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Hydrolysis of *N*-aryl thioncarbamate esters. Modified Marcus equation for reactions with asymmetric intrinsic barriers†

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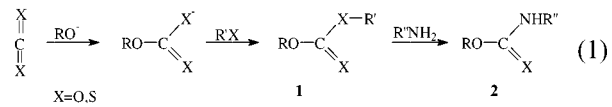
ABSTRACT: The hydrolysis of ethyl *N*-*p*-substituted arylthioncarbamates was studied at 100 °C in the pH range 6.5–12.5. No general catalysis was found, and the presence of an isothiocyanate intermediate was detected, indicating that the alkaline hydrolysis occurs by an *E*1*cb* mechanism. From the pH–rate profiles, the first-order rate constants k_E for the elimination step of the thioncarbamate anion forming the isothiocyanate intermediate were determined. The alkaline hydrolysis of *p*-substituted arylisothiocyanates was studied at 25 °C in 0.1–0.3 M solutions of NaOH and in 0.1–0.3 M aqueous ethanol solutions, at different concentrations of NaOH. The second-order rate constants for the addition reaction with hydroxide (k_{OH}) and ethoxide (k_A) ions were obtained. Leffler plots for the elimination of the ethoxide ion from the arylthioncarbamate anion and for the addition of the ethoxide ion to the arylisothiocyanate were linear. From Leffler's equation, with the sole condition that $d\alpha_L/d\Delta G$ should be constant, a modified Marcus equation (MME) was obtained, where a parameter p (or q for the reverse reaction) defined the asymmetry of the intrinsic barrier. (When $p = 1/2$ the barrier is symmetric and the MME becomes the Marcus equation in the usual form.) For the addition–elimination reaction studied, both Leffler plots were adjusted to MME with the asymmetric parameter $p = 0.694 \pm 0.002$ for the addition and $q = 0.307 \pm 0.002$ for the elimination reaction. The intrinsic barrier was $\Delta G_0^{\neq} = 24.75 \pm 0.02$ kcal mol^{-1} and $|\Delta G_{max}| = 438 \pm 4$ kcal mol^{-1} (1 kcal = 4.184 kJ). The addition reaction was exoergic and, as expected from the high intrinsic barrier, α_L changed very little in the series (0.679–0.683); the transition state was product-like, and it moved towards the reagents with increasing exoergicity. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: arylthioncarbamates; arylisothiocyanates; hydrolysis; Marcus equation

INTRODUCTION

The reactions of carbon disulfide present a close parallelism with carbon dioxide.[1] Some of the products of the reaction with alkoxides, halides and amines [Eqn. (1)] have important biological activity as pesticides.[2] The different reactivities of these oxo and sulfo derivatives are a consequence of the characteristics of the C—X bond involved. For instance, oxygen can stabilize α-carbocations better than sulfur, but this capacity is inverted for carboanions. Sulfur can accept electrons in the empty 3d orbital much better than oxygen, and consequently the thiocarbonyl group is a powerful electron sink.[3] The reaction of esters **1** with amines produces carbamic (X = O) or thioncarbamic (X = S) esters **2**. The sequence of reactions (1) has been used to immobilize an enzyme (Enz-NH_2) to a cellulose matrix [Cel-OC(S)SR] because of the stability of the thioncarbamate group towards hydrolysis.[4]



(1)

In this work, we studied the mechanism of hydrolysis of ethyl *N*-arylthioncarbamate esters and the corresponding arylisothiocyanates that are formed as intermediates. The results allowed the calculation of the rate and equilibrium constants for a one-step addition–elimination reaction that can be analyzed in terms of the Marcus formalism.

EXPERIMENTAL

Materials. All reagents were of analytical grade. Distilled

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water was deoxygenated by boiling and cooling under nitrogen. UV spectra and kinetics were measured using a Cary 219 spectrophotometer. All compounds were identified by ^{1}H NMR and IR spectra.

