4.16	3.71	4.36	4.14		2.30		
H,OEt	5.92	9.96	6.74	6.77	8.11	7.57	4.50	7.88	4.92	4.12		6.27				
Me,OMe	6.01	9.72	7.08	6.05	7.96	7.80	4.54	8.05	5.03	3.95		6.41				
H,OAc	5.92	9.92	5.32	4.91	7.40	8.40	4.99	8.49	5.58	3.95	4.33	6.40		6.28		
Me,OAc	6.01	9.26	5.86	5.17	7.32	7.72	4.82	8.08	4.81	3.73	3.70	6.56				
H,Cl	5.71		4.52		6.14		4.94		5.62	4.72	4.77	6.38		5.09		
Me,Cl	5.38	9.30	4.75	4.28	6.65	7.16	4.46	7.81	5.46	3.46	3.79	5.76				
Cl,Cl	4.07	7.91	2.69	1.88	4.74	5.96	4.16	6.80	5.07	3.97	4.04	5.21				2.02[g]
H,COMe														2.32	3.50	

[a] Values for radicals with no further notation are from the FR review (Reference [6]) except for those for EEst from Reference [23]; *E* values were 're-calculated' as indicated in the text; three significant figures were retained in the correlations to avoid rounding errors, although the last digit is unlikely to be significant in any particular case.

[b] $CH_2{=}CXY$ is designated as 'X,Y.'

[c] Reference [5].

[d] References [37] and [40].

[e] References [41,42].

[f] Value for 1-hexene.

[g] FPr.

[h] FMe.

[i] $k_{exp} > A_{assigned}$; E was set at 0.0.

[j] Values are from an alternate kinetic method (Reference [35]) for Me, *t*-pentyl (as an analog for tBu), and 1-(methoxycarbonyl)-1-heptyl (as an analog for EEst), adjusted to *A* values assumed by FR.

[k] Values are from an alternate kinetic method (Reference [43]), adjusted to *A* values assumed by FR.

Table 2. Estimated ΔH(Me,X,Y) values (kcal mol^{-1})

X,Y	$\Delta_f H$ ($MeCH_2CXYH$)	Source[ab]	$\Delta_f H$ ($CH_2{=}CXY$)	Source[a]	D ($MeCH_2CXY$–H)	Source[cd]	ΔH (Me,X,Y)[e]	Δ [ΔH(Me,X,Y)][f]
H,H	−24.9	A–F	12.5	A–F	100.9		−23.7	0.0
H,Me	−30.2	A–F	4.8	A–F	98.3		−23.9	−0.7
H,Et	−35.1	A–F	−0.1	A–F	98.3	[g]	−23.8	−0.2
Me,Me	−36.8	A–F	−4.1	A–F	95.8		−24.0	−0.6
H,Ph	1.9	A–F	35.3	A–F	87.1	[h]	−33.5	2.3
Me,Ph	−4.2	A–F	27.5	B, C, F[i]	86.2	[j]	−32.6	1.8
Ph,Ph	28.4 (22.4)	G[k]	58.8	C–F	82.5	[l]	−35.0	1.5
H,$SiMe_3$	−67.4 (−79.3)	G[m]	−29.2	[n]	97.5	J[o]	−27.8	−3.7
H,CHO	−49.3	A–F	−18.1	C, E, F	91.9	J[p]	−26.4	2.7
H,CO_2Me	−109.4 (−108.0)	G[q]	−74.9 (−79.6)	C, E, F[r]	94.6	[s]	−27.1	0.9
Me,CO_2Me	−117.7 (−114.7)	B, D, E[t]	−83.1 (−79.1)	C, E, F[r]	92.6		−29.2	−0.8
H,CN	7.7	A–D, F[u]	43.6	A–D, F	92.4	[v]	−30.7	2.5
Me,CN	1.2	H[w]	31.0	C, F	90.4	[vx]	−26.6	4.5
H,OEt	−65.1	A–F	−33.7	A–F	92.5		−26.0	−2.1
Me,OMe	−64.3	H[y]	−35.3	B, C, E, F	90.5	[z]	−25.6	−3.2
H,OAc	−111.2 (−108.7)	I[aabb]	−75.3	A–F	94.0	[cc]	−29.1	−4.9
Me,OAc	−120.0	C, E, F	−83.4	C	93.3	[dd]	−30.5	−4.4
H,Cl	−31.5	A–D, F	5.2 (8.7)	[eeff]	97.2		−26.6	−1.3
Me,Cl	−38.8	A–D, F	−5.5	A, B[ff]	95.2	K[gg]	−25.3	−1.6
Cl,Cl	−35.7	I[hh]	0.6	A–D, F	94.3	[ii]	−29.2	0.7
H,COMe	−61.9	A–F	−33.0	C, E, F	92.3	[jj]	−23.8	

[a] Average value from data compilations listed, unless noted otherwise. A: Reference [49]; B: Reference [50]; C: Reference [51] (used most heavily by FR); D: Reference [52]; E: Reference [53]; and F: literature values cited in Reference [54]. Of course, there is considerable duplication of original sources cited in these compilations.

[b] Average value from estimation methods. Method G: extrapolate from the value for the homolog with two less carbons based on $[\Delta_f H(MeCH_2CH_2Y) - \Delta_f H(MeY)]_{av} = -11.0$ for X = Me, Ph, CH_2OH, CHO, CO_2H, NH_2, OMe, OH, and Cl (from sources A and B). Method H: interpolate between the values for *n*-BuY and *t*-BuY based on values for Y = Me, Ph, NH_2, OH, Cl, and Br (from sources A and B); the value for the *s*-BuY isomer lies 43% of the way on average from *n*-BuY to *t*-BuY. Method I: extrapolate from the value for the homolog with one less carbon based on $[\Delta_f H(MeCH_2CH_2Y) - \Delta_f H(MeCH_2Y)]_{av} = -5.0$ for X = Me, Ph, CH_2OH, CHO, CO_2H, NH_2, OMe, OH, and Cl (from sources A and B).

[c] Recommended values from Reference [47], unless indicated otherwise; the value may be for a lower homolog MeCXY–H rather than $MeCH_2CXY$–H.

[d] Method J: extrapolate from *prim* to *sec* radical based on $[D(ZCH_2{-}H) - D(ZCHR{-}H)]_{av} = 2.4$ for Z = R, Vi, F, Cl, HO, RO, HC(=O), MeC(=O), ROC(=O), RC(=O)O, H_2N, O_2N, and RS. Method K: extrapolate from *sec* to *tert* radical based on $[D(ZCHR{-}H) - D(ZCR_2{-}H)]_{av} = 2.0$ for Z = R, Vi, HO, RO, MeC(=O), ROC(=O), RC(=O)O, H_2N, and O_2N.

[e] From Eqn (3) with $\Delta_f H(MeH) = -17.8$ and D(Me–H) = 105.0.

[f] Difference between ΔH(Me,X,Y) estimated here and that used in the FR review (Reference [6]).

[g] Assumed to be the same as H,Me.

[h] The value for PhCH(Me)–H is based on the value for $PhCH_2$–H (Table 3) and the resonance stabilization increment (Δ(RSE)) from Reference [55].

[i] The average also includes the value from Reference [56].

[j] The value for $PhC(Me)_2$–H is based on the value for $PhCH_2$–H (Table 3) and the Δ(RSE) from Reference [55].

[k] Variations exist in the value for Ph_2CH_2 needed to apply Method G; the value shown used that from Reference [57,58]; the value in parentheses used that from source A.

[l] The average of (a) 82.2 from ΔRSE = 4 compared with cumene (Reference [59]) and (b) 82.8 (Reference [60]).

[m] Variations exist in the value for Me_4Si needed to apply Method G; the value shown uses the average from sources A and C; the value in parentheses uses that from source B.

[n] The average of estimates from sources C and F; no experimental data are available.

Continues

Table 2. (Continued)

[o] Method J applied to the recommended value for $(Me)_3SiCH_2$–H.

[p] Method J applied to the recommended value for H–CH_2CHO (94.3); the latter is based on an EA(R) from References [61,62]; a slightly lower recent EA measurement (Reference [63]) would decrease the value by 0.7. The recommended value for $CH_3CH(–H)CH{=}O$ itself is essentially identical (91.7) but suffers from ambiguities concerning geometrical isomers of the enolate anion and the radical involved in $\Delta_{acid}H$(R–H) and EA(R) measurements as discussed in Reference [64].

[q] Variations exist in the value for $MeCO_2Me$ needed to apply Method G; the value shown uses the average from sources A, B, and E; the value in parentheses uses the average of estimates from sources C and F.

[r] The values shown give $[\Delta_f H(CH_2{=}C(CH_3)CO_2Me) - \Delta_f H(CH_2{=}CHCO_2Me)] = -8.2$; this difference is consistent with that for other such structurally related pairs; the values in parentheses from sources A and/or B lead to an unreasonably small difference of 0.5.

[s] The value is placed between the recommended values of 97.1 for the *prim* H–CH_2CO_2Me and 92.6 for the *tert* H–$C(Me)_2CO_2Et$ (as in Table 3) according to Methods J and K; the value recommended for H–$CHMeCO_2Et$ itself is 95.6.

[t] The value in parentheses is from Method H applied to sources A and C.

[u] The average also includes the value from Reference [74].

[v] We anchored the D scale for nitriles to 94.8 for MCN (as in Table 3) and applied Methods J and K. Reported values for H–CHMeCN itself range widely from 94.9 (Reference [60]) to 89.9 (Reference [75]).

[w] Method H applied to sources A and B; Reference [74] gives 0.6.

[x] Reported values for H–$C(Me)_2CN$ itself range widely from 91.9 (Reference [60]) to 86.5 (Reference [75]).

[y] The value shown is the average from Method H applied to sources A–C and E; method I applied to the value for *i*-PrOMe from source D gives −65.2.

[z] Method *K* applied to H,OEt case; compiled values for *i*-$PrOCMe_2$–H average 93.6, with no recommendation.

[aa] The value shown is the average from Method I applied to sources A, B, D, and E.

[bb] The value in parentheses is the average of estimates from sources C and F.

[cc] The average for ethyl butanoate and pentanoate rather than *n*-propyl acetate; method J applied to the value for $MeCO_2CH_2$–H gave 94.3.

[dd] The average for *i*-propyl acetate and pentanoate rather than *s*-butyl acetate.

[ee] Two ranges of values are reported (as in source B); that shown is the average of the 'low' values from sources B, C, and F (*cf.* Reference [76]); the value in parentheses is the average of the 'high' values from sources A–D.

[ff] The values shown give $[\Delta_f H(CH_2{=}C(CH_3)Cl) - \Delta_f H(CH_2{=}CHCl)] = -10.7$; the alternate value for $CH_2{=}CHCl$ gives −14.2, an unreasonably large difference; *cf.* footnote r.

[gg] Method K applied to the H,Cl case.

[hh] The value shown is the average from Method I applied to sources A–D.

[ii] The average of values for CH_3CCl_2–H, 93.4 (Reference [77]) and 95.1 (Reference [78]).

[jj] The value for MeC(=O)CHMe–H; a slightly higher value of 93.2 was reported based on $\Delta_{acid}H$(R–H) of this ketone (Reference [65]) and the EA(R) of its radical (Reference [66]); a recent computational re-evaluation of α-carbonyl radicals (Reference [79]) recommends a much lower value of 90.3, but the 5.5 difference from the analogously recommended value for acetone seems unreasonably large (*cf.* Method J).

We follow the FR protocol[6] of approximating ΔH(R,X,Y) as the sum of (a) ΔH(Me,X,Y) for the addition of the prototypical methyl radical to each olefin, which highlights the effects of substituents X and Y on the stabilities of the olefin and the adduct radical, and (b) a differential term $\delta[\Delta H(\mathrm{R})] = [\Delta H(\mathrm{R,H,H}) - \Delta H(\mathrm{Me,H,H})]$ for addition of each radical to the prototypical olefin ethylene, which highlights the effects of the stability of the attacking radical and the strength of the newly formed bond.[45] To avoid the direct use of $\Delta_f H$ values for radicals, which are only sparsely tabulated, the expressions for ΔH were transformed[6] into ones that contains only $\Delta_f H$ and bond dissociation enthalpies, D(C—H), for stable molecules.[46] The ΔH(Me,X,Y) term was thus expressed as Eqn (3) and the $\delta[\Delta H$(R)] term as Eqn (4):

$$\Delta H(\mathrm{Me,X,Y}) = \Delta_f H(\mathrm{MeCH_2CXYH}) - \Delta_f H(\mathrm{CH_2=CXY}) - \Delta_f H(\mathrm{MeH}) + \mathrm{D(MeCH_2CXY-H)} - \mathrm{D(Me-H)} \quad (3)$$

$$\delta[\Delta H(\mathrm{R})] = \Delta_f H(\mathrm{RCH_2CH_3}) - \Delta_f H(\mathrm{RH}) - \mathrm{D(R-H)} - \Delta_f H(\mathrm{MeCH_2CH_3}) + \Delta_f H(\mathrm{MeH}) + \mathrm{D(Me-H)} \quad (4)$$

However, there are still significant uncertainties in the required thermochemical database, especially for D(C—H) values, and FR[6] recognized the imprecision inherent in many of the ΔH(Me,X,Y) and $\delta[\Delta H$(R)] assignments.

