

Table 2. Enthalpy and Entropy Contribution to the Binding of Alkaline Earth Metal Cations by DBC at 25°C

Solvent	Cation	$-\Delta H^\circ$ (Kcal mol ⁻¹)	$T\Delta S^\circ$ (Kcal mol ⁻¹)
AN	Ca ²⁺	16.9	-13.7
	Sr ²⁺	8.39	-3.82
	Ba ²⁺	3.04	1.72
DMF	Ca ²⁺	29.3	-26.3
	Sr ²⁺	6.25	-1.93
	Ba ²⁺	4.04	0.55
DMSO	Ca ²⁺	25.1	-22.7
	Sr ²⁺	13.1	-9.26
	Ba ²⁺	1.62	2.78

vent affects the magnitude of $T\Delta S^\circ$.

To look at this phenomenon more closely, correlation between ΔH° and $-T\Delta S^\circ$ for the systems is drawn in Figure 1 which revealed compensation effect.⁸ Highly favorable enthalpy contribution and large but negative entropy contribution result in the smaller stability constants of Ca²⁺ complexes than those of Ba²⁺ complexes in the solvents used. As for Ba²⁺ complexes having relatively low $-\Delta H^\circ$ values, fitting of the metal ion into the cavity is of great importance. The relatively low $-\Delta H^\circ$ and $-T\Delta S^\circ$ of Ba²⁺ complexes reflect its soft character and its weak structure breaking effect in the basic solvents.

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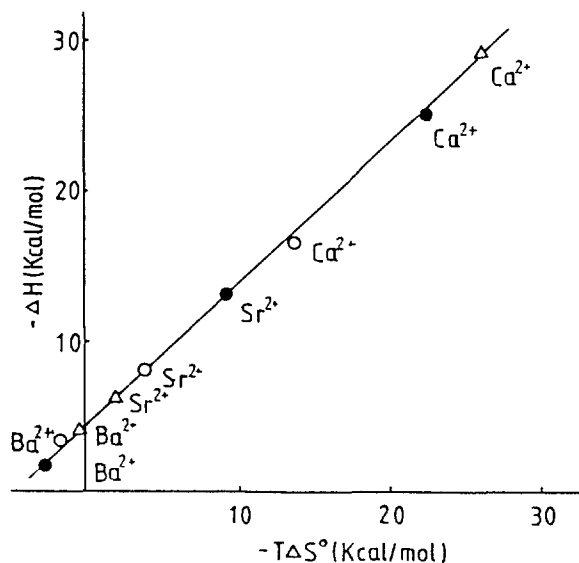


Figure 1. Correlation between ΔH° and $T\Delta S^\circ$ for alkaline earth metal cation-DBC complexes in AN(O), DMF(Δ), and DMSO(\bullet).

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Applicability of Dual Substituent Parameter Equation to S_N2 Reaction

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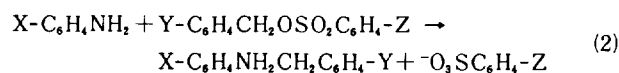
Recently various dual substituent parameter(DSP) equations have been proposed for analyses of substituent effects on rates and equilibria in terms of polar(ρ_{pol} , σ_{pol}) and resonance(ρ_r , σ_r) components.¹⁻⁵ All the DSP equations have basically the same form, (1)

$$\log(k/k_o) = \rho_{pol} \sigma_{pol} + \rho_r \sigma_r + B \quad (1)$$

where B is a constant. The polar component is variously expressed as inductive(ρ_i , σ_i)^{6,7,10} or field effect(f/F)^{6,14} term.

