Kinetics and mechanism of aminolysis of aryl cyclobutanecarboxylates in acetonitrile

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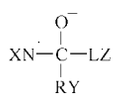
Received (in Cambridge, UK) 3rd April 2000, Accepted 21st August 2000
First published as an Advance Article on the web 16th October 2000

The aminolysis of Z-aryl cyclobutanecarboxylates (**II**) with X-benzylamines is investigated in acetonitrile at 55.0 °C. The rates are uniformly greater by 2.2 times than the corresponding rates of aryl cyclopropanecarboxylates (**III**). All the selectivity parameters, ρ_X (β_X), ρ_Z (β_Z) and ρ_{XZ}, are quite similar for the two substrates **II** and **III**. The k_H/k_D values involving deuterated benzylamines ($XC_6H_4CH_2ND_2$) are greater than unity, but are marginally smaller than those for the reactions of **III**. Low $\Delta H^{\ddagger}$ and large negative $\Delta S^{\ddagger}$ values are obtained and adherence to the reactivity–selectivity principle is observed. All these results are consistent with a stepwise mechanism with rate-limiting expulsion of a leaving group (aryl oxides) from a tetrahedral intermediate, $T^{\pm}$, with a hydrogen-bonded, four-center transition state.

Introduction

The Brønsted plots for the aminolysis of carbonyl compounds are often curved with a change in slope from a large ($\beta_{nuc} \geq 0.8$) to a small ($\beta_{nuc} \leq 0.3$) value, which can be attributed to a change in the rate determining step from breakdown to formation of a tetrahedral zwitterionic intermediate ($T^{\pm}$) in the reaction path as the amine basicity is increased.[1] The stepwise mechanism with rate-limiting expulsion of leaving group (LZ) from $T^{\pm}$ (**I**) is

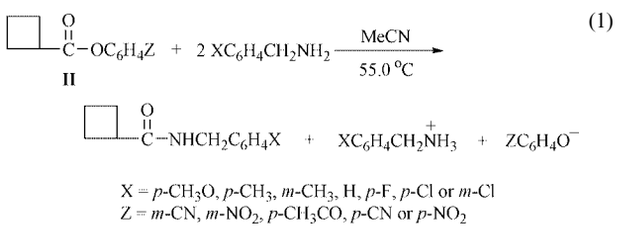


I

more likely to be observed in the aminolysis of a carbonyl compound with (i) a stronger electron acceptor acyl group, RY,[2] (ii) a poor leaving group, LZ,[2] and (iii) a more weakly basic (or nucleophilic) amine (XN).[2b,c] However, the effect of the acyl group, RY, on the mechanism is subtle and is not quite straightforward, since the effect can be both on the substrate and the intermediate, $T^{\pm}$, and the electronic effect can be either inductive or resonance delocalized, or both. This is the reason why it is rather difficult to predict the mechanism simply by taking account of the stereoelectronic effect of the acyl group, RY.

In view of the importance of predicting the effects of the acyl group on the mechanism of aminolysis of carbonyl compounds, we have used many different acyl groups in our studies of the aminolysis mechanism.[2b,3] In previous work, we investigated the effect on the mechanism of the reaction of a cyclopropyl group, RY = cyclo-C_3H_5, with benzylamines in acetonitrile[3h] and found that the cyclopropyl group leads to stepwise aminolysis with rate-limiting breakdown of the intermediate, $T^{\pm}$. In this paper, we extend our work to the aminolysis of aryl cyclobutanecarboxylates, **II**, with benzylamines (BA) in acetonitrile (eqn. (1)).

