Separation of Polar and Enthalpic Effects on Radical Addition Reactions Using Principal Component Analysis†

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Principal component analysis (PCA) was performed on rate constants of radical addition reactions involving various carbon centred radicals and vinyl type alkenes. Reactivity data for reactions of nine radicals with eight alkenes (data set A) and of five radicals with 15 alkenes (data set B) were analysed. In addition, a mixed case (data set C) was also considered with 13 variables of seven alkenes (reactivities of nine radicals toward the alkenes and four thermodynamic properties of the alkenes). It was found that in all cases two principal components account for more than 90% of the total variance in the data. With data sets (A) and (B) the plots of component loadings and component scores showed significant groupings of radicals and alkenes, respectively, according to similarity in reactivity and character. The component scores were found to be significantly correlated with certain thermodynamic properties of the alkenes. The correlations were in agreement with the Frontier Molecular Orbital model, the first principal component being correlated with the electron affinity and the second one with the ionization potential of the alkenes. Thus, PCA was able to decompose the individual reactivities into nucleophilic and electrophilic components. The first principal component also correlates with exothermicity ($-\Delta_rH$) suggesting that the radical addition reactions investigated are partly controlled by Hammond's postulate. With data set (C) a plot of component loadings showed that the rate constants for the less nucleophilic radicals correlate with exothermicity, whereas those for the more nucleophilic radicals correlate with electron affinity. Consequently, the reactivities of the less nucleophilic radicals appear to be well described by Hammond's postulate and those of the more nucleophilic radicals by the FMO model.

By the early 1980s it had been accepted that radical addition reactions can be interpreted in terms of the Frontier Molecular Orbital (FMO) model.[1-6] This model involves SOMO–LUMO interactions for nucleophilic and SOMO–HOMO interactions for electrophilic radicals. If early transition states are assumed and polar factors become effective, a linear correlation can be expected to hold between the activation energy (or the logarithm of rate constant) and the electron affinity (E_e) of alkenes for nucleophilic radicals or the ionization potential (E_i) of alkenes for electrophilic radicals.

On the other hand, a number of theoretical studies[7-10] have been published recently in which certain radical addition reactions have been shown to obey Hammond's postulate[11] rather than, or in addition to, the FMO model. According to Hammond's postulate, the more exothermic is the reaction, the more closely will the transition state resemble the reactants. As a consequence, more exothermic reactions can be expected to have lower activation energies. This relationship is reflected by a linear correlation between activation energy and heat of reaction (Δ_rH) frequently called a Bell or Evans–Polanyi type correlation.

Based on this correlation with the heat of reaction, we use the term of enthalpic effects which act on radical addition reactions controlled by Hammond's postulate. At the molecular level the enthalpic effects correspond to the bond strengths' term referred to by Tedder[12] as one of the major factors influencing radical addition reactions. The bond strengths' term is, in turn, connected to the radical stabilization energy and the heat of reaction.

It is still a matter of controversy in the literature[3,12-14] as to which among the major factors, *i.e.* polar, steric and enthalpic effects influencing radical addition reactions, is dominant in a particular case. We think that principal component analysis[15-17] is a suitable method to contribute to this controversy since it can provide information on the dominance of the individual factors influencing radical addition reactions.

In the past decades principal component analysis (PCA) became a popular method in chemometrics. Nowadays PCA is frequently used to analyse complex data sets to reveal underlying components that reflect the effects of some process(es) acting on the chemical system investigated.[16,17] PCA gives insight into mechanisms governing chemical reactions, provides information on the similarities of chemical structures and/or reactions, and helps classify and characterize reactants, solvents, reactions, *etc.*

In the field of reaction kinetics PCA was used to extract kinetic information from sensitivity coefficients.[18] Other important applications of PCA were reviewed by Malinowski,[16] and some more recent applications can be found in refs. 19–22.

Recent extensive studies[5,6,23-26] on radical addition reactions have provided a reliable basis for a general investigation by PCA. To the best of our knowledge, no PCA results have been published on radical reactions so far.

