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STEREOSELECTIVES AND REACTION RATES IN DIELS–ALDER REACTIONS PROMOTED BY NON-AQUEOUS SOLVENTS AND THEIR AQUEOUS MIXTURES: CORRELATIONS WITH NON-ADJUSTABLE PARAMETERS*

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Stereoselectivities and rates of Diels–Alder reactions in different solvents were correlated with a parameter, Q, defined based on internal pressure, which is normalized with respect to a polarity scale. The polarity scale or index, although purely empirical in nature, can be calculated from the refractive index of the solvent. These correlations were linear for both stereoselectivities and reaction rates. Using expressions derived in this study, it is possible to represent the kinetic profiles of several Diels–Alder reactions in about 75 pure and mixed solvent media. The activation volume of a reaction can be directly estimated from the regression of data on rates and Q in various solvents using the proposed correlations.

1. INTRODUCTION

The Pioneering work of Breslow and Rideout[1] on the acceleration of Diels–Alder (D–A) reactions in aqueous solvent media has generated an upsurge in interest in examining the role of solvent media on the kinetic profiles of these reactions.[2] As part of our attempts to quantify the origin of possible forces responsible for the rate enhancement noted in these reactions, we recently correlated the reaction rates with a measurable property of solvent media, called the internal pressure (*Pi*) for various D–A reactions under different conditions in aqueous and non-aqueous ionic media.[3] We noted that internal pressure coupled with the activation volume of a reaction, ΔV, can describe the rate enhancement in such reactions, suggesting that the internal pressure induced by the ion-containing solvent media may act as a substitute for external pressure.

In literature, the free energy relationship[4] has been used for several years to describe the kinetic profiles of the D–A reactions in a variety of pure and mixed solvent media. Advanced developments, however, have centred around the building and testing of regression models involving four or five parameters.[5–7] Since the concept of internal pressure in correlating the rates of the D–A reactions in salt–solvent media was noted to be successful, it was thought useful to quantify the role of pure and mixed solvents (without any ionic species) in the kinetic parameters of these reactions.

In the present investigation, we therefore attempted to correlate the stereoselectivities and rate data with a solvent parameter, defined on the basis of internal pressure and polarity of the reaction medium. The solvent property used in this approach can be calculated independently from the available basic properties of solvent molecules. It is also shown that the activation volume of a reaction can be easily estimated from the proposed correlations. Several D–A reactions in about 75 solvents were examined in this work.

DEVELOPMENT OF OPERATIONAL EQUATIONS

Let us consider a D–A reaction between a diene, A, and a dienophile, B, in a solvent, S, to produce a cycloadduct via a transition state, TS. The apparent rate constant, k, can be defined as

$$k = k^{\circ}\gamma_A\gamma_B/\gamma_{TS} \tag{1}$$

where k° is the rate constant for an ideal reference system and γ is the activity coefficient of the relevant

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species. The activity coefficient of any species i in solution can be defined in terms of its molar volume and internal pressure, when normalized to a parameter expressing a relative polarity index of the medium. Thus,

$$\ln \gamma_i = v_i \theta_i / RT \qquad (2)$$

where θ_i accounts for the difference in the internal pressure terms of any species (A, B or TS) with respect to that of the solvent or solvent mixture:

$$\theta_i = [(Pi/nr)_i^{1/2} - (Pi/nr)^{1/2}]^2 \qquad (3)$$

and R and T are the universal gas constant and absolute temperature, respectively.

In fact, Pi is the internal pressure of a solvent or a solvent mixture and nr is a parameter indicating the polarity of the medium. the significance of the nr parameter, specific to a medium, will be discussed later during the analysis of experimental data.

For a D–A reaction involving reactants (i) and TS(j), one can write

$$\ln k = \ln k^\circ + \left(\sum_{i=1}^{2} \upsilon_i \theta_i - \sum_{j=1}^{1/2} \upsilon_j \theta_j \right) \Big/ RT \qquad (4)$$

Equation (4) can be explored for different cases, as follows.

