

The thickness decreased on reduction as can be expected considering the release of anions from the polymer film.

The optical properties of the polymers continuously changed with growth of the film. Initial rise and gradual decrease in the later stage of the real part of the refractive index n indicated increase and decrease, respectively, in the compactness of the structure. The imaginary part of the refractive index κ increased with the advancement of polymerization and diminished on reduction of the polymer film as can be expected from the change in the electronic carrier density. However, the changes in κ on reduction of the film were small and in the case of acidic electrolytes even occurred in the reverse direction from what is expected by a simple consideration of the charge carrier density. The imaginary part of the refractive index of polypyrrole seemed to be predominantly determined by the existence of an absorption band around the visible range.

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Kinetics and Mechanism for the Reactions of N-Methyl-N-phenylcarbamoyl Chlorides with Benzylamines in Acetonitrile

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Kinetic studies are carried out on the reactions of N-methyl-N-phenylcarbamoyl chlorides with benzylamines in acetonitrile. The selectivity parameters, ρ_X ($= -0.6 \sim -0.8$), ρ_Y ($= 1.0-1.1$), and ρ_{XY} ($= -0.14$), suggest that the reaction proceeds by an S_N2 mechanism. Kinetic isotope effects, k_H/k_D , involving deuterated nucleophiles ($XC_6H_4CH_2ND_2$) are all inverse type (< 1.0), and the trends of changes in the magnitude are consistent with those expected for the observed negative sign of ρ_{XY} ($= \partial \rho_X / \partial \sigma_Y = \partial \rho_Y / \partial \sigma_X < 0$). The relatively low activation enthalpies also support the proposed mechanism.

Introduction

Solvolyses of N,N-disubstituted carbamoyl chlorides have been studied extensively. A general consensus is that solvolysis of N,N-disubstituted carbamoyl chlorides proceeds primarily through an S_N1 mechanism, which is favored by a strong electron delocalization from nitrogen.¹⁻⁵ However for some systems, evidence in support of a weak nucleophilic participation by solvent has also been presented, and an S_N2 (intermediate) mechanism has been proposed.⁶

In contrast, for the aminolysis reactions of N,N-disubstituted carbamoyl chlorides, an S_N2 mechanism was often sugge-

sted to apply. Hall has suggested a bimolecular mechanism for the reactions of N,N-dimethylcarbamoyl chloride with aliphatic amines.⁷ Johnson *et al.*,³ have shown that N,N-diphenylcarbamoyl chloride reacts directly with amines forming the corresponding N,N-diphenylurea derivatives. On the other hand, Kim *et al.*,⁸ reported that nucleophilic substitution reactions of N,N-dimethylcarbamoyl chloride are bimolecular whereas those of N,N-diphenylcarbamoyl chloride are unimolecular. Aminolyses of N-arylcarbamates, $ArNHCOOAr'$, are known to proceed by the overall second- and third-order processes in aprotic solvents.⁹

In the course of our development works on the application

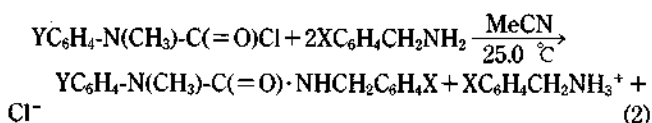
of cross-interaction constants¹⁰ (ρ_{ij} in Eqs. (1), where i and j represent substituents X in the nucleophile, Y in

$$\log(k_{ij}/k_{HH}) = \rho_i\sigma_i + \rho_j\sigma_j + \rho_{ij}\sigma_i\sigma_j \quad (1a)$$

$$\rho_{ij} = \frac{\partial^2 \log k_{ij}}{\partial \sigma_i \partial \sigma_j} = \frac{\partial \rho_i}{\partial \sigma_j} = \frac{\partial \rho_j}{\partial \sigma_i} \quad (1b)$$

the substrate and/or Z in the leaving group), as a mechanistic tool for organic reactions in solution, we found that the sign of ρ_{XY} is normally negative for S_N2 processes whereas it is positive for the acyl transfer reactions with rate-limiting breakdown of an intermediate.¹¹

In this work, we investigated the reactions of *N*-methyl-*N*-phenylcarbamoyl chlorides with benzylamines in acetonitrile, Eq. (2), and the mechanism for the reaction is discussed in terms of the derived cross-interaction constant, ρ_{XY} .



