KINETICS OF REACTIONS OF ACYL ISOTHIOCYANATES WITH AMINES

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The kinetics of reactions of 4-substituted benzoyl, cinnamoyl and phenyl isothiocyanates with aliphatic amines and glycine ethyl ester in organic solvents was studied by the stopped-flow and UV spectroscopic methods. The reaction of acyl isothiocyanates with the nucleophilic reagents employed proved to be $10^3 - 10^4$ times faster than analogous reaction of phenyl isothiocyanates. A linear correlation between $\log k$ and σ_p constants with positive ϱ slope was found. The solvent polarity has only a negligible effect on the reaction. UV spectra as well as gas chromatography of the reaction products proved that under the employed experimental conditions N,N′-disubstituted thioureas are the sole reaction products.

Nucleophilic additions, typical for isothiocyanates, are caused by the presence of a strong electrophilic center at the carbon of the NCS group[1]. The kinetics of these reactions with glycine[2], amines[3–6], OH⁻ ions[7], alcohols[8] and thiols[5,9] were already studied by several authors, both for aliphatic and aromatic isothiocyanates. In spite of the fact that nucleophilic additions of acyl isothiocyanates are known, only little attention has been paid to their quantitative aspects. Contrary to phenyl isothiocyanates, acyl isothiocyanates contain two strongly electrophilic centers; one at the NCS carbon and the second at the carbonyl carbon. The reaction of benzoyl isothiocyanates with amines can in principle afford two different products: N-acylthioureas of N-substituted benzamides. As found by Elmore and Ogle[10], in anhydrous organic solvents benzoyl isothiocyanate reacts with amines to afford exclusively the corresponding disubstituted thioureas (A). When the reaction was performed in aqueous dioxane at pH 8·5, the authors isolated, in addition to the thioureas A, also the N-substituted benzamides (B).

$$C_6H_5CONCS + RNH_2 \rightarrow C_6H_5CONHCSNHR + C_6H_5CONHR$$
$$A \qquad\qquad\qquad B$$
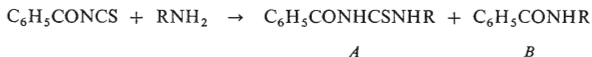
Previously we investigated the reaction of benzoyl isothiocyanates with methanol in anhydrous media[11]. In the present paper we study the kinetics of reactions of sub-

stituted benzoyl and cinnamoyl isothiocyanates with amines in organic solvents in order to compare their reactivity with that of the analogous phenyl isothiocyanates.

