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The magnitude of $\rho_X(\rho_{nuc})$ versus the extent of bond formation in S_N2 Reactions

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The secondary deuterium kinetic isotope effects (SDKIE) involving deuterated aniline nucleophiles are reported for the reactions of benzyl bromides and chlorides and benzoyl chlorides in acetonitrile. The benzyl systems behave normally as to the trend of changes in SDKIE with the magnitude of $\rho_X(\rho_{nuc})$, whereas benzoyl system shows an anomaly; $|\rho_X|$ decreases with increase in the extent of bond making estimated by the SDKIE. This has been ascribed to the negative charge accumulation at the reaction center carbon in the transition state. The magnitude of ρ_{XY} is found to decrease by ca. 0.03 with ten degree rise in the reaction temperature.

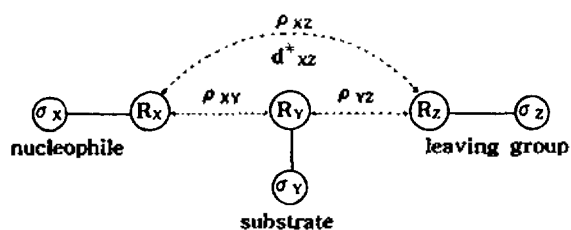
Introduction

Applicability of the magnitude of $\rho_X(\rho_{nuc})$ as a measure of the extent of bond making in the transition state (TS) has an open question.¹ For example, ρ_X can change sign² at certain σ_Y , δ_Y at which $\rho_X=0$, as both σ_X and σ_Y are varied in an S_N2 type reactions, Scheme 1. It is absurd to interpret this sign change of ρ_X at δ_Y as a possibility of the negative degree of bond formation; in reality only the charge reversal takes place, as we often encounter with ρ_Y for S_N2 reactions at a benzylic carbon.

The magnitude of $\rho_X(\rho_{nuc})$ in S_N2 reactions is, however, often loosely related to the extent of bond formation in the TS within a series of reactions.³ For example the magnitude of ρ_X increases in parallel with that of ρ_{XY} , Eq. (1), the cross-interaction constant⁴ between

$$\log(k_{XY}/k_{HH}) = \rho_X\sigma_X + \rho_Y\sigma_Y + \rho_{XY}\sigma_X\sigma_Y \quad (1)$$

substituents (X) in the nucleophile and those (Y) in the substrate, as the substituent Y is varied to a more electron-withdrawing one for reactions of para-Y- substituted 1-⁵ and 2-phenylethyl⁶ and Y-benzyl⁷ arenesulfonates with anilines,



Scheme 1.

$XC_6H_4NH_2$. The magnitude of ρ_{XY} is known to increase with increasing degree of bond formation.⁴ The parallel changes in $|\rho_X|$ and $|\rho_{XY}|$ in fact correctly reflect that a greater $|\rho_X|$ corresponds to a tighter TS for a more electron-withdrawing Y substituent within the series of reactions.

In this paper, we show that for associative S_N2 reaction series, in which negative charge develops at C_n in the TS with $\rho_Y > 0$, an inverse proportionality between $|\rho_X|$ and the extent of bond making is obtained, in contrast to a proportionality between $|\rho_X|$ and the extent of bond making in the TS for a dissociative S_N2 reaction series, in which positive charge develops at the reaction center, C_n , in the TS with $\rho_Y < 0$. Hence care should be exercised in the interpretation of the magnitude of ρ_X as a measure of bond formation within a series of S_N2 reactions.

The secondary α -deuterium kinetic isotope effect (SDKIE) involving deuterated aniline nucleophile, $XC_6H_4NH_2(D_2)$, k_H/k_D , has been shown to be useful in determining the relative extent of bond making in the S_N2 TS.⁸ As a nucleophile, $XC_6H_4NH_2(D_2)$, attacks the reaction center, C_n , the two N-H (D) vibrations, both bending and stretching modes,⁹ are sterically hindered and force constants (and hence vibrational frequencies) increase in the TS.¹⁰ This results in an inverse type of SDKIE, $k_H/k_D < 1/0$,¹⁰ in all normal S_N2 -type reactions, and the size of the inverse SDKIE values reflect the degree of steric hindrance and hence the degree of bond formation; the smaller the SDIKE value, the greater is the extent of bond formation.

We have determined the SDKIE values for the reactions of benzyl chlorides and bromides and benzoyl chlorides in acetonitrile at one temperature. In addition, the rates are measured also at other (1-2) temperatures and the temperature effect of various ρ values are discussed.