Phenylisothiocyanate[5,6]. Carbon disulfide (1.3 mol) and 1.3 mol of ammonia solution (sp. gr. 0.9) were cooled on ice, 0.6 mol of aniline was added with magnetic stirring and the solution was allowed to react for 30 min. After standing for 30 min, the precipitate of ammonium phenyldithiocarbamate was filtered off and dissolved in 800 ml of water. A solution of 0.6 mol of lead sulfide in 400 ml of water was added and the mixture was steam distilled, collecting the distillate in 0.5 M sulfuric acid. The oil was separated, dried over $CaCl_2$ and distilled under vacuum: b.p. 119–121 °C/35 mmHg (lit.[5] 120–121 °C/35 mmHg); λ_{max} (water), 265, 273 nm.

p-N,N-Dimethylphenylisothiocyanate. The procedure was the same as for phenylisothiocyanate. The solid product was dried under vacuum over P_2O_5 and recrystallized from anhydrous ethanol: m.p. 67–68 °C; λ_{max} (water), 295 nm.

p-Chlorophenylisothiocyanate[7]. Carbon disulfide (0.35 mol), 0.6 mol of ammonia solution (sp. gr. 0.9) and 0.30 mol of *p*-chloroaniline were mechanically stirred for 1 h at 30–35 °C. The product was filtered off, washed with a 3% solution of ammonium chloride followed by ethanol and suspended in 250 ml of water at 30 °C. A solution of 0.15 mol of chloroacetic acid and 0.075 mol of sodium carbonate in 35 ml of water was added with stirring. After cooling to room temperature, a solution of 0.15 mol of $ZnCl_2$ in 75 ml of water was added dropwise, with vigorous stirring, for a period of 1 h, maintaining the pH at 7 by the addition of ammonia solution. The product was filtered off and dried under vacuum over P_2O_5, and then extracted with light petroleum (b.p. 30–60 °C). The solvent was evaporated under vacuum and the isothiocyanate was recrystallized from ethanol: m.p. 43–45 °C (lit.[7] 44–45 °C); λ_{max} (aq. EtOH), 272, 283 nm.

p-Nitrophenylisothiocyanate[8]. *p*-Nitroaniline (0.13 mol) was stirred with 700 ml of 10% HCl and the hydrochloride was filtered off and placed in an Erlenmeyer flask that was stoppered after adding 0.13 mol of thiophosgene. The mixture was stirred mechanically and vigorously for 2 days at room temperature. The pale yellow product was filtered off and crystallized from acetone: m.p. 108–110 °C (lit.[8] 112–113 °C); λ_{max} (aq. EtOH), 317 nm.

p-Methylphenylisothiocyanate[8]. Thiophosgene (0.11 mol) was added dropwise to an equimolecular amount of *p*-toluidine dispersed in 250 ml of water, with mechanical stirring, and the mixture was allowed to react at room temperature for 3 days. The oily product was extracted with diethyl ether and recrystallized from the same solvent: m.p. 26–28 °C (lit.[8] 25–26 °C); λ_{max} (EtOH), 269, 280 nm.

p-Methoxyphenylisothiocyanate[8]. The procedure was the same as for p-methylphenylisothiocyanate: bp 279–281 °C (lit.[9] 280–281 °C); λ_{max} (EtOH) 273, 285 nm.

p-Hydroxyphenylisothiocyanate[8]. *p*-Aminophenol (0.1 mol) was stirred with 120 ml of 1 M HCl and 0.1 mol of thiophosgene was added dropwise. The mixture was mechanically stirred for 7 h at room temperature. The oily product was extracted with diethyl ether, the solution was dried over $CaSO_4$ and the solvent was evaporated under vacuum: TLC, R_f 0.5 (benzene); after molecular distillation, the same R_f was found; b.p. 210 °C; λ_{max} (water), 310, 330 nm.