EXPERIMENTAL

Compounds

4-Ethoxybenzoyl isothiocyanate (*I*); b.p. 140—142°C/550 Pa. UV spectrum (CHCl$_3$): λ_{max} 305 nm, log ε 4·38. For C$_{10}$H$_9$NO$_2$S (207·3) calculated: 57·95% C, 4·38% H, 6·76% N; found: 57·51% C, 4·52% H, 6·54% N. 4-Methoxybenzoyl isothiocyanate[12] (*II*), b.p. 114—116°C/295 Pa, m.p. 28—30°C (light petroleum). UV spectrum (dioxane): λ_{max_1} 251 nm, log ε_1 4·11; λ_{max_2} 283 nm, log ε_2 3·86. 4-Methylbenzoyl isothiocyanate[13] (*III*), b.p. 108—110°C/113 Pa. UV spectrum (dioxane): λ_{max_1} 264 nm, log ε_1 4·16; λ_{max_2} 286 nm, log ε_2 3·92. Benzoyl isothiocyanate[14] (*IV*), b.p. 78—80°C/133 Pa. UV spectrum (dioxane): λ_{max_1} 252 nm, log ε_1 4·16; λ_{max_2} 280 nm, log ε_2 3·90. 4-Chlorobenzoyl isothiocyanate[12] (*V*), b.p. 104—106°C/133 Pa. UV spectrum (dioxane): λ_{max_1} 268 nm, log ε_1 4·12; λ_{max_2} 286 nm, log ε_2 3·92. 4-Bromobenzoyl isothiocyanate[15] (*VI*), m.p. 56·5—58°C (CHCl$_3$). λ_{max_1} 270 nm, log ε_1 4·30; λ_{max_2} 290 nm, log ε_2 3·98. 4-Nitrobenzoyl isothiocyanate[16] (*VII*), m.p. 90—91°C (CCl$_4$). UV spectrum (dioxane): λ_{max_1} 263 nm, log ε_1 4·24; λ_{max_2} 295 nm, log ε_2 3·90. 4-Methoxycinnamoyl isothiocyanate[16] (*VIII*), m.p. 47—48°C (light petroleum). UV spectrum (dioxane): λ_{max} 344 nm, log ε 4·48. 4-Methylcinnamoyl isothiocyanate[17] (*IX*), m.p. 46—47°C (light petroleum). UV spectrum (dioxane): λ_{max} 322 nm, log ε 4·46. Cinnamoyl isothiocyanate[17] (*X*), m.p. 41—43°C (light petroleum). UV spectrum (dioxane): λ_{max} 311 nm, log ε 4·37. 4-Chlorocinnamoyl isothiocyanate[18] (*XI*), m.p. 106—108°C (light petroleum). UV spectrum (dioxane): λ_{max} 317 nm, log ε 4·44. 4-Bromocinnamoyl isothiocyanate[17] (*XII*), m.p. 107—110°C (light petroleum). UV spectrum (dioxane): λ_{max} 317 nm, log ε 4·44. 4-Nitrocinnamoyl isothiocyanate[17] (*XIII*), m.p. 145—147°C (ether-toluene). UV spectrum (dioxane): λ_{max} 314 nm, log ε 4·37. 4-Dimethylamino (*XIV*), 4-methyl (*XV*), 4-chloro (*XVI*), 4-bromo (*XVII*) and 4-nitrophenyl (*XVIII*) isothiocyanates were prepared according to the described procedures[19−21]. Phenyl isothiocyanate (*XIX*), n-butylamine, benzylamine and cyclohexylamine were purified by distillation. Dioxane was purified by heating with an alkaline solution of potassium permanganate, dried and fractionated. Acetonitrile was dried over phosphorus pentoxide and distilled through a column. Glycine ethyl ester was liberated from its hydrochloride with gaseous ammonia in chloroform and distilled.

Products

The N-(4-X-cinnamoyl)-N′-butylthioureas *XX—XXV* were prepared by mixing equimolecular amounts of the corresponding 4-substituted cinnamoyl isothiocyanate with n-butylamine in cyclohexane (*XX—XXIV*) or in chloroform (*XXV*). The crude product was precipitated by addition of light petroleum and crystallized from an appropriate solvent. N-(4-Methoxycinnamoyl)-N′-butylthiourea (*XX*), m.p. 132—133°C (ethanol). UV spectrum (dioxane): λ_{max} 327 nm, log ε 4·52. For C$_{15}$H$_{20}$N$_2$O$_2$S (292·4) calculated: 61·62% C, 6·89% H, 9·58% N; found: 61·86% C, 6·48% H, 9·85% N. N-(4-Methylcinnamoyl)-N′-butylthiourea (*XXI*), m.p. 146—147°C (ethanol). UV spectrum (dioxane): λ_{max} 311 nm, log ε 4·53. For C$_{15}$H$_{20}$N$_2$OS (276·4) calculated: 65·18% C, 7·29% H, 10·14% N; found: 64·74% C, 7·81% H, 9·85% N. N-Cinnamoyl-N′-butylthiourea (*XXII*), m.p. 100—101°C (cyclohexane). UV spectrum (dioxane): λ_{max} 298 nm, log ε 4·43. For C$_{14}$H$_{18}$N$_2$OS (262·4) calculated: 64·24% C, 7·04% H, 10·66% N; found: 64·09% C, 6·91% H, 10·68% N. N-(4-Chlorocinnamoyl)-N′-butylthiourea (*XXIII*), m.p. 158—159°C (ethanol). UV