Results and Discussion

The rate constants are summarized in Tables 1-3. The kinetic isotope effects, k_H/k_D , and the Hammett reaction constants, ρ_X and ρ_Y , are given for the reactions of benzyl bromides at 25.0°C, benzyl chlorides at 55.0°C and benzoyl chlorides at 25.0°C, with anilines in acetonitrile in Table 4, 5 and 6 respectively. We note that all the SDIKE values are less than unity, i.e., an inverse type, correctly reflecting an increase in steric inhibition of the two N-H(D) vibrations as the N-C_a bond is formed in the TS in all cases. For the two benzyl series, Tables 4 and 5, the k_H/k_D value decreases with a more electron-withdrawing substituent (Y) in the substrate ($\delta\sigma_Y > 0$), and with a more electron-donating substituent (X) in the nucleophile ($\delta\sigma_X < 0$). The variation of $|\rho_X|$ ($\delta|\rho_X| > 0$) is consistent with the decreasing trend in k_H/k_D reflecting a greater degree of bond making for a substituent with $\delta\sigma_Y > 0$. The decrease in the negative ρ_X for a substituent with $\delta\sigma_X < 0$ is an indication that the increase in the extent of bond cleavage is greater than that in bond formation.

Table 1. Second order rate constants, $k_2 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, for the reaction of Y-Benzyl bromides with deuterated X-Anilines in Acetonitrile at 25.0°C

X	Y	<i>p</i> -CH ₃	H	<i>p</i> -Cl	<i>m</i> -Cl	<i>p</i> -NO ₂
<i>p</i> -CH ₃	H ^a	43.4	37.5	28.8	23.4	15.5
		± 0.2 ^c	± 0.1	± 0.1	± 0.1	± 0.2
	D ^b	46.6	40.4	31.1	25.4	16.9
		± 0.2	± 0.1	± 0.2	± 0.1	± 0.1
H	H	26.3	20.0	15.5	12.3	7.76
		± 0.01	± 0.02	± 0.2	± 0.05	± 0.03
	D	28.0	21.4	16.7	13.3	8.41
		± 0.1	± 0.06	± 0.1	± 0.1	± 0.03
<i>p</i> -Cl	H	12.0	9.77	6.76	5.13	3.02
		± 0.01	± 0.03	± 0.02	± 0.01	± 0.02
	D	12.7	10.4	7.20	5.49	3.24
		± 0.02	± 0.01	± 0.01	± 0.02	± 0.02
<i>m</i> -Cl	H	8.04	6.31	3.89	3.24	1.60
		± 0.01	± 0.02	± 0.01	± 0.03	± 0.01
	D	8.38	6.61	4.10	3.42	1.70
		± 0.01	± 0.02	± 0.01	± 0.01	± 0.01
<i>p</i> -NO ₂	H	2.19	1.50	0.977	0.661	0.316
		± 0.01	± 0.01	± 0.003	± 0.002	± 0.001
	D	2.26	1.55	1.02	0.692	0.332
		± 0.01	± 0.02	± 0.01	± 0.001	± 0.001

^aWith XC₆H₄NH₂. ^bWith XC₆H₄ND₂. ^cStandard deviation.

Table 2. Second order rate constants, $k_2 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, for the reactions of Y-Benzyl chlorides with deuterated X-Anilines in Acetonitrile at 55.0°C

X	Y	<i>p</i> -CH ₃	H	<i>p</i> -Cl	<i>m</i> -Cl	<i>p</i> -NO ₂
<i>p</i> -CH ₃ O	H ^a	46.8	35.5	28.8	25.1	17.4
		± 0.2 ^c	± 0.1	± 0.1	± 0.1	± 0.2
	D ^b	47.8	36.4	29.6	25.8	17.9
		± 0.2	± 0.1	± 0.2	± 0.1	± 0.1

^aWith XC₆H₄NH₂. ^bWith XC₆H₄ND₂. ^cStandard deviation.

