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Kinetics and mechanism of benzylamine additions to ethyl α-acetyl-β-phenylacrylates in acetonitrile

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Kinetic studies of the addition of benzylamines to a noncyclic dicarbonyl group activated olefin, ethyl α-acetyl-β-phenylacrylate (EAP), in acetonitrile at 25.0 °C are reported. The rates are lower than those for the cyclic dicarbonyl group activated olefins. The addition occurs in a single step with concurrent formation of the C_α–N and C_β–H bonds through a four-center hydrogen bonded transition state.

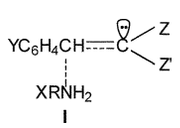
The kinetic isotope effects ($k_H/k_D > 1.0$) measured with deuterated benzylamines ($XC_6H_4CH_2ND_2$) increase with a stronger electron acceptor substituent ($\delta\sigma_X > 0$) which is the same trend as those found for other dicarbonyl group activated series (**1**–**4**), but is in contrast to those for other (noncarbonyl) group activated series (**5**–**9**). For the dicarbonyl series, the reactivity-selectivity principle (RSP) holds, but for others the anti-RSP applies. These are interpreted to indicate an insignificant imbalance for the former, but substantial lag in the resonance delocalization in the transition state for the latter series.

Introduction

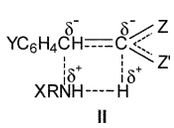
Nucleophilic addition of amines ($XRNH_2$) to olefins (YC_6H_4-CH=CZZ′) activated by electron-withdrawing groups (Z, Z′) is known to proceed in acetonitrile by concerted formation of the C_α–N and C_β–H bonds in a single-step process to a neutral product,[1] eqn. 1.

$$YC_6H_4CH{=}CZZ' + RNH_2 \xrightarrow[MeCN]{k_2} YC_6H_4CH(HNRX)CHZZ' \quad (1)$$

In contrast, the reactions in aqueous solution are reported to occur through a zwitterionic intermediate, $T^{\pm}$, with an imbalanced transition state (TS) in which the development of resonance into the activating groups (Z, Z′) lags behind C_α–N bond formation.[2] The *imbalance* in the TS is mainly caused by the poorly developed resonance into Z, Z′ and solvation with the negative charge largely localized on carbon (C_β), an exaggerated form of which can be given as **I**. The imbalance phenomenon was pronounced in the amine additions in aqueous solution, which was expressed semi-quantitatively by using structure–reactivity coefficients such as Brønsted α and β values.[2] In contrast, the imbalance was hardly observable in the amine addition reactions in acetonitrile, mainly due to the concerted formations of C_α–N and C_β–H bonds.[1]

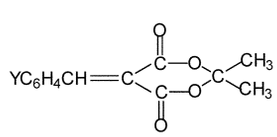


I



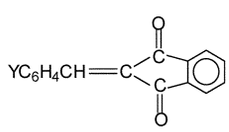
II

Recently, however, we have found that a stronger localized anionic charge on C_β due to the lag in the development of resonance induces a larger kinetic isotope effect involving deuterated amines ($XRND_2$), $k_H/k_D > 2.3$, which is caused by a larger N–H bond stretching (**II**) in the concerted single step addition in acetonitrile.[1a–d] In the absence of, or insignificantly small, imbalance, the isotope effects were smaller ($k_H/k_D < 2.0$)[1e–g] and the trends of change in k_H/k_D with substituents X in the nucleophile and Y in the ring were exactly opposite to those for the reactions with substantial imbalances (*vide infra*). Since we noted that the dicarbonyl activated olefins,[1e–g] Z, Z′ = $(CO)_2$ · R_1R_2, especially with the cyclic structure, **1**[1e] and **2**,[1f] belong to such a class with smaller k_H/k_D values and insignificant imbalances, it is of much interest to verify that the cyclic dicarbonyl structure of the activating group is a prerequisite to the negligible imbalance in the amine additions in acetonitrile. Although we found the same behavior with a noncyclic dicarbonyl activated olefin, **3**[1g] we test further in this work with another acyclic dicarbonyl activated group, **4**, ethyl α-acetyl-β-phenylacrylates. The purpose of this work is to examine (i) whether such a negligible imbalance is limited to the cyclic dicarbonyl activated olefins (**1** and **2**) or not, and (ii) why do dicarbonyl, or cyclic dicarbonyl, activated olefins[1e–g] behave differently from other activated olefins?[1a–d]



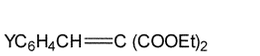
benzylidene-Meldrums' acid [BMA]

1



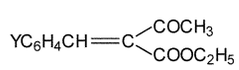
benzylidene-1,3-indandione [BID]