X = *p*-CH₃O, *p*-CH₃, H, *p*-Cl or *m*-Cl

Y = *p*-CH₃O, H, *p*-Cl or *p*-NO₂.

$$k_{\text{obs}} = k_1 + k_2[\text{BA}] \quad (3)$$

Results and Discussion

Table 1. Second order rate constants, k_2 ($\times 10^2 \text{ M}^{-1}\text{s}^{-1}$), for reactions of Y-substituted *N*-methyl-*N*-phenylcarbamoyl chlorides with X-substituted benzylamines in acetonitrile at 25.0 °C

X	Y	<i>p</i> -CH ₃ O	H	<i>p</i> -Cl	<i>p</i> -NO ₂	ρ_Y^{-a}
	<i>p</i> -CH ₃ O		3.72	6.79	15.6	202
<i>p</i> -CH ₃		6.90 ^b	16.8 ^b			
		4.69 ^c	9.90 ^c			
		3.19	5.84	13.3	164	1.12
H		4.70 ^b	12.7 ^b		308 ^b	
		3.45 ^c	7.69 ^c		194 ^c	
		2.53	4.66	10.3	122	1.10
<i>p</i> -Cl			10.5 ^b		205 ^b	
			5.91 ^c		144 ^c	
		1.87	3.34	7.18	80.5	1.10
<i>m</i> -Cl ^d		1.54	2.70	5.93	61.2	1.04
	ρ_X^d	-0.59	-0.62	-0.66	-0.80	$\rho_{XY}^e =$
β_X^e		0.59	0.63	0.66	0.80	-0.14

^aThe σ and σ^- values were taken from: D. H. McDaniel and H. C. Brown, *J. Org. Chem.* 1958, 23, 420. Correlation coefficients were better than 0.998 in all cases. ^bAt 45.0 °C. ^cAt 35.0 °C. ^dThe σ values were taken from: D. H. McDaniel and H. C. Brown, *J. Org. Chem.* 1958, 23, 420. Correlation coefficients were better than 0.999 in all cases. ^eThe pK_a (H₂O, 25.0 °C) values were taken from: A. Fischer, W. J. Galloway and J. Vaughan, *J. Chem. Soc.* 3588 (1964). Correlation coefficients were better than 0.999 in all cases. X = *p*-CH₃O was excluded from the Brønsted plot for ρ_X (benzylamine) due to unreliable pK_a value listed. ^fCorrelation coefficient was better than 0.999.

The reactions of *N*-methyl-*N*-phenylcarbamoyl chlorides with benzylamines (BA) in acetonitrile followed clean second-order kinetics, Eq. (3), with $k_1 = 0$ in acetonitrile. The second-order rate constants, k_2 , determined are summarized in Table 1. Rates are faster with a stronger nucleophile, $\delta\sigma_X < 0$, and with a stronger electron acceptor Y, $\delta\sigma_Y > 0$. This latter fact suggests that negative charge develops at the reaction center carbon in the transition state (TS). The reaction rate is found to be more sensitive to substituent Y than to a substituent on the amine portion of the carbamoyl chlorides ($|\rho_Y| > |\rho_X|$). This may be ascribed to a rather tight TS for the reaction with a relatively large bond making and a low degree of bond cleavage. In contrast to this proposal, a relatively small negative cross-interaction constant ρ_{XY} (-0.14) is obtained.^{10b} This could be due to the two nonconjugating intervening groups (CH₂ in benzylamine and N-CH₃ in the substrate), which are known to reduce ρ values by ca. 2.8.¹⁰ For the reactions of cinnamoyl chlorides, YC₆H₄CH=CHCOCl, with anilines^{11b} the ρ_{XY} value of +0.88 was obtained in acetonitrile at 25.0 °C, which was interpreted to suggest a stepwise reaction with rate-limiting breakdown of the zwitterionic tetrahedral intermediate. On the other hand, a very small negative ρ_{XY} value of -0.04 was observed for the reactions of phenyl chloroformates, YC₆H₄OCOC(=O)Cl, with anilines in acetonitrile at 25.0 °C.^{11c} This small negative ρ_{XY} value was rather difficult to interpret but based on other experimental evidence the reactions was considered to proceed by a direct displacement (S_N2) mechanism.

