

Reaction Kinetics of Cinnamoyl, β -2-Furylacryloyl, and β -2-Thienylacryloyl Chlorides with Anilines in Benzene

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Received August 11, 1977

The reaction rates of cinnamoyl, β -2-furylacryloyl, and β -2-thienylacryloyl chlorides with substituted anilines have been measured in benzene at different temperatures. The reactions follow second-order kinetics. The activation parameters and the slopes of the Hammett and Brønsted plots are similar to those of the benzoylation reaction. The results show that the reaction mechanism of cinnamoyl, β -2-furylacryloyl, and β -2-thienylacryloyl chlorides with aniline is the same as for the benzoylation reaction. The cinnamoyl, β -2-furylacryloyl, and β -2-thienylacryloyl chloride reactivities are similar. The reaction rates of cinnamoyl and β -2-thienylacryloyl chlorides are faster than those of benzoyl and 2-thenoyl chlorides, whereas the reactivity of β -2-furylacryloyl chloride is similar to that of 2-furoyl chloride. The results show that, when a vinylene group is interposed between the reaction center and the heteroaromatic ring, the heteroaromatic nuclei behave as the benzene nucleus. The Hammett treatment of the data shows the variability of σ_{het} values. The data are well correlated by the Taft-Pavelich equation, indicating that the reactivity of the five-membered rings depends on steric and polar effects.

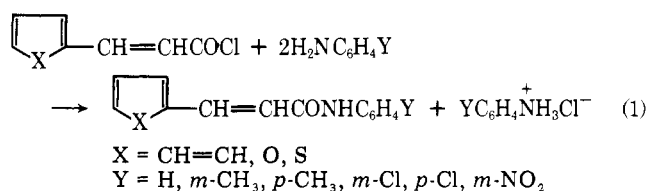
Several studies have been carried out with the purpose of comparing the side-chain reactivity in the furan and thiophene series with that of the benzene series.

Furyl and thienyl groups may be expected to exert two opposing electronic effects. There will be an electron-withdrawing inductive effect caused by the electronegatives of the heteroatoms; second, there will be an electron-donating mesomeric effect due to the ability of the heteroatoms to share their unshared electron pairs. It was pointed out that both the inductive and the resonance effects of the heterocyclic rings may contribute.¹

In the past few years we have studied the kinetics of the reaction of 2- and 3-thienyl³ and 2- and 3-furoyl chlorides^{1,4} with anilines, 2- and 3-chloroacetyl furan, and 2- and 3-chloroacetylthiophenes with triethyl phosphite,⁵ basic⁶ and acid hydrolysis⁷ of 2- and 3-furanilides, and 2- and 3-thenilides. The data indicated that these heterocyclic rings, depending on the pattern of substitution and reaction considered, may act as electron donating or electron withdrawing.

Following this research work in this paper we report the reaction kinetics of cinnamoyl, β -2-furylacryloyl, and β -2-

thienylacryloyl chlorides with anilines in benzene (eq 1) with the aim of studying the influence of the heteroaromatic rings on the reactivity of the acid chlorides where the heteroaromatic systems are separated from the reaction center by the insertion of a vinylene group.



Results and Discussion

The reactions of cinnamoyl, β -2-furylacryloyl, and β -2-thienylacryloyl chlorides with meta- and para-substituted anilines took place quantitatively according to eq 1. The reactions were followed kinetically as previously described^{3,4} and in all cases the compounds gave excellent second-order kinetics.

The second-order rate constants, reported in Tables I, II,

Table I. Second-Order Rate Constants and Activation Parameters for the Reaction of Cinnamoyl Chloride with Meta- and Para-Substituted Anilines in Benzene

No.	Substituent	Registry no.	$\text{p}K_{\text{a}}^{\text{a}}$	$k_2 \times 10^2, \text{L mol}^{-1} \text{s}^{-1}$			E_{A}^{b}	Log A	ΔS^{c}
				15 °C	25 °C	40 °C			
1	H	62-53-3	4.58	7.90	12.5	20.6	6.83	4.09	-41.8
2	<i>m</i> -CH ₃	108-44-1	4.69	15.1	23.1	35.8	6.14	3.85	-42.9
3	<i>p</i> -CH ₃	106-49-0	5.12	36.8	49.3	81.2	5.71	3.89	-42.7
4	<i>m</i> -Cl	108-42-9	3.34	0.491	0.778	1.53	8.16	3.88	-42.8
5	<i>p</i> -Cl	106-47-8	3.98	2.01	3.06	5.79	7.61	4.07	-41.9
6	<i>m</i> -NO ₂	99-09-2	2.50	0.0496	0.0934	0.184	9.34	3.79	-43.2

^a Reference 8. ^b In units of kcal/mol. ^c At 25 °C, in cal mol⁻¹ K⁻¹.