Ethyl N-arylthioncarbamates[8,10]. A 1 mol amount of the corresponding arylisothiocyanate was dissolved in 10 mol of anhydrous ethanol and the mixture was boiled under reflux. The product was crystallized at room temperature and recrystallized from light petroleum (b.p. 40–60 °C). Phenyl: m.p. 68–69 °C (lit. 69–71 °C[11]; 70–71 °C[10]); λ_{max} (water), 272 nm. *p*-Nitro: m.p. 176–177 °C (lit.[10] 175 °C); λ_{max} (EtOH) 336 nm. *p*-Chloro: m.p. 104–105 °C (lit.[11] 104–106 °C); λ_{max} (water), 276 nm. *p*-Methyl: m.p. 83–84 °C (lit.[10] 85 °C); λ_{max} (water), 272 nm. *p*-Methoxy: m.p. 78–80 °C (lit.[12] 81 °C); λ_{max} (water), 273 nm.

Acid dissociation constants of ethyl N-arylthioncarbamates. The dissociation constants were calculated at 25 °C from a series of measurements of the absorbance at λ_{max} of solutions of ca 10^{-5} M of the substrate in the pH range 6–13. The UV spectra showed one isosbestic point. Inversion of the pH after the titration showed that the dissociations were reversible with no noticeable reaction at 25 °C.

Product analysis. The products of the hydrolysis of phenylthioncarbamate were characterized in a preparative run at 0.1 M NaOH and 100 °C. The samples were submitted to molecular distillation. Ethanol was identified by liquid chromatography (Porapak Q column, 157 °C) from the distilled fraction. Aniline was identified from the UV spectrum, from TLC [hexane–acetone (7:3)] and from Rimini assay.[13]

In order to trap the isothiocyanate intermediate, a preparative run of the hydrolysis of phenylthioncarbamate was carried out at 100 °C and pH 8.2 (measured at 25 °C) in the presence of ethylamine. Three samples were taken at 8 h intervals. The samples were extracted with chloroform, concentrated in a rotatory evaporator and then analyzed by TLC [hexane–acetone (7:3)] using aniline and *N*-phenyl-*N*′-ethylthiourea as references. All the samples gave a positive test for thiourea (R_f 0.37) and aniline (R_f 0.50).

Kinetics

Hydrolysis of ethyl N-arylthioncarbamates. Kinetics were studied at 100 °C in the pH range 6.5–12.5. The kinetic solution (50 ml) had a final concentration of ca 10^{-5} M; samples of 3 ml were placed in sealed glass ampoules and immersed in a thermostat at 100 °C. The samples were collected at different times and quenched in a Dewar bath with salted ice. The kinetics were followed by the disappearance of the arylthioncarbamate, by reading the absorbance at λ_{max}. All runs were followed for at least three half-lives and the $\ln\Delta A$ vs time plots produced straight lines that were considered when $r \geq 0.99$. The pH of the buffered solutions was measured at 25 °C and corrected to 100 °C as described elsewhere.[14] The pH (>12) of unbuffered runs was controlled at the end of the experiment and showed no change.

Hydrolysis of arylisothiocyanates. The alkaline hydrolysis of aryisothiocyanates was studied at 25 °C in 0.1–0.3 M solutions of NaOH. The final concentration was about 10^{-4} M. The reaction was followed by the disappearance of the isothiocyanate at λ_{max}, except for the *p*-nitro-, *p-N,N*-dimethyl- and phenylisothiocyanate that were accompanied by product formation. The kinetics were all pseudo-first order and were measured for more than three half-lives. The reaction of arylisothiocyanates with ethoxide ion was studied in 0.1–0.3 M aqueous ethanol solutions at different concentrations of NaOH.

RESULTS AND DISCUSSION

Acid dissociation constants of ethyl *N*-arylthioncarbamates

The acid dissociation constants were obtained at 25 °C for the series of ethyl *N*-arylthioncarbamates from the absorbance–pH titration curves. Since one isosbestic point was found for the UV spectra at different pHs and no reaction was observed after the titration, the reaction corresponded to the dissociation equilibrium of the N—H bond. The pK_a values for the series of thioncarbamate esters are given in Table 1.