Kinetic isotope effects (k_H/k_D) involving deuterate benzylamine nucleophiles (XC₆H₄CH₂ND₂)^{10c} have been determined. The results in Table 2 indicate that the k_H/k_D values are all inverse type ($k_H/k_D < 1.0$) and the magnitude is greater with a more electron withdrawing substituent in the nucleophile (X = *m*-Cl) and with a more electron donating Y substituent. These trends are again in accord with those expected for the S_N2 reactions.^{10c} Since ρ_{XY} is negative, a relatively weaker nucleophile ($\delta\sigma_X > 0$) should lead to a lesser degree of bond formation ($\delta\rho_Y < 0$), Eqs. (1b) and (4). Thus the relatively larger k_H/k_D values for X = *m*-Cl in Table 2 than those corresponding values for X = H can be ascribed to a decrease in the N-H(D) bending vibrational frequency since the nucleophile, benzylamine, is farther away from the carbonyl car-

Table 2. Kinetic isotope effects (k_H/k_D) on the second order rate constants (k_2) for reactions of Y-substituted *N*-methyl-*N*-phenylcarbamoyl chlorides with X-substituted benzylamines (NH₂CH₂C₆H₄X and ND₂CH₂C₆H₄X) in acetonitrile at 25.0 °C

X	Y	k_H	k_D	k_H/k_D
		($\times 10^2 \text{ M}^{-1} \text{ s}^{-1}$)	($\times 10^2 \text{ M}^{-1} \text{ s}^{-1}$)	
H	<i>p</i> -CH ₃ O	2.53 ± 0.02 ^a	2.72 ± 0.03	0.930 ± 0.005 ^b
H	H	4.66 ± 0.03	5.12 ± 0.02	0.910 ± 0.003
H	<i>p</i> -Cl	10.3 ± 0.2	11.6 ± 0.3	0.888 ± 0.008
H	<i>p</i> -NO ₂	122 ± 4	152 ± 5	0.803 ± 0.006
<i>m</i> -Cl	<i>p</i> -CH ₃ O	1.54 ± 0.02	1.64 ± 0.03	0.939 ± 0.005
<i>m</i> -Cl	H	2.70 ± 0.01	2.90 ± 0.02	0.931 ± 0.008
<i>m</i> -Cl	<i>p</i> -Cl	5.93 ± 0.03	6.59 ± 0.04	0.900 ± 0.010
<i>m</i> -Cl	<i>p</i> -NO ₂	61.2 ± 0.9	71.7 ± 3	0.854 ± 0.007

^aStandard deviation. ^bStandard error.

Table 3. Activation parameters^a for the reactions of Y-substituted N-methyl-N-phenylcarbamoyl chlorides with X-substituted benzylamines in acetonitrile

X	Y	ΔH^\ddagger , kcal mol ^{-1b}	$-\Delta S^\ddagger$, cal deg ⁻¹ K ^{-1c}
<i>p</i> -CH ₃	<i>p</i> -CH ₃ O	6.4	21
<i>p</i> -CH ₃	H	9.0	11
H	<i>p</i> -CH ₃ O	5.1	26
H	H	10.6	12
H	<i>p</i> -NO ₂	7.9	9.1
<i>p</i> -Cl	H	7.4	20
<i>p</i> -Cl	<i>p</i> -NO ₂	10.0	2.7

^aCalculated values at 25.0 °C. ^bProbable errors are ± 0.4 kcal mol⁻¹. ^cProbable errors are ± 1.1 cal mol⁻¹K⁻¹.

bon in the TS, *i.e.*, a lesser degree of bond formation, for X=*m*-Cl compared to that for a more electron donating X substituent (X=H). Likewise a stronger electron donating Y substituent ($\delta\sigma_Y < 0$) leads to a relatively larger k_H/k_D value indicating a relatively low degree of bond making, $\delta\rho_X > 0$, Eqs. (1b) and (5).

$$\rho_{XY} = \frac{\partial \rho_Y}{\partial \sigma_X} = \frac{(-)}{(+)} = < 0 \quad (4)$$

$$\rho_{XY} = \frac{\partial \rho_X}{\partial \sigma_Y} = \frac{(+)}{(-)} = < 0 \quad (5)$$