<i>p</i> -CH ₃	H	33.1	25.1	20.4	17.4	12.1
		± 0.2	± 0.3	± 0.2	± 0.1	± 0.3
D		33.7	25.7	20.7	17.9	12.4
		± 0.2	± 0.1	± 0.2	± 0.2	± 0.1
H	H	20.0	15.8	12.0	9.78	6.61
		± 0.01	± 0.02	± 0.2	± 0.05	± 0.03
D		20.2	16.0	12.2	9.94	6.72
		± 0.1	± 0.06	± 0.1	± 0.1	± 0.03
<i>p</i> -Cl	H	12.0	9.32	6.03	4.68	2.88
		± 0.01	± 0.03	± 0.02	± 0.01	± 0.02
D		12.1	9.42	6.12	4.77	2.93
		± 0.02	± 0.01	± 0.01	± 0.02	± 0.02
<i>m</i> -Cl	H	8.32	5.75	3.98	3.31	1.91
		± 0.01	± 0.02	± 0.01	± 0.03	± 0.01
D		8.37	5.79	4.01	3.34	1.93
		± 0.01	± 0.02	± 0.01	± 0.01	± 0.01

^aWith XC₆H₄NH₂. ^bWith XC₆H₄ND₂. ^cStandard deviation.

Table 3. Second order rate constants, $k_2 (\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$, for the reaction of Y-Benzoyl chlorides with deuterated X-Anilines in Acetonitrile at 25.0°C

X	Y	<i>p</i> -CH ₃	H	<i>p</i> -Cl	<i>m</i> -Cl	<i>p</i> -CN	<i>p</i> -NO ₂	<i>m,m</i> - (NO ₂) ₂
<i>p</i> -CH ₃ OH ^a		23.9	65.2	186	401			
		± 0.1 ^c	± 0.2	± 1	± 4			
D ^b		26.4	71.8	202	432			
		± 0.2	± 0.06	± 2	± 2			
<i>p</i> -CH ₃	H	15.3	38.7	110	233			
		± 0.1	± 0.2	± 1	± 2			
D		17.0	42.8	120	253			
		± 0.2	± 0.2	± 1	± 1			
H	H	6.03	14.0	34.5	63.1	238	386	
		± 0.01	± 0.2	± 0.2	± 0.3	± 2	± 2	
D		6.73	15.6	38.0	68.8	256	408	
		± 0.01	± 0.06	± 0.1	± 0.2	± 2	± 2	
<i>p</i> -Cl	H	2.01	4.28	10.6	20.2	63.4	107	
		± 0.01	± 0.03	± 0.2	± 0.3	± 0.3	± 2	
D		2.26	4.78	11.7	22.2	68.9	114	
		± 0.02	± 0.01	± 0.1	± 0.1	± 0.2	± 1	
<i>m</i> -Cl	H	1.08	2.37	5.13	8.96	27.4	42.2	
		± 0.01	± 0.02	± 0.01	± 0.03	± 0.2	± 0.2	
D		1.22	2.66	5.67	9.85	30.0	45.6	
		± 0.01	± 0.006	± 0.01	± 0.01	± 0.1	± 0.1	
<i>m</i> -NO ₂	H	0.204	0.397	0.706	1.17	2.71	4.01	25.5
		± 0.002	± 0.004	± 0.004	± 0.01	± 0.03	± 0.03	± 0.3
D		0.244	0.474	0.814	1.33	3.05	4.49	27.6
		± 0.002	± 0.001	± 0.001	± 0.01	± 0.01	± 0.01	± 0.1
<i>p</i> -NO ₂	H	0.150	0.248	0.482	0.789	1.73	2.52	15.4
		± 0.001	± 0.002	± 0.003	± 0.001	± 0.02	± 0.02	± 0.2
D		0.183	0.301	0.572	0.914	1.97	2.87	17.2
		± 0.001	± 0.002	± 0.002	± 0.001	± 0.01	± 0.01	± 0.1

^aWith XC₆H₄NH₂. ^bWith XC₆H₄ND₂. ^cStandard deviation.

Table 4. The kinetic isotope effects (k_H/k_D) and Hammett reaction constants for the reaction of Y-Benzyl bromides with deuterated X-Anilines in Acetonitrile at 25.0°C

X\Y	<i>p</i> -CH ₃	H	<i>p</i> -Cl	<i>m</i> -Cl	<i>p</i> -NO ₂	ρ_Y^b
<i>p</i> -CH ₃ O	0.932	0.928	0.926	0.921	0.917	-0.48
	± 0.008 ^a	± 0.007	± 0.007	± 0.007	± 0.004	(-0.46) ^c
H	0.939	0.935	0.928	0.925	0.923	-0.55
	± 0.009	± 0.008	± 0.008	± 0.005	± 0.003	(-0.55)
<i>p</i> -Cl	0.945	0.939	0.939	0.934	0.932	-0.65
	± 0.007	± 0.003	± 0.008	± 0.007	± 0.006	(-0.64)
<i>m</i> -Cl	0.959	0.955	0.949	0.947	0.941	-0.75
	± 0.005	± 0.009	± 0.008	± 0.003	± 0.009	(-0.74)
<i>p</i> -NO ₂	0.971	0.966	0.964	0.958	0.955	-0.91
	± 0.005	± 0.009	± 0.003	± 0.009	± 0.008	(-0.90)
ρ_X^b	-1.37	-1.45	-1.55	-1.63	-1.79	
	(-1.39) ^c	(-1.46)	(-1.57)	(-1.64)	(1.81)	