In this report we examine applicability of four major DSP equations, Yukawa-Tsuno-Jencks(YTJ),^{8,9} Taft,¹⁰⁻¹³ Swain-Lupton(SL)¹⁴ and Afanas'ev¹⁵ correlation, to S_N2 reactions by

applying the equations to rate data for reactions of benzyl benzenesulfonates with anilines,(2).¹⁶⁻¹⁸



where X = *p*-CH₃O, *p*-CH₃, H, *p*-Cl, *m*-NO₂

Y = *p*-CH₃, H, *p*-Cl, *p*-NO₂

Z = *p*-CH₃, H, *p*-Cl, *m*-NO₂

Application of the four DSP equations to the rate data of reaction (2) gave the results summarized in Table 1. Correlation coefficients for the multiple linear regression of the calculated

Table 1. Polar and Resonance Components and their ratio R for Various dual Substituent Parameter Equations Applied to Reactions of Benzyl Tosylate with Anilines in Methanol(reaction 2)

X	ρ_Y^{+a}	Yukawa-Tsuno-Jencks ^b			Taft ^c		
		ρ^n	ρ^r	$R = \rho^r/\rho^n$	ρ_I	ρ_R^+	$R = \rho_R^+/\rho_I$
<i>p</i> -CH ₃ O	-0.69	-0.717	-1.813	2.53	-0.803	-0.932	1.16
<i>p</i> -CH ₃	-0.78	-0.804	-1.974	2.46	-0.897	-1.031	1.15
H	-0.84	-0.916	-2.025	2.21	-1.042	-1.052	1.01
<i>p</i> -Cl	-1.06	-1.148	-1.904	1.66	-1.258	-1.184	0.94
<i>m</i> -NO ₂	-1.25	-1.455	-2.199	1.51	-1.643	-1.322	0.80
correlation coefficient		0.987 ± 0.005			0.976 ± 0.008		

X	ρ_Y^{+a}	Swain-Lupton ^d			Afanas'ev ^e		
		<i>f</i>	<i>r</i>	$R = r/f$	ρ^*	<i>r</i> *	$R = r^*/\rho^*$
<i>p</i> -CH ₃ O	-0.69	-0.656	-1.510	2.30	-0.028	-0.686	24.5
<i>p</i> -CH ₃	-0.78	-0.734	-1.668	2.28	-0.034	-0.758	22.3
H	-0.84	-0.881	-1.670	1.90	-0.090	-0.779	8.7
<i>p</i> -Cl	-1.06	-1.078	-1.866	1.73	-0.138	-0.878	6.4
<i>m</i> -NO ₂	-1.25	-1.460	-2.021	1.38	-0.258	-0.990	3.8
correlation coefficient		0.966 ± 0.009			0.981 ± 0.007		

^aReference 18. These were obtained by $\log(k/k_0) = \rho_Y^+ \sigma^+$ with Y = H, *p*-Cl and *p*-NO₂. ^bReference 8. ^cReference 10. ^dReference 14. ^eReference 15. For *b*-*e* Y = *p*-CH₃, H, *p*-Cl and *p*-NO₂; we have made similar calculations for the reaction (2) in 80% and 50% MeOH-MeCN Mixtures and found the same trends as in this Table.

Table 2. Polar and Resonance Components and their ratio R for YTJ and SL Equations Applied to Reaction (2) in methanol

X	Z	ρ_Y^{+a}	Yukawa-Tsuno-Jencks			Swain-Lupton		
			ρ^n	ρ^r	$R = \rho^r/\rho^n$	<i>f</i>	<i>r</i>	$R = r/f$
<i>p</i> -CH ₃ O	<i>p</i> -CH ₃	-0.69	-0.660	-1.289	1.95	-0.456	-1.309	2.87
	H	-0.56	-0.512	-1.341	2.62	-0.311	-1.191	3.83
	<i>m</i> -NO ₂	-0.35	-0.277	-1.432	5.17	-0.080	-1.023	12.80
<i>m</i> -NO ₂	<i>p</i> -CH ₃	-1.25	-1.301	-0.819	0.63	-1.123	-1.681	1.50
	H	-1.21	-1.239	-0.694	0.56	-1.082	-1.553	1.44
	<i>m</i> -NO ₂	-1.11	-1.162	-0.680	0.59	-1.001	-1.468	1.47

^aReference 18. For Y = H, *p*-Cl and *p*-NO₂ with $\log(k/k_0) = \rho_Y^+ \sigma^+$. We have made similar calculations for X = *p*-CH₃, H, *p*-Cl and Z = *p*-Cl for reaction (2) in 80% and 50% MeOH-MeCN mixtures and found the same trends as in this Table.

vs observed values are in general satisfactory. Reference to Table 1 reveals that in all cases both polar and resonance components increase (more negative) with the increase in the magnitude of ρ_Y^+ value (and hence the positive charge on the reaction center C_o) as the substituent X in the nucleophile is varied from an electron donating (*p*-CH₃O) to an electron withdrawing (*m*-NO₂) one. This is in full accord with our expectation, since a greater positive charge reflects a stronger effect of the substituent Y irrespective of the transfer mechanism.¹⁹ Since the polar effect is propagated along a chain of carbon atoms by successive polarization, the effect died off exponentially with the number of bonds *n* traversed.