We have re-evaluated ΔH(Me,X,Y) based on more recent data compilations and sources for the three variable terms in Eqn (3), as shown in Table 2; data gaps and inconsistencies are indicated in the footnotes. Zytowski and Fischer[20] provided their estimates of these three terms and the derived values of ΔH(Me,X,Y). However, the final values used by FR[6] involve a number of adjustments whose source was not indicated. Hence, the specific terms that lead to some troublesome differences between our estimates and those of FR cannot be pinpointed. For cases where the $\Delta_f H$(MeCH$_2$CXYH) term is unavailable, we made 'group additivity' estimates by extrapolation from homologs with one or two fewer methylene groups or, for *s*-BuY cases (X = Me), by interpolation between reported values for the *n*-BuY and *t*-BuY isomers. Significant discrepancies exist for Ph,Ph and H,SiMe$_3$ with lesser ones for Me,CO$_2$Me and H,OAc; the bases for our choices are given in the footnotes. For the $\Delta_f H$(CH$_2$=CXY) term, significant literature discrepancies exist for H,Cl and for the H,CO$_2$Me and Me,CO$_2$Me pair; consistency in the incremental effect of changing X from H to Me was the basis for our choices. For the D(MeCH$_2$CXY—H) term, we gave preference to recommendations in the recent compilation of Luo.[47] Several values are for lower homologs that retain the identical substitution pattern at the radical center. For others for which the closest analog with a recommended D(C—H) value has a lower degree of alkylation at the radical center, we made adjustments with the use of average increments between *prim*, *sec*, and *tert* radical centers, based on several examples of D(C—H) values for ZCH$_2$—H, ZCHR—H, and ZCR$_2$—H series. Our estimated values of ΔH(Me,X,Y) are given in the next to last column of Table 2, and the differences from the FR values[6] are given in the last column. These differences, both positive and negative, illustrate the ambiguities in the experimental thermochemical database.[48] We estimate that additions to the cyano-, phenyl-, and formyl-substituted olefins are less exothermic than FR did, while the reverse is true for the acetoxy-, alkoxy-, and trimethylsilyl-substituted olefins.

We have also re-evaluated $\delta[\Delta H$(R)] as shown in Table 3. Our values tend to be systematically lower than those of FR,[6] that is, they generally suggest a lesser reduction in exothermicity of addition for R compared with Me. This is particularly true for EEst, which however seems out of line with the values for MEst and PEst; the difference for FAc is probably not real because the data plots in the FR review[6] suggest that their tabulated value is a typographical error (as in footnote u in Table 3). Note that $\delta[\Delta H$(FMe)] = −11.2 kcal mol^{-1} is the only negative value for this parameter and reflects the particularly strong CF$_3$—CH$_2$CHXY bond; for example, the C—C bond in CF$_3$CH$_3$ is known to be ≈12 kcal mol^{-1} stronger than that in CH$_3$CH$_3$.[80]

Some of the experimental D(R—H) values in Tables 2 and 3 are related to EA(R) (as described in Table 5) via the identity: $\mathrm{D(R-H)} \equiv \Delta_{\mathrm{acid}}H(\mathrm{R-H}) + EA(\mathrm{R}) - \mathrm{IP(H)}$, that is, the derivation of one or the other was based on $\Delta_{\mathrm{acid}}H$(R—H), the enthalpy for acid dissociation. We have attempted to maintain internal consistency for these values.

FR[6] compiled IP and EA values for the radicals and olefins that were, because of gaps in the database, a mixture of experimental values, both from the literature and obtained by the Fischer group, and computational values (for the radicals). We have updated this list for the olefins in Table 4. For IP(Olefin), FR relied heavily on the Lias compilation;[51] we considered others as well, especially the NIST Webbook.[50] Except for rounding errors, our values coincide with those of FR except for Me,CO$_2$Me (as in footnote f of Table 4) and H,OEt.[97] For EA(Olefin), FR used literature sources or new measurements by the Fischer group and/or collaborators. We have retained these values, except for a small upgrade to that for H,H (as in footnotes c and d in Table 4). Note that, except for Ph,Ph and H,CHO, all olefin EA values are negative, that is, the radical anion is not a bound state.

IP data for radicals are more scarce than for olefins, and FR[6] used a mixture of experimental and computational values. Our updated values in Table 5 differ only in rounding errors except for POH (as in footnote d) and Hx. Our value for PCN is in accord with that in the original Fischer source,[11] although a higher value was used in the FR review.[6] In some cases, only the FR values, computed (PEst, EEst, MEst, and FAc) or estimated (cMal), were available. EA data for radicals are still more scarce, and the FR choices[6] are again a mixture of experimental, computational, and estimated values. Our updated values are in Table 5. The FR values were used for POH, PEst, EEst, and cMal, while the sources of the others are indicated. Significant differences (as in footnotes of Table 5) occur (a) for tBu and PCN, for which reported experimental values were derived from [D(R—H) − $\Delta_{\mathrm{acid}}H$(R—H)] and we adjusted these to be internally consistent with the D(R—H) values in Tables 2 and 3; (b) for MOH, for which the source of the FR value is ambiguous; and (c) for FMe. We note with some concern the lack of consistency for the difference [EA(RCH$_2^\bullet$) − EA(RCMe$_2^\bullet$)]: −10.1 for R = OH, −2.5 for R = Me, +2.7 for R = CN, and +7.8 for R = CO$_2$R.

MECHANISTIC AND CORRELATING MODELS

If we accept the prevailing qualitative wisdom of a role for both enthalpy and polar effects, the issue becomes how to quantitatively describe them and relate their combined effect to independent variables in useful predictive models. We only consider models for which the independent variables are experimentally accessible (except for a few entries in Tables 4

Table 3. Estimated $\delta[\Delta H(\mathrm{R})]$ values (kcal mol^{-1})

R	$\Delta_f H(\mathrm{RCH_2CH_3})$	Source[a]	$\Delta_f H(\mathrm{RH})$	Source[a]	D(R–H)	Source[a]	$\delta[\Delta H(\mathrm{R})]$[b]	$\Delta\{\delta[\Delta H(\mathrm{R})]\}$[c]
Me	−24.9	[d]	−17.8	A–F	105.0	[e]	0.0	0.0
Bn	1.9	[d]	12.0	A–F	89.8	[e]	12.2	−1.2
tBu	−44.2	A–F	−32.2	A–F	95.7		4.4	0.6
POH	−79.0	A, C–F	−65.1	A–F	91.7	[f]	6.5	2.2
MOH	−61.0	A–F	−48.1	A–F	96.1	[e]	3.1	−0.2
PEst[g]	−122.6 (−127.8)	I[h]	−109.0	C, E, F	92.6	[i]	5.9	−1.7
EEst[g]	−117.7 (−114.7)	[d]	−103.4	I[j]	94.6	[k]	3.2	−5.7
MEst[g]	−109.4 (−108.0)	[d]	−98.2	A–C, E, F	97.1	[l]	3.9	−2.3
PCN	−5.6	I[m]	5.8	A–D, F	90.4	[n]	10.2	−2.9
MCN	7.7	[d]	17.7(15.7)	A–C[o]	94.8	[p]	7.3	0.1
cMal	−210.3	[q]	−200.8	[q]	92.5	[q]	10.0	0.0[q]
FAc	−205.0	G[r]	−194.0	[s]	97.2	[t]	3.9	−5.6[u]
Cum	−9.7	A, B, D, E[v]	1.0	A–F	86.2	[w]	15.3	−1.9
cHx	−41.1	A–F	−29.5	A–F	97.5	[x]	3.0	
Hx[y]	−49.8	A–F	−39.9	A–F	100.7	[z]	1.5	0.3
FMe/FPr[aa]	−183.1	[bb]	−166.2	A–D, F	106.4	[cc]	−11.2	−1.6

[a] For identification of data sources and Methods, as in Table 2.

[b] From Eqn (4) with $\Delta_f H(\mathrm{MeCH_2CH_3}) = -24.9$, $\Delta_f H(\mathrm{MeH}) = -17.8$ and $\mathrm{D(Me{-}H)} = 105.0$.

[c] Difference between $\delta[\Delta H(\mathrm{R})]$ estimated here and that used by FR (Reference [6]).

[d] As in Table 2.

[e] Reference [81].

[f] Reference [82].

[g] For the Me rather than the *t*-Bu ester.

[h] The value is the average from Method I applied to sources A–C and E–F; the value in parentheses is based on variant values in sources B and D.

[i] For the Et rather than the *t*-Bu ester.

[j] The value is the average from Method I applied to sources A, B, and E.

[k] As in footnote s in Table 2.

[l] *Cf.* Reference [83].

[m] The value is the average from Method I applied to sources A and B.

[n] As in footnote v in Table 2.

[o] The value in parentheses is a variant value from source B; *cf.* Reference [84].

[p] References [84] and [85,86].

[q] The values are from the calorimetric data and the recommended D(R–H) in Reference [21].

[r] The value is the average from Method G applied to sources C and F.

[s] Estimates from sources C and F; no experimental data are available.

[t] The value derived from $\Delta_{\mathrm{acid}}H(\mathrm{RH})$ in Reference [65] was adjusted to the more recent value of EA(R) in Reference [87].

[u] Consideration of Fig. 12 in the FR review (Reference [6]) suggests that the value of $\delta[\Delta H(\mathrm{R})] = 9.6$ given in their Table 2 is a misprint and should be nearer 5.

[v] The value for $\mathrm{PhC(CH_3)_3}$ adjusted for the difference between the values for $\mathrm{(CH_3)_3CH_2CH_3}$ and $\mathrm{(CH_3)_3CCH_3}$.

[w] As in footnote j in Table 2.

[x] Two recent reports by the same group gave 97 (Reference [88]) and 98 (Reference [89]). A value of 95.5 in an earlier summary for a series of alkyl radicals (References [90,91]) becomes 97.6 if adjusted to current values for acyclic *sec* and *tert* radicals.

[y] 1-Hexyl as a surrogate for 5-hexen-1-yl.

[z] The value is for $\mathrm{CH_3CH_2CH_2CH_2{-}H}$.

[aa] The values are for FMe; given the absence of data relevant to FPr, the same final value of $\delta[\Delta H(\mathrm{R})]$ was assumed.

[bb] No values are reported for $\mathrm{CF_3CH_2CH_3}$. Group additivity procedures (Reference [54]) seriously underpredict the stability of $\mathrm{CF_3CH_3}$, giving −168.2 rather than the experimental value of −178.2 (Reference [92]), presumably because they do not account for the electrostatic stabilization of unsymmetrical fluorinated paraffins (Reference [93]). The value shown is a group additivity estimate, offset by the same increment. Recent computational values include −183.1 (Reference [94]) and −187.9 (Reference [95]).

[cc] *Cf.* Reference [96].

Table 4. Selected IP and EA values for olefins (kcal mol^{-1})

X,Y	IP($CH_2{=}CXY$)	Source[a]	EA($CH_2{=}CXY$)	Source[b]
H,H	242	A–C, F	−39.9	cd
H,Me	224	A–C, F	−45.9	c
H,Et	220	A–C, F	−43.8	e
Me,Me	213	A–C, F	−50.5	c
H,Ph	195	A–C, F	−5.8	c
Me,Ph	190	B–C, F	−5.3	
Ph,Ph	185	B–C, F	8.3	
H,$SiMe_3$	219	B–C, F	−26.5	e
H,CHO	233	A–C, F	0.7	
H,CO_2Me	228	A–C, F	−11.3	
Me,CO_2Me	224	A–C, F[f]	−8.8	
H,CN	252	A–C, F	−4.8	c
Me,CN	238	A–C, F	−3.9	
H,OEt	207	A–C[g]	−51.7	
Me,OMe	199	B, C, F	−57.2	
H,OAc	212	A–C, F	−27.4	
Me,OAc	210	C	−34.8	
H,Cl	230	A–C, F	−29.5	d
Me,Cl	225	h	−33.2	
Cl,Cl	226	A–C, F	−17.5	
H,COMe	221	ij	≈0	k

[a] For identification of data sources, as in Table 2.

[b] Unless noted otherwise, the values are those used by the Fischer group and obtained by them and/or collaborators, presumably by the method of Reference [98].

[c] Reference [99].

[d] Reference [100].

[e] Reference [101].

[f] Identical to the value used in the original Fischer publications (References [11] and [13–16]); the value of 219 in the FR review (Reference [6]) may involve a typographical error.

[g] Reference [102] FR (Reference [6]) used 203.

[h] Reference [103].

[i] Reference [104].

[j] Reference [105].

[k] A recent computation (Reference [106]) gave −3.0; the failure to observe a low-energy band in the electron transmission spectrum (Reference [105]) suggests a slightly positive value.

and 5) and do not address those that rely on computationally derived variables.[3,4,121,126]

All correlations below will address the E values for the full (expanded beyond FR[6]) 16-radical, 21-olefin, 247-reaction data set in Table 1 with the updated thermochemical quantitites in Tables 2–5, unless where exceptions are specifically noted. As measures of the quality of correlation, we will use r^2, the coefficient of determination, of the $E_{predict}$ *versus* E plot; sd(ΔE), the standard deviation of $\Delta E = (E_{predict} - E)$; and the coefficients of the $E_{predict}$ *versus* E plot. Several of these are collected in Table 6. As a baseline, note that the total range of E values in Table 1 is only 10 kcal mol^{-1} and sd(E) is only 2.02 kcal mol^{-1} for the entire data set. While plots of $E_{predict}$ *versus* E should ideally have a zero intercept and unit slope, we will see in Table 6 a consistent trend toward positive intercepts and slopes less than unity, that is, a tendency for the models to over-predict the lower E values and under-predict the higher ones; the extreme 'non-correlation' occurs of course for: $E_{predict} = E_{average} = 4.88 + 0(E)$ with sd(ΔE) = 2.02 kcal mol^{-1}.