^a Standard error = $1/k_D[(\Delta k_H)^2 + (k_H/k_D)^2(\Delta k_D)^2]^{1/2}$.⁽¹⁸⁾ ^b The σ values were taken from "Handbook of Organic Chemistry" McGraw-Hill, New York, 1987, Table 7-1. The correlation coefficients were better than 0.996 in all cases. ^c ρ_X and ρ_Y values are for reactions with XC₆H₄ND₂.

It has been shown that for benzyl systems, the cross-interaction constant ρ_{XZ} , Eq. (2), is negative⁴ so that a stronger nucleophile ($\delta\sigma_X < 0$) and/or nucleofuge ($\delta\sigma_Z > 0$) lead to a later TS along the reaction

$$\rho_{XZ} = \frac{\partial \log k_{XZ}}{\partial \sigma_X \cdot \partial \sigma_Z} = \frac{\partial \rho_Z}{\partial \sigma_X} = \frac{\partial \rho_X}{\partial \sigma_Z} \quad (2)$$

coordinate, i.e., the extent of bond-making and/or -breaking is greater,⁴ which is indeed what we observed for the trends of changes in the k_H/k_D , $|\rho_X|$ and $|\rho_Y|$ values.

For benzoyl series, Table 3 reveals that the k_H/k_D value

Table 5. The kinetic isotope effects (k_H/k_D) and Hammett reaction constants for the reactions between Y-Benzyl chlorides and deuterated X-Anilines in Acetonitrile at 55.0°C

X\Y	<i>p</i> -CH ₃	H	<i>p</i> -Cl	<i>m</i> -Cl	<i>p</i> -NO ₂	ρ_Y^b
<i>p</i> -CH ₃ O	0.979	0.975	0.973	0.973	0.972	-0.44
	± 0.009 ^a	± 0.006	± 0.009	± 0.005	± 0.007	(-0.44) ^c
<i>p</i> -CH ₃	0.982	0.977	0.976	0.972	0.976	-0.45
	± 0.007	± 0.004	± 0.004	± 0.005	± 0.003	(-0.45)
H	0.990	0.988	0.984	0.986	0.984	-0.51
	± 0.004	± 0.009	± 0.004	± 0.003	± 0.005	(-0.51)
<i>p</i> -Cl	0.992	0.989	0.985	0.985	0.983	-0.67
	± 0.009	± 0.004	± 0.005	± 0.006	± 0.003	(-0.66)
<i>m</i> -Cl	0.994	0.993	0.993	0.991	0.990	-0.66
	± 0.004	± 0.005	± 0.008	± 0.004	± 0.004	(-0.66)
ρ_X^b	-1.15	-1.19	-1.34	-1.38	-1.51	
	(-1.16) ^c	(-1.20)	(-1.35)	(-1.40)	(-1.53)	

^{a,b,c} Same as the footnotes in Table 4.

becomes systematically smaller, and hence the degree of bond formation becomes systematically greater in the TS, with a weaker nucleophile (e.g. X = *p*-NO₂) and with a more electron-donating substituent in the substrate (e.g. Y = *p*-CH₃) exhibiting the smallest value ($k_H/k_D = 0.82$) for the reactants with X = *p*-NO₂ and Y = *p*-CH₃. These trends indicate that the extent of bond making is the greater the weaker is the nucleophile and the stronger is the electron-donating power of the substituent (Y) in the substrate. The former trend is consistent with that expected from the More O'Ferrall-Jencks diagram¹¹ and from a positive ρ_{XZ} value, Eq. (2), but the latter trend is contrary to the putative proportionality between $|\rho_X|$ and the extent of bond making; $|\rho_X|$ in fact decreases, in contrast to an increase expected from the propo-

Table 6. The kinetic isotope effects (k_H/k_D) and Hammett reaction constants for the reaction of Y-Benzyl chlorides with deuterated X-Anilines in Acetonitrile at 25.0°C

