Kinetic study of organotin catalyzed alcohol-isocyanate reactions
Part 2: Inhibition by foreign substances in acetonitrile and toluene

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Abstract

The influence of substances such as carboxylic acids, esters, thiol, on the rate of reaction of cyclopentanol with phenylisocyanate was studied in acetonitrile and toluene at 25°C with dibutyltin di(2-ethylhexanoate) (DBTDEH) as catalyst. Carboxylic acids induce an important rate reduction, as already observed [A.-C. Draye, J.-J. Tondeur, J. Mol. Catal. A: Chem. 138 (1999) 135; A.-C. Draye, J.-J. Tondeur, React. Kinet. Catal. Lett., submitted for publication]. The present results, dealing with the effect of added foreign substances, bring new evidences confirming Davies' reaction scheme [A.J. Bloodworth, A.G. Davies, Proc. Chem. Soc. (1963) 264; A.J. Bloodworth, A.G. Davies, J. Chem. Soc. (1965) 5238] in which the first step would be an alcoholysis of carboxylate groups of the catalyst. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Kinetics; Catalysis; Organotin; Alcohol; Isocyanate; Urethane

1. Introduction

The alcohol-isocyanate reaction, catalyzed by dialkyltin dicarboxylates, has been the subject of previous hypotheses which can be summarized as follows. (a) The catalysis results from the formation, among a lot of Sn-reactants complexes [1–6]—the composition of which could be questioned—of one type of productive association yielding urethane. (b) Some authors suggest ionic intermediates to arise either from the catalyst dissociation into $\equiv Sn^+$ and $RCOO^-$ [7–9], eventually induced by alcohol–Sn complexation [10,11], or from the dissociation of a tin–alcohol aggregate into a complex anion and H^+ [12,13]. (c) For Bloodworth and Davies [14,15] the reaction proceeds through an alcoholysis of a Sn–OOC bond followed by addition of isocyanate to produce *N*-stannylcarbamate reacting in turn with alcohol to yield urethane and regenerate tin alkoxide (Scheme 1). This hypothesis is confirmed by recent works of Houghton and Mulvaney [16,17] who point out that a thiol added even in very small amounts decelerates the kinetics. This rate reduction would arise from the substitution of the carbox-

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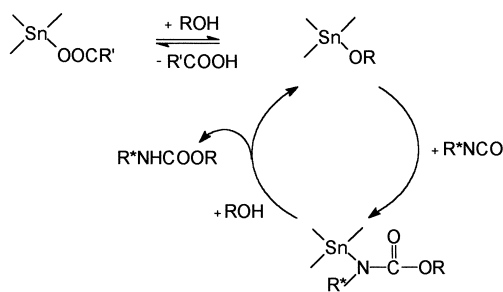
Scheme 1.

ylates by more nucleophilic thiolates which would inactivate the catalyst by forming unreactive organotins. Davies' scheme is also supported by the dependence of the catalytic rate constant on the amount of added acid [18,19] which is likely to reduce the concentration of active tin alkoxides, so reducing the rate. Ionic mechanisms, which are moreover most unlikely in apolar solvents, are excluded.

In the present work, the influence of foreign species (RCOOH, esters, thiol...) on the catalyzed reaction of cyclopentanol with phenyl-

isocyanate was studied at 25°C in acetonitrile and in toluene and the results are compared with the previous ones [18,19].

2. Experimental

2.1. Reactants

Acetonitrile (Acros spectrophotometric grade) distilled over P_2O_5, maleic acid (Acros synthesis); di(n-butyl) maleate and diethyl fumarate (Merck, synthesis), 1-butanethiol (Merck, synthesis), cyclopentanol, phenylisocyanate, di(n-butyl)tin di(2-ethylhexanoate) (DBTDEH), toluene, acids, ethyl acetate were described previously [18,19].