Table II. Second-Order Rate Constants and Activation Parameters for the Reaction of β -2-Furylacryloyl Chloride with Meta- and Para-Substituted Anilines in Benzene

No.	Substituent	$\text{p}K_{\text{a}}^{\text{a}}$	$k_2 \times 10^2, \text{L mol}^{-1} \text{s}^{-1}$			E_{A}^{b}	Log A	ΔS^{c}
			15 °C	25 °C	40 °C			
1	H	4.58	7.23	11.1	18.5	6.71	3.95	-42.4
2	<i>m</i> -CH ₃	4.69	12.8	19.5	31.5	6.42	3.99	-42.2
3	<i>p</i> -CH ₃	5.12	34.6	47.5	77.4	5.79	3.93	-42.5
4	<i>m</i> -Cl	3.34	0.454	0.690	1.34	7.78	3.55	-44.3
5	<i>p</i> -Cl	3.98	1.79	2.61	4.96	7.26	3.75	-43.3
6	<i>m</i> -NO ₂	2.50	0.0431	0.0765	0.161	9.44	3.79	-43.2

^a Reference 8. ^b In units of kcal/mol. ^c At 25 °C, in cal mol⁻¹ K⁻¹.

Table III. Second-Order Rate Constants and Activation Parameters for the Reaction of β -2-Thienylacryloyl Chloride with Meta- and Para-Substituted Anilines in Benzene

No.	Substituent	pK_a^a	$k_2 \times 10^2, \text{L mol}^{-1} \text{s}^{-1}$			E_A^b	Log A	ΔS^*c
			15 °C	25 °C	40 °C			
1	H	4.58	6.91	10.3	18.3	6.99	4.14	-41.6
2	<i>m</i> -CH ₃	4.69	10.6	16.4	26.4	6.50	3.97	-42.3
3	<i>p</i> -CH ₃	5.12	26.1	36.4	60.3	6.02	3.98	-42.3
4	<i>m</i> -Cl	3.34	0.394	0.621	1.22	8.12	3.75	-43.3
5	<i>p</i> -Cl	3.98	1.63	2.32	4.64	7.57	3.94	-42.5
6	<i>m</i> -NO ₂	2.50	0.0385	0.0735	0.152	9.72	3.98	-42.3

^a Reference 8. ^b In units of kcal/mol. ^c At 25 °C, in cal mol⁻¹ K⁻¹.

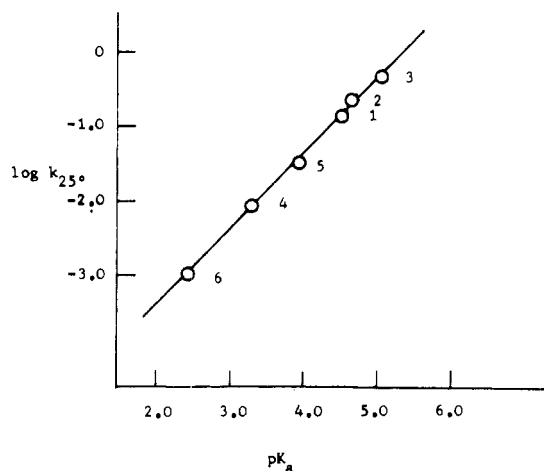


Figure 1. Plot of $\log k_{25}$ for the reaction of cinnamoyl chloride with anilines in benzene against the logarithm of their dissociation constants in water at 25 °C (Brønsted plot).

and III, show that electron-donating substituents accelerate and electron-withdrawing groups retard the reactions. The results indicate that the reactivity sequence is cinnamoyl chloride \geq β -2-furylacryloyl chloride \geq β -2-thienylacryloyl chloride. The difference of reactivity among them is small being the ratio $k/k' = 1.13 \pm 0.09$ and $k/k'' = 1.27 \pm 0.14$, where k are the reaction constants at 25 °C of cinnamoyl chloride, k' are the reaction constants at 25 °C of β -2-furylacryloyl chloride, and k'' are the reaction constants at 25 °C of β -2-thienylacryloyl chloride.