Hammett-type correlations

Hammett-type sigma constants of substituents X and Y have commonly been used as correlating variables for constant radical-varying olefin data sets, especially to explore polar effects. The example most relevant to our data set is that of Heberger, Lopata, and Jaszberenyi (HLJ)[127] who used several subsets of the Fischer data. These used the format $\log k = (\rho_{polar}\sigma_{para}) + (\rho_{enthalpy}\sigma^{\bullet}) + \log k^0$, where the classical Hammett σ_{para} was chosen to capture polar effects,[128] $\sigma^{\bullet}$ was chosen to capture enthalpy effects where it is *either* the radical stability constant of Creary *et al.*[129–131] or Arnold, Dust, and Wayner (ADW),[132,134] and k^0 should ideally equal k for the unsubstituted H,H olefin (all $\sigma = 0$), which was not included in the data sets.[135]

Table 5. Selected IP and EA values for radicals (kcal mol^{-1})

R	IP(R)	Source[a]	EA(R)	Source[a]
Me	227	A–C, F	1.8	A, B
Bn	167	B, C, F	21.0	A–C
tBu	155	B, C, F[b]	−3.5	B[c]
POH	146	[d]	6.9	[e]
MOH	174	B, C, F[f]	−3.2	[g]
PEst[h]	178	[i]	30.9	[i]
EEst[h]	189	[i]	33.2	[i]
MEst[h]	226	[i]	38.7	[j]
PCN	196	[k]	32.8	B, C[l]
MCN	237	[m]	35.5	A–C
cMal	254	[n]	>41.5	[o]
FAc	251	[i]	60.6	A[p]
Cum	152	B, C, F	20.8	B
cHx	165	[q]	−7.2	[r]
Hx[s]	183	B, C, F[t]	−1.3	[u]
FMe/FPr[v]	209	[w]	42.0	[x]

[a] For identification of data sources, as in Table 2.

[b] Reference [107].

[c] The value is based on $\Delta_{acid}H$(R–H) from Reference [108] and D(R–H) used above; FR used 0.

[d] Based on the difference in $\Delta_f H$ values for the radical (as in D(Me_2COH–H) above) and cation (Reference [109]); the larger FR value (149.4) was taken from Reference [110] which apparently used a smaller D(R–H) value derived from early group additivity estimates.

[e] Value in the FR review (Reference [6]); the original source was not found.

[f] Reference [81].

[g] Computational value from Reference [25]; for Me and MCN, the computed values were within 0.9 of the experimental values; *cf.* Reference [111]; Fischer used −3.2 in Reference [13] but +2.3 in the FR review (Reference [6]) without specifying the source.

[h] For the Me rather than the *t*-Bu ester.

[i] Computational value provided by FR (Reference [6]); no experimental data are available.

[j] Reference [83]; FR (Reference [6]) used a computed value of 39.2.

[k] Reference [112].

[l] Compiled value of 24.9 was based on D(R–H) = 82.5; adjustment to D(R–H) used above adds 7.9.

[m] References [84] and [113,114].

[n] Approximation provided in Reference [21] for open-chain malonate.

[o] Estimated to be greater than value for MEst in Reference [21].

[p] Reference [69]; also used by FR (Reference [6]); a computed value in Reference [22] is troublesomely larger (73.3).

[q] Reference [115]; a higher value in source B was from an earlier measurement in Reference [116].

[r] Based on $\Delta_{acid}H$(R–H) from Reference [117] and D(R–H) used above; a larger computational value of +3.0 was reported in Reference [118].

[s] 1-Hexyl was used as a surrogate for 5-hexen-1-yl.

[t] FR (Reference [6]) used a larger value of 196.0.

[u] The value is based on $\Delta_{acid}H = 415.6$ for $CH_3CH_2CH_2$–H (Reference [108]) and D(*prim*-R–H) = 100.7 (Reference [47]).

[v] The values are for FMe; in the absence of data relevant to FPr, the same values were assumed for it.

[w] Values in the various compilations are widely variable; that selected is from Reference [119].

[x] The value is from Reference [120]; FR (Reference [6]) used a larger value of 64.6 which is likely a vertical value.

This model thus treats the enthalpy and polar effects on log *k* (or *E*) as *additive*, and, since the authors used the *sum* of σ values for X and Y, it also assumes that each 'effect' is additive for X and Y and does not saturate. By the use of 'stepwise linear regression analysis,' they concluded that the best correlations for certain radicals required only the ($\rho_{polar}\sigma_{para}$) term (e.g., tBu and POH), certain others required only the ($\rho_{enthalpy}\sigma^{\bullet}$) term (e.g., MCN), and still others required both (e.g., Me and Bn). The final r^2 values varied widely from 0.27 to 0.96. The authors' conclusion[127] was that 'radical reactivity correlates (i) with Hammett σ alone for strongly nucleophilic radicals where polar effects dominate, (ii) with Hammett σ and one of the radical $\sigma^{\bullet}$ scales for moderately nucleophilic (or electrophilic) radicals, and (iii) with one of the radical $\sigma^{\bullet}$ scales for weakly nucleophilic radicals where enthalpy effects dominate.' While semi-quantitatively revealing, this model cannot of course address a new radical because only the 'effects' of X and Y in the olefin partner are considered.

We applied this model to the full data set, with the exclusion of the small data sets for Cum and Hx and of the data for H,CHO and H,COMe for which all the Hammett constants are not available.

Table 6. Correlation parameters for various models applied to the full data set in Table 1 with values of independent variables from Tables 2–5 and 12[a]

Row	Model and conditions	Independent variables	Derived and/or adjustable parameters	r^2	sd(ΔE) (kcal mol^{-1})	E_{predict} (kcal mol^{-1})
1	Hammett	σ_{para} and $\sigma^{\bullet}$ for X, Y, and substituents on R	$\rho_{\text{polar,R}}$, $\rho_{\text{polar,olefin}}$, $\rho_{\text{enthalpy,R}}$, $\rho_{\text{enthalpy,olefin}}$, E^0	0.35	1.68	$3.28 + 0.35(E)$
2	Evans–Polanyi	ΔH	$E^0_{\Delta H}$, $\alpha_{\Delta H}$	0.29	1.71	$3.48 + 0.29(E)$
3	CT SOMO–LUMO	IP(R), EA(Olefin)	$E^0_{\text{R}^+,\text{O}^-}$, $\alpha_{\text{R}^+,\text{O}^-}$	0.013	2.01	$4.82 + 0.013(E)$
4	CT SOMO–HOMO	IP(Olefin), EA(R)	$E^0_{\text{R}^-,\text{O}^+}$, $\alpha_{\text{R}^-,\text{O}^+}$	0.0002	2.02	$4.88 + 0.0002(E)$
5	‘Modified *Q*–*e*’ (Eqn (5))[b]	ΔH, IP(Olefin), EA(Olefin)	*a*–*d*; as in text	0.40	1.57	$2.94 + 0.40(E)$
6	‘Modified *Q*–*e*’ (Eqn (5))[c]	ΔH, IP(Olefin), EA(Olefin), IP(R), EA(R)	*a*–*d*; as in text	0.38	1.59	$3.03 + 0.38(E)$
7	Updated FR; revised Evans–Polanyi ‘upper boundary’; *C*s and γs optimized for each R[d]	ΔH, IP(R), EA(Olefin), IP(Olefin), EA(R)	$E^0_{\Delta H}$ and $\alpha_{\Delta H}$,[e] four or eight *C*s and γs for each R[d]	0.84	0.89	$-0.03 + 1.01(E)$
8	LAF	ΔH, IP(R), EA(Olefin), IP(Olefin), EA(R)	$E^0_{\Delta H}$ and $\alpha_{\Delta H}$ from regression; none arbitrary	0.45	1.54	$2.09 + 0.57(E)$
9	Adjusted LAF[f]	ΔH, IP(R), EA(Olefin), IP(Olefin), EA(R)	Scaling factor for ΔE_{polar}	0.33	2.87	$0.00 + 1.00(E)$
10	Original Marcus (Eqn (17))	ΔH	E^0	0.28	1.78	$2.87 + 0.41(E)$
11	Modified Marcus (Eqn (18))	ΔH	E^0	0.28	1.72	$3.22 + 0.32(E)$
12	Updated FR as for row 7, but with Evans–Polanyi ‘upper boundary’ replaced with one from the original Marcus equation	ΔH, IP(R), EA(Olefin), IP(Olefin), EA(R)	$E^0_{\Delta H}$,[g] four or eight *C*s and γs for each R[d]	0.82	0.98	$-0.15 + 1.03(E)$
13	Updated FR as for row 7, but with Evans–Polanyi ‘upper boundary’ replaced with one from the modified Marcus equation	ΔH, IP(R), EA(Olefin), IP(Olefin), EA(R)	$E^0_{\Delta H}$,[h] four or 8 *C*s and γs for each R[d]	0.83	0.92	$-0.01 + 1.00(E)$
14	Revised FR; revised Evans–Polanyi ‘upper boundary’; single set of optimized[i] $C_{\text{n}} = fC^*_{\text{n}}$, $C_{\text{e}} = fC^*_{\text{e}}$, $\gamma_{\text{n}} = f\gamma^*_{\text{n}}$, and $\gamma_{\text{e}} = f\gamma^*_{\text{e}}$ used for all R and olefins with $f = 1$; as in row 3 of Table 11	ΔH, IP(R), EA(Olefin), IP(Olefin), EA(R)	$E^0_{\Delta H}$ and $\alpha_{\Delta H}$,[e] single set of optimized C^*_{n}, C^*_{e}, γ^*_{n}, and γ^*_{e} used for entire data set	0.46	1.74	$1.18 + 0.76(E)$
15	Revised FR as for row 14, but with *f* variable and dependent on a^{H} and a scaling factor *h* (as in text); as in row 5 of Table 11	ΔH, IP(R), EA(Olefin), IP(Olefin), EA(R), a^{H} for each R and adduct radical	$E^0_{\Delta H}$ and $\alpha_{\Delta H}$,[e] single set of optimized C^*_{n}, C^*_{e}, γ^*_{n}, and γ^*_{e} used for entire data set, scaling factor *h*	0.57	1.40	$1.29 + 0.74(E)$
16	Revised FR; same as row 14 except with ‘upper boundary’ from the original Marcus equation; as in row 3 of Table 13	ΔH, IP(R), EA(Olefin), IP(Olefin), EA(R)	$E^0_{\Delta H}$,[g] single set of optimized C^*_{n}, C^*_{e}, γ^*_{n}, and γ^*_{e} used for entire data set	0.46	1.81	$0.96 + 0.80(E)$

(*Continues*)

Table 6. (Continued)

Row	Model and conditions	Independent variables	Derived and/or adjustable parameters	r^2	sd(ΔE) (kcal mol^{-1})	$E_{predict}$ (kcal mol^{-1})
17	Revised FR as for row 16, but with *f* variable and dependent on a^H and a scaling factor *h* (as in text); as in row 5 of Table 13	ΔH, IP(R), EA(Olefin), IP(Olefin), EA(R), a^H for each R and adduct radical	$E^0_{\Delta H'}$[g] single set of optimized C^*_n, C^*_e, γ^*_n, and γ^*_e used for entire data set, scaling factor *h*	0.54	1.46	$1.28 + 0.73(E)$
18	Revised FR; same as row 14 except with 'upper boundary' from the modified Marcus equation; as in row 3 of Table 14	ΔH, IP(R), EA(Olefin), IP(Olefin), EA(R)	$E^0_{\Delta H'}$[h] single set of optimized C^*_n, C^*_e, γ^*_n, and γ^*_e used for entire data set	0.46	1.77	$1.13 + 0.77(E)$
19	Revised FR as for row 18, but with *f* variable and dependent on a^H and a scaling factor *h* (as in text); as in row 5 of Table 14	ΔH, IP(R), EA(Olefin), IP(Olefin), EA(R), a^H for each R and adduct radical	$E^0_{\Delta H'}$[h] single set of optimized C^*_n, C^*_e, γ^*_n, and γ^*_e used for entire data set, scaling factor *h*	0.57	1.41	$1.30 + 0.74(E)$

[a] For the 'non-correlation' $E_{predict} = E_{average} = 4.88 + 0(E)$, sd($\Delta E$) = 2.02 kcal mol^{-1} and characterizes the inherent span of the *E* values.

[b] Use of χ_{Olefin}.

[c] Use of $(\chi_{Olefin} + \chi_R)/2$.

[d] $(\Delta E)_{av}$ for each R was forced to zero by multiplying the FR-assigned *C*s and γs (Table 10) by a scaling factor; hence all *C*s and γs were independent but the originally assigned ratios among them for each R were maintained.

[e] 'Visually' selected 'upper boundary' Evans–Polanyi parameters.

[f] ΔE_{polar} term multiplied by scaling factor of 2.5.

[g] Upper boundary' parameter for original Marcus equation.

[h] Upper boundary' parameter for modified Marcus equation.

[i] Optimized to force $(\Delta E)_{av}$ for full data set to zero.