X\Y	<i>p</i> -CH ₃	H	<i>p</i> -Cl	<i>m</i> -Cl	<i>p</i> -CN	<i>p</i> -NO ₂	m,m-(NO ₂) ₂	ρ_Y^b
<i>p</i> -CH ₃ O	0.905	0.908	0.921	0.928				2.23
	± 0.008 ^a	± 0.008	± 0.010	± 0.010				(2.21) ^c
<i>p</i> -CH ₃	0.900	0.904	0.917	0.921				2.16
	± 0.012	± 0.006	± 0.011	± 0.009				(2.14)
H	0.896	0.897	0.908	0.917	0.930	0.946		1.89
	± 0.003	± 0.013	± 0.008	± 0.004	± 0.010	± 0.007		(1.87)
<i>p</i> -Cl	0.889	0.895	0.906	0.910	0.920	0.930		1.81
	± 0.009	± 0.007	± 0.010	± 0.009	± 0.005	± 0.012		(1.79)
<i>m</i> -Cl	0.885	0.891	0.905	0.910	0.913	0.925		1.66
	± 0.010	± 0.008	± 0.004	± 0.002	± 0.007	± 0.009		(1.64)
<i>m</i> -NO ₂	0.836	0.838	0.867	0.880	0.889	0.893	0.924	1.31
	± 0.010	± 0.009	± 0.005	± 0.010	± 0.010	± 0.007	± 0.011	(1.28)
<i>p</i> -NO ₂	0.820	0.824	0.843	0.863	0.878	0.878	0.895	1.24
	± 0.012	± 0.009	± 0.006	± 0.001	± 0.010	± 0.008	± 0.012	(1.24)
ρ_X^b	-2.11	-2.28	-2.46	-2.57	-2.77	-2.84	-3.22	
	(-2.07) ^c	(-2.24)	(-2.43)	(-2.54)	(-2.74)	(-2.80)	(-3.02)	

^{a,b} and ^c Same as the footnotes in Table 4.

Table 7. Temperature dependence of the Hammett (ρ_X and ρ_Y) coefficients and the Cross-interaction Constants (ρ_{XY})

Reaction	Solvent	T/°C	ρ_X	ρ_Y	ρ_{XY}	
XC ₆ H ₄ NH ₂ + YC ₆ H ₄ CH ₂ Br	MeCN	25.0	-1.45	-0.55	-0.47	0.999 ^a
		35.0	-1.47	-0.56	-0.43	0.999
		45.0	-1.47	-0.56	-0.40	0.999
XC ₆ H ₄ NH ₂ + YC ₆ H ₄ CH ₂ Cl	MeCN	35.0	-1.22	-0.51	-0.44	0.998
		45.0	-1.23	-0.51	-0.42	0.998
		55.0	-1.19	-0.51	-0.39	0.998
XC ₆ H ₄ NH ₂ + YC ₆ H ₄ COCl	MeCN	25.0	-2.26	1.89	-0.85	0.999
		35.0	-2.13	1.86	-0.81	0.999

^aCorrelation coefficients.

tionality, as the degree of bond formation increases, *i.e.*, the inverse SDKIE decreases, with increase in electron-donating power of substituent Y.

For the benzoyl series, in Table 6, ρ_Y is positive indicating that bond making is more advanced than bond cleavage so that the carbonyl carbon (C_a) atom becomes more negatively charged in the TS. For this series, the variation of TS structure is expected to be consistent with that predicted from the More O'Ferrall-Jencks diagram,¹¹ which in turn is consistent with a positive ρ_{XZ} value^{4,8}; a weaker nucleophile ($\delta\sigma_X > 0$) should therefore lead to a greater degree of bond formation,⁴ $\delta|\rho_X| > 0$. This is in agreement with a smaller k_H/k_D value observed for a weaker nucleophile ($\delta\sigma_X > 0$) in Table 6. According to the More O'Ferrall-Jencks diagram, however, a more electron-withdrawing Y substituent ($\delta\sigma_Y > 0$) should lead to a greater degree of bond formation and a lesser degree of bond cleavage.⁴ The increase in $|\rho_X|$ seems to reflect correctly these TS variation for the Y substituent predicted by the More O'Ferrall-Jencks diagram. However the k_H/k_D value increases for a Y substituent with $\delta\sigma_Y > 0$ contradicting the prediction of the More O'Ferrall-Jencks diagram, *i.e.*, the increase in $|\rho_X|$. Since the N-H(D) vibrations become sterically hindered, but cannot become in any way sterically released, as the nucleophile, aniline, approaches C_a in the TS, the increase in k_H/k_D should be the true reflection of the decrease in the extent of bond making. This kind of anomaly was also observed for the reactions of arenesulfonyl chlorides with anilines.¹²