2.2. Procedure

The pseudo-first order constant k_a of the kinetics of phenylisocyanate with excess cy-
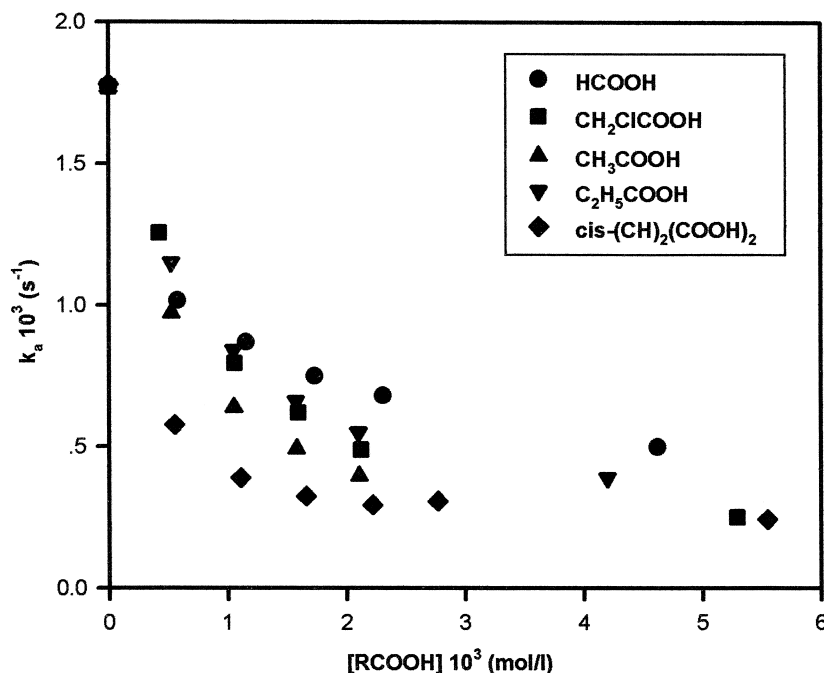

Fig. 1. Influence of carboxylic acids on the observed rate constant. PhNCO 1.63 10^{-3} M + C_5H_9OH 1.95 M/DBTDEH 1.00 10^{-3} M; acetonitrile at 25°C.
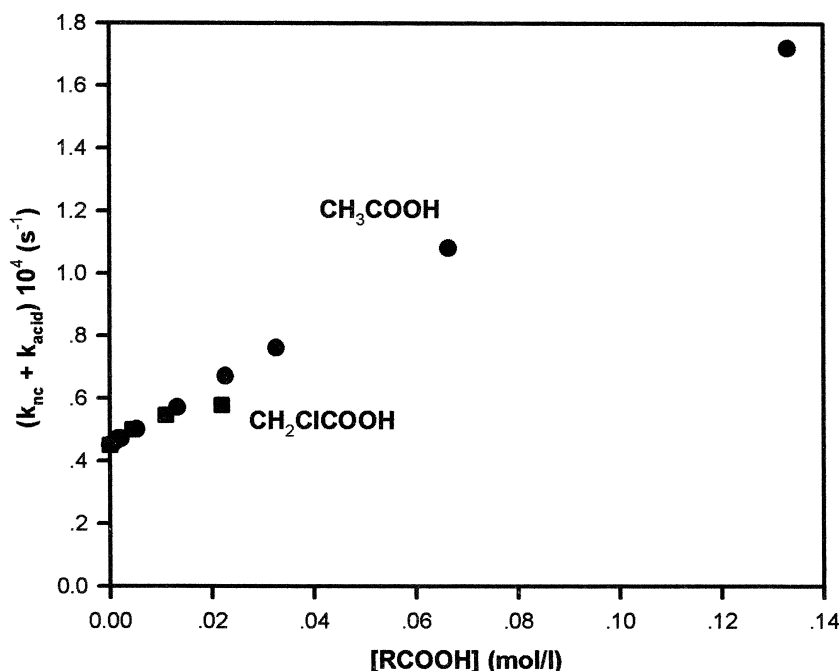
Fig. 2. Catalysis by acetic and chloroacetic acids: observed rate constant ($k_{nc} + k_{acid}$). PhNCO 1.63 10^{-3} M + C_5H_9OH 1.95 M in acetonitrile at 25°C.

clopentanol catalyzed by DBTDEH is obtained in toluene by FTIR spectroscopy [18,19] (–N=C=O at 2261 cm^{-1}); a diode array UV–visible spectrophotometer Beckmann model DU7500 is used in acetonitrile at 25°C. Urethane is the only product [20] and, α being the