spectrum (dioxane): λ_{max} 302 nm, log ε 4·41. For $C_{14}H_{17}ClN_2OS$ (296·8) calculated: 56·65% C, 5·77% H, 9·44% N; found: 56·85% C, 6·04% H, 9·57% N. N-(4-Bromocinnamoyl)-N'-butyl-thiourea (*XXIV*), m.p. 177—179°C (ethanol). UV spectrum (dioxane): λ_{max} 305 nm, log ε 4·48. For $C_{14}H_{17}BrN_2OS$ (341·3) calculated: 49·27% C, 5·02% H, 8·21% N; found: 49·91% C, 5·48% H, 8·14% N. N-(4-Nitrocinnamoyl)-N'-butylthiourea (*XXV*), m.p. 182—183°C (ethanol). UV spectrum (dioxane): λ_{max} 314 nm, log ε 4·38. For $C_{14}H_{17}N_3O_3S$ (307·4) calculated: 54·89% C, 5·26% H, 13·72% N; found: 54·67% C, 5·60% H, 13·28% N.

The N-(4-substituted benzoyl)-N'-(ethoxycarbonylmethyl)thioureas *XXVI—XXXI* were prepared by mixing equimolecular amounts of 4-substituted benzoyl isothiocyanates with glycine ethyl ester in chloroform. After stirring for 30 min the chloroform was evaporated to half of the original volume, the crude products were precipitated by addition of light petroleum and crystallized from ethanol. N-(4-Ethoxybenzoyl)-N'-(ethoxycarbonylmethyl)thiourea (*XXVI*), m.p. 124—126°C. UV spectrum (CHCl₃): λ_{max} 286 nm, log ε 4·45. For $C_{14}H_{18}N_2O_4S$ (309·4) calculated: 54·35% C, 5·86% H, 9·05% N; found: 54·49% C, 5·63% H, 8·74% N. N-(4-Methyl-benzoyl)-N'-(ethoxycarbonylmethyl)thiourea (*XXVII*), m.p. 123—125°C. UV spectrum (CHCl₃): λ_{max} 255 nm, log ε 4·31. For $C_{13}H_{16}N_2O_3S$ (279·3) calculated: 55·89% C, 5·77% H, 10·02% N; found: 55·69% C, 5·53% H, 9·95% N. N-Benzoyl-N'-(ethoxycarbonylmethyl)thiourea[22] (*XXVIII*), m.p. 128—129·5°C. UV spectrum (CHCl₃): λ_{max} 247 nm, log ε 4·40. N-(4-Chlorobenzoyl)--N'-(ethoxycarbonylmethyl)thiourea (*XXIX*), m.p. 137—138·5°C. UV spectrum (CHCl₃): λ_{max} 255 nm, log ε 4·37. For $C_{12}H_{13}ClN_2O_3S$ (300·7) calculated: 47·92% C, 4·35% H, 9·13% N; found: 47·22% C, 4·29% H, 9·12% N. N-(4-Bromobenzoyl)-N'-(ethoxycarbonylmethyl)thiourea (*XXX*), m.p. 146—147°C. UV spectrum (CHCl₃): λ_{max} 261 nm, log ε 4·40. For $C_{12}H_{13}BrN_2O_3S$ (345·2) calculated: 41·75% C, 3·79% H, 8·10% N; found: 41·30% C, 3·82% H, 7·60% N. N-(4-Ni-trobenzoyl)-N'-(ethoxycarbonylmethyl)thiourea (*XXXI*), m.p. 134—135°C. UV spectrum (CHCl₃): λ_{max} 258 nm, log ε 4·39. For $C_{12}H_{13}N_3O_5S$ (311·3) calculated: 46·29% C, 4·20% H, 13·49% N; found: 45·70% C, 4·05% H, 13·23% N.