We used E in place of log k, which, except for sign changes, is equivalent, given the assumption of constant A for each radical. E^0 would then represent the inherent reactivity of a given radical for addition to ethylene *without* any dissection into a polar and an enthalpy component, ρ_{polar} would represent the *incremental* change in the polar effect that results from the replacement of H by X and/or Y, and ρ_{enthalpy} would represent the corresponding *incremental* change in the enthalpy effect. (We assumed that the various $\sigma^{\bullet}$ values for Et and OEt were equal to those for Me and OMe, respectively, and missing values of $\sigma^{\bullet}$(ADW) for Ph and OH were estimated from the linear correlation of the two $\sigma^{\bullet}$ scales ($r^2 = 0.95$).[127]) To provide context, the correlation of each radical with $\sigma^{\bullet}$ alone was tested first to focus on the enthalpy effect. Because all $\sigma^{\bullet}$ are positive (radical-stabilizing), it is not surprising that all the ρ_{enthalpy} values were negative, that is, E_{predict} decreases as the adduct radical becomes more stable. However, the typical correlation was quite poor with sd(ΔE) = 0.85 ± 0.46 kcal mol^{-1} for $\sigma^{\bullet}$(Creary) and 0.83 ± 0.47 kcal mol^{-1} for $\sigma^{\bullet}$(ADW); note that these sd(ΔE) values apply to each *individual* radical, *not* to the much more demanding entire data set as those in Table 6 do. The range of correlation quality was large, with the poorest (sd(ΔE) ≈ 1.95 kcal mol^{-1}) occurring for POH, likely the most nucleophilic radical, and the best (sd(ΔE) = 0.30–0.35 kcal mol^{-1}) for MEst and MCN, likely the most ambiphilic radicals. Analogously, the correlation of each radical with σ_{para} alone was then tested to focus on the polar effect. Because σ_{para} is positive for electron-withdrawing substituents, one would expect negative ρ_{polar} values for nucleophilic radicals, that is, E should decrease because of the dominant R$^+$Olefin$^-$ CT state, and positive ρ_{polar} values for electrophilic radicals, that is, E should decrease because of the dominant R$^-$Olefin$^+$ CT state. Indeed, the order of increasing ρ_{polar} from −5.5 to +1.9 was POH < tBu < MOH < cHx < Me < Bn < EEst < PEst < PCN < MCN < MEst < cMal < FAc < FMe/FPr, with the cross-over from negative to positive occurring between MEst and cMal. This pattern generally coincides with expectations for nucleophilic–electrophilic ordering of the radicals, although it does not overlap exactly with the order of increasing IP(R) shown in Table 5, especially for the positions of Me and FMe/FPr. However, the typical correlation was even poorer than with $\sigma^{\bullet}$ alone (sd(ΔE) = 1.02 ± 0.28 kcal mol^{-1}), and the range of correlation quality was again large, with the poorest (sd(ΔE) ≈ 1.5 kcal mol^{-1}) occurring for POH and the best (sd(ΔE) ≈ 0.5 kcal mol^{-1}) for FMe/FPr and cMal, likely the most electrophilic radicals.

Moving on to the two-parameter HLJ[127] additive approach, we applied standard linear least squares fitting with no assumptions whether one or the other of the ($\rho\sigma$) terms could be neglected. Results are summarized in Table 7, in which the radicals are listed in order of increasing ρ_{polar}; the ordering is the same for either $\sigma^{\bullet}$ scale. Both the quality and the range of the correlations were significantly improved from the single-parameter approaches, with sd(ΔE) = 0.47 ± 0.14 kcal mol^{-1} for $\sigma^{\bullet}$(Creary) and 0.44 ± 0.16 kcal mol^{-1} for $\sigma^{\bullet}$(ADW). The values of ρ_{enthalpy} were again all negative, whereas the sign of ρ_{polar} was again radical dependent. The philicity ordering of the radicals in Table 7, based on increasing ρ_{polar}, was very similar to that from the (much poorer) correlations with ρ_{polar} alone. Plots of E_{predict} *versus* E (not shown but the sd(ΔE) values are given in Table 7) consistently gave slightly positive intercepts and slopes slightly less than unity. As already noted, however, this correlation method lacks predictive power for new radicals because the E^0 term for any radical inherently contains a mixture of polar and enthalpy effects and cannot be predicted *a priori*; in other words, no independent variables associated with R are considered.

Given that the X and Y substituents reside directly on the olefin radical anion or radical cation in the CT states, one might expect an improved two-parameter correlation if σ_{para} were replaced with σ^-_{para} or σ^+_{para}.[128] In fact, use of σ^-_{para} gave sd(ΔE) = 0.49 ± 0.16 kcal mol^{-1} for $\sigma^{\bullet}$(Creary) and 0.44 ± 0.16 kcal mol^{-1} for $\sigma^{\bullet}$(ADW), indistinguishable from the results

Table 7. Correlations of E with a Hammett-type model for X and Y[a]

Radical	ρ_{enthalpy}	ρ_{polar}	$E^{0\text{b}}$	N^{c}	r^2	sd(ΔE)$^{\text{b}}$
POH	−5.61 (−5.38)[d]	−5.72 (−5.75)	6.00 (5.75)	14	0.86 (0.85)	0.86 (0.89)
tBu	−4.76 (−4.88)	−4.62 (−4.57)	6.33 (6.24)	19	0.92 (0.93)	0.54 (0.49)
MOH	−4.98 (−4.98)	−4.32 (−4.28)	7.99 (7.86)	19	0.92 (0.91)	0.53 (0.54)
cHx	−5.00 (−5.10)	−3.65 (−4.05)	6.86 (6.85)	10	0.89 (0.90)	0.54 (0.53)
Bn	−4.55 (−4.43)	−2.09 (−2.12)	10.3 (10.2)	15	0.90 (0.90)	0.40 (0.40)
Me	−3.69 (−3.81)	−2.02 (−1.99)	6.55 (6.48)	19	0.89 (0.93)	0.38 (0.30)
PEst	−4.74 (−4.78)	−1.44 (−1.47)	8.48 (8.36)	14	0.79 (0.84)	0.57 (0.49)
EEst	−4.55 (−4.63)	−1.35 (−1.31)	7.23 (7.13)	17	0.84 (0.88)	0.47 (0.41)
PCN	−4.08 (−4.12)	−1.02 (−1.05)	8.84 (8.74)	15	0.82 (0.88)	0.44 (0.37)
MCN	−3.70 (−3.74)	−0.36 (−0.33)	6.14 (6.05)	19	0.92 (0.93)	0.34 (0.33)
MEst	−3.95 (−4.03)	−0.30 (−0.27)	5.55 (5.47)	19	0.88 (0.91)	0.33 (0.29)
cMal	−1.56 (−1.559	0.37 (0.39)	4.46 (4.43)	18	0.46 (0.49)	0.38 (0.37)
FMe/FPr	−2.49 (−3.12)	1.72 (1.61)	2.17 (2.41)	9	0.88 (0.94)	0.27 (0.19)
FAc	−2.84 (−2.91)	2.11 (2.12)	4.59 (4.53)	16	0.68 (0.70)	0.60 (0.58)

[a] $E = (\rho_{\text{polar}}\sigma_{\text{para}}) + (\rho_{\text{enthalpy}}\sigma^{\bullet}) + E^0$; the first value is from the use of $\sigma^{\bullet}$(Creary); that in parentheses is from the use of $\sigma^{\bullet}$(ADW).

[b] kcal mol^{-1}.

[c] Number of olefins in the data set.

[d] Because the $\sigma^{\bullet}$(ADW) scale is so compressed compared with the $\sigma^{\bullet}$(Creary) scale, the values shown in parentheses for this column are ρ_{enthalpy}(ADW)/10 for easier comparison.

for σ_{para}, and use of σ^{+}_{para} gave only a slight improvement to $\text{sd}(\Delta E) = 0.40 \pm 0.08\ \text{kcal mol}^{-1}$ for $\sigma^{\bullet}$(Creary) and $0.36 \pm 0.08\ \text{kcal mol}^{-1}$ for $\sigma^{\bullet}$(ADW). In fact, the greatest reduction in sd(ΔE) from the use of σ^{+}_{para} for X and Y occurred for the most nucleophilic POH, tBu, and MOH radicals, a counterintuitive result for the expected dominant role of the $R^{+}\text{Olefin}^{-}$ CT state.

If one wished to extend the Hammett approach to the full data set, one could of course add two more parameters, the summations of σ_{para} and of $\sigma^{\bullet}$ for the three substituents on radical R. Doing this, with exclusion of the data for Cum, Hx, FAc, H,CHO, and H,COMe and with use of the $\sigma^{\bullet}$(Creary) scale, gave $E_{\text{predict}} = -1.92\sigma_{\text{para,olefin}} - 4.20\sigma^{\bullet}_{\text{Olefin}} - 0.43\sigma_{\text{para,R}} + 1.97\sigma^{\bullet}_{\text{R}} + 5.95$. The correlation indicators, $r^2 = 0.35$ and $\text{sd}(\Delta E) = 1.68\ \text{kcal mol}^{-1}$, were poor and the final correlation: $E_{\text{predict}} = 3.28 + 0.35(E)$ (row 1 of Table 6) shows serious deviation from a zero intercept and unit slope (as described above).

Principal components analysis

The recent trend in choice of independent variables has been away from the use of empirical parameters such as the Hammett constants for *substituents* on the radical and/or olefin toward the use of experimentally accessible properties of the radical and/or olefin *as a whole*, especially $\Delta_f H$, IP, and EA. For example, Heberger and Lopata[136,137] applied principal components analysis to the rate constants for several of the constant radical-varying olefin subsets of the Fischer data to explore the relative roles of enthalpy effects, expressed as ΔH, and polar effects, expressed as IP(Olefin) and/or EA(Olefin). Two principal components accounted for >90% of the total variance. They concluded that the major one described the nucleophilic character of radicals and correlated with EA(Olefin) and ΔH, which are themselves significantly correlated, while the minor one described the electrophilic character of radicals and correlated with IP(Olefin). (The relative importance of the two components results because the majority of the radicals included in the data sets are nucleophilic.) Plots of the component loadings allowed subdivision of the radicals into a 'more nucleophilic' set that correlated most strongly with EA(Olefin), a 'less nucleophilic' set that correlated most strongly with ΔH, and an 'electrophilic' set that correlated most strongly with $-$IP(Olefin). These authors[136,137] presented the following summary: (a) the role of EA(Olefin) will be the strongest for the most nucleophilic radicals but will decrease with decreasing nucleophilicity, (b) the role of $-$IP(Olefin) will be the strongest for the most electrophilic radicals but will decrease with decreasing electrophilicity, and (c) the role of ΔH will be the strongest for the borderline (ambiphilic) radicals. Following this reasoning, the authors presented a regression equation for each radical of the form: $\log k = a[\text{EA(Olefin)}] + b[-\Delta H] + c[-\text{IP(Olefin)}] + d$, with only certain of the coefficients a–d having non-zero values, dependent on the radical. The values of the non-zero coefficients were considered to support their three summary statements.

Single-variable models

To provide context for quantitative models based on radical and olefin properties, we first demonstrate the well-known limitations of correlations of E with *single* independent variables by carrying out linear least squares analyses for the format $E = E^{0}_{z} + \alpha_{Z}(Z)$ with the data from Tables 1–5. The scatter of the Evans–Polanyi plot ($Z = \Delta H$(R,X,Y)) shown in Fig. 1 visually reinforced the well-known fact that enthalpy alone is a poor predictor of reactivity (row 2 of Table 6). (The dashed correlation lines in Fig. 1 will be discussed below). The plot for $Z = [\text{IP(R)} - \text{EA(Olefin)}]$ to explore the polar effect for a nucleophilic radical–electrophilic olefin interaction showed no correlation (Fig. 2 and row 3 of Table 6), nor did that for $Z = [\text{IP(Olefin)} - \text{EA(R)}]$ to explore the polar effect for the reverse sense of electron transfer (Fig. 3 and row 4 of Table 6).

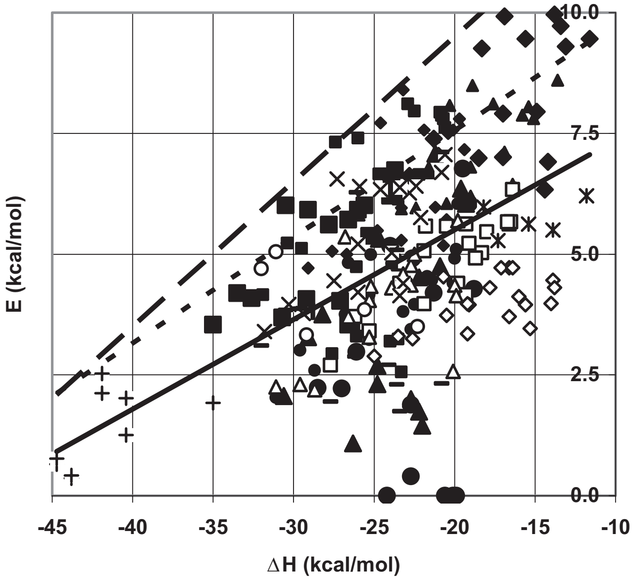

Figure 1. Evans–Polanyi plot of full data set (Table 1) with updated parameters (Tables 2 and 3). ■, Me; ◆, Bn; ▲, tBu; ●, POH; ▪, MOH; ⬩, PEst; ▴, PCN; •, MEst; □, MCN; ◇, cMal; Δ, FAc; x, EEst; *, Cum; –, cHx; ○, Hx; and +, FMe/FPr. ——, actual correlation line, $E = 9.21 + 0.186(\Delta H)$; - - - - - - -, 'upper boundary' line used by FR, $E = 11.95 + 0.22(\Delta H)$; — — — — , 'upper boundary' line used herein, $E = 15.5 + 0.30(\Delta H)$

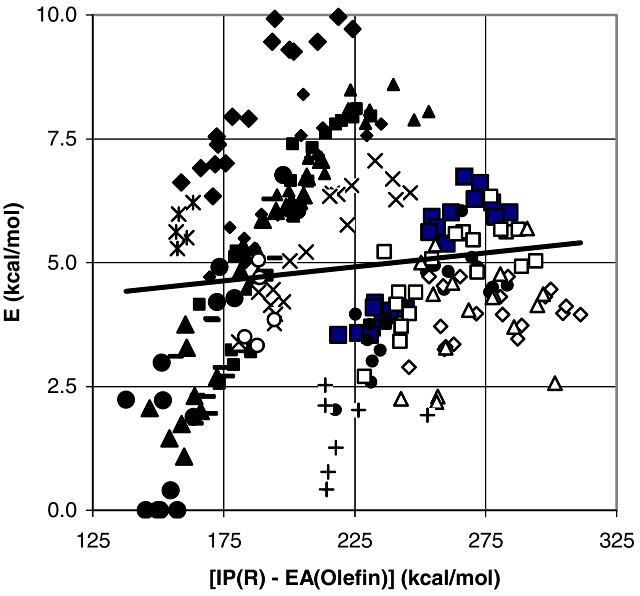

Figure 2. Activation energy data of Table 1 plotted against [IP(R) $-$ EA(Olefin)]. Symbols as in Fig. 1. ——, actual correlation line, $E = 3.64 + 0.00564[\text{IP(R)} - \text{EA(Olefin)}]$.