The decrease in the $|\rho_X|$ value with a more electron-donating Y appears to result from an accumulation of negative charge at C_a in the TS² ($\rho_Y > 0$) due to a relatively strong electronegative, or electron-attracting, carbonyl oxygen atom in benzoyl chlorides. The accumulation of negative charge at the C_a -O moiety leads to an inefficient charge transfer from the nucleophile even at a closer N- C_a distance. Indeed, the inefficient charge transfer requires a closer approach of the nucleophile in the TS.² Hence the inverse proportionality between $|\rho_X|$ and the extent of bond making is intimately related to the negative charge accumulation in the TS for an associative S_N2 reaction series in which bond formation is ahead of bond cleavage ($\rho_Y > 0$) with a relatively tight TS.

For the benzoyl series, the selectivity plots, $\log(k_H/k_D)$ vs σ_Y , give positive slopes,¹³ indicating that the reactions proceed *via* the S_N2 mechanism.¹⁴ It is also interesting to note

Table 8. Second order rate constants, $k_2 \times 10^4$ dm³mol⁻¹s⁻¹, and Hammett reaction constants for the reaction of Y-Benzyl bromides with X-Anilines in Acetonitrile at 35.0°C

X \ Y	<i>p</i> -CH ₃	H	<i>p</i> -Cl	<i>m</i> -Cl	<i>p</i> -NO ₂	ρ_Y
<i>p</i> -CH ₃	72.4 ± 0.3 ^a	60.3 ± 0.2	44.7 ± 0.1	39.8 ± 0.2	25.7 ± 0.2	-0.48 (0.999) ^b
H	43.7 ± 0.01	34.6 ± 0.02	26.9 ± 0.2	21.9 ± 0.1	12.9 ± 0.02	-0.56 (0.999)
<i>p</i> -Cl	20.0 ± 0.01	15.5 ± 0.03	12.8 ± 0.02	9.55 ± 0.01	4.90 ± 0.01	-0.64 (0.993)
<i>m</i> -Cl	12.6 ± 0.03	9.77 ± 0.3	6.61 ± 0.1	5.13 ± 0.1	2.69 ± 0.2	-0.71 (0.999)
ρ_X	-1.41 (0.999) ^b	-1.47 (0.999)	-1.51 (0.996)	-1.63 (0.999)	-1.81 (1.00)	

^aStandard deviation. ^bCorrelation coefficients.**Table 9.** Second order rate constants, $k_2 \times 10^4$ dm³mol⁻¹s⁻¹, and Hammett reaction constants for the reaction of Y-Benzyl bromides with X-Anilines in Acetonitrile at 45.0°C

X \ Y	<i>p</i> -CH ₃	H	<i>p</i> -Cl	<i>m</i> -Cl	<i>p</i> -NO ₂	ρ_Y
<i>p</i> -CH ₃	103 ± 2 ^a	85.6 ± 2	63.5 ± 1	56.5 ± 0.6	36.5 ± 0.5	-0.48 (0.999) ^b
H	62.1 ± 1	49.1 ± 0.6	38.2 ± 0.2	31.1 ± 0.2	18.3 ± 0.3	-0.56 (0.999)
<i>p</i> -Cl	28.4 ± 0.5	22.0 ± 0.3	17.1 ± 0.2	13.6 ± 0.1	6.96 ± 0.1	-0.64 (0.997)
<i>m</i> -Cl	16.9 ± 0.2	13.9 ± 0.2	9.39 ± 0.1	7.29 ± 0.02	3.82 ± 0.2	-0.69 (0.999)
ρ_X	-1.45 (0.999) ^b	-1.47 (0.999)	-1.53 (0.998)	-1.63 (0.999)	-1.81 (1.00)	

^aStandard deviation. ^bCorrelation coefficients.

that the least reactive reactant pair with X = *p*-NO₂ and Y = *p*-CH₃ has the least SDKIE value, *i.e.*, the most selective, in line with the reactivity-selectivity principle (RSP).¹⁵ The magnitude of the first-order selectivity parameters, ρ_X and ρ_Y , is smaller for the more reactive processes with XC₆H₄ND₂ rather than with XC₆H₄NH₂, which is again consistent with the RSP. The cross-interaction constant, ρ_{XY} , is however, identical for the two reaction series with XC₆H₄NH₂ and XC₆H₄ND₂ (for both series, $\rho_{XY} = -0.85$ with $r = 0.999$), demonstrating that the TS structure, *i.e.*, the degree of bond formation, is not affected by the isotopic substitution ($-\text{NH}_2 \rightarrow -\text{ND}_2$).¹⁶

For the benzyl series, however, the RSP does not apply. The ρ_{XY} values are collected in Table 7. We note that ρ_{XY} is negative in all cases but the magnitude of ρ_{XY} is greater for the benzoyl series than for the benzyl series indicating the extent of bond making is greater for the benzoyl series. This is in agreement with the general trend of the smaller k_H/k_D values for the benzoyl series. A small increase in the magnitude of ρ_{XY} for benzyl chloride than bromide also reflects a somewhat greater degree of bond making for the chloride.