Table 1. Acid dissociation and rate constants of the alkaline hydrolysis of ethyl *p*-substituted arylthioncarbamates

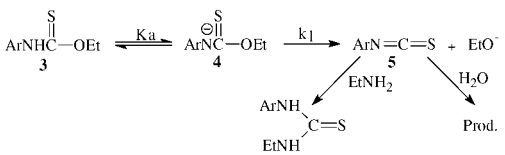
X	σ_p	pK_a [a]	pK_a [b]	$10^4\ k_E$ (l mol^{-1} s^{-1}) [b]
NO_2	0.81	9.2	8.2	0.91 ± 0.02
Cl	0.24	10.5	9.0	1.30 ± 0.01
H	0.00	10.8	9.4	2.02 ± 0.06
Me	−0.17	11.0	9.8	2.45 ± 0.02
MeO	−0.29	11.2	9.9	2.23 ± 0.03
NMe_2	−0.60	11.5[c]	10.1[c]	3.43[c]
O^-	−0.81	11.8[c]	10.4[c]	4.22[c]

[a] Measured at 25 °C.
[b] Calculated from the pH–rate profile at 100 °C.
[c] Extrapolated from the Hammett correlation line.

Alkaline hydrolysis of ethyl *N*-arylthioncarbamates

The reaction was studied at 100 °C and the pH–rate profiles were obtained in the pH range 6.5–12.5. The hydrolyses of ethyl *N*-phenyl- and *N-p*-nitrophenylthiocarbamates were studied with respect to the catalysis by the buffer using phosphate, borate and carbonate in the range 0.01–0.05 M, and no buffer effect was observed. Therefore, the hydrolysis occurs without general catalysis.

The rate constants increase with the pH reaching a pH-independent plateau at pH >11. A typical profile is shown in Fig. 1. This profile is consistent with a $B_{AC}2$ and *E*1*cb* mechanism. Both have been observed for carbamate esters,[15,16] but the detection of isothiocyanate as an intermediate and the absence of general catalysis supports the theory that these ethyl *N*-arylthioncarbamates hydrolyze through the *E*1*cb* mechanism, as has been found for aryl *N*-aryl analogs[17,18] [Eqn. (2)]. According to this mechanism, the pH–rate profile follows Eqn. (3), where K_a is the acid dissociation constant of the N—H bond and k_E is the first-order rate constant of the elimination step. The values of the pK_a and k_E at 100 °C calculated from the pH–rate profiles of the series of thioncarbamate esters studied in this work are given in Table 1.

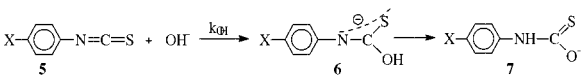


(2)

$$k_{obs} = \frac{k_E K_a}{K_a + a_{H^+}} \quad (3)$$

Hydrolysis of arylisothiocyanates

The reaction with hydroxide ion produced the thioncarbamate anion [Eqn. (4)] that is stable under the reaction conditions. The pH–rate profiles of the alkaline hydrolyses were linear with a slope of +1 (Fig. 2). The second-order rate constants for the reaction are given in Table 2.



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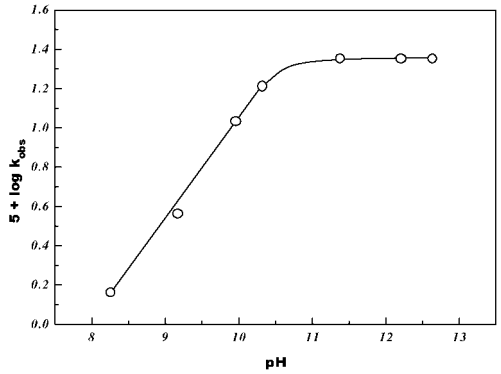


Figure 1. pH–rate profile of the alkaline hydrolysis of ethyl *N*-*p*-methylphenylthioncarbamate at 100 °C. The curve was calculated from Eqn. (3)

The reaction with ethoxide ion was studied in alkaline aqueous ethanol solutions, and the second-order rate constant k_A for the addition of the ethoxide ion was calculated from the observed rate constant according to Eqn. (5), where a and b are the concentrations of ethanol and NaOH in the solution, and K_e is the equilibrium constant of Eqn. (6) (Table 2).