In this paper we report on PCA calculations carried out on rate constants of radical addition reactions involving various carbon centred radicals ($R^1R^2R^3C^\bullet$) and vinyl type alkenes ($CH_2{=}CR^4R^5$). The rate constants were taken mainly from our previous measurements: for the *tert*-butyl radical from refs. 5, 6, for the *tert*-butoxycarbonylmethyl radical from ref. 23, for the benzyl and *para*-substituted benzyl radicals from ref. 24, for the 2-cyanoprop-2-yl radical from ref. 25 and for the 2-hydroxyprop-2-yl radical from ref. 26.

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† Part III of the series Linear Free-energy Relationships in Radical Reactions. For Part II, see K. Héberger, *J. Phys. Org. Chem.*, 1994, 7, 244.

Methods

Principal Component Analysis.—PCA was used as formulated by Harman.[15] The basis of the method is summarized below using the example of the present investigations.

We have collected reactivity data for reactions of n radicals with N alkenes. We construct a data matrix $\boldsymbol{Z}$ of radical reactivities with n columns for radicals and N rows for alkenes. The element z_{ij} of the matrix $\boldsymbol{Z}$ is the reactivity data for the reaction of the jth radical with the ith alkene. The column Z_j of the matrix $\boldsymbol{Z}$ is a reactivity variable for the jth radical. Then, these Z_j reactivity variables are investigated using PCA.

The aim of PCA is to represent the variables investigated in terms of several underlying components. PCA expresses the n original variables as linear combinations of n new variables [eqn. (1)]; where Z_j is the jth variable investigated, C_k is the kth

$$Z_j = \sum_{k=1}^{n} C_k a_{kj} \quad j = 1, 2, \ldots n \tag{1}$$

underlying (principal) component searched for, and the a_{kj} coefficients are the so-called component loadings. The vector of component loadings a_{kj} ($j = 1, 2, \ldots, n$) is denoted by A_k.

The principal components are calculated such that they should be uncorrelated and should account for the total variance of the original variables. More specifically, the first principal component accounts for a maximum of the total variance, the second one is uncorrelated with the first and accounts for a maximum of the residual variance, and so on until the total variance is accounted for.

For a practical problem, it is sufficient to retain only a few components accounting for a large percentage of the total variance.

At first, the correlation or covariance matrix of the Z_j original variables is computed (this matrix is of size $n \times n$ and it contains the correlation coefficients or the covariances of each variable with the others). Then, the a_{kj} component loadings are obtained from the eigenvectors and eigenvalues of the correlation or covariance matrix. The component loading a_{kj} is, in fact, the correlation coefficient or the covariance of Z_j and C_k (depending on whether the correlation or the covariance matrix is analysed). The C_k principal components (their values are the so-called component scores) are obtained from the component loadings and the original variables.

Starting Data.—The reaction (2) was investigated; where the particular radicals and alkenes are listed in Table 1(*a*) and 1(*b*), respectively.

$$R^1R^2R^3C^{\bullet} + CH_2{=}CR^4R^5 \longrightarrow R^1R^2R^3C{-}CH_2{-}C^{\bullet}R^4R^5 \tag{2}$$

Table 2 summarizes the rate constant values collected for the calculations. All values refer to $T = 296$ K except for the 2-cyanoprop-2-yl radical, referring to $T = 315$ K.

Table 2 contains data for nine radicals. There are eight alkenes in the Table for which reactivity data are available for all the nine radicals. This data set was denoted by (A), and it consists of reactivity data for radicals 1–9 [Table 1(*a*)] and alkenes 1, 3–5, 8, 9, 13 and 14 [Table 1(*b*)], *i.e.* in mathematical statistical terms nine variables and eight objects.

On the other hand, Table 2 contains data for 15 alkenes. There are five radicals in the Table for which reactivity data are available for all the 15 alkenes. This data set was denoted by (B), and it consists of reactivity data for radicals 1, 2, 5, 7 and 8 [Table 1(*a*)] and alkenes 1–15 [Table 1(*b*)], *i.e.* five variables and 15 objects.