Hence unless the charge is large, the effect becomes negligible when *n* is still small. For a fixed *n*, the polar effect is therefore strongly dependent on the amount of charge in contrast with the resonance effect, which can easily reach relatively long distance through a conjugative chain and hence

is less dependent on the amount of charge.¹⁹ This difference in the transfer mechanism is reflected in a relatively wide range variation of the polar component compared to that of the resonance component; as a result ratio of the resonance to polar component R is the greatest for the smallest charge and is the smallest for the greatest charge on C_o (i.e., magnitude of ρ_Y^+).

It is interesting to note that the polar component almost parallels the ρ_Y^+ value. The only exception to this however is the magnitude of the polar component in the Afanas'ev equation, which is too small compared to that of other equations.

On the other hand ratios of resonance to polar component, R, for Taft equation with X = *p*-Cl and *m*-NO₂ are less than one, which is difficult to rationalize since the inductive mechanism of the effects of *para*-substituents (Y = *p*-CH₃, H, *p*-Cl and *p*-NO₂) through an aromatic ring can not be normally more important than the resonance transfer mechanism.¹⁹ It

is therefore evident that the Afanas'ev equation underestimates whereas the Taft equation overestimates the polar component.

In this sense, the other two equations, YTJ and SL correlations, appear to be normal, and indeed the corresponding components in these two equations are approximately equal.

Inclusion of effects of substituent variation in the leaving group (Z) on the components of the DSP equations given in Table 2 however puts an end to this apparent similarity of the two equations. Now the YTJ equation shows anomalies in that resonance contributions vary in opposite to polar contributions for X = *p*-CH₃O and the resonance to polar ratios R for X = *m*-NO₂ are less than one. These and other types of anomalies were also found with the Taft and Afanas'ev equations when substituent variation in the leaving group is considered. The SL equation is the only one that behaves normally in every respects. Thus of the four major types of DSP correlations, we must regard the Swain-Lupton equation as the most reliable one for correlating substituent effects on rates for S_N2 reactions.

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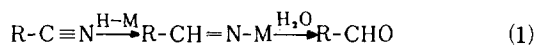
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A New Aldehyde Synthesis from Aliphatic Nitriles with Sodium Diethyldihydroaluminat in the Presence of Diethylaluminum, 2,6-Di-*t*-Butylphenoxide

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Reduction of nitriles to aldehydes is an important functional group transformation and consequently considerable effort has been expended devising methods for these conversions.^{1,2} Such transformations generally take the form of partial reduction of a nitrile to an aldimine followed by hydrolysis of the aldimine to the corresponding aldehyde³ (eq. 1).



Diisobutylaluminum hydride (DIBAH)⁴, and lithium triethoxyaluminumhydride (LTEAH)⁵ are the two major hydride reducing agents for such transformations (both of which have only one hydride per molecule). In contrast to these hydride reagents, sodium diethyldihydroaluminat (OMH-1) has two hydrides per molecule and was reported to reduce benzonitrile

to benzaldehyde in 86% yield, whereas gives only 14% butyraldehyde from butyronitrile.

We tested several aliphatic nitriles with OMH-1, and the yields of aldehydes were constantly low, comparable to those reported with lithium aluminum hydride. However, it was very interesting to note that the yields of aldehydes increased tremendously from the primary nitrile (*n*-capronitrile; 10% conversion) to the secondary (isobutyronitriles; 57%) and tertiary (trimethylacetoneitrile; 68%) nitriles. The steric effect of alkyl group on the cyano group is presumably interfering the second hydride attack. Since nitriles are known to form adducts with Lewis acids⁶, it was felt that bulky Lewis acid-nitrile adduct might accept only one hydride from OMH-1, resulting a new aldehyde synthesis (eq. 2).