(a) For the rate of reaction resulting in *endo* and *exo* stereoisomers via two separate transition states.

In such a case, both A and B are common in both transition states, so terms involving A and B or i are dropped. The transition states yielding *endo* and *exo* forms only appear in the expression which can be written with the help of equation (3) for the relative rate constant ratio, $\ln(k_N/k_X)_{rel}$ defined with respect to that in the ideal transition state as

$$\ln(k_N/k_X)_{rel} = (v_{TS,X}\theta_{TS,X} - v_{TS,N}\theta_{TS,N})/RT \qquad (5)$$

Expansion of above equation with the help of equation (3) written individually for transition states N and X yields

$$\begin{aligned}\ln(k_N/k_X)_{rel} = \{ & v_{TS,X}[(Pi/nr)_{TS,X} \\ & -2(Pi/nr)^{1/2}_{TS,X}(Pi/nr)^{1/2} \\ & + (Pi/nr)] - v_{TS,N}[(Pi/nr)_{TS,N} \\ & - 2(Pi/nr)^{1/2}_{TS,N}(Pi/nr)^{1/2} \\ & + (Pi/nr]\}/RT \qquad (6)\end{aligned}$$

Simplifying the above equation and also setting $v_{TS,X} = v_{TS,N}$, as X and N are isomers, gives

$$\begin{aligned}\ln\ (k_N/k_N)\mathrm{rel} = (& v_{TS,N}\{[(Pi/nr)^{1/2}_{TS,N} \\ & - 2(Pi/nr)^{1/2}_{TS,X}]2(Pi/nr)^{1/2}\} \\ & + \{v_{TS,N}[(Pi/nr)_{TS,X} - (Pi/nr)_{TS,N}]\})/RT \qquad (7)\end{aligned}$$

$$\log(k_N/k_X)_{rel} = 1/2{\cdot}303RT\,(Int. + Sl.Q) \qquad (8)$$

where

$$\begin{aligned} Sl. = v_{TS,N}[&(Pi/nr)^{1/2}_{TS,N} - 2(Pi/nr)^{1/2}_{TS,X} \\ & - 2(Pi/nr)^{1/2}_{TS,X}] \qquad (9a)\end{aligned}$$

$$Int. = v_{TS,N}[(Pi/nr)_{TS,X} - (Pi/nr)_{TS,N}] \qquad (9b)$$

and

$$Q = 2(Pi/nr)^{1/2} \qquad (9c)$$

Hence it is possible to evaluate the values of *Int.* and *Sl.* from an analysis of the experimental rate data for a reaction. Equation (8) is an operational expression yielding a linear plot between $\log(k_N/k_X)$ and Q for a given reaction in different solvents.

(b) For ratios of *endo* and *exo* stereoisomers.

Since *endo* and *exo* ratios are directly proportional to k_N/k_X, one can write

$$\log(\mathrm{N/X}) = (1/a \times 2{\cdot}303RT)(\mathrm{Int.} + Sl.)Q \qquad (10)$$

where a is a proportionality constant. A linear plot between log(N/X) and Q can be obtained as described above.

(c) For a reaction of A and B in a solvent medium with a single TS.

Equation (4), written for expressing ln k_{rel} with respect to Q in the above case, can be solved as

$$\begin{aligned}\ln k_{rel} = 1/RT[& v_A(Pi/nr)_A + v_B(Pi/nr)_B \\ & - v_{TS}(Pi/nr)_{TS} + 0{\cdot}25Q^2(v_A + v_B - v_{TS}) \\ & + Q(v_{TS}(Pi/nr)_{TS}{}^{1/2} - v_A(Pi/nr)_A{}^{1/2} \\ & - v_B(Pi/nr)_B{}^{1/2}] \qquad (11)\end{aligned}$$

Dropping the first three terms of right-hand side of equation (11) as a result of a thermodynamic cycle[8] gives

$$\begin{aligned}\log k_{rel}/Q = 1/2{\cdot}303RT\{&[v_{TS}(Pi/nr)_{TS}{}^{1/2} \\ & - v_A(Pi/nr)_A{}^{1/2} - v_B(Pi/nr)_B{}^{1/2}] \\ & + 0{\cdot}25Q(v_A + v_B - v_{TS})\} \qquad (12)\end{aligned}$$

