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Quantitative Prediction of Leaving Group Orders from Aliphatic Carbon in S_N2 Reactions

by

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Quantitative Prediction of Leaving Group Orders from Aliphatic Carbon in S_N2 Reactions

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Two quantitative correlations of leaving groups effects from aliphatic carbon in bimolecular nucleophilic substitution reactions were given by using Edwards equation;

$$CH_3Y + X^- \xrightarrow{k} CH_3X + Y^-$$

$$\log k/k_0 = \alpha E_x + \beta H_x$$

in which k and k_0 are the reaction rate constants of the substrate with a nucleophile, X and water, respectively, at 25.0°C. E_x is the oxidative dimerization potential and H_x is the basicity of the nucleophile, relative to water. Leaving group reactivity order is a function of oxidation and basicity of the leaving group. In a serie of alkyl substrates, CH_3Y, the substrate constant α depends linearly to the E_{y-} and the substrate constant, log β depends linearly to the H_{y-}.

$$\alpha = 1.11\ E_{Y-} + 0.87$$

$$\log \beta = 0.13\ H_{Y-} - 1.36$$

Using these equations, new substrate constants and then the rate constants of bimolecular nucleophilic substitution reactions on CH_3Y compounds in water, at 25.0°C can be estimated.

INTRODUCTION

This work undertaken in order to establish a quantitative correlation of leaving group effects from aliphatic carbon in bimolecular nucleophilic substitution reactions by

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using Edward's equation. Edwards equation (1–5) is a linear free energy relationship in which nucleophilic reactivity is correlated with a linear combination of the oxidative potential and the basicity of the nucleophile by means of eq (1).

$$\log k/k_0 = \alpha E_x + \beta H_x \qquad (1)$$

$$CH_3Y + X^- \rightarrow CH_3X + Y^- \qquad (2)$$

$$CH_3Y + H_2O \rightarrow CH_3OH + H^+ + Y^- \qquad (3)$$

$$E_x \equiv \varepsilon + 2{,}60 \text{ v.} \qquad (4)$$

$$2X^- \rightleftarrows X_2 + 2e \qquad : \varepsilon \qquad (5)$$

$$H_x \equiv pK_a + 1{,}74 \qquad (6)$$

$$X^- + H^+ \rightleftarrows HX \qquad : pK_a \qquad (7)$$

The rate constants k and k_0 refer to the reactions of a substrate CH_3Y, with a nucleophile, X in eq. (1) and water as a reference nucleophile, in eq. (2); E_x is defined by eq. (4) where ε is the oxidative dimerization potential of the nucleophile in the equilibrium reaction (5), H_x is defined by eq. (6) where pK_a is the acidity constant of the conjugate acid of the nucleophile in the reaction (7). 2.60 v. and 1.74 are correction terms for the ε and pK_a of water. All the data are in water at 25.0°C.

Edwards equation, now called oxibase scale by Davis (7), is quantitatively good for nucleophilic displacaments on aliphatic carbon. Davis (8) also gave the following equation serving as a more general oxibase scale,

$$\log k_1/k_2 = \alpha (\varepsilon_1 - \varepsilon_2) + \beta (pK_{a1} - pK_{a2}) \qquad (8)$$

in which k_1/k_2 is the rate constant for the reaction of a substrate with a nucleophile 1 relative to that for reaction with a nucleophile 2. In this equation, the k_1, k_2, ε and pK_a vaules can be used at the same proper temperature from 0 to 100°C and without the necessity of the reference nucleophile, water.

The use of oxibase scale to predict leaving group orders from carbon in S_N2 reactions was first made by Davis (7).

For the parameters α and β for a serie of alkyl substrates RY, where Y is a variety of leaving groups; he found a linear relationship between α and E_{Y^-} with a slope equal to unity as predicted from theory. The substrates were CH_3Y and $CH_2YCOONa$ and Y was Cl, Br, I and OTs (p-toluenesulphonate). The value of β appeared to be related to the electronegativity difference $(x_Y\text{-}x_R)^2$ and increase as Y becomes more electronegative relative to R.

In this work, the substrate parameters α and β of a serie of alkyl substrates CH_3Y were found from literature as in the case of CH_3Cl, CH_3Br, CH_3I and CH_3OTs or computed as a result of this study on CH_3F and CH_3CN and the dependence of the substrate parameters to the nucleophilic constants of the leaving group (legate) i.e. oxidation potentials and basicity, was investigated. As a leaving group is a nucleophile leaving the reaction center, its reactivity can be correlated with its nucleophilic constants. It was shown that leaving group order is a function of oxidation and basicity of the leaving group.

RESULTS AND DİSCUSSİON

The substrate parameters, α and β of CH_3F and CH_3CN in water at 25°.OC.

Using the kinetic data given by Marshall and Moelwyn-Hughes (9) and the oxibase scale given by Davis (8), the substrate parameters α and β of CH_3F and CH_3CN in water at 25°.OC were computed by least squares adjustment. They were found $\alpha = 1.03$ and $\beta = 0.156$ for CH_3F and $\alpha = 3.45$ and $\beta = 0.462$ for CH_3CN.