The purpose of the present work is to further explore the effect of the acyl group on the aminolysis mechanism by investigating the structure–reactivity behavior of aryl cyclobutanecarboxylates in acetonitrile. We are interested in the effects of the small ring acyl group on the mechanism,



(1)

II

X = *p*-CH_3O, *p*-CH_3, *m*-CH_3, H, *p*-F, *p*-Cl or *m*-Cl
Z = *m*-CN, *m*-NO_2, *p*-CH_3CO, *p*-CN or *p*-NO_2

especially on the sign and magnitude of the cross-interaction constant,[4] ρ_{XZ} in eqns. (2a) and (2b), where X and Z are the

$$\log (k_{XZ}/k_{HH}) = \rho_X\sigma_X + \rho_Z\sigma_Z + \rho_{XZ}\sigma_X\sigma_Z \quad (2a)$$

$$\rho_{XZ} = \partial\rho_Z/\partial\sigma_X = \partial\rho_X/\partial\sigma_Z \quad (2b)$$

substituents in the nucleophile, benzylamine, and leaving group, aryl oxide, respectively. Furthermore, the variation in the kinetic isotope effects, k_H/k_D, involving deuterated benzylamines ($XC_6H_4CH_2ND_2$) with substituents X and Z, and the activation parameters, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, are also determined since they can provide valuable information regarding the transition state (TS) structure.

Results and discussion

The aminolysis of aryl cyclobutanecarboxylates, **II**, with a large excess of benzylamines in acetonitrile obeyed the simple rate law given by eqns. (3) and (4), where [S] and [N] are the

$$\text{Rate} = k_{obs}[S] \quad (3)$$

$$k_{obs} = k_N[N] \quad (4)$$

concentrations of substrate (**II**) and nucleophile (BA), respectively. Plots of k_{obs} against [N] were linear, and the k_N values were determined from the slopes of these plots (eqn. (4)). The k_N values are summarized in Table 1 together with the Hammett (ρ_X and ρ_Z) and Brønsted coefficients (β_X and β_Z). The aminolysis rates summarized in Table 1 are consistently faster by *ca.* a factor of 2.2 than the corresponding values for the reactions of

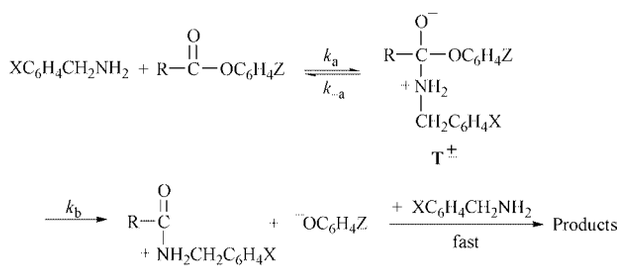
 DOI: 10.1039/b002610g

Table 1 Second-order rate constants, k_N (10^{-3} M^{-1} s^{-1}), for the reactions of Z-aryl cyclobutanecarboxylates with X-benzylamines in acetonitrile at 55.0 °C

	Z						
X	*m*-CN	*m*-NO_2	*p*-CH_3CO	*p*-CN	*p*-NO_2	ρ_Z[a]	β_Z[b]
p-CH_3O	4.60	11.0	33.2	44.2	255	2.40 ± 0.14	−1.18 ± 0.11
p-CH_3	2.71	6.49	16.3	34.6	156	2.41 ± 0.14	−1.20 ± 0.18
	2.01[c]				116[c]		
	1.49[d]				86.6[d]		
m-CH_3	1.69	3.40	11.2	20.4	141	2.72 ± 0.12	−1.33 ± 0.14
H	1.24	3.10	9.17	15.6	119	2.75 ± 0.12	−1.35 ± 0.12
p-F	0.891	2.24	5.89	13.0	83.2	2.76 ± 0.05	−1.34 ± 0.16
p-Cl	0.374	0.983	3.48	6.34	51.5	2.99 ± 0.10	−1.46 ± 0.15
m-Cl	0.215	0.634	1.83	4.42	31.7	3.04 ± 0.03	−1.47 ± 0.19
					22.9[c]		
					16.6[d]		
ρ_X[a]	−2.08 ± 0.02	−1.92 ± 0.08	−1.86 ± 0.10	−1.62 ± 0.06	−1.36 ± 0.08	ρ_{XZ}[e] = 1.02 ± 0.16	
β_X[f]	2.07 ± 0.06	1.78 ± 0.13	1.78 ± 0.08	1.55 ± 0.08	1.48 ± 0.05		