A plot of $\log k_{rel}/Q$ (denoted by Y for convenience) versus Q for a reaction yields a straight line with a slope

$$Sl. = 0{\cdot}25(v_A + v_B - v_{TS}) \qquad (13a)$$

and intercept

$$Int. = [v_{TS}(Pi/nr)_{TS}{}^{1/2} - v_A(Pi/nr)_A{}^{1/2} - v_B(Pi/nr)_B]^{1/2} \qquad (13b)$$

Although the slope is obtained as an adjustable parameter from a least-squares fitting between reaction rates and Q data, one can extract the approximate value of $\Delta V^\ddagger$, which is an important activation parameter of the reaction. This activation parameter, called the activation volume of a reaction, is a useful tool for describing the pressure dependence of the reaction rates.[9] Employing the definition $\Delta V^\ddagger = v_{TS} - v_A - v_B$ in the expression for the slope, one can obtain the value of $\Delta V^\ddagger$ as

$$\Delta V^\ddagger = 2{\cdot}303Sl.RT/0{\cdot}25 \qquad (14)$$

Simple expressions can also be developed in a similar fashion for the reactions, where either A or B is common in two reactions. It is therefore possible to treat the kinetic data on the reaction rates and stereoselectivities.

In the above set of equations, two quantities, *Pi* and *nr*, are used in both pure and mixed solvent media. As discussed earlier, *Pi* is a result of intermolecular forces in the liquid state,[10] which has also received support from the equation of state.[11] Calculations of *Pi* for a solvent are straightforward using the relationship

$$Pi = \alpha T/\beta \qquad (15)$$

where α and β are the thermal expansion coefficient and isothermal compressibility, respectively, of a solvent at temperature T. Alternatively, the Tammann–Tait–Gibson (TTG) model can be used to calculate the *Pi* values with confidence.[12]

In the case of mixed solvents, α and β can be calculated from experimental volumetric and compressibility data. In the absence of experimental data, use can be made of the scaled particle theory (SPT) for generating α and β values in mixtures.[13,14] The agreement between *Pi* values obtained by SPT and experimental data is excellent (within 3%) in several cases.[3] The mixing rule used in calculations of *Pi* for the mixed solvents is reasonably accurate, as evidenced by many studies.[15]

The polarity of a solvent, in general, plays a significant role in influencing the kinetics of a reaction. Several measures to denote the polarity of a solvent medium are available in the literature; a different method, however, was adopted in the current investigation. A relative polarity parameter, *nr*, of a solvent can be defined as the refractive index, n_D, of a solvent divided by n_D of *n*-hexane. We chose *n*-hexane, a non-polar solvent, as a reference solvent. Thus, $nr = n_D$ of a solvent in question/n_D of *n*-hexane. This choice of definition is purely empirical in nature and has been observed to be more suitable in the present case over some other combinations of refractive index and dielectric constant.[16] In the case of mixed solvents, a linear mixing over mole fractions x_i given by

$$nr_m = \sum_i x_i nr_i \qquad (16)$$

As seen earlier, the values of Q for any solvent medium can be calculated from a knowledge of experimental data. It is possible, however, to estimate these values by the following expression obtained from the regression of available data on 100 solvents:

$$Q = 93{\cdot}6 + 364{\cdot}1\, nr \qquad (17)$$

RESULTS AND DISCUSSION

We examined the validity of our approach to several Diels–Alder reactions in a variety of solvents. Equations (8), (10) and (12), representing $\log(k_N/k_X)$, $\log(N/X)$ and $\log k_{rel}$, respectively, were tested against reactions with the corresponding experimental data. In Table 1 are recorded the values of *Int.* and *Sl.* as obtained from the least-squares fitting of rate (k) and stereoselectivity (N/X) data versus Q. Also given in Table 1 are the number of solvents, N, correlation coefficients, r, standard deviation, σ, of fits and source of data. The names of substrates indicated by R and the solvents employed are also included in Table 1. Molecular size data of solvents and their refractive indices were taken from elsewhere.[16]