2



benzylidenediethylmalonate (BDM)

3



ethyl α-acetyl-β-phenylacrylate (EAP)

4

Results and discussion

The reactions studied in the present work followed a simple second-order rate law given by eqns 2 and 3

$$-\mathrm{d[EAP]}/\mathrm{d}t = k_{obs}\,[\mathrm{EAP}] \quad (2)$$

$$k_{obs} = k_2\,[\mathrm{BA}] \quad (3)$$

where [EAP] and [BA] are the concentrations of substrate, **4**, and benzylamine, respectively. No catalysis by a second amine molecule was detected. The second-order rate constants, k_2,

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Table 1 The second order rate constants, $k_2 \times 10^2$ dm^3 mol^{-1} s^{-1} for the addition reactions of ethyl α-acetyl-β-phenylacrylates with X-benzylamines in acetonitrile at 25.0 °C

	Y					
X	*p*-OMe	*p*-Me	H	*p*-Cl	*p*-Br	ρ_Y [a]
	0.767			2.38		
p-OMe	0.559 [b]	1.02	1.47	1.69	2.74	1.03 ± 0.06
	0.408 [c]			1.18		
p-Me	0.612	0.825	1.14	1.77	1.99	0.95 ± 0.05
H	0.439	0.581	0.815	1.22	1.33	0.90 ± 0.05
	0.295			0.749		
p-Cl	0.212	0.372	0.496	0.554	0.807	0.83 ± 0.03
	0.151			0.404		
ρ_X [d]	−0.83	−0.89	−0.94	−0.99	−1.05	
	(±0.03)	(±0.01)	(±0.02)	(±0.05)	(±0.06)	ρ_{XY} [e] = − 0.38 (±0.13)
β_X [f]	0.79	0.84	0.90	0.95	1.01	
	(±0.03)	(±0.02)	(±0.01)	(±0.02)	(±0.03)	

[a] The σ values were taken from ref. 11*a*. Correlation coefficients were better than 0.995 in all cases. [b] At 15.0 °C. [c] At 5.0 °C. [d] The source of σ is the same as for footnote *a*. Correlation coefficients were better than 0.997 in all cases. [e] Correlation coefficients was 0.997. [f] The pK_a values were taken from ref. 11b. Correlation coefficients were better than 0.999 in all cases. pK_a = 9.67 was used for X = *p*-CH_3O. (ref. 11c).

Table 2 Comparison of rates (k_2) and other parameters for the benzylamine additions to **1**–**4** in acetonitrile

	k_2/°C [a]	$\Delta H^{\neq}$ [b]	$-\Delta S^{\neq}$ [c]	k_H/k_D [d]	β_X [e]	ρ_{XY}	Ref.
BMA (**1**)	86.6(20)	~ 4.0	~−37	1.45 ~ 1.74	0.23	−0.33	1*e*
BID (**2**)	1.48(25)	~ 6.2	~−37	1.25 ~ 1.81	1.09	−0.33	1*f*
BDM (**3**)	2.48×10^{-2}(20)	~ 6.4	~−48	1.52 ~ 2.07	0.88	−0.45	1*g*
EAP (**4**)	0.815×10^{-2}(25)	~ 4.9	~−52	1.78 ~ 2.38	0.90	−0.38	This work

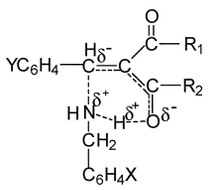
[a] For X = Y = H: M^{-1} s^{-1}. [b] kcal mol^{-1}. [c] cal mol^{-1} K^{-1}. [d] With deuterated benzylamine ($XC_6H_4CH_2ND_2$). [e] For Y = H.

were obtained from the slopes of the linear plots of k_{obs} *vs.* [BA], eqn 3, and are summarized in Table 1. The Hammett ρ_X and ρ_Y values and Brønsted β_X values are also shown in Table 1 together with the cross-interaction constant ρ_{XY}, which is defined as eqns 4 and 5.[3]

$$\log (k_{XY}/k_{HH}) = \rho_X\sigma_X + \rho_Y\sigma_Y + \rho_{XY}\sigma_X\sigma_Y \qquad (4)$$

$$\rho_{XY} = \partial\rho_X/\partial\sigma_Y = \partial\rho_Y/\partial\sigma_X \qquad (5)$$