[a] Sigma (σ and σ^-) values were taken from ref. 14. Correlation coefficients were better than 0.995. [b] The pK_a values were taken from ref. 15. Correlation coefficients were better than 0.979 in all cases. [c] At 45.0 °C. [d] At 35.0 °C. [e] Correlation coefficient was 0.998. [f] The pK_a values were taken from ref. 16. Correlation coefficients were better than 0.992 in all cases. X = *p*-CH_3 were excluded from the Brønsted plot for β_X(benzylamine) due to an unreliable pK_a value listed.

aryl cyclopropanecarboxylates,[3h] **III**, under the same reaction conditions. This uniform increase in the rate of aminolysis for the aryl cyclobutanecarboxylates, **II**, suggests that the mechanism of the aminolysis is the same as that for the aryl cyclopropanecarboxylates, **III**, *i.e.*, rate-limiting expulsion, k_b, of the leaving group, aryl oxides, from a tetrahedral intermediate, $T^{\pm}$ (Scheme 1). Since the cyclobutyl group is a slightly weaker



R = Cyclobutyl, **II**, or cyclopropyl, **III**

Scheme 1

electron donor than the cyclopropyl group (σ_I:σ_R^o[5] values are −0.08:−0.13 and −0.02:−0.12 for the cyclopropyl and cyclobutyl groups, and pK_a's[6] of cyclopropanecarboxylic acid and cyclobutanecarboxylic acid are 4.83 and 4.79, respectively), it can lead to a greater k_N in eqn. (5) by increasing the stability of the intermediate, $T^{\pm}$ in Scheme 1, *i.e.*, a larger K in eqn. (5). It

$$k_N = \frac{k_a}{k_{-a}} k_b = Kk_b \qquad (5)$$

is well known that a stronger electron-acceptor (or a weaker electron-donor) acyl (R) group leads to a greater stabilization of the tetrahedral intermediate, $T^{\pm}$.[2] The stepwise mechanism (Scheme 1) for the aminolysis of the two substrates **II** and **III**[3f] is supported by quite similar values of ρ_X (β_X) and ρ_Z (β_Z). For example, for X = H, the ρ_Z (β_Z) values are 2.8 (−1.4) and 2.8 (−1.3) for **II** and **III**, respectively, and for Z = *p*-CN the ρ_X (β_X) values are −1.6 (1.8) and −1.6 (1.7) for **II** and **III** respectively. Although the magnitude of β_Z may not be reliable since we used pK_a values of phenols determined in water (not in acetonitrile), comparison of β_Z values (β_Z (**II**) ≈ β_Z (**III**)) obtained under exactly the same reaction conditions is justified. In contrast, the β_X values obtained from rate constants in acetonitrile and the pK_a's of the conjugate acids of amines determined in water have been shown to be reliable.[7] The large magnitudes of ρ_X (β_X) and ρ_Z (β_Z) are consistent with the proposed mechanism.[2b,c,3] The corresponding values for the rate-limiting addition of benzylamines to aryl benzoates (or concerted substitution by benzylamines) were β_X = 0.25–0.70.[3b] The importance of bond breaking in the TS (Scheme 1) is reflected in the better Hammett correlations with σ_Z^- than with σ_Z and the large magnitude of ρ_Z^- (=2.4–3.0) suggesting strong negative charge development in the aryl oxide leaving group with a large extent of bond cleavage in the TS.