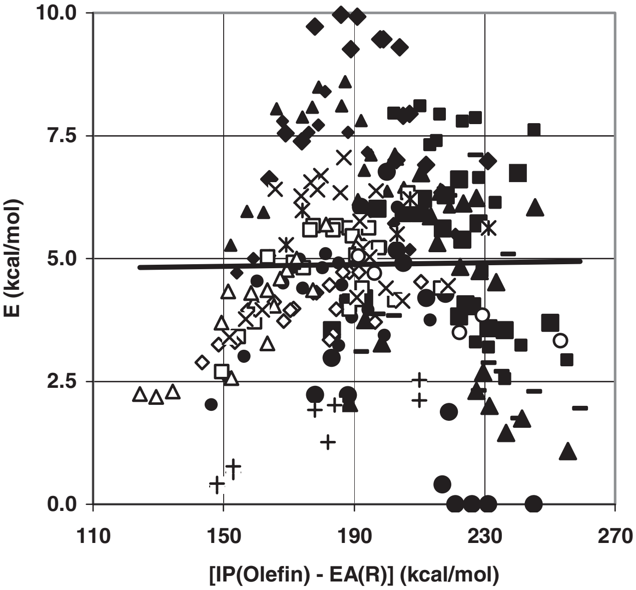

Figure 3. Activation energy data of Table 1 plotted against [IP(Olefin) – EA(R)]. Symbols as in Fig. 1. ——, actual correlation line, $E = 4.71 + 0.00091[\mathrm{IP(Olefin)} - \mathrm{EA(R)}]$

Analogous plots for each *individual* radical and its olefin set gave the E^0_Z and α_Z values shown in Table 8.[138] The parameters with the highest r^2 value for each radical are highlighted. In spite of the much poorer correlation for the total data set in Fig. 2 than in Fig. 1, the majority of the better correlations for constant radical-varying olefin cases occurred for the R^+,Olefin$^-$ CT state, that is, for radicals dominated by their nucleophilic character. The largest α_{R^+,O^-} values (sensitivity to [IP(R) – EA(Olefin)] as the correlating variable) occurred for POH, cHx, tBu, and MOH. In contrast, the three radicals which showed the best correlation with the R^-,Olefin$^+$ CT state as evidence for dominant electrophilic character are FAc, FMe/FPr, and cMal.[139] Only MEst and MCN gave their best (or comparable) correlations in the Evans–Polanyi plots. Thus, these plots at least give a qualitative separation into the nucleophilic, ambiphilic, and electrophilic classes, as clearly expounded by FR.[6]

The correlations summarized in Table 8 follow the typical practice of comparing the reactivity of a selected radical with a suite of olefins. One can equally well use the inverted constant olefin-varying radical mode.[35] The derived parameters are shown in Table 9. Examples of acceptable r^2 values were much rarer than in Table 8, and some counter-intuitive conclusions emerged. For example, a few of the Evans–Polanyi plots had $\alpha_{\Delta H} < 0$, that is, E was predicted to increase with increasing exothermicity. Also, the majority of the plots for the R^+,Olefin$^-$ CT state had negative slopes, that is, E was predicted to increase with decreasing relative energy of the CT configuration; positive slopes occurred only for H,CHO, Me,CO_2Me, H,CN, and Me,CN that are expected to be highly electrophilic, albeit with very low r^2 values. The plots for the R^-,Olefin$^+$ CT state also had some negative slopes, and the only moderately acceptable correlations with positive slopes occurred for H,Me and Me,Me that are expected to be highly nucleophilic. Thus, the contents of Table 9 offer little potential for predicting the reactivity of a new radical with a given olefin.

Multi-variable models

To extend the use of the Evans–Polanyi model (Fig. 1), we used linear combinations of a ΔH(R,X,Y) term with an [IP(R) –

Table 8. Single-variable correlations for individual radicals with the olefin set[a]

	Evans–Polanyi			SOMO–LUMO CT			SOMO–HOMO CT		
Radical	$E^0_{\Delta H}$	$\alpha_{\Delta H}$	r^2	$E^0_{R^+,O^-}$	α_{R^+,O^-}	r^2	$E^0_{R^-,O^+}$	α_{R^-,O^+}	r^2
Me	11.2	0.22	0.40	**−8.6**	**0.054**	**0.85**	5.4	−0.002	0.001
tBu	11.6	0.31	0.28	**−12.6**	**0.094**	**0.88**	11.2	−0.032	0.08
Bn	11.5	0.20	0.23	**−3.1**	**0.061**	**0.83**	11.2	−0.015	0.04
MOH	12.7	0.28	0.22	**−12.2**	**0.091**	**0.82**	13.0	−0.032	0.08
POH	5.9	0.14	0.03	**−14.6**	**0.105**	**0.72**	17.2	−0.069	0.30
MEst	**9.4**	**0.22**	**0.57**	**−5.1**	**0.037**	**0.58**	−0.2	0.024	0.20
EEst	11.8	0.26	0.47	**−6.1**	**0.054**	**0.81**	4.4	0.005	0.01
PEst	11.4	0.22	0.28	**−4.7**	**0.056**	**0.75**	6.8	−0.003	0.001
MCN	**9.6**	**0.23**	**0.68**	−3.8	0.033	0.51	0.1	0.026	0.24
PCN	11.3	0.23	0.46	**−3.2**	**0.047**	**0.76**	6.4	0.003	0.003
cMal	5.8	0.10	0.36	1.8	0.008	0.08	**0.3**	**0.021**	**0.43**
FAc	8.3	0.18	0.33	0.6	0.012	0.04	**−4.6**	**0.054**	**0.79**
Cum	6.6	0.06	0.16	−6.6	0.077	0.33	5.2	0.003	0.03
cHx	5.2	0.06	0.02	**−14.2**	**0.101**	**0.77**	9.4	−0.026	0.09
Hx	0.5	−0.13	0.48	−2.9	0.037	0.04	**10.1**	**−0.028**	**0.86**
FMe/FPr	8.1	0.16	0.36	−3.5	0.022	0.12	**−4.1**	**0.031**	**0.89**
All	9.2	0.19	0.29	3.6	0.006	0.01	4.7	0.001	0.0001

[a] The better correlations for each radical, as judged by r^2, are given in bold; E^0 values are in kcal mol^{-1}.

Table 9. Single-variable correlations for individual olefins with the radical set[a]

	Evans–Polanyi			SOMO–LUMO CT			SOMO–HOMO CT		
Olefin	$E^0_{\Delta H}$	$\alpha_{\Delta H}$	r^2	$E^0_{R^+,O^-}$	α_{R^+,O^-}	r^2	$E^0_{R^-,O^+}$	α_{R^-,O^+}	r^2
H,H	4.5	−0.10	0.11	8.3	−0.008	0.18	2.6	0.017	0.45
H,Me	1.6	−0.21	0.28	12.2	−0.025	0.55	−3.2	0.044	0.81
H,Et	10.6	0.23	0.43	15.2	−0.036	0.37	−1.1	0.039	0.22
Me,Me	1.2	−0.22	0.14	15.1	−0.036	0.61	−5.8	0.060	0.70
H,Ph	9.4	0.19	0.46	7.5	−0.017	0.14	1.6	0.015	0.04
Me,Ph	9.2	0.19	0.45	8.2	−0.021	0.20	0.3	0.023	0.09
Ph,Ph	9.5	0.20	0.26	5.4	−0.010	0.07	2.4	0.007	0.01
H,$SiMe_3$	10.7	0.21	0.20	9.8	−0.017	0.14	4.3	0.009	0.01
H,CHO	10.3	0.31	0.27	−1.0	0.025	0.21	17.0	−0.061	0.38
H,CO_2Me	9.8	0.26	0.30	2.3	0.010	0.03	14.2	−0.048	0.21
Me,CO_2Me	8.0	0.18	0.38	4.0	−0.001	0.001	8.5	−0.023	0.07
H,CN	8.0	0.16	0.25	0.7	0.016	0.09	17.6	−0.060	0.37
Me,CN	8.7	0.24	0.22	0.7	0.015	0.10	12.8	−0.042	0.22
H,OEt	9.4	0.14	0.09	15.4	−0.036	0.54	−0.7	0.039	0.16
Me,OMe	9.0	0.12	0.07	15.1	−0.034	0.49	0.1	0.037	0.14
H,OAc	10.8	0.19	0.14	11.4	−0.023	0.23	0.9	0.020	0.04
Me,OAc	9.7	0.14	0.09	13.0	−0.029	0.40	0.0	0.033	0.14
H,Cl	3.3	−0.09	0.14	6.1	−0.003	0.03	3.7	0.008	0.07
Me,Cl	9.3	0.18	0.15	9.9	−0.018	0.14	5.5	0.002	0.0003
Cl,Cl	9.0	0.18	0.37	4.8	−0.001	0.001	9.1	−0.022	0.07

[a] The E^0 values are in kcal mol^{-1}.

EA(Olefin)] term, with an [IP(Olefin) − EA(R)] term, or with both. These showed no more success than the Evans–Polanyi format alone, the r^2 value being 0.2875, 0.2887, 0.2896, and 0.2898, respectively, and the sd(ΔE) value being 1.71 kcal mol^{-1} in all four cases.

The initial recognition of significant polar effects arose from observations of alternation effects in radical copolymerization, and the most venerable proposed correlation for radical addition is the *Q–e* scheme of Alfrey and Price.[140] However, its physical basis was been questioned,[141,142] and the *Q* and *E* parameters[143,144] are now taken simply as empirical indicators of overall monomer reactivity and the polar effect, respectively. Considerations that arose during recent approaches[145,146] to compute *Q* and *e* led to additional correlations that potentially relate *Q* and *e* to physical observables. Thus, *e* was suggested to correlate linearly with the electronegativity (χ) of the olefin or with the average χ of the olefin and the radical, and ln *Q* was suggested to correlate with a multi-parameter expression involving χ and ΔH. The final proposed 'modified *Q–e*' correlation[145,146] is Eqn (5):

$$E = a + b(\Delta H) + c(\chi) + d(\Delta H)(\chi) \qquad (5)$$

where *a–d* are fitting parameters, and a distinctive feature is the cross-term involving ΔH and χ. While χ can be addressed computationally,[145,146] it is also available experimentally because the Mulliken electronegativity is the average of IP and EA (refer more detailed consideration below). However, fitting the full data set to Eqn (5) led to only slightly better correlation than did the simpler Evans–Polanyi correlation with ΔH alone (*cf.* rows 5 and 6 of Table 6 with row 2).

The Fischer–Radom (FR) model

FR[6] proposed a new method to combine ΔH, IP, and EA as the independent variables, based conceptually on a curve-crossing model and VB state correlation diagram.[147,148] Four configurations are considered as contributors to an early transition state: (a) the starting state, (R + Olefin), whose energy steadily increases as the radical approaches the olefin terminus because of Pauli repulsion in the absence of electron unpairing, (b) an excited state, (R + ^{3}Olefin), whose energy steadily decreases from an initial maximum determined by the olefin triplet–singlet gap toward that of the final adduct radical as bonding between R and one of the termini of the olefin triplet increases, (c) a CT state, (R^+ + $Olefin^-$), characteristic of SOMO–LUMO interaction between a nucleophilic radical and an electrophilic olefin, and (d) a second CT state, (R^- + $Olefin^+$), characteristic of SOMO–HOMO interaction between an electrophilic radical and a nucleophilic olefin. The reaction barrier and the geometry of the transition state result largely from an avoided crossing of states (a) and (b). As substituents on the radical and/or olefin are varied, the relative energy of excited state (b) will be decreased if the olefin triplet energy is decreased and/or if the reaction becomes more exothermic. As a result of the latter, *E* will be decreased by an enthalpy effect. Second, if the relative energy of either (or both) of the CT states, which is high at infinite separation but is lowered by coulombic attraction as the reactants approach each other, becomes low enough at the transition state geometry to allow significant mixing of states, E will also be decreased by a polar effect. In this model, the independent variable to capture the enthalpy effect is the overall ΔH while those to capture the polar effects are [IP(R) − EA(Olefin)] for nucleophilic radicals and [IP(Olefin) − EA(R)] for electrophilic radicals. For ambiphilic radicals, both are relevant. Qualitatively then, E will decrease as ΔH becomes more negative and as the values of (IP − EA) become smaller. (In principle, E should also decrease as the olefin triplet energy decreases, but this parameter is seldom explicitly treated.)