The β_X values were determined by the plots of log k_2 (MeCN) against pK_a (H_2O) of benzylamines. This procedure was found to be reliable, since the pK_a (MeCN) varies in parallel with the pK_a (H_2O) with a reasonably constant difference of ΔpK_a (= pK_a (MeCN) − pK_a (H_2O)) ≅ 7.5.[4] The rates and other relevant parameters for the benzylamine additions to the dicarbonyl activated benzylidene series of substrate (**1**–**4**) in acetonitrile are compared in Table 2. We note that the rates are significantly faster for the cyclic dicarbonyl activated substrates (**1** and **2**) than the noncyclic dicarbonyl activated ones (**3** and **4**). This is clearly the π-overlap effect of the ring structure which alleviates the rate lowering due to the lag in the resonance stabilization.[5] In noncyclic systems the resonance develops late along the reaction coordinate but in the ring system the π-overlap is already maximally built into the olefin so that the structural reorganization that may be needed to achieve this overlap in noncyclic systems is not required and hence the activation barrier is lowered. The sign of ρ_{XY} is negative in all cases, which is consistent with those reported for nucleophilic bond formation processes.[3] The magnitudes of ρ_{XY} for the cyclic series (−0.33) are somewhat smaller than those for the noncyclic series (−0.45 and −0.38), which could be an indication of an earlier TS for the cyclic compounds. This is supported by smaller k_H/k_D values for **1** and **2** than for **3** and **4**. The kinetic isotope effect, k_H/k_D, involving deuterated nucleophiles ($XC_6H_4CH_2ND_2$) reflects bond stretching of the N–H (N–D) bond of the amine in the TS due to the hydrogen bonding of the amine proton toward the anionic center developing on C_β forming a four-membered type (**II**), or alternatively hydrogen bonding to a carbonyl oxygen forming a six-membered type, (**III**), structure, albeit the latter possibility has been shown to be less likely[1g] (*vide infra*). The k_H/k_D values determined in this work are collected in Table 3. We note that the k_H/k_D values are smaller (1.78 ~ 2.24) for a stronger nucleophile ($\delta\sigma_X < 0$) than for a weaker nucleophile (1.82 ~ 2.38) *i.e.*, $\delta\sigma_X < 0 \longrightarrow \delta (k_H/k_D) < 0$. Admittedly the differences are marginal but *the same trend is clear* Exactly the same tend was found for the benzylamine additions to other dicarbonyl activated series in acetonitrile, irrespective of whether the dicarbonyl group has a ring structure (BMA (**1**) and BID (**2**))[1e,f] or not (BDM (**3**)[1g] and EAP (**4**)).



III

In nucleophilic substitution reactions, the two product stabilizing factors are (i) a stronger nucleophile ($\delta\sigma_X < 0$) and (ii) a better leaving group ($\delta\sigma_Z > 0$), for which the TS shift is predicted based on thermodynamic models,[6] such as the Hammond postulate,[6a] the Bell–Evans–Polanyi[6b] (BEP) principle *etc*. According to these models, a stronger nucleophile ($\delta\sigma_X < 0$) leads to an earlier TS with a lower degree of bond formation (and bond cleavage of the leaving group), which in the present case should give a lower degree of C_α–N bond formation with a low degree of progress in the hydrogen bonding by the N–H (D) proton *i.e.*, a smaller k_H/k_D value for a stronger nucleophile ($\delta\sigma_X < 0 \longrightarrow \delta (k_H/k_D) < 0$) as was observed with all the dicarbonyl activated compounds, **1**–**4**. This means that the TS structures, or the TS positions along the reaction coordinate, are largely determined by the product stability, and a

Table 3 Kinetic isotope effects on the second-order rate constants (k_2) for the reactions of ethyl α-acetyl-β-phenylacrylates with deuterated X-benzylamines in acetonitrile at 25.0 °C

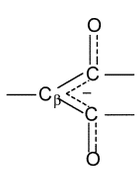
X	Y	$k_H \times 10^2/M^{-1}s^{-1}$	$k_D \times 10^2/M^{-1}s^{-1}$	k_H/k_D
p-OMe	*p*-OMe	0.767(±0.005)	0.341(±0.002)	2.24 ± 0.02[a]
p-OMe	*p*-Me	1.02(±0.004)	0.481(±0.005)	2.12 ± 0.02
p-OMe	H	1.47(±0.01)	0.753(±0.006)	1.95 ± 0.02
p-OMe	*p*-Cl	2.38(±0.02)	1.34(±0.02)	1.78 ± 0.03
p-Cl	*p*-OMe	0.295(±0.001)	0.124(±0.001)	2.38 ± 0.02
p-Cl	*p*-Me	0.372(±0.002)	0.170(±0.001)	2.19 ± 0.02
p-Cl	H	0.496(±0.004)	0.251(±0.003)	1.98 ± 0.03
p-Cl	*p*-Cl	0.749(±0.005)	0.412(±0.003)	1.82 ± 0.02

[a] Standard deviations.

greater reactivity is accompanied by a lower selectivity, *i.e.*, the reactivity–selectivity (RSP)[7] holds for the dicarbonyl activated olefins.