Table 2 Kinetic isotope effects on the second-order rate constants (k_N) for the reactions of Z-aryl cyclobutanecarboxylates with deuterated X-benzylamines ($XC_6H_4CH_2ND_2$) in acetonitrile at 55.0 °C

X	Z	k_N(H)/ 10^{-3} M^{-1} s^{-1}	k_N(D)/ 10^{-3} M^{-1} s^{-1}	k_H/k_D
H	*p*-NO_2	119 ± 2[a]	100 ± 2	1.19 ± 0.04[a]
H	*p*-CN	15.6 ± 0.3	12.2 ± 0.4	1.28 ± 0.05
H	*p*-CH_3CO	9.17 ± 0.05	7.05 ± 0.03	1.30 ± 0.06
H	*m*-NO_2	3.10 ± 0.02	2.25 ± 0.04	1.38 ± 0.04
H	*m*-CN	1.24 ± 0.04	0.849 ± 0.004	1.46 ± 0.05
p-CH_3O	*p*-CN	44.2 ± 0.3	36.2 ± 0.3	1.22 ± 0.04
p-CH_3	*p*-CN	34.6 ± 0.3	27.9 ± 0.5	1.24 ± 0.06
p-Cl	*p*-CN	6.34 ± 0.03	4.84 ± 0.03	1.31 ± 0.04
m-Cl	*p*-CN	4.42 ± 0.02	3.03 ± 0.03	1.46 ± 0.04

[a] Standard deviation.

The cross-interaction constant ρ_{XZ} (=1.02) determined by subjecting 35 items of k_N (k_{XZ}) data in Table 1 to multiple linear regression analysis using eqn. (2a) is also similar to that for **III** (1.06), which provides further support for the proposed mechanism. Typically, the aminolyses of various substrates with benzylamines in acetonitrile, which are believed to proceed by rate-limiting expulsion of the leaving group, gave positive ρ_{XZ} values ranging from *ca.* 0.7 to 1.5.[3d,5,8] In contrast, the aminolysis which proceeds concertedly in acetonitrile gave a negative ρ_{XZ} value.[9] We also note in Table 1 that the rate increase is invariably accompanied by a decrease in the selectivities, ρ_X (β_X) and ρ_Z^- (β_Z), and hence the reactivity–selectivity principle (RSP) holds.[10] Adherence to the RSP is considered another criterion for the stepwise mechanism with rate-limiting expulsion of the leaving group[11] (aryl oxides).

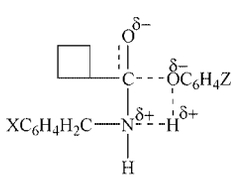
The kinetic isotope effects (k_H/k_D) for the reactions of Z-aryl cyclobutanecarboxylates, **II**, with deuterated benzylamines ($XC_6H_4CH_2ND_2$) in Table 2 are all greater than unity, k_H/k_D > 1.0, implying that the rate-limiting step is not a simple

Table 3 Activation parameters[a] for the reactions of Z-aryl cyclobutanecarboxylates with X-benzylamines in acetonitrile

X	Z	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$-\Delta S^{\ddagger}$/ cal mol^{-1} K^{-1}
p-CH_3	*m*-CN	5.4 ± 0.4[b]	54 ± 1[b]
p-CH_3	*p*-NO_2	5.3 ± 0.5	46 ± 1
m-Cl	*m*-CN	6.4 ± 0.6	56 ± 2
m-Cl	*p*-NO_2	5.9 ± 0.4	48 ± 1

[a] Calculated by the Eyring equation. [b] Standard deviation.

concerted S_N2 process, or a stepwise mechanism with rate-limiting formation of $T^{\pm}$.[4b] This is because in such cases inverse kinetic isotope effects ($k_H/k_D < 1.0$) are expected due to an increase in the N–H(D) vibrational frequency as a result of steric crowding as the nucleophile approaches the reaction center[4b] (the carbonyl carbon). The kinetic isotope effects observed ($k_H/k_D = 1.2–1.5$) are larger than those expected from a simple stepwise acyl transfer mechanism ($k_H/k_D \approx 1.0$)[4b] with rate-limiting breakdown of $T^{\pm}$. The magnitudes of k_H/k_D in Table 2 are again slightly smaller than those corresponding values for the reactions of aryl cyclopropanecarboxylates[3h] (**III**). Admittedly the differences are marginal (*ca*. 0.02) but persistent. The variations in k_H/k_D with substituents X ($k_H/k_D = 0.21\sigma_X + 1.27$, $r = 0.991$) and Z ($k_H/k_D = -0.37\sigma_Z^- + 1.64$, $r = 0.977$) are in agreement with those for the reactions of **III**. Thus, these results support the proposed mechanism with a hydrogen-bonded four-center type TS structure, **IV**, with a slightly lower degree of proton transfer than that for the reaction of **III**.