The substrate parameters of a serie of alkyl substrates CH_3Y and their dependence to the nucleophilic constants of leaving group, Y.

The substrate parameters α and β of a serie of alkyl substrates, CH_3Y and the oxidative dimerization potentials, ε_{Y^-} and basicity constants, $pK_{a_{Y^-}}$ of leaving groups, Y, all in water at 25.0°C are given in Table 1.

TABLE 1

Substrate parameters α and β (Edwards) of CH_3Y compounds and oxidative dimerization potential ε_{Y^-} and basicity constant $pK_{a_{Y^-}}$ of leaving groups, Y, in water at 25.0°C.

CH_3Y	α	β	Ref.	ε_{Y^-}[b]	pKa_{Y^-}[c]
CH_3F	1.03	0.156	This work	—2.87	3.2
CH_3Cl	2.25	0.008	d	—1.36	—7.0
CH_3Br	2.50	0.006	d	—1.09	—9.0
CH_3I	2.95	—0.003	e	—0.54	—9.5
CH_3CN	3.45	0.462	This work	0.19	9.2
CH_3OTs[a]	1.50	0.013	d	—2.30[g]	—7[f]

[a] OTs: p- toluenesulphonate, [b] R.G. Pearson, et al:, J. Am. Chem. Soc. 90, 319 (1968), ($E_{Y^-} = \varepsilon_{Y^-} - 2.60$), [c] J. Bjerrum, G. Schwarzenbach and L. Sillen, Stability constants, Part II, The Chemical Society, 1958, [d] R. E. Davis, et al., J. Am. Chem. Soc. 87, 3010 (1965), [e] J. O. Edwards, ibid., 76, 1540 (1954), [f] J. March, Advanced Organic Chemistry, McGraw Hill, 1968, p.219, [g] We estimated 0.30 v. for the E af tosylate anion ($\varepsilon = -2.30$ v.) by refinement of the data given by Davis (ref. d) about the CH_3Y and $CH_3YCOONa$ substrates..

The plot of α vs. the ε_{Y^-}, oxidative dimerization potential of the leaving group, Y in water at 25.0°C for a serie of alkyl substrates, CH_3Y is presented in Fig. 1A. It is shown that substrate parameters α of CH_3F and CH_3CN follow the linear dependence of α to the oxidation potential ε_{Y^-} of leaving group, which is already given by Davis (7), i. e. the substrate parameter, α depends linearly to the ε_{Y^-} with a slope nearly equal to unity (theoretically equal).
The equation for this plot is:

$$\alpha = 1.11\ \varepsilon_{Y^-} + 3.76 \qquad (9)$$

or

$$\alpha = 1.11\ E_{Y^-} + 0.87 \qquad (10)$$

The plot of the log. of β vs. the pKa_{Y^-}, basicity constant of the leaving group, Y in water at 25.0°C for a serie of alkyl substrates CH_3Y is presented in Fig. 1B. There is a good fit to the equation,

$$\log \beta = 0.13\ pKa_{Y^-} - 1.13 \qquad (11)$$

or

$$\log \beta = 0.13\ H_{Y^-} - 1.36 \qquad (12)$$

though iodide is highly out of the line.

