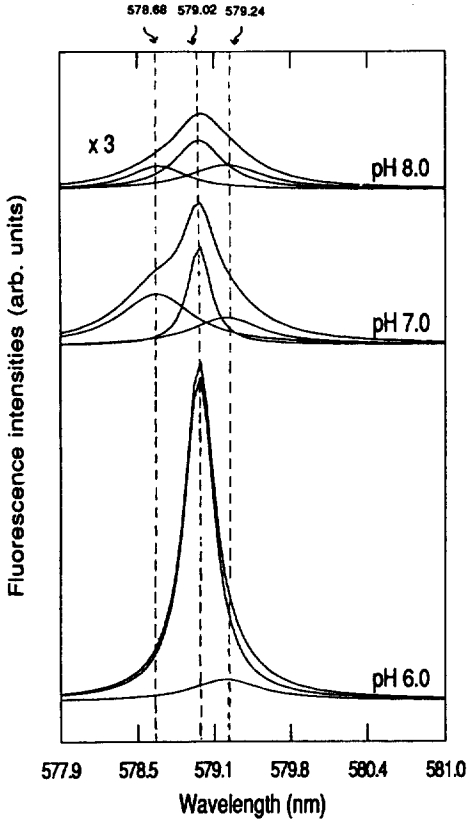

Figure 6. The deconvoluted excitation spectra of Eu(III)-glutarate in Figure 4.

shown in Figure 6. It reveals the main peak corresponding to Eu(glutarate)$^+$ with a small shoulder peak (Eu(glutarate)$_2^-$) at pH 6.0, but at a higher pH of 7.0, the shoulder peak at 578.68 nm can be seen clearly, revealing the occurrence of Eu(III) hydroxo complex formation. At still higher pH of 8.0, all three peak components (Eu(glutarate)$^+$, Eu(glutarate)$_2^-$ and Eu(III)-hydroxo) can be seen in reduced intensities due to precipitation. It shows that the effect of hydrolysis is more pronounced in weakly complexing ligand systems.

Through this spectral investigation, it has been shown that Eu^{3+} ion hydrolyzes but slightly at pH below 6.0. The excitation peak at 578. 63 nm at pH greater than 6.0 was identified as that due to the presence of Eu(III) hydroxo complexes. It was also shown that the formation of Eu(III) hydroxo complex poses less complication during complexation studies between trivalent metal ions and organic ligands, if the investigations are conducted at pH 6.0 or below.

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Kinetics and Mechanism of the Reactions of S-Phenyl Dithiobenzoates with Benzylamines in Acetonitrile

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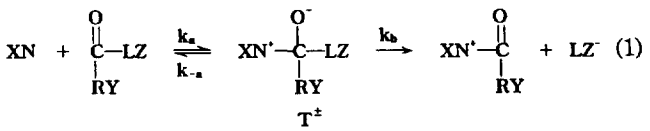
Kinetic studies are carried out on the reaction of S-phenyl dithiobenzoates with benzylamines in acetonitrile at 30.0 ℃. Small magnitude of ρ_X (β_X) as well as ρ_Z (β_Z) obtained suggests rate-limiting nucleophilic attack of the thiocarbonyl carbon. This is supported by the unusually small magnitude of ρ_{XY} and ρ_{YZ}, albeit their signs do not agree with those expected. Moreover, the inverse secondary kinetic isotope effects ($k_H/k_D<1.0$) involving deuterated benzylamine nucleophiles are also in line with the proposed mechanism.

Introduction

The acyl transfer reactions involving amine nucleophiles have been extensively studied due to their biological as well as synthetic relevance.[1] The acyl transfer reactions with a series of structurally similar amines are often found to ex-

hibit a nonlinear Brönsted type plot showing a break from a large ($\beta_{nuc}\approx$0.8-1.0) to a small ($\beta_{nuc}\approx$0.1-0.3) rate dependence on basicity of the amines at pK_o as the amine basicity is increased.[2] The break at pK_o, where $k_{-a}=k_b$ (eq. 1), has been attributed to a change in the rate-determining step from breakdown (k_b) to formation (k_a) of a tetrahedral intermediate, $T^{\pm}$, in the reaction path,[2] eq. (1) where X, Y and Z represent substituents in the nucleophile, substrate and nucleofuge, respectively.