For the PCA calculations the logarithms of rate constants were used. Then, the variables were standardized to obtain centred and scaled variables with mean zero and standard

Table 1 Radicals and alkenes involved in the calculations and thermodynamic properties of alkenes

(*a*) Radicals

No.	Notation	Name
1	Bu^t	*tert*-Butyl
2	HP	2-Hydroxyprop-2-yl
3	MeOBz	*para*-Methoxybenzyl
4	FBz	*para*-Fluorobenzyl
5	Bz	Benzyl
6	MeBz	*para*-Methylbenzyl
7	CNP	2-Cyanoprop-2-yl
8	BCM	*tert*-Butoxycarbonylmethyl
9	CNBz	*para*-Cyanobenzyl

(b) Alkenes

No.	R^4, R^5	Name	E_e[a,b]	E_i[a,h]	$-\Delta_\mathrm{r}H$[a,l]	$\Delta_\mathrm{f}H$[a,h]
1	H, CN	Acrylonitrile	−20.26[c]	1053	87	184
2	Me, Ph	Methylstyrene	−22.19	790.2	88	113
3	H, Ph	Styrene	−24.12[d]	813.3	90	148
4	H, CO_2Me	Methyl acrylate	−47.28	955.2	67	−312
5	Cl, Cl	1,1-Dichloroethylene	−73.32[e]	944.5	68	2.0
6	H, $Si(OEt)_3$	Triethoxy(vinyl)silane	−107.1[f]	970.6[i]		
7	H, $SiMe_3$	Trimethyl(vinyl)silane	−110.0	916.6	32	−123
8	H, OCOMe	Vinyl acetate	−114.8	886.7	44	−315
9	H, CH_2CN	Allyl cyanide	−126.4	984.1		156
10	Me, Cl	2-Chloropropene	−138.9	941.6[j]	48	−21.0[m]
11	Me, OCOMe	Prop-2-enyl acetate	−145.7	878.0	66	−349
12	H, CH_2SiMe_3	Allyl(trimethyl)silane	−165.9[g]	868.3[k]		
13	H, Bu^t	*tert*-Butylethylene	−166.9[g]	911.7	52	−61.0
14	H, OEt	Vinyl ethyl ether	−216.1	849.0	54	−141
15	Me, OMe	Prop-2-enyl methyl ether	−239.3	833.6	55	−146

[a] All data are in kJ/mol and are measured at 298 K. [b] Ref. 23 unless indicated otherwise. [c] Ref. 27(*a*). [d] Ref. 27(*b*). [e] Ref. 27(*c*). [f] Ref. 6. [g] Ref. 27(*d*). [h] Ref. 27(*e*) unless indicated otherwise. [i] Ref. 26. [j] Ref. 27(*f*). [k] Ref. 27(*g*). [l] Ref. 25. [m] Ref. 27(*h*).

Table 2 Rate constant values[a] for reaction (2), used in the calculations. For the notations see Table 1

	Radical								
Alkene (R^4, R^5)	Bu^t[b]	HP[e]	MeOBz[f]	FBz[f]	Bz[f]	MeBz[f]	CNP[h]	BCM[i]	CNBz[f]
H, CN	1.0×10^6	1.0×10^8	1800	3250	2200	2100	2020	5.12×10^5	1400
Me, Ph	6.79×10^4[c]	4.0×10^8			850[g]		2310	3.5×10^6	
H, Ph	1.32×10^5	2.2×10^6	2300	2400	1300	2300	2410	1.95×10^6	3400
H, CO_2Me	1.04×10^6[d]	1.0×10^7	2450	1200	450	3000	367	4.5×10^5	680
Cl, Cl	3.50×10^5	2.15×10^5	1050	810	550	490	603	2.43×10^5	890
H, $Si(OEt)_3$	2.75×10^4	8.26×10^4			44[g]		323	6.7×10^4[j]	
H, $SiMe_3$	9600	2.49×10^4			33[g]		75	8.4×10^4	
H, OCOMe	4200	7500	36	27	14	25	41	6.0×10^4	20
H, CH_2CN	1.12×10^4[c]	2.33×10^4	28	8	3	10	88	3.8×10^4	10
Me, Cl	1.14×10^4	2.22×10^4			43[g]		120	1.32×10^5	
Me, OCOMe	1700	4850			46[g]		79	8.2×10^4	
H, CH_2SiMe_3	1120[c]	1300			56[g]		47	8.2×10^4	
H, Bu^t	150	1070	15	25	18	49	87	3.8×10^4	57
H, OEt	390	320	12	18	14	32	108	1.34×10^5	260
Me, OMe	220	1080			21[g]		82	1.21×10^5	

[a] All rate constant values are in $dm^3\ mol^{-1}\ s^{-1}$, and are measured at 296 K, except for the values for CNP measured at 315 K. [b] Refs. 5, 6 unless indicated otherwise. [c] Ref. 28(*a*). [d] Ref. 28(*b*). [e] Ref. 26. [f] Ref. 24 unless indicated otherwise. [g] Ref. 28(*c*). [h] Ref. 25. [i] Ref. 23 unless indicated otherwise. [j] Ref. 28(*d*).