The FR model specifically formulated E as the *arithmetic product* of (a) the enthalpy effect, expressed as a foundational Evans–Polanyi relationship between E and ΔH, and (b) rate-enhancing polar effects, expressed as multiplicative factors lying between 0 and 1, as shown below (Eqn (6)):

$$E = E_{\Delta H}(F_{\mathrm{n}})(F_{\mathrm{e}}) = [E^0_{\Delta H} + \alpha_{\Delta H}(\Delta H)](F_{\mathrm{n}})(F_{\mathrm{e}}) \tag{6}$$

$$E_{\Delta H} = E^0_{\Delta H} + \alpha_{\Delta H}(\Delta H) = 11.95 + 0.22(\Delta H) \tag{7}$$

$$E_{\mathrm{CT,n}} = \mathrm{IP(R)} - \mathrm{EA(Olefin)} - C_{\mathrm{n}} \tag{8}$$

$$E_{\mathrm{CT,e}} = \mathrm{IP(Olefin)} - \mathrm{EA(R)} - C_{\mathrm{e}} \tag{9}$$

$$F_{\mathrm{n}} = 1 - \exp\left[-\left(\frac{E_{\mathrm{CT,n}}}{\gamma_{\mathrm{n}}}\right)^2\right] \tag{10}$$

$$F_{\mathrm{e}} = 1 - \exp\left[-\left(\frac{E_{\mathrm{CT,e}}}{\gamma_{\mathrm{e}}}\right)^2\right] \tag{11}$$

The multiplicative factors were labeled F_{n} for nucleophilic radical behavior and F_{e} for electrophilic behavior. First, an Evans–Polanyi plot of all the E *versus* ΔH data was prepared (as in Fig. 1) and an observer-dependent straight line was 'visually' selected to represent the 'upper boundary' of this scatter plot, that is, the dependence of $E_{\Delta H}$ on ΔH in the hypothetical absence of polar effects (Eqn (7)). The specific $E^0_{\Delta H}$ and $\alpha_{\Delta H}$ values shown in Eqn (7) were estimated by FR from their set of experimental E and estimated ΔH values for the first 11 radicals in Table 1; this particular choice for the 'upper boundary' is shown in Fig. 1 as the short dashed line. The CT energy levels were expressed as Eqns (8) and (9) where C is the coulombic stabilization term between the separated charges at their distance in the transition state. To illustrate the data trends for the case of a nucleophilic radical (for which F_{e} can be held at unity), a plot of $E/E_{\Delta H}$, which from Eqn (6) is equal to F_{n} if $F_{\mathrm{e}} = 1$, *versus* [IP(R) − EA(Olefin] generates a curve that starts at 1 for high [IP(R) − EA(Olefin)] (no nucleophilic polar effect) but decreases toward 0 as [IP(R) − EA(Olefin)] decreases (maximum nucleophilic polar effect). To fit such sigmoidal curves that describe the F values as a function of (IP − EA) and C, the heuristic functions shown in Eqns (10) and (11) were used where γ_{n} and γ_{e} are somewhat ill-defined interaction parameters between the CT and the ground-state configurations. Since the positions of these sigmoidal curves along the (IP − EA) axis varied from radical to radical, individual l values of C_{n} and γ_{n} were empirically assigned to *each* nucleophilic radical (those characterized by particularly low values of [IP(R) − EA(Olefin)]); individual values of C_{e} and γ_{e} were assigned to *each* electrophilic radical (those characterized by particularly low values of [IP(Olefin) − EA(R)]); and individual values of all four parameters were assigned to *each* ambiphilic radical. (We note an ambiguity for Me which was assigned only nucleophilic parameters even though for almost all olefins [IP(Me) − EA(Olefin)] > [IP(Olefin) − EA(Me)]; this may be offset in the model by the typical inequality $C_{\mathrm{n}} > C_{\mathrm{e}}$.) In addition, to improve data fits further, a second set of systematically lower C and γ values was assigned to *each* radical for use whenever the olefins H,Ph, Me,Ph, and Ph,Ph were involved. This differentiation was postulated to be necessary for reactions involving delocalization of the radical spin and/or the transferred charge over the reactants, such that the coulombic stabilization and the interaction parameter were diminished by increased distance (as described below). (In principle for the relationship $E/E_{\Delta H} = 1 - \exp\{-[(\mathrm{IP} - \mathrm{EA} - \mathrm{C})/\gamma]^2\}$, one might have attempted to assign the constants C and γ for each radical non-arbitrarily by a nonlinear least squares fitting technique. While our attempts to do this led in some cases to values similar to those assigned by FR, in other cases the best fit gave physically unrealistic values. FR apparently took a more empirical, but not specifically prescribed assignment approach.) Although the values of C and γ are thus experimentally constrained and there was considerable overlap from radical to radical among the values assigned, these parameters were by no means universal, especially the γ values. Hence, they introduce numerous essentially adjustable fitting parameters without concrete connection to physical observables. While, as we shall see, this variability of the C and γ parameters allows for rather good correspondence between E_{predict} and E and provides a very useful means of representing the data, it conversely limits the extension of the model because there is no explicit method to assign the required C and γ values required for a radical not in the data set.

The final correlation of E_{predict} *versus* E by FR[6] for their data for the first 11 radicals in Table 1 with the use of their values of E, ΔH, IP, and EA is shown as Fig. 15 in Reference [6] and achieved $\sigma(\Delta E) = 0.57\ \mathrm{kcal\,mol^{-1}}$, equivalent to only a 2.6-fold variation in k at ambient temperature. The C and γ parameters assigned are listed in Table 10. For the 10 assignments made for nucleophilic behavior, 8 of the C_{n} values for non-phenylated olefins are identical and the range is <1.2-fold; however, only four of the corresponding γ_{n} values are identical and the range is >twofold. Similar variation exists for the electrophilic values, expecially γ_{e}. (With the same inputs, we obtained $(\Delta E)_{\mathrm{av}} = -0.07\ \mathrm{kcal\,mol^{-1}}$ and $\mathrm{sd}(\Delta E) = 0.62\ \mathrm{kcal\,mol^{-1}}$; the reason for this small difference from $0.57\ \mathrm{kcal\,mol^{-1}}$ is not apparent). Given that the C and γ values are already variable, one could allow even more fitting flexibility by forcing the $(\Delta E)_{\mathrm{av}}$ term for *each* of the radicals to zero by multiplying all its FR-assigned C and γ factors by a scaling factor slightly different from unity (In this 'scaling operation' which we will use again below, all the ratios among the four (or often eight) C and γ parameters assigned by FR to each radical are maintained.) However, the improvement to $(\Delta E)_{\mathrm{av}} = 0.00$ (assured by the protocol used) and $\mathrm{sd}(\Delta E) = 0.59\ \mathrm{kcal\,mol^{-1}}$ was minimal. Given the uncertainties introduced by possible small solvent effects, small variations in A factors, and uncertainties in the thermochemical inputs (as described above), this agreement for such a large data set is truly impressive, but, as already noted, the assignment of variable C and γ parameters introduces considerable flexibility in fitting that is not founded in the independent variables. In other words, because of its large number of adjustable parameters ($E^0_{\Delta H}$, $\alpha_{\Delta H}$, and the numerous C and γ values), the FR model might be characterized as better for correlation than prediction.

We next applied the FR protocol to the same 11 radicals but with use of our updated values for E, ΔH(Me,X,Y), $\delta[\Delta H(\mathrm{R})]$, IP, and

Table 10. Parameters assigned by FR (Reference [6]) for use in Eqns (8)–(11)[a]

Radical	C_n	γ_n	C_e	γ_e
Me	150 (138)	74 (46)		
tBu	138 (127)	46 (23)		
Bn	127 (115)	35 (17)		
MOH	138 (127)	46 (23)		
POH	138 (127)	46 (23)		
MEst	138 (127)	69 (35)	104 (92)	69 (69)
EEst	138 (127)	55 (35)	104 (92)	58 (58)
PEst	138 (127)	35 (17)	104 (92)	46 (46)
MCN	138 (127)	69 (46)	104 (97)	69 (69)
PCN	138 (127)	46 (23)	104 (97)	58 (58)
cMal			92 (81)	99 (81)
FAc			104 (92)	69 (58)
Cum	127 (115)	30 (30)		
Hx	138 (127)	58 (29)		
FMe/FPr			104 (92)	69 (69)
cHx[b]	144 (132)	60 (35)		

[a] Values in kcal mol^{-1}; those in parentheses are for use with H,Ph, Me,Ph, and Ph,Ph.
[b] Not assigned by FR; arbitrarily assigned by us as average of Me and tBu.

EA (Tables 1–5). The Evans–Polanyi plot is significantly perturbed by small changes in ΔH and several points now fall above the 'upper boundary' chosen by FR (as shown in Fig. 1). Therefore, we 'visually' selected a revised 'upper boundary' as $E_{\Delta H} = 15.5 + 0.30$ (ΔH) (as described below) which leads to increased $E_{\Delta H}$ values. Repeating the protocol with the FR-assigned C and γ values led to $(\Delta E)_{av} = 1.10$. However, this significant offset was fully expected because increasing $E_{\Delta H}$ for essentially the same E values would require smaller F_n and/or F_e values, reflective of larger polar effects, to maintain a good correlation, that is, the empirical C and/or γ factors would need to be increased (Eqns (8)–(11)). Thus, we applied the same 'scaling operation' noted above to force the $(\Delta E)_{av}$ term for each radical to zero by applying a scaling factor to all its C and γ parameters. The final result of these modifications was an increase in sd(ΔE) from 0.59 to 0.93 kcal mol^{-1}. Hence, unfortunately our updating of the thermochemical parameters significantly degraded rather than improved the FR correlation; this highlights the continuing need for improvements in the thermochemical database for substituted radicals and olefins.

Finally, we applied the FR protocol to the full 16-radical data set with the updated values of E and independent variables. The Evans–Polanyi plot shown in Fig. 1 suggests the need to revise the FR-assigned 'upper boundary' for the enthalpy effect (the short dashed line), and as already noted above we selected $E_{\Delta H} = 15.5 + 0.30$ (ΔH) (the long dashed line). Then applying the 'scaling operation' to the FR-assigned C and γ factors gave the best correlation contained herein for the full data set of sd(ΔE) = 0.89 kcal mol^{-1}, along with an ideal zero intercept and unit slope of the $E_{predict}$ *versus* E plot (row 7 of Table 6). Hence, the addition of five radicals to the original 11-radical FR set had minimal impact on the correlation behavior of the model when the arbitrary assignments of C and γ were made in the same way. The final output for the full data set and updated independent variables is illustrated in Fig. 4.

The Lalevee–Allonas–Fouassier (LAF) model

The Allonas group[149–151] formulated E not as an arithmetic product but as an *arithmetic difference* of an Evans–Polanyi $E_{\Delta H}$ contribution, diminished by a ΔE_{polar} contribution (Eqn (12)).[152] The key first step was to derive ΔE_{polar} on an *absolute basis* by adoption of the Parr–Pearson treatment of absolute electronegativity (χ) and absolute hardness (η),[153,154] which can be derived from experimental IP and EA values (in eV units) by

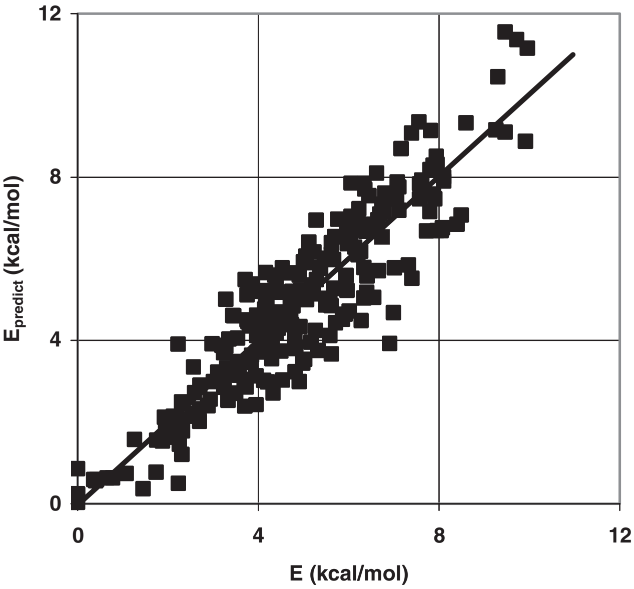

Figure 4. Correlation of the full data set with the FR model including a revised Evans–Polanyi 'upper boundary,' and optimized C and γ parameters

Eqns (13) and (14). These are then used to estimate the extent of CT (δ) and the magnitude of $\Delta E_{\mathrm{polar}}$ by Eqns (15) and (16):

$$E = E_{\Delta H} - \Delta E_{\mathrm{polar}} = [E^0_{\Delta H} + \alpha_{\Delta H}(\Delta H)] - \Delta E_{\mathrm{polar}} \quad (12)$$

$$\chi = \frac{(\mathrm{IP} + \mathrm{EA})}{2} \quad (13)$$

$$\eta = \frac{(\mathrm{IP} - \mathrm{EA})}{2} \quad (14)$$

$$\delta = \frac{(\chi_{\mathrm{Olefin}} - \chi_{\mathrm{R}})}{[2(\eta_{\mathrm{Olefin}} + \eta_{\mathrm{R}})]} \quad (15)$$

$$\Delta E_{\mathrm{polar}} = \frac{(\chi_{\mathrm{Olefin}} - \chi_{\mathrm{R}})^2}{[4(\eta_{\mathrm{Olefin}} + \eta_{\mathrm{R}})]} \quad (16)$$

In this formulation, CT is promoted by the difference in electronegativities and opposed by the sum of the hardnesses.[155] Once $\Delta E_{\mathrm{polar}}$ was determined non-empirically for each reaction from Eqn (16), the corresponding $E_{\Delta H}$ was 'back-calculated' as $(E + \Delta E_{\mathrm{polar}})$ (as in Eqn (12)). Finally, subjecting these individual $E_{\Delta H}$ values to the Evans–Polanyi format allowed derivation of 'smoothed' values of $E^0_{\Delta H}$ and $\alpha_{\Delta H}$ for use in Eqn (12) to make the required connection to the independent variable ΔH. In distinct contrast to the FR model, this LAF model has *no* adjustable parameters, as even the $E^0_{\Delta H}$ and $\alpha_{\Delta H}$ parameters result directly from calculations traceable to ΔH, IP, and EA values rather than from 'visual' estimation. This model was tested by the authors[149–151] on their computational results for addition of a wide range of radicals to a modest range of olefins but was not applied to experimental data.