Table 1
Influence of acids on the observed (k_a) and catalyzed (k_c) rate constant

[CH$_3$COOH] 10^3 (mol/l)	k_a 10^4 (s^{-1})	k_c 10^4 (s^{-1})	[CH$_2$ClCOOH] 10^3 (mol/l)	k_a 10^4 (s^{-1})	k_c 10^4 (s^{-1})
0	18.23	17.75	0	18.23	17.75
0.42	12.56	12.11	0.52	11.97	11.51
1.06	7.94	7.48	1.05	8.26	7.80
1.59	6.19	5.72	1.58	6.55	6.09
2.12	4.89	4.42	2.10	5.51	5.03
5.29	2.50	2.00	4.20	3.89	3.39
13.3	1.52	0.95	10.5	2.44	1.90
22.7	1.28	0.61	21	1.57	0.99
32.7	1.24	0.48			
66.5	1.38	0.30			
133	1.87	0.15			

$k_c = k_a - (k_{nc} + k_{acid})$, PhNCO 1.63 10^{-3} M + C_5H_9OH 1.95 M/DBTDEH 1.00 10^{-3} M; acetonitrile, 25°C.

ratio of reacted isocyanate, the absorbance writes (282 nm):

$$A_{282} = [NCO]_0\{\alpha\varepsilon_{NCO} + (1-\alpha)\varepsilon_{Ure}\}$$

and

$$\alpha = (A_{282} - [NCO]_0\varepsilon_{Ure})$$
$$/\{[NCO]_0(\varepsilon_{NCO} - \varepsilon_{Ure})\}.$$

3. Results

In acetonitrile at 25°C the addition of carboxylic acids gives the results of Fig. 1. The rate constant diminishes in the same sequence as in toluene at 55°C, i.e., formic > chloroacetic > acetic > propionic > maleic, which is not related to pK_a. As in toluene at 55°C [18,19], a catalytic power of carboxylic acids is observed at high molarities in the absence of tin catalyst (Fig. 2). The overall reaction rate is so the sum of three terms and the Sn-catalyzed rate constant k_c must be calculated by subtracting the

Table 2
Influence of water on the observed rate constant k_a

$[H_2O]\ 10^3$ (mol/l)	0	58.2	135	267
$k_a\ 10^4$ (s^{-1})	18.23	13.70	11.76	11.47

PhNCO 1.63 10^{-3} M + C$_5$H$_9$OH 1.95 M/DBTDEH 1.00 10^{-3} M; acetonitrile, 25°C.

contribution of the uncatalyzed and of the acid catalyzed reaction $(k_{nc} + k_{acid})$ from the observed rate constant k_a (Table 1).

As in toluene, ethyl acetate does not exert any significant effect on the reaction rate in acetonitrile. On the contrary, dibutyl maleate clearly slows down, but much less than the corresponding acid (Figs. 1 and 3), while dibutyl fumarate is inactive. As in the case of maleic acid (Fig. 1), the *cis* structure is a determining parameter of the inhibiting activity, owing to a chelate effect replacing the initial intramolecular dicarbonyl–Sn complex.