Table 3 Variances accounted for by the individual principal components in data sets (A), (B) and (C)

	Data set (A)[a]		Data set (B)[b]		Data set (C)[c]	
Principal component	Variance accounted for	Percent of total variance	Variance accounted for	Percent of total variance	Variance accounted for	Percent of total variance
C1	7.9937	88.819	4.2616	85.231	10.3418	79.552
C2	0.6397	7.107	0.4203	8.406	1.4147	10.883
C3	0.1375	1.528	0.1556	3.113	0.8570	6.593
C4	0.1150	1.278	0.1011	2.023	0.2384	1.834
C5	0.0685	0.761	0.0614	1.227	0.0901	0.693
C6	0.0255	0.283			0.0580	0.446
C7	0.0201	0.223			0.0000	0.000
C8	0.0000	0.000				

[a] Data set (A) includes nine radicals and eight alkenes, therefore eight principal components were obtained. [b] Data set (B) includes five radicals and 15 alkenes, therefore five principal components were obtained. [c] Data set (C) includes nine radicals and four thermodynamic properties (altogether 13 variables) as well as seven alkenes, therefore seven principal components were obtained.

deviation one. The PCA calculations were carried out on the correlation matrices of the variables of radical reactivities (log *k* values).

The resulting principal components can be interpreted in terms of the original variables, *i.e.* the reactivities of radicals toward the various alkenes. In order to reveal the physical meaning of the principal components obtained they were also investigated as a function of certain thermodynamic properties of the alkenes. Thus, multiple linear regression calculations[29] were performed with the C_k principal components as dependent variables and the thermodynamic properties of alkenes as independent variables. The following thermodynamic properties were considered: electron affinity (E_e), ionization potential (E_i), heat of formation ($\Delta_f H$), and exothermicity [($-\Delta_r H$), the negative of the heat of reaction for alkenes with the 2-cyanoprop-2-yl radical chosen as a model]. These data were taken from refs. 6, 23, 25–27, and are listed in Table 1.

Combining the data in Tables 1 and 2, a third data set (C) was also constructed which contains reactivity data for as many radicals and alkenes as possible in addition to the above thermodynamic properties of the alkenes. Table 2 contains seven alkenes for which all the E_e, E_i, ($-\Delta_r H$) and $\Delta_f H$ data as well as the rate constants toward all the nine radicals are available. Thus, this data set consists of log *k* values for radicals 1–9 [Table 1(*a*)] and alkenes 1, 3–5, 8, 13 and 14 [Table 1(*b*)] as well as the E_e, E_i, ($-\Delta_r H$) and $\Delta_f H$ properties of the same alkenes, *i.e.* altogether 13 variables and seven objects.

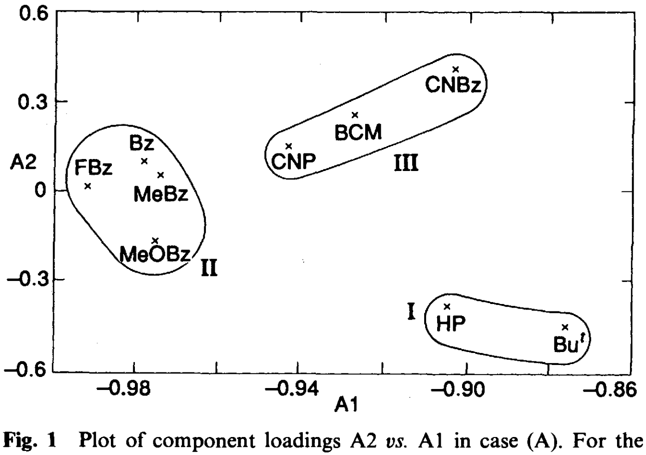

Fig. 1 Plot of component loadings A2 *vs.* A1 in case (A). For the notations see Table 1.