(1)

In a previous work,[3] we concluded based on the sign and magnitude of cross-interaction constants, ρ_{XY} (>0), ρ_{YZ} (<0) and ρ_{XZ} (>0), eq. (2),[4] that the reactions of S-phenyl dithiobenzoates with aniline nucleophiles in acetonitrile proceed by a mechanism in which breakdown of the intermediate, $T^{\pm}$, is rate limiting. In view of the mechanistic change observed

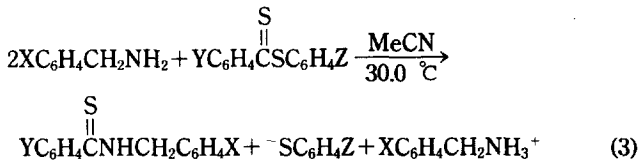
$$\log(k_{ij}/k_{HH})=\rho_i\sigma_i+\rho_j\sigma_j+\rho_{ij}\sigma_i\sigma_j \quad (2a)$$

$$\rho_{ij}=\frac{\partial\rho_i}{\partial\sigma_i}=\frac{\partial\rho_i}{\partial\sigma_j} \quad (2b)$$

where i, j=X, Y or Z in eq. (1)

experimentally,[2] and also theoretically predicted,[5] for the acyl transfer reactions with a more basic nucleophile than nucleofuge, it is of much interest to see whether such a mechanistic change takes place or not when we use strongly basic amine nucleophiles in the reactions of S-phenyl dithiobenzoates in acetonitrile.

In this work, we report the results of kinetic studies on the acyl transfer reactions of S-phenyl dithiobenzoates with benzylamines in acetonitrile at 30.0 ℃, eq. (3). We have app-



(3)

lied various mechanistic criteria including those involving the sign and magnitude of the cross-interaction constants, ρ_{XY}, ρ_{YZ} and ρ_{XZ}, and concluded that the mechanistic change-over to rate-limiting formation of $T^{\pm}$ (or concerted process) indeed takes place by using more basic amines, benzylamines.

Results and Discussion

The second-order rate constants, k_2, determined by eq. (4), for the reactions of S-phenyl dithiobenzoates with benzylamines (BA) in acetonitrile at 30.0 ℃ are summarized in Table 1. The intercepts, k_0, were zero in all cases and no third-order kinetics were observed indicating that there is no general base catalysis by benzylamine or amide product. A good second-order kinetics, eq. (4), and product analysis support the general mechanism given by eq. (3) with no other side reactions or complications.

Table 1. The second order rate constants, $k_2\times10^2$ dm^3 mol^{-1}s^{-1} for the reactions of Z-S-phenyl Y-dithiobenzoates with X-benzylamines in acetonitrile at 30.0 ℃

Y	Z	X			
		p-OMe	*p*-Me	H	*p*-Cl
Me	*p*-Me	40.2	33.6	24.9	17.5
	H	47.7	40.9	31.8	22.6
	p-Cl	59.6	51.9	41.0	32.5
	p-Br	61.1	53.0	42.3	33.2
H	*p*-Me	47.2	40.1	29.9	21.0
	H	56.8	48.9	38.2	26.9
	p-Cl	69.7	61.8	50.2	38.5
	P-Br	70.5	62.7	50.9	39.3
p-Cl	*p*-Me	58.8	50.7	38.1	26.4
	H	71.8	61.4	49.4	34.7
	p-Cl	87.8	78.2	63.3	49.0
	p-Br	88.4	78.9	63.9	49.5

Table 2. The Hammett (ρ_X, ρ_Y and ρ_Z) and Brönsted (β_X and β_Z) coefficients for the reactions of Z-S-phenyl Y-dithiobenzoates with X-benzylamines

(i) ρ_X and (β_X) values[a]

Y/Z	*p*-Me	H	*p*-Cl	*p*-Br
p-Me	−0.73(0.26)	−0.65(0.24)	−0.53(0.19)	−0.53(0.19)
H	−0.71(0.26)	−0.65(0.24)	−0.52(0.19)	−0.51(0.19)
p-Cl	−0.71(0.25)	−0.63(0.24)	−0.52(0.19)	−0.51(0.19)