Table 2 shows that the effect of water, compared to that of acids or of thiol, is small but not negligible.
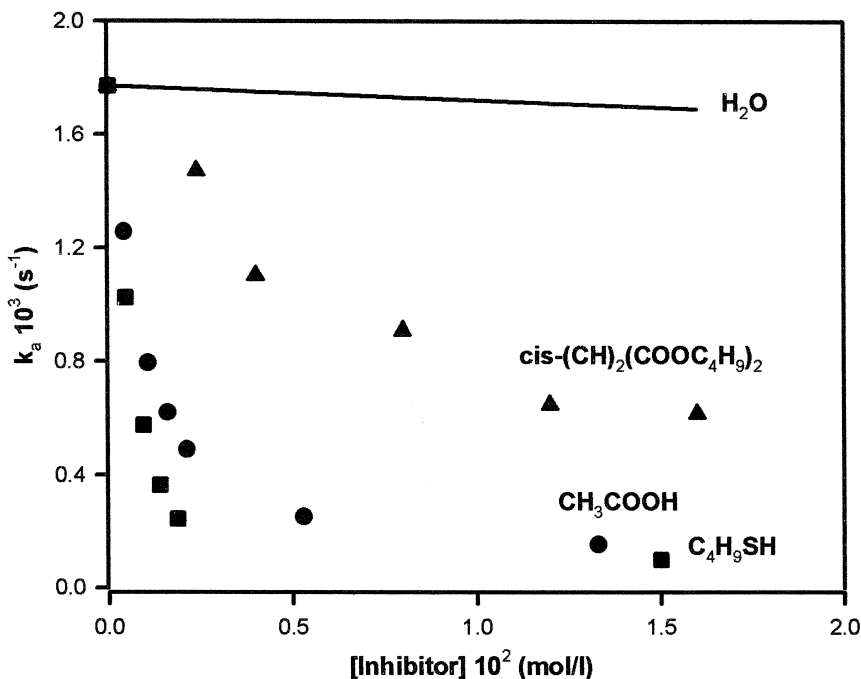

Fig. 3. Influence of various substances on the observed rate constant. PhNCO 1.63 10^{-3} M + C$_5$H$_9$OH 1.95 M/DBTDEH 1.00 10^{-3} M, acetonitrile, 25°C.
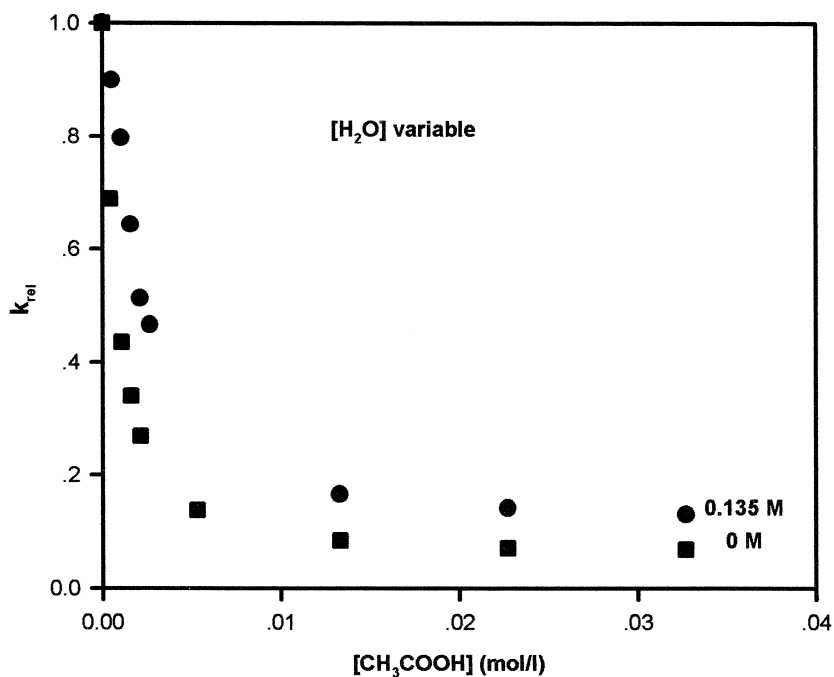
Fig. 4. Influence of acetic acid and water on the relative rate constant. $k_{rel} = k_a$ (with acid)$/k_a$ (without acid). PhNCO 1.63 10^{-3} M + C_5H_9OH 1.95 M/DBTDEH 1.00 10^{-3} M; acetonitrile, 25°C.
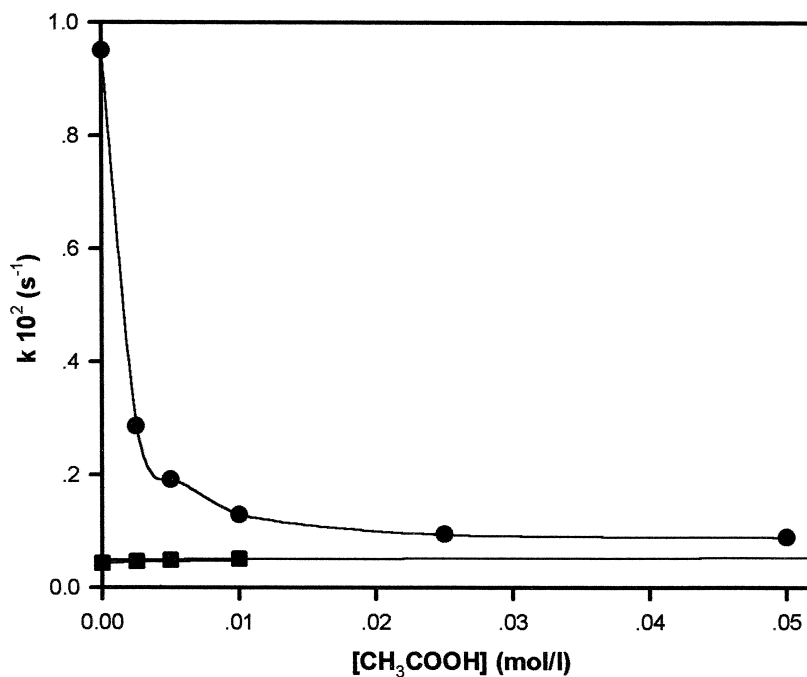