$$k_{obs} = (k_A K_e a + k_{OH})b \tag{5}$$

$$EtOH + OH^- \overset{K_e}{\rightleftharpoons} EtO^- + H_2O \tag{6}$$

Modified Marcus equation

The values of k_E for the hydrolyses of the arylthioncarbamate anions and k_A for the addition of ethoxide ion to arylisothiocyanates permitted the calculation of the free energy reaction profiles and equilibrium constants for the one-step elimination–addition reaction (7), where $K_{AE} = k_A/k_E$ (Fig. 3, Table 3).

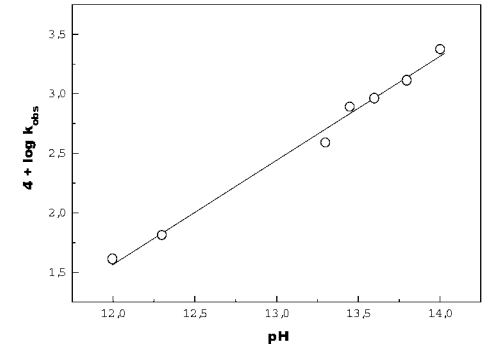
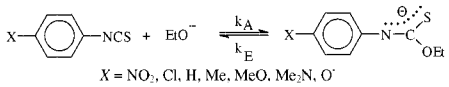


Figure 2. pH–rate profile of the alkaline hydrolysis of *N*-*p*-chlorophenylisothiocyanate at 25 °C

Table 2. Second-order rate constants of the solvolysis of *p*-substituted arylisothiocyanates at 25 °C

X	σ_p	$10^2\ k_{OH}$ (l mol^{-1} s^{-1})[a]	k_A (l mol^{-1} s^{-1})[b]
NO_2	0.81	99.4 ± 3.2	24.3 ± 3.0
Cl	0.24	19.9 ± 0.3	4.92 ± 0.32
H	0.00	10.4 ± 0.20	3.01 ± 0.24
Me	−0.17	6.63 ± 0.31	1.34 ± 0.12
MeO	−0.29	6.14 ± 0.71	1.79 ± 0.13
NMe_2	−0.60	4.64 ± 0.19	0.59 ± 0.04
O^-	−0.81	0.92 ± 0.02	0.30 ± 0.04

[a] [NaOH] = 0.1–0.8 M.
[b] [EtOH] = 0.1–03 M; [NaOH] = 0.1–0.3 M; [EtO$^-$] from Eqns (5) and (6), $K_e = 1.48 \times 10^{-2}$ l mol^{-1}.



(7)

We will consider first the Leffler equation [Eqn. (8)]:[19]

$$\delta G^{\neq} = \alpha_L\ \delta G_P + (1 - \alpha_L)\delta G_R \tag{8}$$

where α_L is a parameter that expresses the contribution of free energy in the transition state. It varies between 0 and 1, and is interpreted as the defining the position of the TS in the reaction coordinates. There is no condition in the Leffler equation that $G_P = G_R$ when $\alpha_L = 1/2$, as has been interpreted.[20,21] In this case, $\delta G^{\neq} = 1/2\delta(G_P + G_R)$, but it does not imply that G_P must be equal to G_R. If G_P were

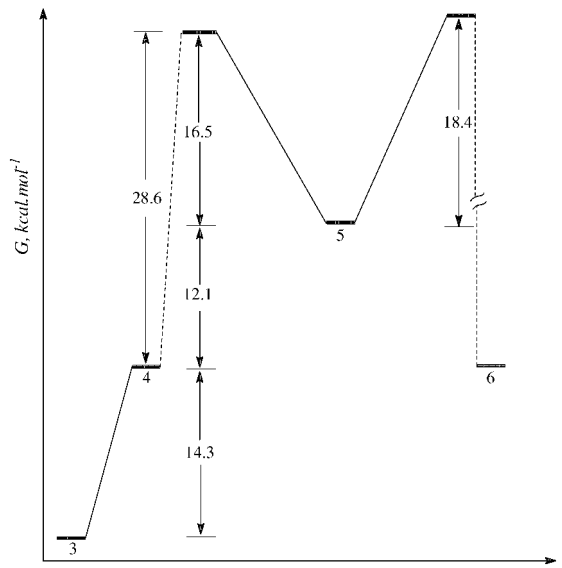
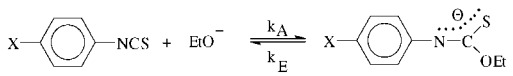