Kinetics

The absorption spectra were measured on a Superscan 3 instrument (Varian Techtron, Australia). The reactions of the acyl isothiocyanates *II—XIII* with amines were followed by the stopped-flow technique (model 1705, Applied Photophysics, Great Britain). Concentration of the isothiocyanates was $1 \cdot 10^{-4}$—$2·5 \cdot 10^{-5}$M, of the amines $1 \cdot 10^{-1}$—$2·5 \cdot 10^{-3}$M: the reaction was thus pseudomonomolecular. The measurements were performed in organic solvents at 25°C, at 285 to 300 nm for benzoyl isothiocyanates and at 315—340 nm for cinnamoyl isothiocyanates. The reaction course was recorded by a Telequipment DM 64 oscilloscope. Rate constants were calculated from the relation log [log (V_∞/V_t)] $= C - k't/2·303$, where V_t is the intensity of the transmitted light at the time t and V_∞ is the intensity at the end of the reaction. The values of the apparent rate constant k' were obtained from the slope of the linear plot of log [log (V_∞/V_t)] against time t, the actual rate constant k was calculated by dividing k' by concentration of the amine. The kinetics of reaction of phenyl isothiocyanates *XIV—XIX* with amines was followed spectroscopically (UV) on a Superscan 3 spectrophotometer by measuring the isothiocyanate concentration drop at the corresponding wavelength in cyclohexane. Starting concentration: phenyl isothiocyanates $5 \cdot 10^{-5}$M, amines $5 \cdot 10^{-3}$M. The kinetic measurements were performed in thermostated 1 cm cells at $25 \pm 0·2$°C. The apparent rate constants k' were calculated using equation for a reaction of the first order, the actual rate constants k were obtained by division of the k' values by amine concentration. The kinetics of reaction of 4-substituted benzoyl isocyanates *I, III—VII* with glycine ethyl ester (concentration 10^{-3}M) was followed in chloroform at 25°C, i.e. under conditions employed for the phenyl isothiocyanates.

Determination of Reaction Products from 4-Chlorobenzoyl Isothiocyanate and Glycine Ethyl Ester in Aqueous Dioxane

The reaction was performed in aqueous dioxane, containing various amount of water (0, 5, 10, 25, 50, 70%). The initial concentration of 4-chlorobenzoyl isothiocyanate and glycine ethyl ester in the reaction mixture was $1 . 10^{-2}$M and $2 . 10^{-2}$M, respectively. The ratio of the formed

TABLE I

Effect of Cyclohexylamine Concentration on the Reaction Rate of 4-Chlorocinnamoyl Isothiocyanate in Cyclohexane

k', k Rate constants at 25°C; initial concentration of isothiocyanate $2 \cdot 5 . 10^{-5}$M.

Cyclohexylamine M . 10^3	Relative excess of amine	k' s^{-1}	k $l\,mol^{-1}\,s^{-1}$
5	200	1·726	345
4	160	1·442	361
3	120	1·107	369
2·5	100	0·904	362
2	80	0·711	356
1·5	60	0·543	362
1	40	0·374	374
0·5	20	0·186	371

TABLE II

Rate Constants (k', s^{-1}; k, $l\,mol^{-1}\,s^{-1}$) of Reactions of 4-Substituted Benzoyl, Cinnamoyl and Phenyl Isothiocyanates with n-Butylamine in Cyclohexane at 25°C

Values of slopes ϱ and correlation coefficients r of the linear relationships log k vs σ_p.

Substituent	Benzoyl[a]		Cinnamoyl[b]		Phenyl[c]	
	k'	k	k'	k	$10^4 k'$	$10^3 k$
$(CH_3)_2N$	—	—	—	—	0·095	3·8
CH_3O	1·89	380	1·01	403	—	—
CH_3	2·60	520	1·14	456	1·22	24·4
H	8·48	848	1·39	558	2·74	54·9
Cl	6·35	1 270	2·00	801	7·98	159·6
Br	5·40	1 080	2·14	856	11·12	222·5
NO_2	9·32	1 860	—	—	203·90	4 080

[a] $\varrho_{benzoyl} = 0.641$, $r = 0.944$; [b] $\varrho_{cinnamoyl} = 0.636$, $r = 0.995$; [c] $\varrho_{phenyl} = 2.027$, $r = 0.996$.

thiourea *XXIX* and ethyl *p*-chlorohippurate (*XXXII*) was determined by gas chromatography on a Fractovap 2200 (Carlo Erba, Milano) instrument (1·2 m glass column packed with 3% OV-1 on Chromaton N-Super (0·125—0·160 mm), temperature 175°C, nitrogen pressure 147·1 kPa, hydrogen flow rate 0·05 l min^{-1}), using a Minigrator (Spectra-Physics, USA) integrator and ethyl stearate as internal standard.