Fig. 5. Influence of acetic acid on the observed rate constant. (■) Without tin catalyst: (●) with tin catalyst. PhNCO 0.011 M + C_5H_9OH 1.95 M/DBTDEH 1.00 10^{-3} M; toluene, 25°C.

Table 3
Influence of thiol on the observed (k_a) and on the catalyzed rate constant (k_c)

$[C_4H_9SH]\ 10^3$ (mol/l)	$k_a\ 10^4$ (s^{-1})	$k_c\ 10^4$ (s^{-1})
0	18.23	17.36
0.46	9.60	8.73
0.93	5.40	4.55
1.40	3.40	2.53
1.86	2.30	1.43
15	0.93	0.06
75	0.88	0.01
150	0.87	0

$k_c\ (s^{-1}) = k_a - 8.7\ 10^{-5}$, PhNCO $1.63\ 10^{-3}$ M + C_5H_9OH 1.95 M/DBTDEH $1.00\ 10^{-3}$ M; acetonitrile, 25°C.

Small concentrations of 1-butanethiol strongly diminish the pseudo-first order rate constant (Fig. 3). Since it is a very weak acid but a strong nucleophilic species, it becomes obvious that the acidic character cannot be responsible for the reaction inhibiting power. At high added contents, thiol is shown not to catalyze this alcohol-isocyanate reaction.

However, thiols react with isocyanates and the observed rate constant tends towards a limiting value of $8.7\ 10^{-5}\ s^{-1}$ which corresponds to the added contributions of the uncatalyzed alcohol-isocyanate reaction and of the thiol-isocyanate reaction. So, the catalytic rate constant k_c has been calculated by subtracting it from k_a (Table 3).

The simultaneous introduction of acetic acid with water 0.135 M induces a smaller effect than acetic acid alone (Fig. 4), though each exerts separately an inhibiting effect.

In toluene at 25°C, some experiments were performed with PhNCO and CH_3COOH and the kinetics was studied with and without organotin catalyst. The obtained values for $(k_{nc} + k_{acid})$ and for $k_c = k_a - (k_{nc} + k_{acid})$ are collected in Fig. 5.
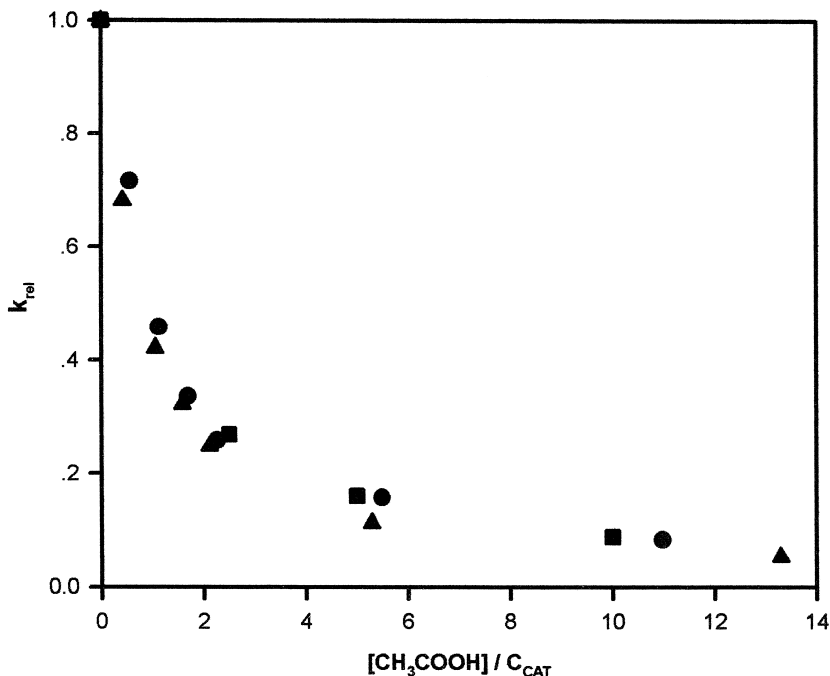