The activation parameters, ΔH^\ddagger and ΔS^\ddagger , in Table 3 were determined using the k_2 values (Table 1) at three temperatures. The enthalpies of activation are relatively low which is consistent with low degree of bond cleavage.¹² The ΔS^\ddagger value for the reaction of reactants with X=*p*-Cl and Y=*p*-NO₂ is small negative, which may again suggest a low degree of bond cleavage in the TS; the activation process in such case will have relatively small change in solvation, since the bond cleavage of Cl⁻ in MeCN may not involve significant solvation changes.¹³

In summary, the negative sign of ρ_{XY} and the inverse k_H/k_D values (<1.0) with the trends of changes in the magnitude of k_H/k_D that are expected from the negative ρ_{XY} are consistent with the direct displacement (*S_N2*) mechanism.

Experimental

Materials. Solvent, acetonitrile was Aldrich HPLC grade, which was further distilled over phosphorus pentoxide. The benzylamine nucleophiles, Aldrich GR, were used without further purification. Preparations of deuterated benzylamines were as described previously.^{11b,c} The analysis (NMR and GC Mass spectroscopy) of the deuterated benzylamines showed more than 99% deuterium content, so that no corrections to kinetic isotope effects for incomplete deuterium were made.

The substrate, N-methyl-N-phenylcarbamoyl chloride, was Aldrich GR purchased, which was recrystallized before use. Y-Substituted N-methyl-N-phenylcarbamoyl chlorides were prepared by reacting Y-substituted N-methyl-N-phenylanilines with triphosgene followed by small amount of triethylamine in ethyl acetate. The product, *p*-methyl(Y) N-methyl-N-

phenylcarbamoyl chloride was obtained by column chromatography (silicagel, 30% ethyl acetate/*n*-hexane). The other products, *p*-substituted(Y) N-methyl-N-phenylcarbamoyl chlorides were purified by recrystallization from *n*-hexane. The substrates synthesized were confirmed by spectral and elementary analysis as follows.

***p*-CH₃OC₆H₄N(CH₃)C(O)Cl.** liquid. δ_H (CDCl₃) 6.7-7.0 (C₆H₄, 4H, m), 3.8 (CH₃O, 3H, s), 3.2 (CH₃, 3H, s). ν_{max} (neat) 3040 (C-H), 2850 (C-H, aromatic), 1740 (C=O). m/z 199 (M⁺). (Calc. for C₉H₁₀ClNO: C, 54.3; H, 5.0. Found: C, 54.3; H, 5.1%).

***p*-ClC₆H₄N(CH₃)C(O)Cl.** mp 68-70 °C. δ_H (CDCl₃) 6.7-7.3 (C₆H₄, 4H, m), 3.2 (CH₃, 3H, s), ν_{max} (KBr) 3050 (C-H), 2920 (C-H, aromatic), 1740 (C=O). m/z 203 (M⁺). (Calc. for C₈H₇Cl₂NO: C, 47.3; H, 3.4. Found: C, 47.2; H, 3.4%).

***p*-NO₂C₆H₄N(CH₃)C(O)Cl.** mp 102-104 °C. δ_H (CDCl₃) 6.8-7.6 (C₆H₄, 4H, m), 3.2 (CH₃, 3H, s). λ_{max} (KBr) 3100 (C-H), 2950 (C-H, aromatic), 1740 (C=O). m/z 214 (M⁺). (Calc. for C₈H₇ClN₂O₃: C, 44.9; H, 3.3. Found: C, 44.8; H, 3.2%).

Kinetic procedures. Rates were measured conductimetrically in acetonitrile. The conductivity bridge used in this work was a self-made computer automatic A/D converter conductivity bridge. Pseudo-first order rate constants, k_{obs} were determined by the Guggenheim method¹⁴ with a large excess of benzylamine; [N-methyl-N-phenylcarbamoyl chloride] = 2.0×10^{-4} mol dm⁻³ and [benzylamine] = 0.01-0.40 mol dm⁻³. Second order rate constants, k_2 , were obtained from the slope of a plot of k_{obs} vs [benzylamine] with more than four concentrations of benzylamine, Eq. (3). The k_2 values in Table 1 are the averages of more than triplicate runs and were reproducible to within $\pm 3\%$.