(ii) ρ_Z and (β_Z) values[a]

Y/X	*p*-OMe	*p*-Me	H	*p*-Cl
p-Me	0.44(−0.18)	0.48(−0.20)	0.55(−0.23)	0.69(−0.29)
H	0.43(−0.18)	0.48(−0.20)	0.56(−0.24)	0.67(−0.28)
p-Cl	0.43(−0.18)	0.47(−0.20)	0.55(−0.23)	0.68(−0.29)

(iii) ρ_Y values[a]

X/Z	*p*-Me	H	*p*-Cl	*p*-Br
p-OMe	0.42	0.45	0.43	0.41
p-Me	0.45	0.45	0.45	0.44
H	0.47	0.48	0.47	0.45
p-Cl	0.45	0.47	0.45	0.44

[a]The correlation coefficients were better than 0.995 in all cases.

$$k_{obsd}=k_0+k_2[BA] \quad (4)$$

The Hammett (ρ_i) and Brönsted (β_i) coefficients based on the observed macroscopic rate constant, k_2 (in Table 1), are collected in Table 2. We found no break in the Brönsted-type plot so that no mechanistic change is anticipated. The magnitude of ρ_X (ρ_{nuc}) as well as of β_X (β_{nuc}) is small and especially that of β_X is within the range normally observed for the acyl transfer reactions with nucleophilic attack of the carbonyl carbon, which can be either rate-limiting formation of the tetrahedral intermediate, $T^{\pm}$, or concerted pro-

Table 3. The cross-interaction constants, ρ_{XY}, ρ_{YZ} and ρ_{XZ}, for the reactions of Z-S-phenyl Y-dithiobenzoates with X-benzylamines in acetonitrile at 30.0 ℃

(i) ρ_{XY} values[a]

Z	ρ_{XY}
p-Me	0.06
H	0.06
p-Cl	0.05
p-Br	0.05

(ii) ρ_{YZ} values[a]

X	ρ_{YZ}
p-OMe	−0.02
p-Me	−0.02
H	−0.02
p-Cl	−0.03

(iii) ρ_{XZ} values[a]

Y	ρ_{XZ}
p-Me	0.50
H	0.50
p-Cl	0.49

[a] The correlation coefficients were better than 0.997 in all cases.

cess[2] ($\beta_X \cong 0.1$-0.3). The two types of mechanisms are kinetically indistinguishable.[6] Similarly, the magnitudes of ρ_Z (ρ_{lg}) and β_Z (β_{lg}) are also small lending further support to the proposed concerted mechanism.[7]

Applying steady-state approximation to $T^{\pm}$ in eq. (1), we can show that the magnitude of ρ_X (β_X) and ρ_Z (β_Z) should be much smaller for the-limiting nucleophilic attack (k_a) than for the rate-limiting breakdown (k_b). For the latter mechanism the macroscopic rate constant, k_2, is a complex quantity, $k_2 = k_a/k_{-a}k_b = K \cdot k_b$, assuming $k_{-a} \gg k_b$.[10] Thus eq. (5) shows that ρ_X based on k_2, which is the rate constant in the rate-limiting breakdown mechanism, is greater by *ca.* three times than ρ_X based on k_a, which is the rate constant involved in the rate-limiting nucleophilic attack, for which the assumptions of $k_{-a} \ll k_b$ and $k_2 = k_a$ apply.[10]

$$\rho_X(k_2) = \frac{\partial \log k_2}{\partial \sigma_X} = \frac{\partial \log k_a}{\partial \sigma_X} - \frac{\partial \log k_{-a}}{\partial \sigma_X} + \frac{\partial \log k_b}{\partial \sigma_X}$$
$$= \rho_X(k_a) - \rho_X(k_{-a}) + \rho_X(k_b)$$
$$= (-) - (+) + (-) \quad (5)$$

The concerted or the step-wise mechanism with rate-limiting formation of $T^{\pm}$ is quite reasonable in view of the fact that the nucleophiles, benzylamine, are far more basic ($pK_a \cong 9.1$-9.5 for $XC_6H_4CH_2NH_3^+$ in water at 25.0 ℃[8] than the nucleofuges, thiophenol used in this work ($pK_a \cong 5.9$-7.0 for ZC_6H_4SH in water at 25.0 ℃).[9] Due to the narrow pK_a ranges of nucleophiles and nucleofuges employed in this work, no mechanistic change-over is found.