Contrary to this, a larger k_H/k_D value was observed with a stronger nucleophile ($\delta\sigma_X < 0 \longrightarrow \delta\ (k_H/k_D) > 0$) for the benzylamine additions in acetonitrile to olefins activated by other (than dicarbonyl) groups: BMN (**5**), benzylidenemalononitrile ($YC_6H_4CH{=}C(CN)_2$)[1b]; NS (**6**), β-nitrostyrene ($YC_6H_4CH{=}CH(NO_2)$)[1a] NSB (**7**), β-nitrostilbene ($YC_6H_4CH{=}C(C_6H_5)NO_2$)[1c]; CNS (**8**), β-cyano-4′-nitrostilbene ($YC_6H_4CH{=}C(CN)\cdot C_6H_4NO_2$)[1c] ECC (**9**), ethyl-α-cyanocinnamate, ($YC_6H_4CH{=}C(CN)COOEt$).[1d] A later TS with a greater degree of bond formation with a greater extent of hydrogen bonding by the N–H (D) proton leading to a larger value of k_H/k_D ($\delta(k_H/k_D) > 0$) with a stronger nucleophile ($\delta\sigma_X < 0$) represents an anti-Hammond effect[6a] or an intrinsic effect,[3b] *i.e.*, a greater reactivity leads to a greater selectivity, and an anti-RSP.[3b] This is no doubt related to the stronger anionic charge development on C_β with a stronger nucleophile due to the lag in the delocalization of charge onto the activating groups, which are not dicarbonyls. This kind of charge imbalance causes a reduction in the intrinsic rate[2,5] (k_o), and hence the effect on selectivity should be intrinsic so that the anti-Hammond effect,[6a] or anti-RSP, should hold as we have observed with the trend of changes in the magnitude of k_H/k_D for **5**–**9**, as well as the substantially larger magnitude ($k_H/k_D \cong 2.3 \sim 2.8$) than for the dicarbonyl series ($k_H/k_D \cong 1.2 \sim 2.4$). It is therefore clear that the dicarbonyl group, irrespective of whether it has a ring structure (as in **1** and **2**) or not (**3** and **4**), has very small TS imbalance effect in the amine additions in acetonitrile. This is evident since for the dicarbonyl activated series the thermodynamic models, which are based on product stability, *i.e.*, the Hammond effect and the BEP principle,[6] hold. This means that due to strong resonance delocalization through dicarbonyl groups in the TS the charge imbalance effect becomes small. The resonance delocalization is especially efficient with ring structure[5] as we noted above.

Dicarbonyl groups attached to a carbanionic center are known to have enormous charge transfer stabilization energies due to the two strong vicinal $n_C \longrightarrow \pi^*_{C=O}$ charge transfer interactions,[8] $-\Delta E_{CT} > 250$ kcal mol^{-1} at the NBO-B3LYP/6-311+G** level.[9] Due to the delocalization of anionic charge on the carbanionic center, C_β, into the two carbonyl groups, the dicarbonyl moiety becomes planar, **IV**.



IV

However, if it has a built-in planar structure as in the cyclic dicarbonyls (**1** and **2**), the reorganization required to form such a planar structure is not required, which should result in a lower activation barrier,[5] as we noted above (Table 2). In fact the noncyclic dicarbonyls such as dimethyl malonate, **10** ($CH_2(COOCH_3)_2$), and 1,3-cyclohexadione, **11** ($CH_2(COCH_2CH_3)_2$), have nonplanar twisted structures ranging 35–86° (calculated at the B3LYP/6-311+G** level).[9] When these are deprotonated the planar structures, **IV**, are formed so that there should be some reorganization energies required. This should increase the activation barrier. Thus the anionic center developing on C_β in the noncyclic dicarbonyl activated series (**3** and **4**) should have lower rate than the cyclic dicarbonyl series (**1** and **2**) as observed in Table 2.