Reactions between R1 + R2 i.e. cyclopentadiene and methyl acrylate, is a commonly studied D–A reaction. The reaction rates fitted for this system are shown in Figure 1, where the Y term and Q correlate in a linear fashion with $\gamma = 0{\cdot}965$. Two systematic and consistent data sets from independent sources[4b,6d] on N/X ratios for the same reaction were investigated. The results of such an exercise are demonstrated in Figure 2, where the calculated log(N/X) values are plotted against those obtained from the experimental work. The analysis of log(N/X) data both from Berson *et al.*[4b] and Cativiela *et al.*[6d] offered intercepts and slopes to within a difference of 0·003 and $0{\cdot}05 \times 10^{-2}$, respectively. A combined data fit was also carried with a total number of 28 solvents. Slightly larger deviations between the observed and calculated (N/X) values in methanol–water (30%) and dioxane were noted, but the overall results remained almost unaltered without these two solvents.

Application of the present approach to the $\log(k_N/k_X)$ data of this reaction against the Q values for 18 solvents yielded a good linear relationship with $\sigma = 0{\cdot}060$ (Figure 1). The solvents used for the reaction included aqueous mixtures of methanol, acetone and dioxane in several compositions, in addition to many pure solvents. For the reaction of R1 with methyl vinyl ketone (R3), the log(N/X) versus Q plot is shown in Figure 1. In this case, the maximum deviation from the linearity was observed at higher Q values by two solvents. A linear relationship is obtained with $r = 0{\cdot}989$ and 0·065 with log(N/X) for this reaction in 16 solvents, except trifluoroethanol and hexafluoropropan-2-ol. With all 18 solvents $r = 0{\cdot}980$ and 0·045 are obtained for the reaction. A linear relationship is obtained for log(N/X) data as a function of Q for the reactions of cyclopentadiene with methyl methacrylate (R4) and transcrotonate (R5) in ten solvents for each reaction.[4b] The calculated and experimental log(N/X) values fall close to or at an angle of 45°, showing the quality of fits. Reactions of R1 with R2 , R4 and R5 are noted to show pro-, anti- and borderline cases of the Alder rule. The slopes obtained in our studies indicate that their values increase on going from pro- , borderline to anti-Alder rules. Since Q is essentially a pressure parameter, it is possible to compute the ratios of the volumes

Table 1. Summary of analysis of Diels–Alder reactions by applications of equations (8), (11) and (12)[a]

Property (log)	No. of solvents	*Int.*	*Sl.* ×10⁴	*r*	σ	Ref.
R1 + R2						
N/X	18	2·0405	-107·7	0·990	0·025	6d
N/X	10	2·0379	-105·5	0·987	0·042	4b
k_{rel}	18	-0·0352	1·203	0·965	0·060	6b
k_N/k_X	10	2·0367	-105·4	0·984	0·080	4b
R1 + R3						
N/X	18	2·5597	-143·3	0·980	0·045	6d
R1 + R4						
N/X	10	1·0033	-78·20	0·989	0·048	4b
R1 + R5						
N/X	10	1·2210	-87·28	0·981	0·041	4b
R1 + R6						
k_{rel}	17	-0·0539	1·5415	0·971	0·085	6c
N/X	17	-2·6144	143·8	0·900	0·026	6c
R1 + R7						
k_{rel}	6[b]	0·0251	-4·0473	0·969	0·053	6a
N/X	6[b]	0·7644	-52·71	0·970	0·052	6a
k_{rel}	6[c]	0·0207	-3·1672	0·961	0·058	6a
N/X	6[c]	0·7647	-49·98	0·979	0·050	6a
R8 + R9						
k_{rel}	26	-0·0426	1·4377	0·948	0·091	7e
R8 + R10						
k_{rel}	26	-0·0388	1·5653	0·979	0·056	7e
R8 + R11						
k_{rel}	16	-0·0468	1·3209	0·972	0·077	7a
R8 + R12						
k_{rel}	10	-0·0387	1·0951	0·920	0·129	7d
R8 + R13						
k_{rel}	10	-0·0428	1·1589	0·919	0·147	7d
R14 + R17						
k_{rel}	27	-0·0468	1·571	0·963	0·064	7b
R15 + R17						
k_{rel}	27	-0·0530	1·3490	0·946	0·090	7b
R16						
k_{rel}	21	-0·0458	0·8481	0·944	0·103	7c
R1 + R18						
k_{rel}	13	-0·0201	3·5176	0·952	0·083	5a
R1 + R19						
N/X	7	2·7293	124·2	0·966	0·065	5b