IV

Activation parameters, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, determined for the present reaction series from the slope and intercept, respectively, of Eyring plots are shown in Table 3. The low $\Delta H^{\ddagger}$ (5–6 kcal mol^{-1}) and large negative $\Delta S^{\ddagger}$ (−46–−56 e.u.) values are also similar to those for the reactions of **III**[3h] and in line with the rate-limiting breakdown of $T^{\pm}$ assisted by concurrent proton transfer,[3h,8a,12] **IV**. In the concerted (S_N2) and the stepwise mechanisms in which no such assistance for expulsion of the leaving group by concurrent proton transfer occurs, the $\Delta H^{\ddagger}$ values are somewhat higher (8–16 kcal mol^{-1}) and the $\Delta S^{\ddagger}$ values are smaller negative values (−15–−34 e.u.).[3b,d,f,g,9,13]

In summary, the reactions of aryl cyclobutanecarboxylates (**II**) with benzylamines in acetonitrile proceed by a stepwise mechanism with rate-limiting expulsion of the leaving group (aryl oxide) which is assisted by a concurrent proton transfer, **IV**. The faster rates and (albeit marginally but consistently) lower k_H/k_D values found with **II** compared with those for **III** are due to the slightly weaker electron-donating ability of the cyclobutane ring than the cyclopropane ring. The large magnitude of ρ_X (β_X) and ρ_Z (β_Z), the normal kinetic isotope effects ($k_H/k_D > 1.0$) involving deuterated benzylamines, the large positive ρ_{XZ} value, adherence to the RSP in all cases, and low $\Delta H^{\ddagger}$ and large negative $\Delta S^{\ddagger}$ values are all consistent with the proposed mechanism.

Experimental

Materials

Merck GR acetonitrile was used after three distillations. The benzylamine nucleophiles, Aldrich GR, were used without further purification.

Preparation of deuterated benzylamine

Benzylamine was dissolved in excess D_2O under a nitrogen atmosphere and left for 5 hours at 25.0 °C. The deuterated benzylamine was extracted with dry ethyl ether and dried again over $MgSO_4$. After expulsion of solvent, the analysis (NMR) of dried deuterated benzylamine showed more than 99% deuterium content, and the k_H/k_D values were thus not corrected for the deuterium content.

Aryl cyclobutanecarboxylates were prepared by reacting phenols with cyclobutanecarbonyl chloride. The substrates synthesized were confirmed by spectral analyses as follows.

***p*-Cyanophenyl cyclobutanecarboxylate.** δ_H(250 MHz, $CDCl_3$) 7.25–7.70 (4H, m, C_6H_4), 3.5–3.6 (1H, m, CH), 2.3–2.5 (4H, m, $2CH_2$), 1.9–2.1 (2H, m, CH_2); ν_{max}(neat)/cm^{-1} 2900 (CH), 2300 (CN), 1730 (C=O); $m/z = 201$ (M^+) (Calc. for $C_{12}H_{11}NO_2$; C, 71.6; H, 5.47. Found: C, 71.7; H, 5.46%).

***m*-Cyanophenyl cyclobutanecarboxylate.** δ_H(250 MHz, $CDCl_3$) 7.25–7.70 (4H, m, C_6H_4), 3.5–3.6 (1H, m, CH), 2.3–2.5 (4H, m, $2CH_2$), 1.9–2.1 (2H, m, CH_2); ν_{max}(neat)/cm^{-1} 2900 (CH), 2300 (CN), 1730 (C=O); $m/z = 201$ (M^+) (Calc. for $C_{12}H_{11}NO_2$; C, 71.6; H, 5.47. Found: C, 71.7; H, 5.46%).