The activation parameters, listed in Tables I, II, and III, show a regular variation with the substituent in the aniline, as noted in the furoyl¹ and thenoyl chloride³ reactions.

The large negative entropies of activation are as expected in reaction involving polar transition states and similar to those found previously in 2-² and 3-thenoyl³ and 2- and 3-furoyl chloride¹ reactions.

As for the thenoyl^{2,3} and furoyl chlorides¹ reactions, linear relationships were also found in the reactions of cinnamoyl, β -2-furylacryloyl, and β -2-thienylacryloyl chlorides with anilines between $\log k$ at 25 °C and the pK_a values at 25 °C in water of the corresponding protonated anilines⁸ indicating that also the reaction rates of these acid chlorides with aniline depend on the electron density on the nitrogen atom. The slopes of the Brønsted plots, 1.04 ($r = 0.998$), 1.06 ($r = 0.999$), and 1.03 ($r = 0.999$), for cinnamoyl, β -2-furylacryloyl, and β -2-thienylacryloyl chlorides, respectively, are similar to those found for benzoylation and thenoyl^{2,3} and furoyl chloride¹ reactions. The plot of $\log k$ at 25 °C of the reaction of cinnamoyl chloride with anilines against the pK_a values at 25 °C in water of the corresponding protonated anilines are reported in Figure 1.

The plot of $\log k$ at 25 °C for the reactions of cinnamoyl, β -2-furylacryloyl, and β -2-thienylacryloyl chlorides against

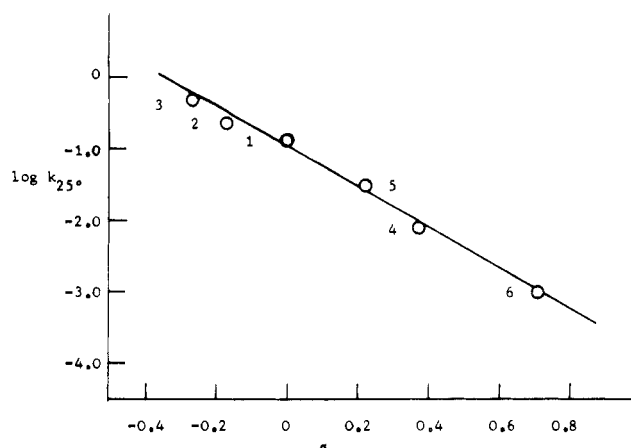


Figure 2. Hammett plot for the reaction of cinnamoyl chloride with anilines at 25 °C in benzene.

Hammett's σ constants are linear with slopes of -2.77 ($r = 0.995$), -2.86 ($r = 0.995$), and -2.74 ($r = 0.994$), respectively. Figure 2 reports the plot of $\log k$ at 25 °C for the reaction of cinnamoyl chloride with anilines against Hammett's σ constants. The values of the slopes are similar to those found for benzoylation⁹⁻¹¹ and thenoyl^{2,3} and furoyl chlorides¹ reactions.

From these results it is evident that cinnamoyl, β -2-furylacryloyl, and β -2-thienylacryloyl chlorides react with aniline in benzene with the same mechanism as the reaction of benzoylation involving the attack of the lone pair of the electrons of the amine group on the carbonyl carbon atom.¹²

The reaction rates of cinnamoyl and β -2-thienylacryloyl chlorides are faster than those of benzoyl¹³ and 2-thenoyl chlorides,² whereas the reactivity of β -2-furylacryloyl chloride is similar to that of 2-furoyl chloride¹ being the ratio $k/k' = 1.18 \pm 0.16$, where k are the reaction rate constants at 25 °C of 2-furoyl chloride and k' are the reaction rate constants at 25 °C of β -2-furylacryloyl chloride.

In the reaction of 2- and 3-furoyl^{1,4} and 2-^{2,4} and 3-thenoyl^{3,4} chlorides with aniline we have found the reactivity sequence 2-furoyl chloride > benzoyl chloride > 3-thenoyl chloride \approx 3-furoyl chloride > 2-thenoyl chloride indicating that, in comparison with the benzene nucleus, the thienyl group behaves as electron donating, whereas the furyl group behaves as electron donating in the 3-furoyl chloride and as electron withdrawing in the 2-furoyl chloride. From the results here obtained it is clear that the reactivity of heterocyclic acid chlorides, when the heteroaromatic system is separated from the reaction center by the insertion of a vinylene group, is similar to that of benzene derivatives, indicating that the heteroaromatic nuclei behave as the benzene nucleus. The same trend was observed in the saponification of ethyl ester of cinnamic, β -2-furylacrylic, and β -2-thienylacrylic acids.¹⁴