Both the PCA and the regression calculations were carried out using the DrugIdea program package developed for the IBM PC and compatibles.[30]

Results

We found that in all cases (A), (B) and (C) two principal components account for more than 90% of the total variance in the data, as shown in Table 3. Therefore, the first two principal

Table 4 Component loading and component score values for the first two principal components for data sets (A), B) and (C). Dimensionalities are given in parentheses. For the notations see Table 1.

	Data set (A) (9 × 8)		Data set (B) (5 × 15)		Data set (C) (13 × 7)	
Loadings	A1	A2	A1	A2	A1	A2
1 Bu^t	−0.8761	−0.4454	−0.8667	0.4791	−0.9078	−0.3420
2 HP	−0.9049	−0.3821	−0.9505	0.1528	−0.9401	−0.3015
3 MeOBz	−0.9751	−0.1726			−0.9637	−0.1559
4 FBz	−0.9918	0.0147			−0.9957	−0.0687
5 Bz	−0.9782	0.0969	−0.9394	−0.1082	−0.9959	−0.0180
6 MeBz	−0.9744	0.0494			−0.9660	−0.0832
7 CNP	−0.9430	0.1506	−0.9527	−0.1274	−0.9593	0.2514
8 BCM	−0.9274	0.2558	−0.9039	−0.3734	−0.8987	0.3038
9 CNBz	−0.9040	0.4067			−0.8966	0.3398
10 E_e					−0.9143	−0.2271
11 E_i					−0.3974	−0.7073
12 $-\Delta_r H$					−0.9462	0.2815
13 $\Delta_f H$					−0.6067	0.5182
Scores	C1	C2	C1	C2	C1	C2
1 H, CN	−1.1538	−0.4630	−1.5910	0.7143	−1.1413	−0.5459
2 Me, Ph			−1.6895	−1.3918		
3 H, Ph	−1.1415	1.0657	−1.4300	−1.2495	−1.0214	1.6007
4 H, CO_2Me	−0.8239	−0.8074	−1.0092	1.1909	−0.5449	−1.2018
5 Cl, Cl	−0.5476	−0.0542	−0.7382	0.7123	−0.3923	−0.1646
6 H, $Si(OEt)_3$			0.0732	0.9421		
7 H, $SiMe_3$			0.4344	0.6269		
8 H, OCOMe	0.8742	−0.6494	0.7980	0.6627	1.0508	−0.8249
9 H, CH_2CN	1.0267	−1.3242	0.7958	1.4834		
10 Me, Cl			0.2541	0.2534		
11 Me, OCOMe			0.5986	−0.2299		
12 H, CH_2SiMe_3			0.7551	−0.4203		
13 H, Bu^t	0.9527	0.7114	1.0578	−0.7036	1.0307	0.1546
14 H, OEt	0.8132	1.5211	0.8500	−1.2703	1.0183	0.9819
15 Me, OMe			0.8409	−1.3205		

components were retained in all the three cases to describe the original variables. For these principal components the component loading and component score values are given in Table 4.

Data Set (*A*).—A plot of the component loadings (A2 *vs.* A1) is shown in Fig. 1. A significant grouping of the radicals can be seen from the figure, according to similarity in reactivity: (I) more nucleophilic radicals (*tert*-butyl, 2-hydroxyprop-2-yl); (II) 'benzylic' radicals (benzyl, *para*-methylbenzyl, *para*-fluorobenzyl, *para*-methoxybenzyl); (III) less nucleophilic radicals (borderline cases)[13] (2-cyanoprop-2-yl, *tert*-butoxycarbonylmethyl, *para*-cyanobenzyl).

The component scores were found to be significantly correlated with various thermodynamic properties of the alkenes. The first principal component correlates with electron affinity and exothermicity, the second principal component with ionization potential [eqns. (3)–(5)]; where N is the number

$$C1 = (-0.012\,62 \pm 0.002\,705)\,E_e - (1.245 \pm 0.3205) \quad (3)$$
$$N = 8, r = 0.885, F = 21.8, s = 0.502$$

$$C1 = (-0.030\,75 \pm 0.011\,06)\,(-\Delta_r H) - (0.006\,248 \pm 0.002\,594)\,E_e + (1.291 \pm 0.9436) \quad (4)$$
$$N = 7, r = 0.971, F = 32.8, s = 0.289$$

$$C2 = (-0.009\,324 \pm 0.003\,741)\,E_i + (8.621 \pm 3.470) \quad (5)$$
$$N = 8, r = 0.713, F = 6.21, s = 0.757$$

of points included in the regression calculations, r is the (multiple) correlation coefficient, F is the overall Fisher's test value, s is the standard error of the estimate and the values in parentheses are the regression coefficients and their standard errors. Note that one alkene (allyl cyanide) had to be omitted from eqn. (4) since no $(-\Delta_r H)$ value was available (see Table 1).