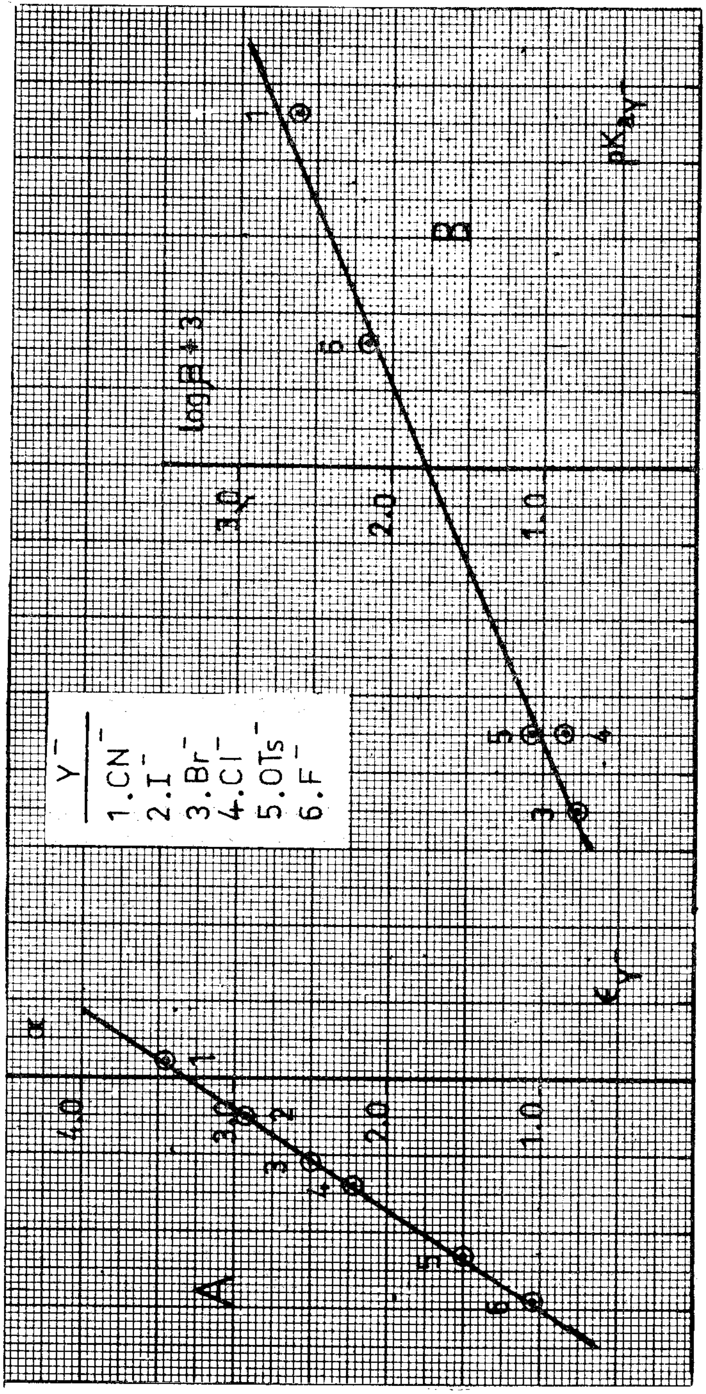

Fig. 1 A. The plot of α vs. the ε_{Y^-}; B. The plot of $\log\beta$ vs. the pKa_{Y^-} in water at 25.0°C for a serie of alkyl substrates, CH_3Y.

Using the eq. (9) and eq. (11), an *a piori* estimate of the two substrate constants α and β and then a quantitative prediction of the rates of nucleophilic displacement reactions on CH_3Y compounds in water at 25.0°C can be made. These values can be also used for C_2H_5Y and $CH_2YCOONa$ compounds in some approximation. Using these α and β values or the new ε and pK_a values, the predictive ability of the oxibase scale is increased.

REFERENCES

[1] **J. O. Edwards,** *J. Am. Chem.* Soc., 76, 1540 (1954).

[2] **J. O. Edwards and R. G.** Pearson, *ibid.*, 84, 16 (1962).

[3] **J. E. Leffler and E. Grunwald.** *Rates and Equilibria of Organic Reactions,* John Wiley, NewYork, 1963, p. 251.

[4] **P. R. Wells,** *Linear Free Energy Relationships.* Academic Press, London, 1968, Chap. 5.3.

[5] **C. Duboc,** *Bull. Soc. Chim.* France, 1970 (5) 1768.

[6] **N. B. Chapman and J. Shorter** (eds.), *Advances in Linear Free Energy Relationships,* Plenum Press, London, 1972, Chap. 6.

[7] **R. E. Davis,** *J. Am. Chem. Soc.* 87, 3010 (1965).

[8] **R. E. Davis,** *ibid.*, 91, 91 (1969).

[9] **B. W. Marshall and E. A. Moelwyn-Hughes,** *J. Chem. Soc.* 1965, 7119.

ÖZET

Bimoleküler nükleofilik substitüsyon reaksiyonunda alifatik karbon üzerinde ayrılan grubun etkinliğini belirtmek için Edwards bağıntısı yardımıyla iki kantitatif bağıntı verilmiştir. Edwards bağıntısı nükleofilik reaktifliği nükleofilin yükseltgenmesine ve bazikliğine bağlıyan bir lineer serbest enerji bağıntısıdır:

$$CH_3Y + X^- \xrightarrow{k} CH_3X + Y^-$$

$$\log k/k_0 = \alpha E_x + \beta H_x$$

Burada k ve k_0, substratın X nükleofili ve suyla 25,0°C de reaksiyon hız sabitleri, E_x, nükleofilin suya göre yükseltgen çiftlenme potansiyeli ve H_x suya göre baziklik sabitidir. Ayrılan grubun etkinliğinin, yükseltgenme ve bazikliğinin bir fonksiyonu olduğu gösterilmiştir. Bir seri CH_3Y bileşiklerinde substrat parametreleri, α, E_{Y^-} ye ve log. β, H_{Y^-} ye lineer bağlıdır:

$$\alpha = 1{,}18\ E_{Y^-} + 0{,}87.$$

$$\log \beta = 0{,}13\ H_{Y^-} - 1.36.$$

Bu eşitlikler yardımıyla, CH_3Y bileşiklerine ait yeni substrat parametreleri ve dolayısıyle suda 25,0°C de bimoleküler nükleofilik reaksiyon hız sabitleri önceden bulunabilir.

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