We applied the LAF model to the full 16-radical data set. The δ values from Eqn (15) ranged from 0.12 for the highly nucleophilic–electrophilic tBu-H,CN and POH-H,CN pairs to -0.16 for the highly electrophilic–nucleophilic FAc-H,Ph, FAc-Me,Ph, FAc-Ph,Ph, FAc-Me,Me, FAc-Me,OMe, and cMal-Me,OMe pairs.[156] The $\Delta E_{\mathrm{polar}}$ contributions from Eqn (16) ranged from trivial for ambiphilic radicals to a maxima of 2.8 kcal mol^{-1} (tBu-H,CN and POH-H,CN) for cases with $\delta > 0$ and 6.3 kcal mol^{-1} (cMal-Me,OMe) for cases with $\delta < 0$. The individual $E_{\Delta H}$ values from Eqn (12) then led to the Evans–Polanyi correlation $E_{\Delta H} = 11.06 + 0.214(\Delta H)$ ($r^2 = 0.40$). As can be seen from Fig. 5 where this correlation line is overlaid on the data set, it lies significantly below that deduced as the Evans–Polanyi 'upper boundary' in Fig. 1, and numerous E values lie above it. Hence, it is at best an approximation to such an 'upper boundary' in the FR sense, and the physical basis of the model comes under some shadow. Nevertheless, continuing the formalism of Eqn (12), we obtained the correlation shown in Fig. 6 and row 8 of Table 6, which is slightly better than those from the 'modified *Q*–*e*' model. However, compared with Fig. 4 from the FR model, there is considerably more scatter and much poorer correlation by all criteria, and the non-trivial bias toward over-predicting the lower E values and under-predicting the higher ones ($E_{\mathrm{predict}} = 2.09 + 0.57(E)$) persisted. Thus, while the output from applying the LAF model is clearly inferior to that from applying the FR model, the statistical significance of this conclusion must be strongly tempered by the fact that the LAF model has *no* adjustable parameters while the FR model has several for each individual radical.

The position of the Evans–Polanyi 'upper boundary' line in Fig. 5 suggests that the $\Delta E_{\mathrm{polar}}$ term from Eqn (16) that is added to E to obtain $E_{\Delta H}$ via Eqn (12) was generally too small. This Evans–Polanyi line could of course be 'raised' by adjusting $\Delta E_{\mathrm{polar}}$ by an arbitrary coefficient. For example, using a multiplier of 2.5 produced the ideal $E_{\mathrm{predict}} = 0.00 + 1.00(E)$ (row 9 of Table 6) but the sd(ΔE) value of 2.87 kcal mol^{-1} was unacceptable and numerous unrealistic negative values of E_{predict} resulted. Hence, such a 'correction' is inappropriate.

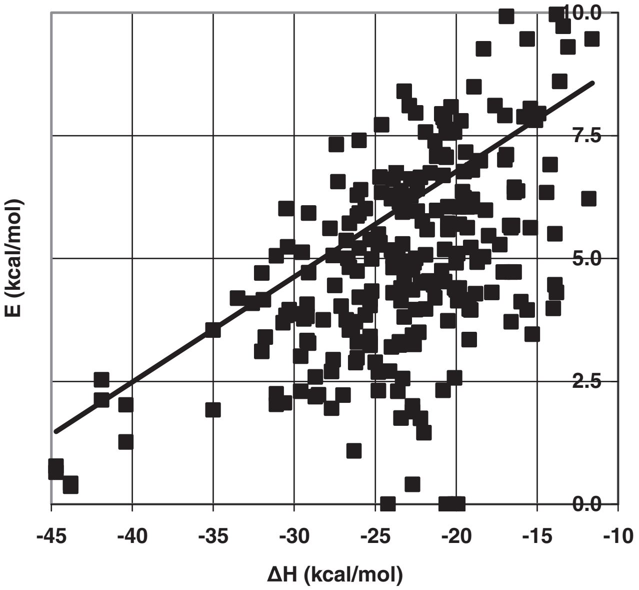

Figure 5. Activation energy data of Table 1 overlaid with the Evans–Polanyi 'upper boundary' deduced from the FAL model. ——, $E = 11.06 + 0.214(\Delta H)$

ADJUSTMENTS TO THE FR MODEL

Varying the functional form of the enthalpy effect

Both the FR and LAF models express the enthalpy effect by the classic *linear* Evans–Polanyi equation. This is of course an approximation, especially for the more highly exothermic

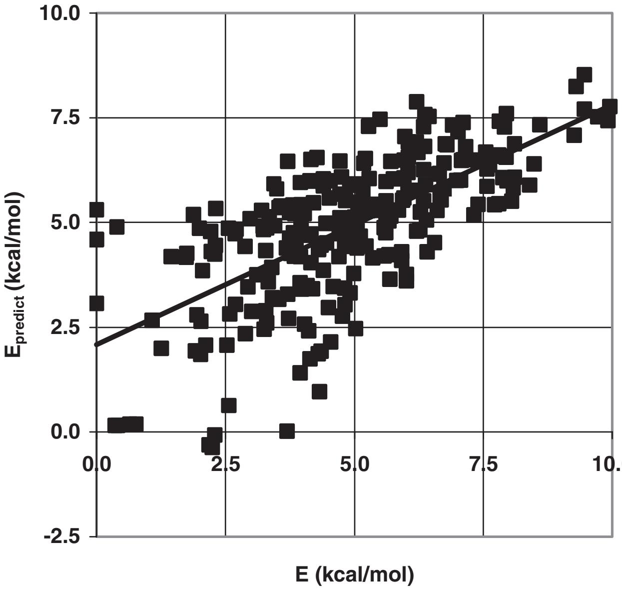

Figure 6. Correlation of the full data set with the FAL model

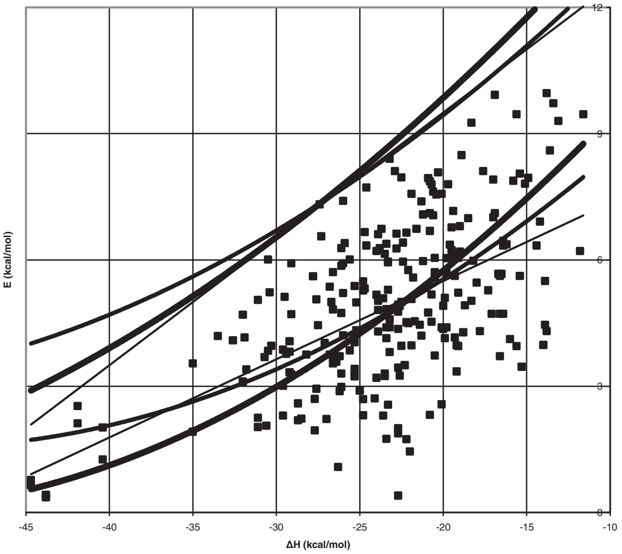

Figure 7. Activation energy data of Table 1 with varying E–ΔH relationships. Heavy curves: original Marcus equation, $E^0 = 13.95\ \text{kcal mol}^{-1}$ for best fit, $E^0 = 18.5\ \text{kcal mol}^{-1}$ for assigned 'upper boundary.' Medium curves: modified Marcus equation, $E^0 = 12.97\ \text{kcal mol}^{-1}$ for best fit, $E^0 = 17.5\ \text{kcal mol}^{-1}$ for assigned 'upper boundary.' Light curves: Evans–Polanyi best fit and assigned 'upper boundary' from Fig. 1

reactions, and it might be more appropriate to use a nonlinear function of the Marcus type. Marcus[157,158] extended his formulation of electron transfer reactions to atom transfer reactions in Eqn (17) and also suggested a modification in Eqn (18) which was better behaved at the extremes of high exothermicity or endothermicity:[159]

$$E = E^0\left[1+\left(\frac{\Delta H}{4E^0}\right)\right]^2 \tag{17}$$

$$E = E^0 + (0.5\Delta H) + \left\{\frac{E^0}{\ln 2}\right\}\left\{\ln\left[\cosh\left(0.5\times\ln 2\times\frac{\Delta H}{E^0}\right)\right]\right\} \tag{18}$$

In either of the above cases, the intrinsic barrier E^0 is the only adjustable parameter needed to relate E to ΔH. Our best fit of the E–ΔH data to the original Marcus Eqn (17), achieved by selecting E^0 to force $(\Delta E)_{av}$ to 0 for the full data set, gave $E^0 = 13.95\ \text{kcal mol}^{-1}$ and the correlation indicators in row 10 of Table 6; the nonlinear correlation is shown in Fig. 7. Results of analogous application of the modified Marcus Eqn (18) gave $E^0 = 12.97\ \text{kcal mol}^{-1}$, the correlation indicators in row 11 of Table 6, and the nonlinear correlation shown in Fig. 7. We also 'visually' assigned 'upper boundaries' of $E^0 = 18.5$ and $17.5\ \text{kcal mol}^{-1}$, respectively, also shown in Fig. 7. For comparison, the best fit and 'upper boundary' Evans–Polanyi lines from Fig. 1 are superimposed on Fig. 7. Thus, these three methods of expressing the E–ΔH relationship are quite similar (*cf.* rows 2, 10, and 11 of Table 6). If the curved Marcus 'upper boundaries' are a more accurate representation of the enthalpy effect than is the linear Evans–Polanyi 'upper boundary,' then greater polar effects would be implied in the FR treatment[6] for the most and least exothermic reactions, with the former being dominated by the additions of FMe/FPr.

The FR protocol was repeated for the full data set with the use of the 'upper boundaries' from the original Marcus equation and from the modified Marcus equation rather than with the Evans–Polanyi 'upper boundary' discussed above. To address the need for increased C and γ values, we again applied the 'scaling operation' to all FR-assigned C and γ parameters. The correlation parameters in rows 12 and 13 of Table 6 can be compared with those in row 7 for the parallel Evans–Polanyi treatment. Thus, switching from the Evans–Polanyi formulation of the enthalpy effect to either of the Marcus formulations led to insignificant changes in the correlation indicators.

Reducing the multiplicity of C and γ values

As already noted, application of the FR model to the full data set with a revised Evans–Polanyi 'upper boundary' and scaling of the values of the FR-assigned C and γ parameters for each radical could produce $(\Delta E)_{av} = 0$ and $\text{sd}(\Delta E) = 0.89\ \text{kcal mol}^{-1}$ (row 1 of Table 11). However as also noted, there is a need to assign adjustable C and γ parameters to each radical, as well as different ones for the phenylated olefins, with no physical basis. Thus, it would be desirable to tie these assignments to an experimental observable and thereby reduce the number of adjustable fitting parameters. To establish the simplest baseline, we explored assigning *a single set* of C_n, C_e, γ_n, and γ_e parameters to *all* radicals, and with *no special values* for the phenylated olefins. One such trial set, based on averages of the parameters originally assigned by FR[6] (as shown in Table 10), is shown in row 2 of Table 11. This major decrease in the number of adjustable parameters led to a major deterioration of $\text{sd}(\Delta E)$ to1.82 kcal mol^{-1} (of course the positive value of $(\Delta E)_{av} =\ 0.81\ \text{kcal mol}^{-1}$ was expected from the change in the Evans–Polanyi 'upper boundary' as noted above). We then searched for 'optimised,' but still universal, values of C_n, C_e, γ_n, and γ_e that first forced $(\Delta E)_{av}$ for the full data set to 0 and then also gave the minimum value of $\text{sd}(\Delta E)$.[160] The result was $\text{sd}(\Delta E) = 1.74\ \text{kcal mol}^{-1}$) (row 3 of Table 11 and row 14 of Table 6). In summary, use of a *single* empirically optimized value for each of the C_n, C_e, γ_n, and γ_e parameters for all radicals and olefins (in this exercise C_n decreased and the others increased) led to an increase in $\text{sd}(\Delta E)$ of $\approx 0.85\ \text{kcal mol}^{-1}$ compared with the use of *multiple* values that were tailored to each radical and further modified for the phenylated olefins.

To then systematically re-introduce radical and/or olefin specificity into the C and γ parameters, we defined $C_n = fC^*_n$, $C_e = fC^*_e$, $\gamma_n = f\gamma^*_n$, and $\gamma_e = f\gamma^*_e$, where C^*_n, C^*_e, γ^*_n, and γ^*_e are a single set of constants for the entire data set (e.g., row 3 of Table 11) that can be modulated by a variable scaling factor f that is reactant specific but *derivable from an experimental observable*. A central feature of the assignments of C and γ by FR[6] is that smaller values were used for the phenylated olefins; also, the values assigned to the radicals were the smallest for Bn. FR related this trend to the resonance delocalization of benzylic radicals. We note however that many of the other radicals involved in the data set are also somewhat delocalized (by classic π-resonance, hyperconjugation, or interaction with adjacent lone pairs of electrons) so that a clean dissection of C and γ into 'benzylic' and 'non-benzylic' values may be oversimplified. Nevertheless, a tempting fact for our purposes is that 'delocalization' of radicals is known to correlate with an experimental observable, the ESR hyperfine coupling constant (a^H). Decreased a^H, either for hydrogens on the radical center (a^H_α) or for hydrogens on a

Table 11. Results from the FR model for the full data set (Table 1) with a revised Evans–Polanyi 'upper boundary' as a function of the assignment of *C* and γ values based on ESR data[a]

Row	*f*(R)	*f*(Olefin)	C_n^*	C_e^*	γ_n^*	γ_e^*	$(\Delta E)_{av}$	sd(ΔE)
1	1	1	[b]	[b]	[b]	[b]	0.00	0.89
2	1	1	135[c]	100[c]	47[c]	66[c]	0.81	1.82
3	1	1	127[d]	111[d]	55[d]	76[d]	−0.01	1.74
4	$\neq 1$;[e] $h = 1$	$\neq 1$;[e] $h = 1$	127[f]	111[f]	55[f]	76[f]	3.20	1.77
5	$\neq 1$;[e] $h = 0.37$	$\neq 1$;[e] $h = 0.37$	145[g]	110[g]	68[g]	94[g]	0.00	1.40

[a] Values are in kcal mol^{-1}.
[b] Variable parameters tailored to each radical with distinction of phenylated and non-phenylated olefins.
[c] Constant parameters for all radicals and olefins; values are weighted average of parameters used by FR (Reference [6]) but revised Evans–Polanyi 'upper boundary' was used.
[d] Constant parameters for all radicals and olefins; values were 'optimized' to achieve $(\Delta E)_{av} = 0$ for revised Evans–Polanyi 'upper boundary'; as in text.
[e] Value of *f* derived from ESR data, via *g*; as in text.
[f] Same as row 3.
[g] Constant parameters for all radicals and olefins; values were 'optimized' to achieve $(\Delta E)_{av} = 0$ for revised Evans–Polanyi 'upper boundary' by variation of *h*; as in text.

freely rotating methyl substituent (a_β^H), is an indicator of decreased spin density on the radical center[161] because of delocalization of spin 'into' substituents. Correlations exist between a_α^H or a_β^H and radical 'stability' as reflected in D(C—H) or RSE[162] (although deviations occur for a_α^H for radicals with heteroatom substituents that lead to non-planarity). Therefore, we explored whether the desired scaling factor *f* might be derivable from a^H values. Note immediately however that there is little theoretical basis for this approach because the underlying cause for decreased *C* and γ values for benzylic species that was envisioned by FR[6] was a decrease of the coulombic and orbital interactions in the *charged* CT states because of increased distance between centers of charge at the transition state for these delocalized cases. Hence, we are making the gross (and in some cases clearly incorrect) approximation that there are parallels in the extent of delocalization in $R^\bullet$, R^+, and R^-.[163]

In this modification, the *f* value for each radical will ultimately then be based on an a^H value, normalized for convenience to a^H for ethyl radical (Et). However, since it is not obvious in this crude model that attenuations of *C* and γ should scale *directly* with a delocalization factor derived from a^H, we further defined $f \equiv [1 + h(g - 1)]$, where *g* is the actual spin density on the radical center that can be derived from a^H while *h* is a variable scaling factor;[164] for example for $g = 0.8$, variation of *h* from 0.5 to 1 to 1.5 would change *f* from 0.9 (a less than proportional effect) to 0.8 to 0.7 (a more than proportional effect). Since the attacking and adduct radicals in the data set include *prim*, *sec*, and *tert* radicals, we selected the relationships between *g* and a^H as follows: if the radical had a β-methyl substituent, it took first priority and $g = a_\beta^H / a_\beta^H(\mathrm{Et})$,[165] but if the radical had no β-methyl substituent, the α-hydrogens were used and $g = a_\alpha^H / a_\alpha^H(\mathrm{Et})$.[166] The ESR data used are compiled in Table 12.