***p*-Nitrophenyl cyclobutanecarboxylate.** Mp 60–62 °C; δ_H(250 MHz, $CDCl_3$) 7.24–7.80 (4H, m, C_6H_4), 3.4–3.6 (1H, m, CH), 2.3–2.6 (4H, m, $2CH_2$), 2.0–2.2 (2H, m, CH_2); ν_{max}(KBr)/cm^{-1} 2900 (CH), 1730 (C=O); $m/z = 221$ (M^+) (Calc. for $C_{11}H_{11}NO_4$; C, 59.7; H, 4.98. Found: C, 59.8; H, 4.99%).

***m*-Nitrophenyl cyclobutanecarboxylate.** δ_H(250 MHz, $CDCl_3$) 7.24–7.80 (4H, m, C_6H_4), 3.4–3.6 (1H, m, CH), 2.3–2.6 (4H, m, $2CH_2$), 2.0–2.2 (2H, m, CH_2); ν_{max}(neat)/cm^{-1} 2900 (CH), 1730 (C=O); $m/z = 221$ (M^+) (Calc. for $C_{11}H_{11}NO_4$; C, 59.7; H, 4.98. Found: C, 59.8; H, 4.99%).

***p*-Acetylphenyl cyclobutanecarboxylate.** δ_H(250 MHz, $CDCl_3$) 7.25–7.70 (4H, m, C_6H_4), 3.5–3.6 (1H, m, CH), 2.3–2.5 (4H, m, $2CH_2$), 1.9–2.1 (2H, m, CH_2); ν_{max}(neat)/cm^{-1} 2900 (CH), 1730 (C=O), 1690 ($COCH_3$); $m/z = 218$ (M^+) (Calc. for $C_{13}H_{14}O_3$; C, 71.6; H, 6.42. Found: C, 71.6; H, 6.43%.)

Rate constants

Rates were measured conductimetrically at 55.0 ± 0.05 °C. The conductivity bridge used in this work was a laboratory-made computer automatic A/D converter conductivity bridge. Pseudo-first order rate constants, k_{obs}, were determined by the curve fitting analysis of the computer data with a modified version of the Origin program, which fits conductance *vs.* time data to the equation $A = A_\infty + (A_0 - A_\infty)\exp(-k_{obs} \times t)$, where A is the observed conductivity and A_∞, $A_0 - A_\infty$, and k_{obs} are iteratively optimized to achieve the best possible least-squares fit with a large excess of benzylamine (BA); [aryl cyclobutanecarboxylate] $\approx 1 \times 10^{-3}$ M and [BA] = 0.03–0.24 M. Second-order rate constants, k_N, were obtained from the slope of a plot of k_{obs} *vs.* [BA] with more than five concentrations of benzylamine, eqn. (4). The k_N values in Table 1 are the averages of more than three runs and were reproducible to within ±3%.

Product analysis

p-Nitrophenyl cyclobutanecarboxylate was reacted with excess *p*-methylbenzylamine with stirring for more than 15 half-lives at 55.0 °C in acetonitrile, and the products were isolated by evaporating the solvent under reduced pressure. The product mixture was separated by column chromatography (silica gel, 20% ethyl acetate–*n*-hexane). Analysis of the products gave the following results.

Cyclobutyl-C(O)NHCH$_2$C$_6$H$_4$-*p*-CH$_3$. Mp 180–182 °C; δ_H(250 MHz, $CDCl_3$–DMSO-d_6) 7.25–7.70 (4H, m, C_6H_4), 5.80

(1H, br s, NH), 4.20 (2H, s, CH_2), 2.30 (3H, s, CH_3); 3.5–3.6 (1H, m, CH), 2.3–2.5 (4H, m, $2CH_2$), 2.0–2.3 (2H, m, CH_2); ν_{max}(KBr)/cm^{-1} 3200 (NH), 2900 (CH), 1730 (C=O); m/z = 203 (M^+) (Calc. for $C_{13}H_{17}NO$; C, 76.9; H, 8.37. Found: C, 76.8; H, 8.36%).

Acknowledgements

We thank the Korean Science and Engineering Foundation (981-0303-019-2) for support of this work.

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