All first-order susceptibility factors, ρ , β , m , s , etc. are

Table 10. Second order rate constants, $k_2 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, and Hammett reaction constants for the reaction of Y-Benzyl chlorides with X-Anilines in Acetonitrile at 35.0°C

X \ Y	p-CH ₃	H	p-Cl	m-Cl	p-NO ₂	ρ_Y
p-CH ₃ O	15.8 ± 0.3 ^a	13.5 ± 0.2	10.9 ± 0.1	9.54 ± 0.2	6.61 ± 0.2	-0.40 (0.999) ^b
p-CH ₃	12.2 ± 0.3	9.54 ± 0.2	7.75 ± 0.1	6.61 ± 0.2	4.60 ± 0.2	-0.44 (0.996)
H	7.60 ± 0.01	6.01 ± 0.02	4.56 ± 0.2	3.72 ± 0.1	2.51 ± 0.02	-0.51 (0.997)
p-Cl	4.56 ± 0.01	3.16 ± 0.03	2.29 ± 0.02	1.78 ± 0.01	1.09 ± 0.01	-0.65 (0.994)
m-Cl	3.16 ± 0.01	2.19 ± 0.2	1.51 ± 0.1	1.26 ± 0.02	0.726 ± 0.2	-0.66 (0.995)
ρ_X	-1.08 (0.999) ^b	-1.22 (0.999)	-1.34 (0.999)	-1.38 (0.998)	-1.52 (0.999)	

^aStandard deviation. ^bCorrelation coefficients.**Table 11.** Second order rate constants, $k_2 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, and Hammett reaction constants for the reaction of Y-Benzyl chlorides with X-Anilines in Acetonitrile at 45.0°C

X \ Y	p-CH ₃	H	p-Cl	m-Cl	p-NO ₂	ρ_Y
p-CH ₃ O	33.4 ± 0.3 ^a	25.1 ± 0.2	19.9 ± 0.1	17.3 ± 0.2	12.0 ± 0.2	-0.45 (0.993) ^b
p-CH ₃	22.9 ± 0.3	17.3 ± 0.2	14.1 ± 0.1	12.0 ± 0.2	8.35 ± 0.2	-0.45 (0.994)
H	13.8 ± 0.01	10.9 ± 0.02	8.71 ± 0.2	6.75 ± 0.1	4.56 ± 0.02	-0.51 (0.997)
p-Cl	8.28 ± 0.01	5.74 ± 0.03	4.16 ± 0.02	3.23 ± 0.01	1.98 ± 0.01	-0.65 (0.994)
m-Cl	5.74 ± 0.01	3.97 ± 0.2	2.75 ± 0.1	2.31 ± 0.02	1.20 ± 0.2	-0.70 (0.998)
ρ_X	-1.21 (0.994) ^b	-1.23 (0.999)	-1.34 (0.999)	-1.38 (0.998)	-1.56 (0.999)	

^aStandard deviation. ^bCorrelation coefficients.**Table 12.** Second order rate constants, $k_2 (\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$, and Hammett reaction constants for the reaction of Y-Benzyl chlorides with X-Anilines in Acetonitrile at 35.0°C

X \ Y	p-CH ₃	H	p-Cl	m-Cl	ρ_Y
p-CH ₃ O	34.0 ± 0.1 ^a	69.3 ± 0.6	252 ± 1		2.21 (0.997) ^b
H	14.4 ± 0.1	33.3 ± 0.2	82.2 ± 0.7	151 ± 0.3	1.86 (0.999)
p-Cl	4.79 ± 0.01	10.2 ± 0.03	25.2 ± 0.2	48.0 ± 0.3	1.83 (0.999)
m-Cl	2.58 ± 0.01	5.64 ± 0.02	12.2 ± 0.01	21.3 ± 0.03	1.66 (0.998)
m-NO ₂	0.458 ± 0.002	0.931 ± 0.004	1.68 ± 0.004	2.65 ± 0.01	1.37 (0.995)

ρ_X	-2.11 (0.999) ^b	-2.13 (0.999)	-2.43 (0.998)	-2.48 (0.999)
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^aStandard deviation. ^bCorrelation coefficients.

known to decrease at higher reaction temperature,¹⁷ but the trends in the changes of $|\rho_X|$ and $|\rho_Y|$ in Table 7 are not so clear-cut. In contrast, the magnitude of ρ_{XY} decreases uniformly by ca. 0.03 per 10°C rise in temperature, which is again a correct reflection of a decrease in the extent of bond making as the reaction temperature rises.