Fig. 6. Influence of the ratio $[CH_3COOH]/C_{CAT}$ on the relative rate constant. $k_{rel} = k_c$ (with acid)$/k_c$ (without acid). PhNCO + C_5H_9OH 1.95 M/DBTDEH $1.00\ 10^{-3}$ M, (■) toluene (▲) acetonitrile, 25°C; (●) 1,6-diisocyanatohexane + C_5H_9OH 1.95 M/DBTDEH $8.74\ 10^{-4}$ M; toluene, 55°C [16,17].

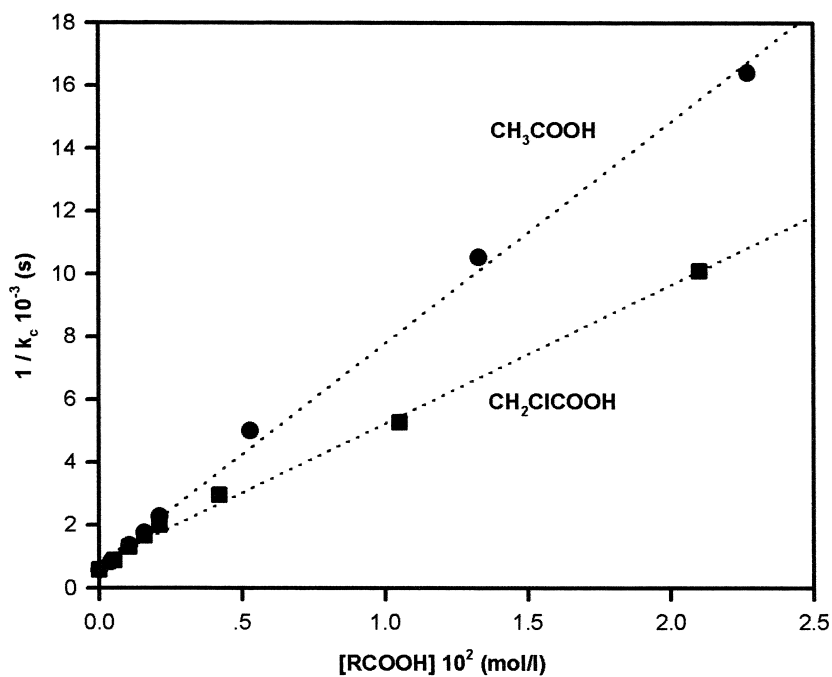Fig. 7. Influence of acetic and chloroacetic acids on $1/k_c$. PhNCO 1.63 10^{-3} M + C_5H_9OH 1.95 M/DBTDEH 1.00 10^{-3} M; acetonitrile, 25°C.
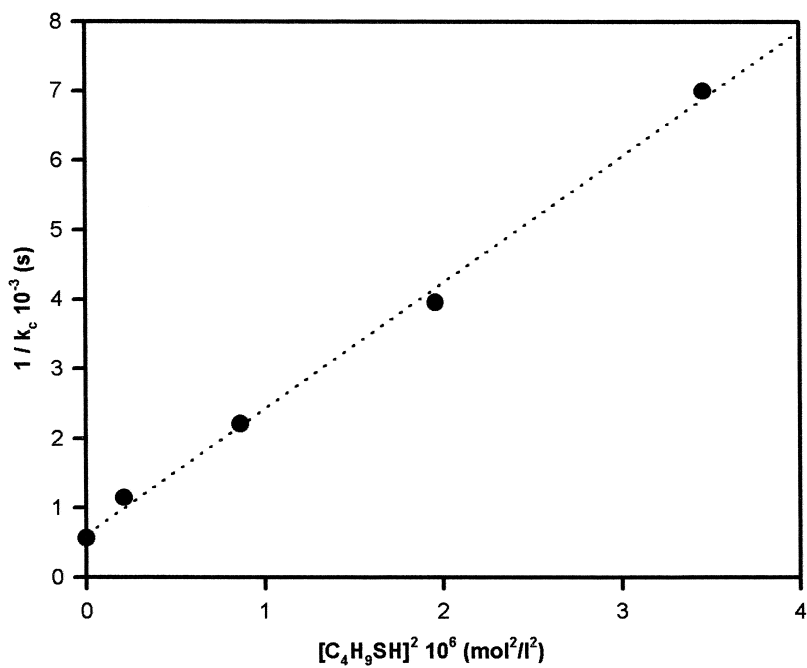