The reactivity sequence (2-furyl > phenyl > 2-thienyl) of the reaction of acid chlorides with aniline⁴ was observed in

Table IV. Application of the Taft-Pavelich Equation to the Reaction of Acid Chlorides (Ar-COCl) with Aniline in Benzene at 25 °C

No.	Ar	σ^*	E_s	Log k	Log $k - \delta E_s$
1	Phenyl	0.60 ^a	-2.55 ^a	-1.20 ^c	1.42
2	2-Furyl	1.08 ^b	-3.16 ^b	-0.876 ^c	2.38
3	3-Furyl	0.65 ^b	-2.71 ^b	-1.39 ^c	1.40
4	2-Thienyl	0.93 ^b	-3.39 ^b	-1.59 ^c	1.91
5	3-Thienyl	0.65 ^b	-2.73 ^b	-1.36 ^c	1.45
6	5-Methyl-2-thienyl	0.84 ^b	-3.58 ^b	-1.99 ^d	1.70
7	5-Chloro-2-thienyl	1.26 ^b	-3.53 ^b	-1.23 ^d	2.40
8	5-Nitro-2-thienyl	1.65 ^b	-3.19 ^b	-0.374 ^d	2.91

^a J. Shorter, "Advances in Linear Free Energy Relationship", N. B. Chapman and J. Shorter, Ed., Plenum Press, London, 1972, p 76. ^b Reference 15. ^c Reference 1. ^d G. Alberghina, A. Arcoria, S. Fisichella, and G. Scarlata, *Gazz. Chim. Ital.*, **103**, 319 (1973).

Table V. Application of the Taft-Pavelich Equation to the Reaction of Acid Chlorides (R-COCl) with *m*-Nitroaniline in Benzene at 20 °C

No.	R	σ^*	E_s	Log k	Log $k - \delta E_s$
1	CH ₃	0 ^a	0 ^a	-1.91 ^c	-1.91
2	<i>n</i> -C ₃ H ₇	-0.115 ^a	-0.36 ^a	-2.02 ^c	-1.66
3	<i>n</i> -C ₄ H ₉	-0.130 ^a	-0.39 ^a	-2.17 ^c	-1.78
4	<i>i</i> -C ₄ H ₉	-0.125 ^a	-0.93 ^a	-2.42 ^c	-1.49
5	C ₆ H ₅ CH ₂	0.215 ^a	-0.38 ^a	-1.68 ^c	-1.30
6	CH ₃ CH=CH	0.36 ^a	-1.63 ^a	-2.32 ^c	-0.693
7	ClCH ₂	1.05 ^a	-0.24 ^a	-0.38 ^c	-0.140
8	Cl ₃ C	2.65 ^a	-2.06 ^a	-0.558 ^c	1.50
9	C ₆ H ₅	0.60 ^a	-2.55 ^a	-3.49 ^c	0.945
10	2-Furyl	1.08 ^b	-3.16 ^b	-3.24 ^d	-0.0863
11	3-Furyl	0.65 ^b	-2.71 ^b	-3.80 ^d	-1.10
12	3-Thienyl	0.65 ^b	-2.73 ^b	-3.69 ^d	-0.965
13	C ₆ H ₅ CH=CH	0.41 ^a	-1.89 ^a	-3.18 ^e	-1.29

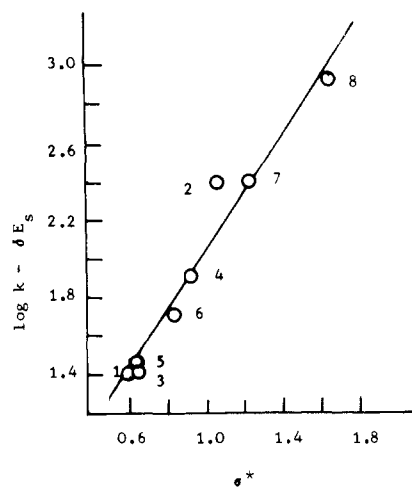
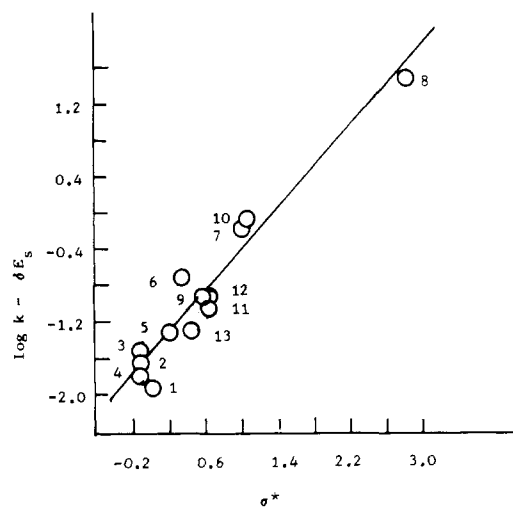
^a J. Shorter, "Advances in Linear Free Energy Relationship", N. B. Chapman and J. Shorter, Ed., Plenum Press, London, 1972, p 76. ^b Reference 15. ^c H. S. Venkataraman and C. N. Hinshelwood, *J. Chem. Soc.*, 4977 (1960). ^d Reference 1, interpolated at 20 °C from activation parameters. ^e This work, interpolated at 20 °C from activation parameters.