(continued)

Table 1. *Continued*

Property (log)	No. of solvents	*Int.*	*Sl.* ×10⁴	*r*	*σ*	Ref.
R20 + R21						
k_{rel}	15	−0·0261	1·6671	0·948	0·090	18
R1 + R22						
k_{rel}	15	−0·0558	1·5415	0·949	0·088	19
R1 + R23						
k_{rel}	10	−0·0588	1·3990	0·940	0·105	19
R1 + R24						
k_{rel}	10	−0·0510	1·0491	0·955	0·065	19

[a] r = Correlation coefficient; σ = standard deviation. Substrates: R1 = cyclopentadiene; R2 = methyl acrylate; R3 = methyl vinyl keton; R4 = methyl methacrylate; R5 = methyl transcrotonate; R6 = (-)-menthyl acrylate; R7 = methyl (*E*)-α-cynanocinnamate; R8 = 2,3-dimethylbutadiene; R9 = diethyl azodicarboxylate; R10 = 4-bromonitrosobenzene; R11 = 1,4-naphthoquinone; R12 = 5-hydroxy-1,4-naphthoquinone; R13 = 5-methoxy-1,5-naphthoquinone; R14 = 4-(*p*-nitro)benzylidene-1-phenylpyrazol-5-one; R15 = 4-(*o*-methoxy)benzylidene-1-phenylpyrazol-5-one; R16 = 1-phenyl-4-2-(3-methyl-2-butenyloxy)benzylidenepyrazolone; R17 = isobutyl vinyl ether; R18 = diethyl fumarate; R19 = monoethyl maleate; R20 = anthracene; R21 = tetracyanoethylene; R22 = acrolein: R23 = crotonaldehyde; R24 = methacrolein. Solvents: acetic acid; acetone; acetone–water (10–90%); acetonitrile; *tert*-amyl alcohol; benzene; benzonitrile; benzyl alcohol; benzyl chloride; bromobenzene; isobutanol; *sec*-butanol; *tert*-butanol; chloroform; chlorobenzene; cyclohexane; cyclohexanone; cyclohexanol; 1,2-dichloroethane; diethyl ether; diglyme; 1,2-dichloromethane; dioxane; dioxane–water (10–90%); DMF; DMSO; 1,2-dimethoxyethane; ethanol; ethyl acetate; ethylene dichloride; fluorobenzene; formamide; hexane; hexafluoropropan-2-ol; mesitylene; methanol; methanol–water (10–90%); methyl acetate; nitrobenzene; nitromethane; *tert*-pentyl alcohol; *n*-propanol; propan-2-ol; proprionitrile; propylene carbonate; pyridine; sulpholane; toluene; triethylamine; trifluoroethanol; water; *p*-xylene.

[b] Acetone–water mixture.

[c] Dioxane–water mixture.

for *endo* and *exo* forms from the kinetic data.[5b] As expected, these volume ratios fall approximately in the order >1, 1 and <1 for pro-, borderline and anti-Alder types of reactions, respectively. Appropriate differentiation[17] of log (k_N/k_X) with respect to Q yielded v_N/v_X ratios of 1·19, 0·88 and 0·98 for pro-, anti- and borderline cases for R1 + R2, R1 + R4 and R1 + R5, respectively.