The cross-interaction constants determined by subjecting the macroscopic rate constants, k_2, to multiple regression using equation 2a (with appropriate X, Y or Z for i and j eq. (2a))[4] are summarized in Table 3. We note that the signs of ρ_{XY} (>0), ρ_{YZ} (<0) and ρ_{XZ} (>0) are all consistent with those for the acyl transfer mechanism with rate-limiting expulsion of the nucleofuges.[10] However, the magnitudes of ρ_{XY} and ρ_{YZ} are unusually small; they are in fact smaller by *ca.* one-tenth than those for the other similar reactions proceeding by the rate-limiting expulsion of the nucleofuges.[10,11] Thus the unusually small magnitudes of ρ_{XY} and ρ_{YZ} suggest that the rate-limiting nucleophilic attack is plausible albeit rate-limiting breakdown of $T^{\pm}$ is implicated by their signs.[10] In agreement with the mechanism proposed the magnitude of ρ_{XY} is small indicating that the degree of bond formation in the TS is low[4] and the TS is in an early stage along the reaction coordinate. The magnitude of ρ_{YZ} is nearly zero so that the extent of bond cleavage is also small[4] in the TS.

Table 4. The secondary kinetic isotope effects for the reactions of Z-S-phenyl Y-dithiobenzoates with deuterated X-benzylamines in acetonitrile at 30.0 ℃

X	Y	Z	k_H ($\times 10^2$ $M^{-1}s^{-1}$)	k_D ($\times 10^2$ $M^{-1}s^{-1}$)	k_H/k_D
p-OMe	*p*-Me	*p*-Br	61.1(± 0.01)[a]	73.7(± 0.06)	0.829± 0.003[b]
p-OMe	*p*-Cl	*p*-Br	88.4(± 0.01)	94.0(± 0.05)	0.940± 0.002
p-Cl	*p*-Me	*p*-Me	17.5(± 0.02)	21.5(± 0.03)	0.814± 0.001
p-Cl	*p*-Cl	*p*-Me	26.4(± 0.03)	30.2(± 0.03)	0.874± 0.002

[a] Standard deviation. [b] Standard error.

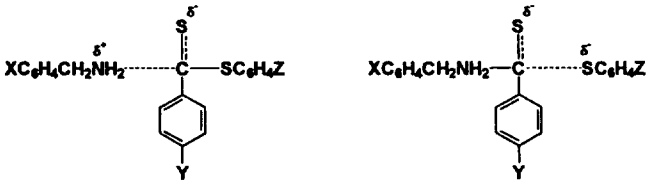
A further support for the rate-limiting nucleophilic attack is provided by the inverse secondary kinetic isotope effect, $k_H/k_D < 1.0$, involving deuterated nucleophiles, benzylamines, Table 4. The inverse effect is consistent with nucleophilic attack in the rate determining step, since in the nucleophilic attack the N-H vibrations in benzylamines are sterically hindered so that vibrational frequencies increase.[12] In contrast, the k_H/k_D values involving deuterated nucleophiles were normal ($k_H/k_D > 1.0$) in all the acyl transfer reactions that proceed through rate-limiting expulsion of the nucleofuges.[11]

We therefore conclude that the reactions of S-phenyl dithiobenzoates with benzylamines in acetonitrile proceed by the rate-limiting nucleophilic attack at the carbonyl carbon, despite the signs of the cross-interaction constants indicated otherwise. As has been noted often previously,[5,11b] no kinetic mechanistic criteria can be sufficient;[13] the signs of ρ_{XY} and ρ_{YZ} are just such an example. This brings us the importance of applying as many mechanistic criteria as possible for the prediction of a correct mechanism for a reaction.