RESULTS AND DISCUSSION

The high reactivity of acyl isothiocyanates towards amines makes an investigation of these reactions by usual kinetic methods very difficult and we have therefore applied the stopped-flow technique. As reagents we chose aliphatic amines because they are transparent in the UV region. The reactions were performed in anhydrous organic solvents; under these conditions N-acyl-N'-alkylthioureas were formed as the sole products. This was proved also by identity of the UV spectra of the reac-

TABLE III

Rate Constants (k, l mol^{-1} s^{-1}) for Reactions of 4-Substituted Benzoyl and Cinnamoyl Isothiocyanates with n-Butylamine in Solvents of Various Polarity at 25°C

Substituent	Toluene	Dioxane	CH_3CN	CH_2Cl_2
Benzoyl isothiocyanates				
CH_3O	792	1 103	850	—
CH_3	1 030	2 673	952	—
H	1 390	3 334	2 893	—
Cl	1 538	4 315	3 113	—
Br	1 291	4 134	2 872	—
NO_2	2 766	11 330	16 090	—
ϱ	0·495	0·828	1·195	—
r	0·953	0·947	0·974	—
Cinnamoyl isothiocyanates				
CH_3O	632	1 132	668	245
CH_3	751	1 330	852	281
H	832	—	1 080	338
Cl	1 016	2 330	1 580	399
Br	1 053	2 480	1 760	452
NO_2	2 040	—	5 430	740
ϱ	0·468	—	0·855	0·452
r	0·993	—	0·977	0·995

tion mixtures from kinetic measurements with the spectra of authentic thioureas. On the basis of the present experience with reactions of isothiocyanates with amines[3] we expected that the studied reactions follow kinetic equation for a second order reaction. This assumption was proved by study of the effect of the amine concentration on k' or k in the reaction of 4-chlorocinnamoyl isothiocyanate with cyclohexylamine (Table I). We found that the first order reaction constant k' was directly proportional to the amine concentration, whereas the second order reaction constant k remained unchanged.

The kinetic data found for the reaction of benzoyl, cinnamoyl and phenyl isothiocyanates with amines are given in Tables II–V. As seen from the rate constants k and the slopes of the linear plots of log k against the Hammett σ_p constants, electron

TABLE IV

Rate Constants (k, l mol^{-1} s^{-1}) for Reactions of 4-Substituted Benzoyl, Cinnamoyl and Phenyl Isothiocyanates at 25°C

Substi-tuent	Benzoyl				Cinnamoyl					Phenyl
	C_6H_{12}	toluene	dioxane	CH_3CN	C_6H_{12}	toluene	dioxane	CH_2Cl_2	CH_3CN	C_6H_{12}
With cyclohexylamine										
$(CH_3)_2N$	—	—	—	—	—	—	—	—	—	0·0048
CH_3O	171	236	654	390	207	342	544	120	292	—
CH_3	265	541	1 149	524	272	383	652	134	392	0·030
H	393	583	1 410	1 012	278	479	—	140	490	0·051
Cl	736	967	1 621	1 119	452	558	895	188	584	0·154
Br	718	815	1 676	1 086	447	591	899	194	591	0·207
NO_2	2 287	1 632	5 360	3 230	—	1 641	—	338	2 202	2·820
ϱ	1·049	0·696	0·760	0·829	0·661	0·634	—	0·434	0·787	2·012
r	0·994	0·923	—	0·978	0·982	0·981	—	0·992	0·997	0·997
with benzylamine										
$(CH_3)_2N$	—	—	—	—	—	—	—	—	—	0·0029
CH_3O	149	371	722	293	153	225	566	91	300	—
CH_3	255	442	1 311	396	177	268	769	97	342	0·014
H	268	500	1 559	902	259	343	—	106	362	0·023
Cl	588	700	1 644	1 069	336	416	823	137	503	0·086
Br	483	651	1 607	960	357	435	924	131	516	0·091
NO_2	1 600	1 241	4 190	3 550	—	1 197	—	200	1 045	1·330
ϱ	0·944	0·493	0·620	0·989	0·720	0·672	—	0·334	0·519	1·945
r	0·985	0·996	0·948	0·977	0·993	0·990	—	0·996	0·992	0·994