Although the correlation coefficient of eqn. (5) is rather low, the equation is significant at the 5% level. Moreover, the correlation coefficient of the corresponding eqn. (8) based on the larger data set (B) is much higher, and the same conclusions can be drawn from the two equations.

The regression coefficient of E_e in eqn. (3) is quite different from that in eqn. (4). The reason is that the E_e and $(-\Delta_r H)$ variables in eqn. (4) are intercorrelated ($r = -0.795$). In spite of this intercorrelation, however, the signs of the two regression coefficients are the same, therefore both equations lead to the same interpretation.

The correlations of C1 and C2 with E_e and E_i are in agreement with the Frontier Molecular Orbital model. The equations show that C1 and C2 can be considered as descriptors of the nucleophilic and electrophilic radical reactivity, respectively. That means the radical reactivities analysed are composed of a nucleophilic and an electrophilic component. In other words, each radical involved in the present study bears both a nucleophilic and an electrophilic character, although they are generally considered as nucleophilic, *i.e.* the SOMO–HOMO interaction cannot be neglected in the case of nucleophilic radicals either.

Furthermore, eqn. (4) shows that Hammond's postulate also applies here, by showing that an increase in $(-\Delta_r H)$ corresponds to a decrease in C1, *i.e.* the more exothermic is the reaction, the higher will be the rate of reaction since all the corresponding component loading values are negative.

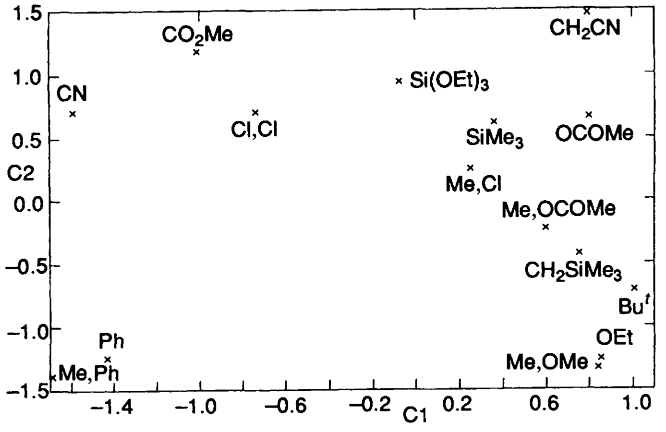

Fig. 2 Plot of component scores C2 *vs.* C1 in case (B). For the notations see Table 1.

Data Set (B).—The component loading plot obtained is quite similar to that for data set (A).

A plot of the component scores (C2 *vs.* C1) is shown in Fig. 2. It can be seen from the figure that C1 divides the olefins into two groups in accordance with their similarity in reactivity toward the radicals involved in the present study: (I) 'fast-reacting' alkenes (acrylonitrile, methylstyrene, styrene, methyl acrylate, 1,1-dichloroethylene); (II) 'slow-reacting' olefins [triethoxy(vinyl)silane, trimethyl(vinyl)silane, vinyl acetate, allyl cyanide, 2-chloropropene, prop-2-enyl acetate, allyl(trimethyl)silane, *tert*-butylethylene, vinyl ethyl ether, prop-2-enyl methyl ether]. Of course, the above classification of olefins would be reversed in the case of electrophilic radicals.

The correlations obtained between the component scores and the thermodynamic properties of the alkenes are as shown in eqns. (6)–(8). Note that three alkenes [triethoxy(vinyl)silane, allyl cyanide, allyl(trimethyl)silane] had to be omitted from eqn. (7) since no $(-\Delta_rH)$ values were available (see Table 1).

$$C1 = (-0.013\,12 \pm 0.001\,833)E_e - (1.503 \pm 0.2421) \quad (6)$$
$$N = 15, r = 0.893, F = 51.2, s = 0.467$$

$$C1 = (-0.025\,14 \pm 0.007\,125)(-\Delta_rH) - (0.008\,759 \pm 0.001\,765)E_e + (0.4757 \pm 0.6001) \quad (7)$$
$$N = 12, r = 0.961, F = 53.7, s = 0.329$$

$$C2 = (0.011\,88 \pm 0.002\,120)E_i - (10.769 \pm 1.927) \quad (8)$$
$$N = 15, r = 0.841, F = 31.4, s = 0.561$$

Thus, the same conclusions can be drawn for data set (B) as for data set (A). This supports the validity of the conclusions since in the former case more radicals, while in the latter case more alkenes were involved in the calculations.