The rate-limiting nucleophilic attack proposed for the reactions studied in this work, eq. (3), is in striking contract to the rate-limiting breakdown of the tetrahedral intermediate, $T^{\pm}$, predicted for the reactions of phenyl ($YC_6H_4C(O)OC_6H_4Z$)[11a] and thiophenyl benzoates ($YC_6H_4C(O)SC_6H_4Z$)[11b] with benzylamines under similar reaction conditions. We can think of the following reasons for the mechanistic change: Firstly the pK_a values used in the comparison of basicities for benzylamines ($pK_a \cong 9.1$-9.5),[8] phenoxides ($pK_a \cong 7.2$-10.2)[14] and thiophenoxides ($pK_a \cong 5.9$-7.0)[9] are those determined in water, not in acetonitrile. The relative basicities may differ in different medium, especially in a protic (water) and an aprotic (acetonitrile) medium. Secondly $YC_6H_4C{=}O$ group may be acting as a relatively strong electron donor. It has

been shown theoretically[5] as well as experimentally[2c,15,16] that an electron-donating non-leaving group, RY in eq. (1), favors the expulsion of a higher pK_a group by depressing the TS level involving cleavage of such a group. Thus if the YC_6H_4-C=O group acts as a stronger electron donor than the YC_6H_4-C=S group, the TS 1 level will be lowered more in the oxy-$T^{\pm}$ than in the thio-$T^{\pm}$ leading to the step-wise mechanism with rate-limiting expulsion of the nucleofuge,[16] TS 2.

In summary, the reaction of S-phenyl benzoates with benzylamines in acetonitrile proceeds by the rate-limiting nucleophilic attack on the carbonyl carbon. Although the signs of ρ_{XY} and ρ_{YZ} did not agree with those expected for the mechanism proposed, the small magnitudes of ρ_X (β_X) and



TS 1 TS 2

ρ_Z (β_Z) together with the unusually small ρ_{XY} and ρ_{YZ} support the mechanism proposed. We stress the importance of applying as many mechanistic criteria as possible to predict a correct mechanism since no kinetic criteria can be a sufficient condition.

Experimental

Materials. Merck G. R acetonitrile was used after three distillations. The benzylamine nucleophiles, Aldrich G. R, were used without further purification. Preparation of deuterated benzylamines were as described previously.[17] The analysis (NMR spectroscopy) of the deuterated benzylamines showed more than 99% deuterium content, so that no corrections to kinetic isotope effects for incomplete deuteration were made.

The S-phenyl dithiobenzoates were prepared by reacting thiophenyl benzoates with Aldrich GR Lawesson reagent. Thiophenyl benzoate was reacted with Lawesson reagent with stirring under refluxing condition in toluene. The organic layer was separated and the aqueous layer was extracted with 10 mL portion of methylene chloride. The solution was dried briefly over magnesium sulfate, and the products in pure form were isolated by evaporating the solvent under reduced pressure. Other substrates were prepared by similar method as above. The product mixture was treated with column chromatography. Melting points and spectral data for compounds synthesized are as reported previously.[3]

Kinetic procedures. Rates were measured conductimetrically at 30.0± 0.05 ℃ in acetonitrile. Pseudo-first order rate constants, k_{obs}, were determined by the Guggenheim method[18] with a large excess of benzylamine; [S-thiophenyl benzoate]=5.0×10^{-4} mol dm^{-3} and [benzylamine]=0.03-0.35 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. (4). The k_2 values in Table 1 are the averages of more than triplicate runs and were reproducible to within ± 3%.

Product analysis. S-Thiophenyl benzoate (Y=*p*-CH_3, Z=*p*-Br) was reacted with excess benzylamine with stirring for more than 15 half-lives at 30.0 ℃ in acetonitrile, and the products were isolated by evaporating the solvent under reduced pressure. The product mixture was treated with column chromatography (silica gel, 20% ethyl acetate/n-hexane). Analysis of the product gave the following results. $CH_3C_6H_4C(S)NHCH_2C_6H_5$; PMR (400 MHz, $CDCl_3$), 2.37 (3H, s, CH_3), 3.62 (1H, br, NH), 5.00 (2H, d, CH_2, J=5.12 Hz), 7.17-7.69 (9H, m, phenyl ring). ^{13}C NMR (100 MHz, $CDCl_3$), 198.89 (C=S), 141.78, 136.30, 129.13, 129.02, 128.38, 128.19, 126.17, 120.68 (phenyl ring), 51.03 (CH_2), 21.34 (CH_3).