Fig. 8. Influence of 1-butanethiol on $1/k_c$. PhNCO 1.63 10^{-3} M + C_5H_9OH 1.95 M/DBTDEH 1.00 10^{-3} M; acetonitrile, 25°C.

4. Discussion

4.1. Inhibition by carboxylic acids

A nucleophilic C=O–Sn inhibition must be rejected since, as in toluene at 55°C [18,19], added esters (except the *cis* form dibutyl maleate) do not lower the reaction rate. The catalyst DBTDEH is unsensitive to these mono-carbonyl compounds and so should it also be in the case of the used acids. More, Fig. 6 confirms that the reaction quenching cannot be caused by the formation of acid-catalyst blocked complexes, since this complexation should be hindered by a temperature increase.

An ionic mechanism and an inhibition by ions issued from acids has been discarded in toluene but could a priori occur in a polar medium like acetonitrile, able to solvate $RCOO^{(-)}$ anions and to accept H^+ and in which an ionic dissociation of potential intermediates remains possible. However, the lack of relationship between acidity and inhibition and the slight acceleration due to water (Fig. 4), which should on the contrary promote RCOOH dissociation and thus increase rate lowering effects, confirm that the ionic hypothesis is unfounded.

Other facts support this statement: (a) in acetonitrile, 1-butanethiol has a larger inhibiting power than acetic acid (Fig. 3), this confirming that the proton donating power does not influence the kinetics in a significant manner, (b) a spectroscopic evaluation of acidity functions H_0 was undertaken for chloroacetic acid with 4-(2-pyridylazo)-N,N-dimethylaniline ($pK_{BH^+} = 4.43$). Preliminary values are $H_0 = 4.05 - 0.95$ log C_{acid} in toluene and $H_0 = 2.6 - 1.5$ log C_{acid} in acetonitrile. This confirms that acidity goes together with medium polarity and that, even for large acid contents in toluene and in acetonitrile, the H^+ donating power is very weak and cannot justify the reaction deceleration, (c) inhibiting effects are quantitatively similar in toluene and in acetonitrile (Fig. 6) and are not influenced in a significant way by solvent changes, which excludes an intervention of

ions and refutes the assumption of a prevailing role of the acidic character, this latter normally being polarity dependent.

A blocking effect due to a hypothetical complexation of NCO groups by acids must not be considered since the polarity of the used isocyanates is unconcerned about the observed kinetic inhibition, as shown by the similar behaviour depicted by Fig. 6 for the aliphatic and the aromatic one.