other nucleophilic substitution at the carbonyl group, as in the reaction of aryl chloromethyl ketones with triethyl phosphite,⁵ in the alkaline hydrolysis of esters¹⁵ and in the reduction of aryl methyl ketones by sodium borohydride.¹⁶

The Hammett equation was applied to 5-heteroaromatic rings^{17,18} and, considering the heterocycle as a substituted benzene, σ_{het} constants for the replacement of a CH=CH group in the benzene ring by the heteroatoms were calculated by

$$\sigma_{\text{het}} = (\log k - \log k_0) / \rho \quad (2)$$

where $\log k$ is the reaction rate at 25 °C of the heteroaromatic compounds, $\log k_0$ is the reaction rate at 25 °C of the unsubstituted benzene derivative, and ρ is the reaction constant of benzene derivatives. The σ_{het} values for the reaction of furoyl and thenoyl chlorides with aniline in benzene⁴ are $\sigma_{\alpha-0} = 0.31$, $\sigma_{\beta-0} = -0.05$, $\sigma_{\alpha-S} = -0.20$, and $\sigma_{\beta-S} = -0.04$ using the $\rho = 1.42$ and $\log k_0 = -1.31$ values.¹⁹ The Hammett treatment was also applied to other nucleophilic substitutions at the carbonyl group and the results show the variability of σ_{het} values.²⁰



**Figure 3.** Plot of $(\log k - \delta E_s)$ for the reaction of acid chlorides with aniline in benzene at 25 °C against σ^* constants.**Figure 4.** Plot of $(\log k - \delta E_s)$ for the reaction of acid chlorides with *m*-nitroaniline in benzene at 20 °C against σ^* constants.

The Taft-Pavelich²¹ (eq 3) equation that takes into account both polar (σ^*) and steric effects (E_s) was recently used to correlate the kinetic data of reactions of heteroaromatic compounds to the carbonyl group.²⁰

$$\log k/k_0 = \rho^* \sigma^* + \delta E_s \quad (3)$$

We applied eq 3 in the reactions of acid chlorides with aniline at 25 °C (Table IV) and with *m*-nitroaniline at 20 °C in benzene (Table V). Table V contains only the value of cinnamoyl chloride, because the σ^* and E_s values for β -2-furylvinyl and β -2-thienylvinyl groups are not known. The data are well correlated by eq 3, obtaining $\rho = 1.52$ (standard deviation, $s = 0.12$), $\delta = 1.03$ ($s = 0.11$), $\log k_0 = 0.489$ for the reaction of acid chlorides with aniline and $\rho = 1.19$ ($s = 0.09$), $\delta = 1.01$ ($s = 0.06$), and $\log k_0 = -1.68$ for the reaction of acid chlorides with *m*-nitroaniline. The plots of $\log k$ at 25 °C and at 20 °C for the reactions of acid chlorides with aniline and *m*-nitroaniline, respectively, cleaned from the contribution of the steric effect ($\log k - \delta E_s$) against σ^* constants give linear relationships with $r = 0.98$ (Figure 3) for the reaction of acid chlorides with aniline and $r = 0.97$ (Figure 4) for the reaction of acid chlorides with *m*-nitroaniline, indicating that the reactivity of five-membered rings depends on steric and polar effects. Conjugative effects cannot be excluded because E_s values for aromatic and unsaturated groups include conjugative contributions.²²