Cativiela *et al.*[6a] studied the rates and N/X selectivity of the D–A reaction of R1 with R7 in six aqueous mixtures of acetone and dioxane. For the sake of illustration, in Figure 1 are shown both the rates and selectivities as a function of Q in one type of solvent medium for each kinetic property. As can be seen from these curves and the results given in Table 1, both the reaction rates and N/X ratios vary linearly with respect

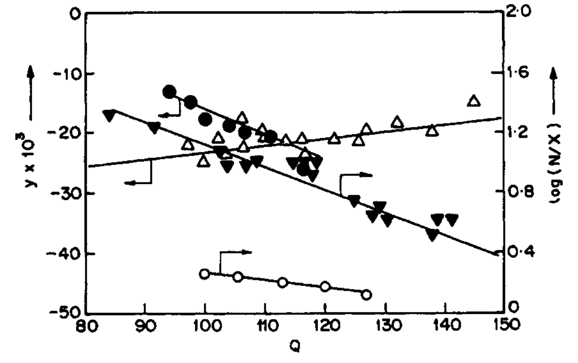

Figure 1. Plots of Y ($\log k_{rel}/Q$) against Q for reaction R1 + R2 (△) Ref. 6b; reaction R1 + R7 (acetone–water) (●) Ref. 6a; log(N/X) versus Q for reactions of R1 + R7 (dioxane–water) (○) Ref. 6a; log(N/X) versus Q for R1 + R3 (▼) Ref. 6d

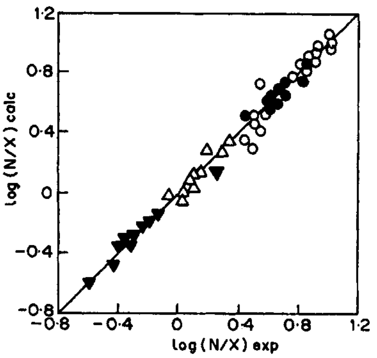

Figure 2. Plots of $\log(N/X)_{calc.}$ obtained from the present work against the experimental data for reaction of R1 + R2 ((●) Ref. 4b; (○) Ref. 6d; reaction of R1 + R4 (▼) Ref. 4b; reaction of R1 + R5 (▽) Ref. 4b

to Q with an average σ.0·050. Although the values of log(N/X) plotted against Q do not vary significantly, it should be noted that the correlation can be considered acceptable for such cases in view of its success in describing the large variations in log(N/X) in several systems.

Solvent effects were also observed in asymmetric D–A reactions. For such a reaction of R1 with R6 in a variety of solvent media, of both pure and mixed, the plots of log (N/X) and $\log(k_N/k_X)$ against Q are depicted in Figure 3. Both the kinetic parameters yield straight lines, involving all 17 solvents, either pure or as aqueous mixtures.

Schneider and Sangwan[5] reported reaction rates and N/X ratios for the reactions of R1 with R18 and R19 and correlated them successfully using a multiple regression model. The solvents they chose were aqueous mixtures of methanol and dioxane in addition to pure solvents. In our study, as seen in Figure 3, the correlations for log(N/X) and Y are noted to be successful. For reactions of R1 with R18 and R19, the proposed equations can account for rates and stereoselectivities with $\sigma = 0{\cdot}083$ and 0·065, respectively.

Several reactions were conducted in a variety of solvents, where a diene has been chosen as a common reactant. Such reactions involve, e.g., isobutyl vinyl ether (R7), cyclopentadiene (R1) and 2,3-dimethylbutadiene (R8) as the diene. The performance of our equations is demonstrated in Figures 3 and 4, where Y values are plotted against Q for R17 with R14 and R8 with R9, R10 and R11. These reactions, chosen for the purpose of illustration, all yield excellent linear relationships. In Figure 3, both the reactions, i.e. R14 + R17 and R15 + R17, can be fitted by the proposed equations yielding $\sigma = 0{\cdot}064$ and 0·090, respectively. Similar results are shown in the form of Y versus Q plots in Figure 4 for several reactions. The reactions of R8 with R9, R10 and R11 can be easily represented in terms of our equations. For these three reactions, the σ values vary between 0·056 to 0·091. For the R8 + R12 reactions, however, a slightly greater scatter of the experimental data points was noted, yielding $\sigma = 0{\cdot}129$. A similar situation was noted for the R8 + R13 reaction.