Product analysis. N-methyl-N-phenylcarbamoyl chloride was reacted with excess *p*-methylbenzylamine with stirring for more than 15 half-lives at 25.0 °C in acetonitrile, and the products were isolated by evaporating the solvent under reduced pressure. The product mixture was treated with column chromatography (silicagel, 40% ethyl acetate/*n*-hexane). The same method was used for other product. Analysis of the products gave the following results.

C₆H₅N(CH₃)C(O)NHCH₂C₆H₄-*p*-CH₃. $R_f = 0.35$ (40% ethyl acetate/*n*-hexane). liquid. δ_H (CDCl₃) 7.0-7.2 (C₆H₅, C₆H₄, NH, 10H, m), 4.3 (CH₂, 2H, d), 3.2 (NCH₃, 3H, s), 2.2 (CH₃, 3H, s). ν_{max} (neat) 3220 (N-H), 3050 (C-H), 2950 (C-H, aromatic), 1690 (C=O). m/z 254 (M⁺).

***p*-NO₂-C₆H₄N(CH₃)C(O)NHCH₂C₆H₄-*p*-CH₃.** $R_f = 0.37$ (40% ethyl acetate/*n*-hexane). liquid. δ_H (CDCl₃) 7.0-7.5 (C₆H₅, C₆H₄, NH, 9H, m), 4.3 (CH₂, 2H, d), 3.2 (NCH₃, 3H, s), 2.2 (CH₃, 3H, s). ν_{max} (neat) 3220 (N-H), 3050-3100 (C-H), 2950 (C-H, aromatic), 1690 (C=O). m/z 299 (M⁺).

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Stability and Electrochemical Characteristics of Polyaniline Salt Films in 1 N HCl Solution

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Thin films of polyaniline (PANI) salts were *in situ* deposited on a Pt plate during either chemical polymerization or electrochemical polymerization. The oxidation states of the salt films were controlled by the applied DC potential. AC impedance of the Pt/PANI electrode were measured in monomer-free 1 N HCl solution in order to investigate the electroodic properties of the films at the following applied DC potentials: 0, 0.45 and 0.75 V *vs.* SCE. Very small differences in film conductivity according to its oxidation state were observed by analysis of the impedance spectra, the reasons of which are complicated by enriched water content in the film and possible decrease in the film thickness during the measurements. The electrochemical activity of the film/solution interface varied with its oxidation state. Stability of the film in 1 N HCl solution was also evaluated by impedance and cyclic voltammetry measurements.

Introduction

Among organic conducting polymers, polyanilines (PANIs) have been extensively studied as prospective materials for various electrochemical applications such as electrochromic devices, energy storages, photocorrosion protection, and electrochemical sensors.¹⁻⁷ Their electrochemical properties, stability in air, and various processing methods have been also illuminated in the literature.⁸⁻¹² It was reported that electrochemical characteristics of polyaniline films can be effectively investigated by impedance measurements.¹³ Mensfeld *et al.*¹⁴ used impedance spectroscopy (IS) technique to examine the effectiveness of polybutadiene coating on metal surface and showed the applicability of this technique. Pasquali *et al.*¹⁵ also used impedance spectroscopy and cyclic voltammetry to investigate storage characteristics of substituted polyanilines under several different environments. Goldenberg *et al.*¹⁶ compared the electrochemically grown films with the films

prepared by several methods and demonstrated possibility of using a number of simple techniques to produce electroactive thin films of polyanilines.

Even though PANI is referred to as the most stable material within the class of conducting polymers,⁹ only a few studies devoted to stability have been reported.^{15,17,18} Stability in aqueous or organic solutions at open circuit or at given potentials should be thoroughly investigated in order to assess its full applicability in practical uses. Resistance to degradation in sulfuric and organic solutions was reported in the literature,¹⁵ in which unpleasant degradation would be serious problem in its practical applications. In this work, IS technique and cyclic voltammetry were utilized in order to investigate stability in acidic chloride solution and the electroodic properties of PANI salt films at three different oxidation states (emeraldine, pernigraniline, and leucoemeraldine).