More probable is an action of the whole COOH function, which would induce the displacement of the balanced alcoholysis towards an inactive carboxylate form of the catalyst. As in toluene at 55°C, Davies' reaction sequence is in agreement with the present results: (a) the inhibiting power of CH_3COOH does not depend on isocyanate polarity (Fig. 6) which fits the proposed scheme since carboxylic acids would only act on tin alkoxide, (b) in acetonitrile the rate increases with the amount of water added to acid (Fig. 4), in accordance with an increased solvation or dissociation reducing the contents of COOH groups. Let us notice that in this case an acid catalysis of a supposed alcoholysis first step, due to an increased presence of H^+, is unlikely since added HCl [18,19] should induce a rate increase in place of the observed lowering, (c) the inhibition sequence by carboxylic acids roughly follows the nucleophilicity of carboxylate anions. This can be due to the formation from Sn alkoxide of a new catalytically inactive carboxylate all the more stable that the anion is nucleophilic.

Davies' scheme should be completed, in the presence of added acids (R″COOH), by a side equilibrium affecting Sn alkoxide intermediate, i.e.:

$$R''COOH + \equiv SnOR$$
$$\rightleftharpoons \equiv SnOOCR'' + ROH \quad K_i$$
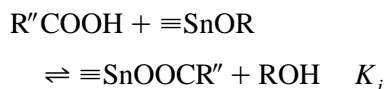
This corresponds to our results since the reciprocal catalytic rate constant $1/k_c$ depends linearly on the acid content in all cases [18,19]. An example of this dependence is given in

Fig. 7. The related rate equation is (C_{CAT} is the molarity of added catalyst):

$$k_c = k_2[SnOR] = \frac{k_2 K_1[ROH]_0 C_{CAT}}{[R'COOH] + K_1 K_i[R''COOH] + K_1[ROH]_0}.$$

(1)

4.2. Inhibition by 1-butanethiol (R''SH)

The observed effect (Figs. 3 and 8) would arise [16,17] from a side reaction of tin carboxylate:

$$=Sn(OOCR')_2 + 2R''SH$$
$$\rightleftharpoons\ =Sn(SR'')_2 + 2R'COOH \quad K_i$$
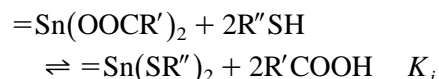
yielding an almost inactive $=Sn(SR'')_2$ because of a much larger affinity towards Sn of RS than of RO. Conversely to the case of carboxylic acids, the reciprocal rate constant varies linearly with the square of the molarity of added thiol (Fig. 8).

The catalytic rate constant writes [18,19]:

$$k_c = k_2[SnOR]$$
$$= \frac{k_2 K_1[Sn(OOCR')][ROH]_0}{[R'COOH]}$$

(2)

The free catalyst content is decreased by the amount of formed $=Sn(SR'')_2$ and, neglecting the stationary N-stannylcarbamate intermediate in the balance equation of the catalyst and considering that the substitution of R''COO groups by R''S reaches a largely right shifted equilibrium, the free catalyst concentration becomes:

$$[Sn(OOCR')]$$
$$= \frac{K_i C_{CAT}[R'COOH]^2}{(K_i + K_1[ROH]_0)[R'COOH] + [R''SH]^2}.$$

(3)

One gets after substitution an equation which fits in with Fig. 8 in which $1/k_c$ is shown to depend on $[R''SH]^2$:

$$k_c$$
$$= \frac{k_2 K_1[ROH]_0 K_i C_{CAT}[R'COOH]}{(K_i + K_1[ROH]_0)[R'COOH] + [R''SH]^2}.$$

(4)

Consequently, the reaction inhibition by thiols also supports the proposed mechanism.

4.3. Effect of water

The amount of added water is large in view of the amount of other added substances which showed to inhibit efficiently the studied reaction (Table 2). In the frame of the proposed mechanism, the observed rate decrease likely results from a competition between alcoholysis and hydrolysis of dialkyltin dicarboxylate.

5. Conclusion

The present study of the inhibition, in a polar solvent, of alcohol-isocyanate reactions catalyzed by a dialkyltin dicarboxylate (DBTDEH) confirms the validity of the already proposed reaction scheme [14,15]. The first alcoholysis step of a Sn-carboxylate bond yields the corresponding alkoxide, able to add isocyanate to produce N-stannylcarbamate which would in turn react with alcohol to yield urethane and regenerate tin alkoxide. The action of acids results from a lowering of the concentration of productive alkoxide. The results related to other added substances, like thiol and water, support these conclusions.

Acknowledgements

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