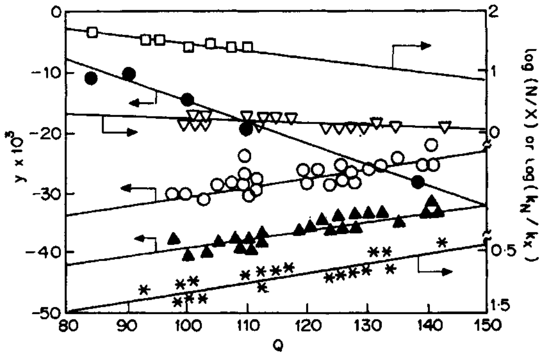

Figure 3. Plots of Y and $\log(k_N/kX)$ or log(N/X) against Q for reactions of R1 + R18 (●) Ref. 5a; R14 + R17 (○) Ref. 7b; R15 + R17 (▲) Ref. 7b; and log(N/X) as a function of Q R1 + R19 (□) Ref. 5b; R1 + R6 (▽) Ref. 6c; $\log(k_N/k_X)$ against Q for R1 + R6 (*) Ref. 6c

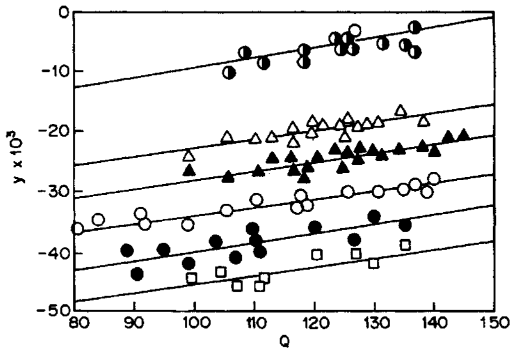

Figure 4. Plots of experimental Y values against Q for reactions of R8 + R9 (▲) Ref. 7e; R8 + R10 (△) Ref. 7e; R8 + R11 (○) Ref. 7a; R1 + R22 (●) Ref. 19; R1 + R23 (□) Ref. 19; R20 + R21 (◑) Ref. 19.

From plots given for several reactions, maximum random scattering was noted in the cases of cyclopentadiene with acrolein (R20) and crotonaldehyde (R23). The values of r and σ in these reactions, however, suggest the ability of our equations to analyse experimental data. Good correlations are also noted for the reaction of R20 with R21 in as many as 15 solvents.

The linear correlations between rate or *endo/exo* quantities and Q parameters of various solvents show that our equations are applicable not only to pure nonelectrolytic solvent media, but also to their aqueous mixtures used frequently in synthetic work. This also implies that the linear mixing rule employed for calculating nr and Pi in aqueous solvent mixtures holds good. Hence this implication simplifies the procedure for the calculation of the Q parameters.

As discussed earlier, several modifications of multiple linear regression methods using solvent properties have been reported for describing kinetic parameters. In this paper, it was not our intention to present a detailed comparative performance of our method with those already existing. It should be mentioned however, that the modification of equations involving two to four solvent parameters offers better fits of the kinetic data.

Recently, the Abboud–Abraham–Kamlet–Taft (AAKT) model has been applied[6d] for fitting the N/X ratios of the reactions of R1 with R2 and R3. This model employs parameters indicating hydrogen bond-donating

Table 2. Activation volumes, $\Delta V^{\ddagger}$, obtained with the present method for several Diels–Alder reactions