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Ultrahigh Vacuum Study for the Model Systems of Ziegler-Natta Catalyst

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The surface structure of the adsorption site for the identification of active sites involved in the Ziegler-Natta catalyst was studied by surface science techniques. As an example of a real catalyst, $TiCl_3$ single crystals were prepared in a gradient furnace designed for this study and characterized by Auger Electron Spectroscopy (AES) and Low Energy Electron Diffraction (LEED) under ultrahigh vacuum condition. The chlorine covered Ti (0001) surface was employed as a model catalyst for the study of Ziegler-Natta catalyst. The diffuse LEED (DLEED) technique for the surface structural determination was applied to this disordered chlorine adsorbed on Ti (0001) surface. The diffuse scattering intensities were measured by a TV-computer method using a low light level video camera. From an analysis of two catalyst systems, the informations for the surface structure of the model catalyst surfaces were derived.

Introduction

Ziegler-Natta catalyst is known as a catalyst which can polymerize olefins with very high activity and selectivity under a wide range of conditions. The catalytic phenomena was initially discovered by Ziegler based on the observation of an anormalous effect of an colloidal nickel on the Aufbau reaction[1] and this work was developed to the stereospecific polymerization of propylene and higher α-olefins[2] using titanium chloride by Natta.

Ziegler-Natta catalysts are generally formed by combining a metal alkyl or hydride, which is an activator, with a transition metal salt under an inert atmosphere.[3] The $TiCl_3/AlR_3$ system is a commercially used catalyst. Usually colloidal particles of α-$TiCl_3$ are disperced into the hydrocarbon solvent and then ethylene or propylene gas is bubbled through the mixture. The polymer forms rapidly around the surface of the finely disperced particles, entraining the catalyst and masking the initial stages of the reaction.

The stereospecificity which Ziegler-Natta catalyst shows in the olefin polymerization is usually explained by the interactions between nonbonded atoms at the catalytic site. Catalytic mechanism proposed by Cossee and Arlman[4~6] is most widely accepted and this is described by the coordination theory between α-olefin and titanium to the active center. However, the fundamental questions about the nature of the active sites still remained unsolved and hence the atomic structure of titanium/chloride surfaces should be understood precisely to identify active sites.

In this paper, I approached to this question to elucidate the nature of the titanium/chloride surfaces by two ways. One way was done with the $TiCl_3$ crystal itself. This is the direct method and has the advantage that we can study the real catalyst. On the other hand, it has some disadvantage that $TiCl_3$ crystals are very hard to work with, because they are only commercially available as very small crystalites and very water sensitive. The other way was done with an appropriate model catalyst system, which is an indirect method, to investigate such active sites. This strategy can be used to simulate a $TiCl_3$ surface under ultrahigh vacuum (UHV) condition, directly forming a chlorine layer on the Ti single crystal surface. This is a common approach due to the convenience and stability of the simulated sample. This model catalyst also has an advantage in that adsorbates can be isolated on a surface of known geometry.

In this study, both methods have been employed to understand the surface structures present in the titanium/chlorine system using the surface-sensitive techniques under ultrahigh vacuum condition.

Experimental

Preparation of Single Crystals. Anhydrous, hydrogen-reduced, not-activated, powdered $TiCl_3$ (Alpha Products, U.S.A.) was used in growing $TiCl_3$ single crystals. A specially prepared pyrex tube, which can withstand a high temperature, was employed to grow $TiCl_3$ single crystals. The sample tubes had been stored in the drying oven at 130 ℃ and heated with a hot air gun before use. All manipulations of $TiCl_3$ crystals were carried out under Argon atmosphere in a dry box. The sample tube was vacuum sealed by an oxygen/acetylene torch and placed in the hot region of the gradient furnace. The gradient furnace which is used in sublimation and recrystallization of $TiCl_3$ crystals is shown in