Figure 3. Free energy reaction profile of alkaline hydrolysis of ethyl *N*-*p*-chlorophenylthioncarbamate; **3**–**6**, according to Eqns (2) and (4)

Table 3. Kinetic and equilibrium parameters for the reaction shown



X	$\Delta G_A^{\neq}$ (kcal mol^{-1})	$\Delta G_E^{\neq}$ (kcal mol^{-1})	K_{AE} (l mol^{-1})[a]	ΔG_{AE} (kcal mol^{-1})
NO_2	15.565	28.912	6.06×10^9	−13.347
Cl	16.511	28.648	7.86×10^8	−12.137
H	16.802	28.321	2.77×10^8	−11.519
Me	17.282	28.178	9.68×10^7	−10.896
MeO	17.110	28.247	1.45×10^8	−11.137
NMe_2	17.768	27.928	2.80×10^7	−10.160
O^-	18.169	27.774	1.10×10^7	−9.605

[a] At 25 °C; $K_{AE} = k_A/k_E$.

equal to G_R, Eqn. (8) would be expressed as $\delta G^{\neq} = \delta G_P = \delta G_R$, which is meaningless because in this case α_L is undetermined. The condition when $\alpha_L = 1/2$ and $G_P = G_R$ applies only when the reaction can be related to a similar reaction.

The derivative of Eqn. (8) defines $\alpha_L = d\Delta G^{\neq}/d\Delta G$. Since α_L is a continuous, single-valued function of ΔG, and assuming that α_L is constant for a small change of ΔG, upon integration Eqn. (9) is obtained:

$$\Delta G^{\neq} = \alpha_L \Delta G + \Delta G_0^{\neq} \tag{9}$$

where $\Delta G_0^{\neq}$ is the kinetic barrier at $\Delta G = 0$. In the formalism of Marcus, this barrier is defined as a constant called the 'intrinsic barrier'.[22] From Table 3, the Leffler plots produce Eqns (10) and (11) for the addition and elimination reaction, respectively (Fig. 4).

$$\Delta G_A^{\neq} = (0.686 \pm 0.015)\Delta G_{AE} + (24.75 \pm 0.17) \qquad r = 0.999 \tag{10}$$

$$\Delta G_E^{\neq} = (0.314 \pm 0.015)\Delta G_{EA} + (24.75 \pm 0.17) \qquad r = 0.994 \tag{11}$$

For a large change of ΔG, assuming that $d\alpha_L/d\Delta G$ is constant,[20] and therefore that α_L changes linearly with ΔG, integration leads to Eqn. (12):

$$\alpha_L = \frac{\Delta G}{2|\Delta G_{max}|} + p \quad \left(\text{and } \beta_L = \frac{-\Delta G}{2|\Delta G_{max}|} + q\right) \tag{12}$$

where $|\Delta G_{max}|$ is the absolute value of the maximum barrier and p (or q for the reverse reaction) is a parameter that measures the asymmetry of the barrier. The barrier is symmetrical only when $p = 1/2$ and $\Delta G = 0$. Substituting α_L and integrating the differential $d\Delta G^{\neq} = \alpha_L d\Delta G$, Eqn. (13) for the relationship between $|\Delta G_{max}|$ and the intrinsic barrier was obtained:

$$\Delta G_0^{\neq} = \left(\frac{3}{4} - p\right)|\Delta G_{max}| \tag{13}$$

and by substitution and integration, the result is Eqn. (14):

$$\Delta G^{\neq} = \Delta G_0^{\neq} + p\Delta G + \left(\frac{3/4 - p}{4\Delta G_0^{\neq}}\right)\Delta G^2 \tag{14}$$

which is the expression of the modified Marcus equation (MME). When $p = 1/2$, the barrier is symmetric and Eqn. (14) becomes the Marcus equation in the usual form.