accepting substituents enhance the reaction rate, confirming thus its nucleophilic mechanism. The results represent the first quantitative data concerning the effect of the carbonyl group in acyl isothiocyanates on the NCS group reactivity towards strong nucleophiles. It follows from comparison of rate constant values that acyl isothiocyanates reacts thousand to ten thousand times faster than phenyl isothiocyanates. The lower rate constants for cinnamoyl isothiocyanates as compared with those for benzoyl isothiocyanates can be explained in the following manner. In cinnamoyl isothiocyanates the mesomeric interaction between the hydrocarbon moiety and the carbonyl group plays the dominant role, suppressing thus the electrophilic nature of the NCS carbon. In the case of benzoyl isothiocyanates the decisive

TABLE V

Rate Constants (k', s^{-1}; k, l mol^{-1} s^{-1}) for Reactions of 4-Substituted Benzoyl Isothiocyanates with Glycine Ethyl Ester in Chloroform at 25°C

($\varrho = 0.501$, $r = 0.969$)

Substituent	$10^2 k'$	k
CH$_3$CH$_2$O	1·07	10·7
CH$_3$	1·29	12·9
H	1·65	16·5
Cl	2·30	23·0
Br	2·43	24·3
NO$_2$	3·52	35·2

TABLE VI

Percentage of N-(4-Chlorobenzoyl)-N'-(ethoxycarbonylmethyl)thiourea (*XXIX*) and Ethyl 4-Chlorohippurate (*XXXII*), Arising in the Reaction of 4-Chlorobenzoyl Isothiocyanate with Glycine Ethyl Ester in Aqueous Dioxane

% Water in dioxane	% *XXIX*	% *XXXII*
0	100	0
5	93·6	6·4
10	90·2	9·8
25	85·8	14·2
50	79·5	20·5
70	72·5	27·5

factor is the mesomeric interaction between the NCS and CO groups, the aromatic moiety interacting with the CONCS group mainly by means of the π-inductive effect. These facts are in accord with our previous results concerning the IR spectra of the mentioned compounds[17,23]. The lower slopes ϱ of the Hammett plots log k vs σ_p in the case of acyl isothiocyanates (Tables II–V) indicate that the presence of carbonyl group lowers the sensitivity towards substituents as compared with phenyl isothiocyanates.

Further, we studied the solvent effects in the reactions of acyl isothiocyanates with amines in five solvents of various polarity (Tables III and IV). No linear correlation between the log k values and the solvent polarity constants E_T, was found. The rate of the studied reactions depended also on the basicity of the employed amine and increased in the order: glycine ethyl ester < benzylamine < cyclohexylamine, butylamine.

The reaction of 4-chlorobenzoyl isothiocyanate with glycine ethyl ester in dioxane was used to study the effect of water content in the solvent on the formation of the two possible reaction products: N-(4-chlorobenzoyl)-N'-(ethoxycarbonylmethyl)-thiourea (*XXIX*) and ethyl *p*-chlorohippurate (*XXXII*). As shown by gas chromatography, reaction in anhydrous dioxane afforded exclusively the thiourea, *i.e.* product of addition of glycine ethyl ester to the NCS group. With increasing amount of water there occurs also the reaction at the carbonyl carbon, leading to ethyl *p*-chlorohippurate (maximum 27·5%; Table VI). The exclusive formation of the thiourea *XXIX* in the anhydrous solvent was confirmed also by the fact that UV spectrum of the reaction product of kinetic measurement was identical with that of the authentic sample of *XXIX*.

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