Table VI. Physical Constants of Anilides^{a,b}

No.	X	Ph—CH=CHCONHC ₆ H ₄ X		 —CH=CHCONHC ₆ H ₄ X		 —CH=CHCONHC ₆ H ₄ X	
		Mp, °C	Registry no.	Mp, °C	Registry no.	Mp, °C	Registry no.
1	H	151 ^c	3056-73-3	128 ^g	15341-86-3	143 ^f	28424-57-9
2	<i>m</i> -CH ₃	114 ^d	57830-64-5	111 ^g	15341-96-5	136 ^f	64741-17-9
3	<i>p</i> -CH ₃	162 ^d	6876-68-2	156 ^g	15341-94-3	143 ^h	28424-60-4
4	<i>m</i> -Cl	120 ^e	64741-15-7	104 ^g	15341-89-6	101 ^h	64741-16-8
5	<i>p</i> -Cl	185 ^e	53691-91-1	173 ^g	15341-87-4	173 ^f	64741-20-4
6	<i>m</i> -NO ₂	177 ^f	55000-38-9	165 ^f	64741-18-0	154 ^f	64741-19-1

^a All the compounds were crystallized from aqueous ethanol. ^b Satisfactory data for N ($\pm 0.2\%$) were reported. ^c A. P. De Jonge, A. Verhge, and B. Van der Ven, *Recl. Trav. Chim. Pays-Bas*, **83**, 949 (1964). ^d P. I. Ittyerah and K. C. Pandya, *J. Indian Chem. Soc.*, **30**, 717 (1953). ^e M. V. George and P. I. Ittyerah, *Agra Univ. J. Res. Sci.*, **4**, 551 (1955). ^f This work. ^g L. F. Golovyashkina, *Uzh. Khim. Zh.*, **11**, 24 (1967). ^h T. Yabuuchi, *Chem. Pharm. Bull.*, **8**, 169 (1960).

Experimental Section

Materials. Cinnamoyl chloride (Aldrich commercial product), bp 256–8 °C, was purified twice by distillation.

The β -2-furylacryloyl and β -2-thienylacryloyl chlorides were prepared by refluxing 2 g of the corresponding acids (Aldrich commercial products) with 10 mL of thionyl chloride for several hours. The excess of thionyl chloride was removed by water bath distillation, and the acid chlorides were purified under reduced pressure: β -2-furylacryloyl chloride, bp 128–30 °C (6 mmHg);²³ β -2-thienylacryloyl chloride, bp 126 °C (30 mmHg).²⁴

The anilines (Carlo Erba commercial products) were purified to constant melting point on boiling point by recrystallization or fractionation.

The solvent was benzene (R. P. Carlo Erba); no special purification was undertaken.²

Kinetic Procedure. The reactions were followed kinetically, as previously,^{3,4} by filtering the completely insoluble aniline hydrochloride, dissolving it in water, and estimating the chloride with 0.01 N mercury(II) nitrate, using diphenylcarbazone as indicator, in the presence of bromophenol blue.

The second-order rate constants were calculated with constant molar ratios of the reactants (1:2): 1 mol of acid chloride with 2 mol of aniline. For the *m*- and *p*-toluidine reactions the initial concentrations of the reactants after mixing were acid chloride 0.0025 M and aniline 0.005 M.

All compounds gave excellent second-order kinetics.

All rates were run in duplicate to the least 75–80% completion with less than 3% deviation between the two rate constants.

All rate constants were calculated by a least-squares computer program with a Hewlett-Packard 9100 B.

The activation parameters were calculated from a least-squares treatment of $\log k$ against T^{-1} . The estimated precision is ca. ± 0.7 kcal mol⁻¹ in E_A and ± 2.5 cal mol⁻¹ in ΔS^\ddagger .

Product Analysis. Standard solutions of the appropriate aniline and acid chloride in benzene were placed in a glass-stoppered bottle and maintained at the kinetic temperature until completion. After concentration of the benzenic solution to small volume, the anilides were filtered, washed free from aniline hydrochloride with water, dried, and recrystallized from aqueous ethanol. In all cases the amount of the anilide was $\geq 95\%$ of that expected from the formation of 1 mol of anilide per mol of acid chloride consumed. Physical constants and analytical data of the anilides are reported in Table VI.

Acknowledgments. The authors are grateful to the Consiglio Nazionale delle Ricerche for financial support.

Registry No.—Cinnamoyl chloride, 102-92-1; β -2-furylacryloyl chloride, 20689-54-7; β -2-thienylacryloyl chloride, 28424-61-5; benzene, 71-43-2.

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