Experimental

Materials and kinetic procedures were as described previously.^{8,12} The rate data, Tables 8-12, are presented as Supplementary Materials.

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Comparison of the Stability Constants of Cd(II)-, Cu(II)-, and Pb(II)-Humate Complexes

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A comparative investigation of the complexations of divalent metal ions (Cd, Cu, and Pb) by a well characterized soil humic acid (HA) from Okchun Metamorphic Belt was carried out in 0.05 M KNO₃ and pH of 4.5 using ion selective electrodes. A continuous distribution model based on the Scatchard Plot was used to determine the stability constants, because the constants obtained by this modeling technique takes the variations in binding energies into consideration without regards to the manner in which M(II) ion is bound on HA. The mean value of log *K*, were 4.05 ± 0.60, 4.92 ± 0.36, and 5.63 ± 0.34 l mol⁻¹ for Cd(II)-, Pb(II), and Cu(II)-humate complexes respectively. The values of intrinsic constant (log *K*_{int}; binding at strongest site) were 7.12 ± 0.30, 6.59 ± 0.32, and 5.07 ± 0.56 l mol⁻¹ in the order Cu(II) > Pb(II) > Cd(II) ion.

Introduction

The rapidly industrialization nations of Asia are becoming more aware of the consequences of the discharge of heavy metals into freshwater systems, and their subsequent migration to other environmental compartments such as irrigated agricultural lands.¹ The bioavailability of environmentally sensitive metals (e.g. Cd, Cu, Pb, Zn, and Ni) is strongly influenced by the chemical speciation of a given metal, defined as the partitioning of total metal into all possible chemical forms in a given system. In an irrigated agricultural land, one of the major components is the species of metals complexed to humic substances. There are many investigations of the complexation of divalent Cd, Cu and Pb with humic (HA) and fulvic (FA) acids reported in the literature.²⁻⁶ However, conflicting information has been obtained regarding the nature of M(II) binding by humic substances.^{5,7,8} Many types of modeling techniques have been used in the calculation of stability constants of the complexes thus formed.^{5,9-11} The humic and fulvic acids used in these investigations are different, and their properties depend on their origin and on the source materials.¹² All these factors make it difficult to compare the results of one investigation with those of others carried out with different humic substances or methods.

A recent study of the probe of metal binding sites on humic acids were carried out using ¹¹³Cd NMR spectroscopic method, and the preliminary results seem to suggest that there are several types of carboxylate moieties for binding of Cd(II) ions on HA. Therefore, the stability constants of M(II)-humate complexes were evaluated using a continuous

distribution model based on the Scatchard Plot. This modeling technique was chosen because this method takes into consideration the variations in the binding energies without regards to manner in which M(II) ions are bound on HA.

The purpose of this work is the determination of the stability constants of the complexes between environmentally sensitive divalent metal ions (Cd, Cu, and Pb) and a representative soil humic acid from the Okchun Metamorphic Belt in Korea. The concentrations of Cd(II), Cu(II), and Pb(II) species were determined using ion selective electrodes (non-separation method).

Experimental

Materials and reagents. The humic acid used in this investigation was extracted from topsoils (0-5 cm) obtained from Okchun Metamorphic Belt by base digestion (1 M NaOH, 48 h) under N₂ atmosphere. The HA was recovered by acid precipitation (HCl), then was washed repeatedly with acid to remove trace of inorganic impurities, followed by extensive dialysis against double deionized water to remove other impurities such as Cl⁻ ion, and the final product was freeze-dried in protonated form. It has been characterized by chemical and spectroscopic methods.¹³

The stock HA solution was prepared by dissolving 0.0548 ± 0.0001 g of accurately weighed HA with a minimum quantity of 0.1 M KOH (~3 ml, 1 h) and further diluting it with 0.05 M KNO₃ to 100 ml, and pH adjusted to 4.5 with HNO₃ and KOH solutions. The stock Cd, Cu, and Pb solutions were prepared by dissolving accurately weighed nitrate salts in