Reactions	$-\Delta V^{\ddagger}$ ($cm^3 mol^{-1}$)	Reactions	$-\Delta V^{\ddagger}$ ($cm^3 mol^{-1}$)
R1 + R2	27.54	R1 + R6	35.79
R1 + R7 (acetone–water)	91.5	R1 + R7 (dioxane–water)	72.3
R8 + R9	33.35	R8 + R10	36.29
R8 + R11	35.70	R8 + R12	29.58
R8 + R13	31.34	R14 + R17	37.16
R15 + R17	31.91	R16	20.96
R1 + R18	79.9	R20 + R21	38.71
R1 + R22	41.68	R1 + R23	37.82
R1 + R24	28.29		

and -accenting abilities together with dipolarity of the reaction media. The use of these three parameters gives accurate fits of log(N/X) data. The calculated values of log(N/X) obtained by our method are in excellent agreement with those obtained by the use of the AKKT model. For example, in the case of a reaction involving R1 and R2, our values of $r = 0\cdot990$ and $\sigma = 0\cdot019$ are comparable to those obtained by the AKKT model, as $r = 0\cdot997$ and $\sigma = 0\cdot019$, obtained using four adjustable parameters. Such an agreement between the values of the rate constants is also seen for other reactions. In general, the predictions of the kinetic profiles of the D–A reactions by other models are based on the multiparameter treatment, whereas comparable predictions can be obtained by using a single solvent property.

The correlations presented here are primarily based on the concept of internal pressure of solvents. Treatment of reaction rate data using equation (12) can also give the activation volume, $\Delta V^{\ddagger}$, of a reaction. The mechanism to facilitate the D–A reaction in terms of $\Delta V^{\ddagger}$ was given by Van Eldik and Le Noble.[9] In Table 2 are listed the $\Delta V^{\ddagger}$ values for these reactions as estimated from equation (14). The D–A reactions are accompanied by negative activation volumes,[7] as also confirmed by the $\Delta V^{\ddagger}$ values listed in Table 2. These negative $\Delta V^{\ddagger}$ values are due to the compact transition states found in such reactions. The kinetic behaviour in these reactions can thus be thought to be related to the combined effects of $\Delta V^{\ddagger}$ and internal pressure. The magnitudes of $\Delta V^{\ddagger}$ for several reactions obtained from this work seems to be in an acceptable range when compared with the literature values.[9] For instance, the experimental $\Delta V^{\ddagger}$ values for the reaction of anthracene-9-methanol with *N*-ethylmaleimide have been reported as $-36\cdot0$, $-31\cdot4$ and $-28\cdot4$ $cm^3 mol^{-1}$, in water, *n*-butanol and heptane, respectively.[20] The reaction was conducted at 45 °C and external pressures ranging from 1 to 900 bar. The analysis of these data by the present method yields $\Delta V^{\ddagger}$ values of $-34\cdot0$, $-29\cdot9$ and $-27\cdot4$ $cm^3 mol^{-1}$, respectively. The solvent parameter *Q* under the reaction conditions was computed from the volumetric information reported elsewhere.[16]

The close agreement between the calculated and experimental values reaffirms two aspects: (a) reliable estimates of the volume of activation for a reaction can be obtained by the proposed correlation and (b) the internal pressure of a solvent system and the external pressure play the identical roles in the reaction kinetics of D–A reactions. The role of internal pressure assumes significance in its correlation with the reaction rates, when $\Delta V^{\ddagger}$ is negative.

CONCLUSION

We have attempted to correlate the rate and stereoselectivity data of several Diels–Alder reactions in a variety of non-aqueous solvents and their aqueous mixtures. Important features of this study can be summarized as follows:

1. No adjustable parameter is required to describe the kinetic profiles of the D–A reactions.
2. The internal pressure for a solvent system can be accurately calculated *a priori*. The polarity is incorporated in the internal pressure by a relative polarity index, defined by treating the refractive index of *n*-hexane as a reference solvent. The choice of the reference solvent is purely empirical in nature.
3. The solvent property, a combination of internal Pressure and relative polarity index, although measurable by experiments, can also be estimated by a linear relationship evaluated from the regression of about 100 solvents.

Our current objective is to gain insight into the role of multicomponent solvent media, including ions and melts, in the kinetic profiles of these reactions. The correlations presented here are part of our attempts in this direction. The results obtained from our ongoing studies on complex solvent media are interesting and will be published in the near future.

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