Data Set (C).—A plot of the component loadings (A2 *vs.* A1) is shown in Fig. 3. Two definite groups of points can be seen in the Figure. The group of less nucleophilic radicals (2-cyanoprop-2-yl, *tert*-butoxycarbonylmethyl, *para*-cyanobenzyl) also includes exothermicity $(-\Delta_rH)$. In other words, the rate constants for these radicals can be expected to be well correlated with exothermicity. This suggests that Hammond's postulate is adequate for describing the reactivities of less nucleophilic radicals.

This result is in accordance with the finding of Giese *et al.*[13] and Wong *et al.*[14] who stated that radical stabilization and reaction exothermicity rather than polar effects are dominant in influencing the reactivity of less nucleophilic radicals toward alkenes.

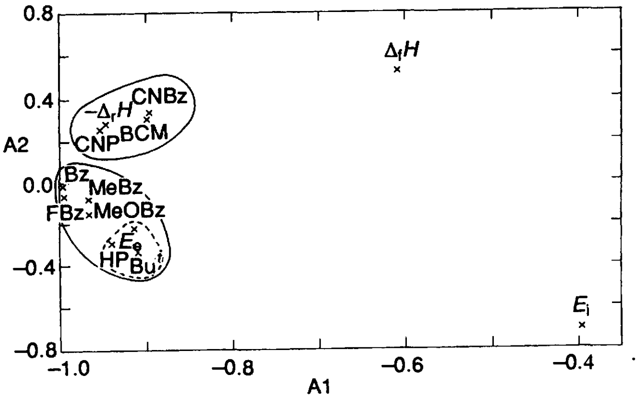

Fig. 3 Plot of component loadings As *vs.* A1 in case (C). For the notations see Table 1.

On the other hand, the second group consists of the more nucleophilic radicals (*tert*-butyl, 2-hydroxyprop-2-yl, benzyl, *para*-methylbenzyl, *para*-fluorobenzyl, *para*-methoxybenzyl) and of electron affinity (E_e). The points of the two most nucleophilic radicals are the closest to the point of electron affinity in accordance with the finding that polar effects play a decisive role in the respective reactions.[5,6,26] Therefore, the rate constants for these radicals can be expected to be well correlated with electron affinity. This implies that the FMO model is suitable for describing the reactivities of more nucleophilic radicals.

Fig. 3 also shows that the points representing heat of formation (Δ_fH) and ionization potential (E_i) are outliers. As to E_i, this is not surprising since none of the radicals in Table 1 is electrophilic. Δ_fH, as a term in the heat of reaction, was also expected to be an outlier.

The present analysis revealed the role of polar and enthalpic effects only in influencing radical addition reactions, and no steric effects were indicated. The reason is that this study was limited to vinyl type alkenes in which steric effects cannot play a decisive role.

Conclusions

Principal component analysis (PCA) was found to be capable of classifying the radicals and alkenes according to reactivities and characters.

The first two principal components, which explain nearly the total variance in the data, were found to be correlated with the electron affinity and ionization potential of alkenes as well as with exothermicity. This is in agreement with both the Frontier Molecular Orbital model and Hammond's postulate.

The results indicate that the rate constants for the less nucleophilic radicals will be well correlated with exothermicity, whereas the rate constants for the more nucleophilic radicals correlate with electron affinity. Thus, the reactivities of the less nucleophilic radicals appear to be well described by Hammond's postulate and those of the more nucleophilic radicals by the FMO model.

The final conclusion is that PCA was able to decompose the individual reactivities into nucleophilic and electrophilic components and to show that even nucleophilic radicals bear a definite electrophilic character. Furthermore, PCA could also reveal two major effects, *i.e.* the polar and enthalpic effects influencing radical addition reactions, as described by the FMO model and Hammond's postulate, respectively.

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