Since the modification under consideration would involve a diminution of *C* and γ by an increase in effective distance involving delocalization in both the attacking and the adduct radical, we made the further simplifying assumption that $f_{total} = (f_R)(f_{Adduct})$. We then took C_n^*, C_e^*, γ_n^*, and γ_e^* as the 'optimized' base set in row 3 of Table 11, g_R for R and g_{Adduct} for the adduct radical from the ESR data in Table 12, and $h = 1$ (i.e., $f = g$), and we obtained $(\Delta E)_{av} = 3.20$ and sd(ΔE) = 1.77 kcal mol^{-1} (row 4 of Table 11). This major over-prediction of *E* resulted from an under-prediction of the polar effects because the *g* values are less than unity for all radicals (except Me); therefore, the *C* and γ values were all decreased from their 'starred' values, the F_n and F_e factors were thereby increased, and hence the polar effects were decreased. Restoring the polar effect terms to their original range, although now *structurally discriminated* by the application of *g*, would require increasing most or all of the C^* and γ^* values. Their 'optimum' values were again sought[160] but with now the added leverage of forcing $(\Delta E)_{av}$ for the full data set to zero by optimizing the adjustable *h* parameter. They are shown in row 5 of Table 11 and row 15 of Table 6 and led to a final sd(ΔE) = 1.40 kcal mol^{-1}.[168] Thus, applying the variable, but ESR-based, *f* factors, and an empirically fitted *h* value to a constant set of derived C_n^*, C_e^*, γ_n^*, and $\gamma_e{}^*$ values led to an improvement in sd(ΔE) of ≈0.35 kcal mol^{-1} (*cf.* rows 3 and 5 of Table 11). In summary, decreasing the number of arbitrary *C* and γ parameters from 4 (or 8) for *each* radical to a total of only 5 for *all* radical-olefin pairs (C_n^*, C_e^*, γ_n^*, $\gamma_e{}^*$, and *h*) degraded sd(ΔE) by ≈0.5 kcal mol^{-1} (*cf.* rows 1 and 5 of Table 11), that is, another factor of 2.3 in *k* at ambient temperature. However, this alteration should improve the predictive capability because the only additional input required for new cases, the ESR a^H values for the radicals involved, is typically readily available. On the other hand, we hesitate to conclude that the modest changes involved and the pragmatic optimization approach used provide any firm evidence for the physical basis of this modification, that is, for a true dependence of *C* and γ on the extent of delocalization of the radicals.

The procedure just described to determine the effectiveness of the ESR-based *f* factor was applied analogously except with the Evans–Polanyi 'upper boundary' replaced by either that from the

Table 12. ESR hyperfine coupling constants used to define *g*

Radical	a_{α}^{H} (gauss)	$a_{\beta\mathrm{-Me}}^{\mathrm{H}}$ (gauss)	Reference
Et	22.3	26.9	a
Me	22.8		a
Bn	16.3		a
tBu		22.7	b
POH		19.6	a
MOH	20.9		c
PEst		21.5	b
PCN		20.7	b
MEst	21.3		b
MCN	21.0		b
cMal	19.4		b
FAc	19.2		b
EEst	20.5	24.4	b
Cum		16.0	a
cHx	21.3		a
Hx	22.1		a
$CF_3^{\bullet}$			d
$RCH_2CH_2^{\bullet}$	22.1		a
$RCH_2CH(\bullet)Me$	21.8	24.6	a
$RCH_2CH(\bullet)Et$	21.8		b
$RCH_2C(\bullet)Me_2$		22.5	a
$RCH_2C(\bullet)(Me)(OMe)$		20.4	b
$RCH_2C(\bullet)(Me)(OAc)$		22.4	b
$RCH_2CH(\bullet)OEt$	18.7		c
$RCH_2CH(\bullet)OAc$	19.6		c
$RCH_2CH(\bullet)Cl$	21.6		c
$RCH_2CH(\bullet)SiMe_3$	20.2		b
$RCH_2C(\bullet)(Me)(Cl)$		22.7	b
$RCH_2C(\bullet)Cl_2$		19.8	a
$RCH_2CH(\bullet)CO_2Me$	20.5		b
$RCH_2C(\bullet)(Me)(CO_2Me)$		22.0	b
$RCH_2CH(\bullet)CN$	20.2		b
$RCH_2C(\bullet)(Me)(CN)$		20.8	b
$RCH_2CH(\bullet)CHO$	17.7		b
$RCH_2CH(\bullet)Ph$	16.3		a
$RCH_2C(\bullet)(Me)(Ph)$		16.0	a
$RCH_2C(\bullet)Ph_2$		15.3	a
$RCH_2CH(\bullet)COMe$	18.8		a

[a] Reference [167].
[b] Reference [7–23].
[c] Back-calculated from the a^{H}–D relationships in Reference [162].
[d] *g* assigned as 1.

original Marcus equation or the modified Marcus equation (as in Fig. 7). The results are shown in Tables 13 and 14, respectively, in the same format as Table 11. Results of the use of a *single* empirically optimized value for each of the C_n, C_e, γ_n, and γ_e parameters for all radicals and olefins, along with the original Marcus equation, are shown in row 3 of Table 13 and row 16 of Table 6, while the parallel results for the modified Marcus equation are shown in row 3 of Table 14 and row 18 of Table 6. Parallel results of the application of the *f* factor, without and with an optimized *h* factor, are shown in rows 4 and 5 of Tables 13 and 14 (also rows 17 and 19 of Table 6). In summary, use of the modified Marcus equation led to results indistinguishable from use of the Evans–Polanyi equation, whereas use of the original Marcus equation gave slightly poorer correlation.

FINAL OBSERVATIONS

We noted above that the more the quality of a correlation as judged by sd(ΔE) improved, the more E_{predict} *versus* *E* curve

Table 13. Results from the FR model for the full data set (Table 1) with an original Marcus equation 'upper boundary' as a function of the assignment of C and γ values based on ESR data[a]

Row	f(R)	f(Olefin)	C^*_n	C^*_e	γ^*_n	γ^*_e	$(\Delta E)_\mathrm{av}$	sd(ΔE)
1	1	1	[b]	[b]	[b]	[b]	0.00	0.98
2	1	1	135[c]	100[c]	47[c]	66[c]	1.01	1.89
3	1	1	131[d]	112[d]	53[d]	76[d]	0.01	1.81
4	≠1;[e] $h = 1$	≠1;[e] $h = 1$	131[f]	112[f]	53[f]	76[f]	3.45	1.82
5	≠1;[e] $h = 0.37$	≠1;[e] $h = 0.37$	139[g]	113[g]	76[g]	94[g]	0.00	1.46

[a] Values are in kcal mol^{-1}.

[b] Variable parameters tailored to each radical with distinction of phenylated and non-phenylated olefins.

[c] Constant parameters for all radicals and olefins; values are weighted average of parameters used by FR (Reference [6]) but 'upper boundary' from the original Marcus equation was used.

[d] Constant parameters for all radicals and olefins; values were 'optimized' to achieve $(\Delta E)_\mathrm{av} = 0$ for original Marcus equation 'upper boundary'; as in text.

[e] Value of f derived from ESR data, via g; as in text.

[f] Same as row 3.

[g] Constant parameters for all radicals and olefins; values were 'optimized' to achieve $(\Delta E)_\mathrm{av} = 0$ for the original Marcus equation 'upper boundary' by variation of h; as in text.

moved toward the ideal of a zero intercept and unit slope. This is illustrated in Fig. 8 for selected cases selected from Table 6 for the range from the 'non-correlation' to the best fit by the FR model.

It appears to us that progress toward an even better correlation may well be limited by the level of uncertainty in the independent variables considered. The uncertainties in many of the estimated ΔH, IP, and EA values are likely to be at least $\pm 1\ \text{kcal mol}^{-1}$. These may in fact often be larger than the uncertainties in the experimental E values, which themselves cover a rather small range. The fact that our updating the ΔH, IP, and EA data compared with the FR assignments led to deterioration of the correlation parameters supports this hypothesis. Hence, improvements in the thermochemical database remain highly desirable, whether by more precise experimental data or by the steadily improving power of computational approaches.

In any case, comparison of models for the radical addition reaction involves an inevitable tradeoff between their ability to correlate existing data and to predict new data and the number of arbitrary fitting parameters they contain. The FR and LAF models emphasized herein represent extremes along this spectrum.

Table 14. Results from the FR model for the full data set (Table 1) and the modified Marcus equation 'upper boundary' as a function of the assignment of C and γ values based on ESR data[a]

Row	f(R)	f(Olefin)	C^*_n	C^*_e	γ^*_n	γ^*_e	$(\Delta E)_\mathrm{av}$	sd(ΔE)
1	1	1	[b]	[b]	[b]	[b]	0.00	0.92
2	1	1	135[c]	100[c]	47[c]	66[c]	0.85	1.82
3	1	1	135[d]	106[d]	48[d]	80[d]	0.02	1.77
4	≠1;[e] $h = 1$	≠1;[e] $h = 1$	135[f]	106[f]	48[f]	80[f]	3.27	1.73
5	≠1;[e] $h = 0.36$	≠1;[e] $h = 0.36$	148[g]	108[g]	62[g]	99[g]	0.00	1.41

[a] Values are in kcal mol^{-1}.

[b] Variable parameters tailored to each radical with distinction of phenylated and non-phenylated olefins.

[c] Constant parameters for all radicals and olefins; values are weighted average of parameters used by FR (Reference [6]) but 'upper boundary' from the modified Marcus equation was used.

[d] Constant parameters for all radicals and olefins; values were 'optimized' to achieve $(\Delta E)_\mathrm{av} = 0$ for modified Marcus equation 'upper boundary'; as in text.

[e] Value of f derived from ESR data, via g; as in text.

[f] Same as row 3.

[g] Constant parameters for all radicals and olefins; values were 'optimized' to achieve $(\Delta E)_\mathrm{av} = 0$ for the modified Marcus equation 'upper boundary' by variation of h; as in text.

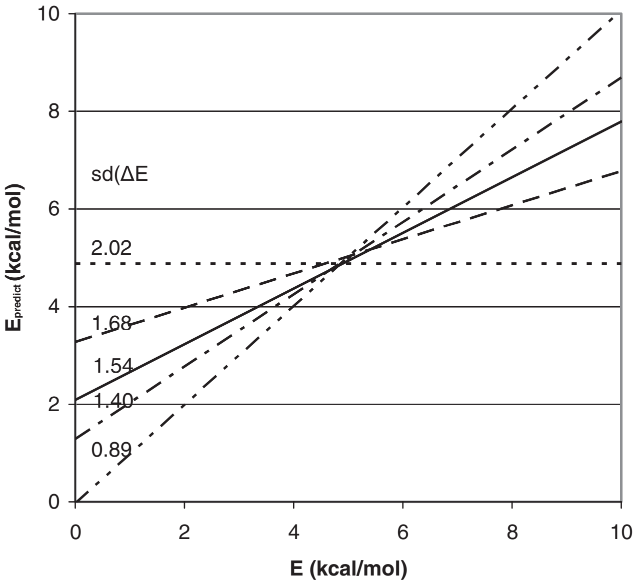

Figure 8. Correlation lines from various models. – – – – – –, 'non-correlation,' footnote a, Table 6; — — — —, full Hammett correlation, row 1, Table 6; ——, LAF model, row 8, Table 6; — – — – —, modified FR model with C and γ restricted by a^H, row 15, Table 6; — – – — – – —, full FR model with C and γ unrestricted, row 7, Table 6

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[165] Values of for methylene or methine hydrogens cannot be used because they are strongly affected by preferred rotational conformations.
[166] Although hetero-atom substituents offer the potential for a_{α}^{H} to be perturbed by non-planarity at the radical center, the radicals MOH, RCH$_2$CH(●)OEt, RCH$_2$CH(●)OAc, and RCH$_2$CH(●)Cl all fit well on the reported relationships between and D(R-H) (Reference 162).
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