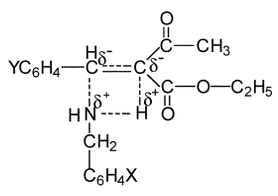
Table 4 Activation parameters[a] for the reactions of ethyl α-acetyl-β-phenylacrylates with X-benzylamines in acetonitrile

X	Y	$\Delta H^{\neq}$/kcal mol^{-1}	$-\Delta S^{\neq}$/cal mol^{-1} K^{-1}
p-OMe	*p*-OMe	4.9	52
p-OMe	*p*-Br	5.3	48
p-Cl	*p*-OMe	4.9	54
p-Cl	*p*-Br	4.6	53

[a] Calculated by the Eyring equation. The maximum errors calculated (by the method of Wiberg[12]) are ±0.6 kcal mol^{-1} and ±3 e.u. for $\Delta H^{\neq}$ and $\Delta S^{\neq}$, respectively.

Although the trends in the change in k_H/k_D with variation of substituent Y in the substrate for the dicarbonyl series (**1**–**4**)[1e,g] and others (**5**–**9**)[1a–d] are opposite, it is rather ambiguous as to the effect of Y on the RSP. An electron donor Y ($\delta\sigma_Y < 0$) should increase negative charge on C_α leading to a lower rate of attack by the nucleophile, benzylamine, but should be weakly stabilizing the neutral product by donating electrons to electron-withdrawing activating groups.

The activation parameters, $\Delta H^{\neq}$and $\Delta S^{\neq}$, are shown in Table 4. Since the reaction proceeds by a concurrent bond formation of N–C_α and H–C_β bonds, the $\Delta H^{\neq}$ values are rather low, but the $-\Delta S^{\neq}$ values are large due to a constrained hydrogen bonded TS structure, **V**. In this structure the amine hydrogen is bonded to C_β not to a carbonyl oxygen as in the six-membered TS structure, **III**. The charge on C_β in the TS should be stronger due to the lag (although it may be small, it is not absent entirely) in the resonance delocalization of anionic charge into the activating groups, and hence should lead to a larger k_H/k_D value with a greater degree of N–H (D) bond cleavage than expected from a synchronous resonance delocalization. The hydrogen bonding to a carbonyl oxygen will be very weak since in the TS delocalization will not be complete.



V

Lastly the timing of the two processes, anionic charge development on C_β and hydrogen bonding to the C_β, is rather difficult to clearly envisage. These two would not take place in the absence of N–C_α bond formation. The electronic shift to form an anionic center should follow immediately and then a proton shift to C_β. Since both shifts, electron and proton, are fast, at best these two could conceivably occur synchronously with bond formation.

Experimental

Materials

Merck GR acetonitrile was used after three distillations. The benzylamine nucleophiles, Aldrich GR, were used after recrystallization.

Preparation of ethyl α-acetyl-β-phenylacrylates

The ethyl α-acetyl-β-phenylacrylates were prepared by the literature method of Horning *et al*.[10] Equimolecular amounts of benzaldehyde (10 mmol) and ethyl acetoacetate(10 mmol) were dissolved in the minimal amount of pyridine and refluxed for 1 h. Solvent was removed under reduced pressure and product was separated by column chromatography (silica gel, 10% ethylacetate-*n*-hexane) (yield >85%). IR (Nicolet 5BX FT-IR) and ^{1}H and ^{13}C NMR (JEOL 400 MHz) data were found to agree well with the literature values.[10]

Kinetic measurements

The reaction was followed spectrophotometrically by monitoring the decrease in the concentration of ethyl α-acetyl-β-phenylacrylate, [EAP], at λ_{max} of the substrate to over 80% completion. The reaction was studied under pseudo-first-order conditions, [EAP] = 8.0×10^{-5} M and [BA] = 0.02–0.05 M at 25.0 ± 0.1 °C. The pseudo first-order rate constant, k_{obs}, was determined from the slope of the plot ($r > 0.995$) ln[EAP] (2.303 log [EAP] *vs*. time. Second-order rate constants, k_N, were obtained from the slope of a plot ($r > 0.993$) of k_{obs} *vs*. benzylamine with more than four concentrations of more than three runs and were reproducible to within ± 3%.

Product analysis

The analysis of final products was difficult due to partial decomposition during product separation and purification. We therefore analysed the reaction mixture by NMR (JEOL 400 MHz) at appropriate intervals under exactly the same reaction conditions as the kinetic measurement in MeCN at 25.0 °C. Initially we found a peak for CH in the reactant, *p*-$CH_3OC_6H_4CH{=}C(COCH_3)CO_2C_2H_5$, at 7.48 ppm, which was gradually reduced, and two new peaks for CH–CH in the product, *p*-$CH_3OC_6H_4(MeOC_6H_4CH_2NH)CH{-}CH(COCH_3)CO_2C_2H_5$, grew at 3.46 and 4.77 ppm as the reaction proceed. No other peaks or complications were found during the reaction except the 3 peak height changes indicating that the reaction proceeds with no other side reactions.

Acknowledgements

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