Both Leffler plots of $\Delta G_A^{\neq}$ vs ΔG_{AE} and $\Delta G_E^{\neq}$ vs ΔG_{EA} were adjusted to Eqn. (14) with the asymmetric parameter $p = 0.694 \pm 0.002$ for the direct reaction and $q = 0.307 \pm 0.002$ for the reverse reaction. The intrinsic barrier was $\Delta G_0^{\neq} = 24.75 \pm 0.02$ kcal mol^{-1} (1 kcal =

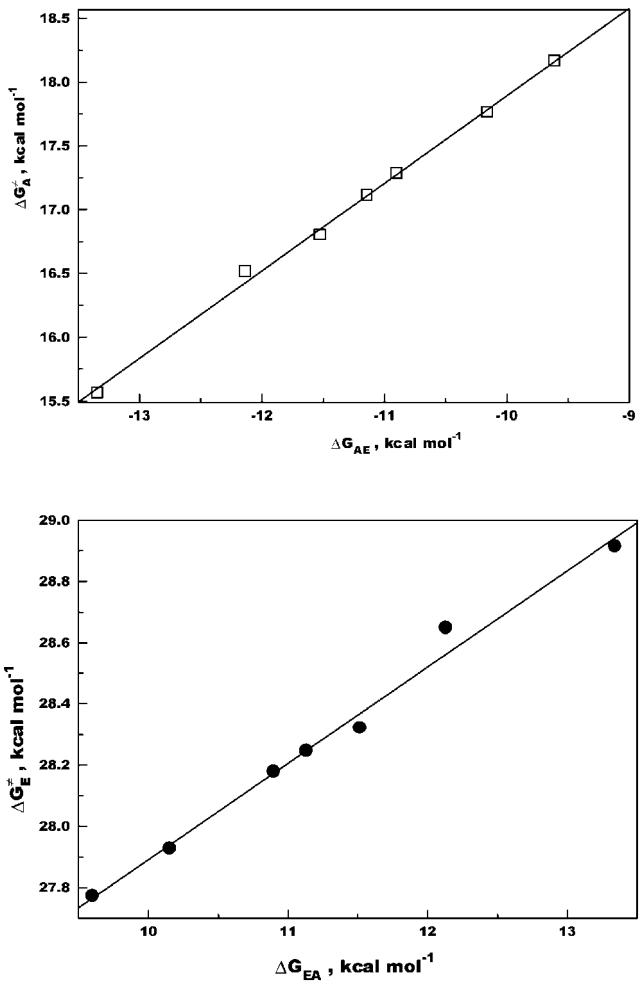


Figure 4. Leffler plots for the addition–elimination reaction: □, *p*-X-phenylisothiocyanates + EtO^-; ●, *p*-X-phenylthiocarbamate anions

4.184 kJ). Leffler and MME plots produce the same value for the intrinsic barrier. However, the slope of the Leffler plot is interpreted as an average of the α_L changes in the series, whereas when the MME is considered, the adjustment indicates the asymmetry of the kinetic barrier. The situation is similar to the comparison of a Brønsted plot and the Marcus equation for proton transfer.

The addition reaction is exoergic and the transition state is more product like on the α_L scale. As expected from the high intrinsic barrier, the maximum barrier is 438 ± 4 kcal mol^{-1}, α_L changes very little in the series (0.679–0.683) and according to the Leffler–Hammond hypothesis it moves towards the reagents with increasing exoergicity.

It has been contended that for a reaction series that does not possess an identity set such as cation–anion recombination and nucleophilic addition to unsaturated systems, an intrinsic barrier cannot be determined, and consequently the Marcus equation[23] cannot be satisfied, but this is true only when considering symmetric barriers.

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