

Kinetic study of organotin-catalyzed alcohol–isocyanate reactions Part 1: Inhibition by carboxylic acids in toluene

Anne-Cécile Draye, Jean-Jacques Tondeur *

Université de Mons-Hainaut, B-7000 Mons, Belgium

Received 9 December 1997; accepted 29 April 1998

Abstract

The influence of species such as carboxylic acids, esters and quaternary ammonium salts has been studied on the rate of the reaction between cyclopentanol and 1,6-diisocyanatohexane catalyzed by di-*n*-butyltin di(2-ethylhexanoate) in toluene at 55°C. The results give a new evidence in agreement with Davies' mechanism in which the active catalytic form results from an alcoholysis of Sn carboxylate. © 1999 Elsevier Science B.V. All rights reserved.

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

1. Introduction

Although the kinetics and the mechanism of organotin-catalyzed isocyanate–alcohol reactions in solution have been the subject of numerous papers [1–22], some obscure points remain regarding the actual sequence of reaction steps.

Some commonly accepted views may be emphasized and refer to (i) the state of the reactants in solution, (ii) internal bipyramidal complexes, resulting from the free 5d orbitals of Sn, pentavalent for monocarboxylates and hexavalent for dicarboxylates, (iii) a probable initial step consisting of a nucleophilic alcohol to Sn complexation, which in the case of dicarboxylates must supplant the original C=O to Sn complex. The proposed mechanisms can gather among a few features.

(1) Alcohol–tin and other complexes determine the reaction rate [1–8,23]. As stated in Refs. [2–5], the ROH–Sn bond would result from a partial charge transfer from O to Sn, either lengthening the hydroxylic bond and favouring its attack by isocyanate or increasing the lability of the H atom and so making it more reactive towards the negative N or O atoms of isocyanate. This is not enough for explaining all experimental results, especially the frequently observed nonlinear dependence of the reaction rate on the concentration of catalyst and of alcohol. Indeed, a ceiling effect is in most cases recorded at high concentrations and was interpreted [2–5,23] as resulting from the concentration

* Corresponding author

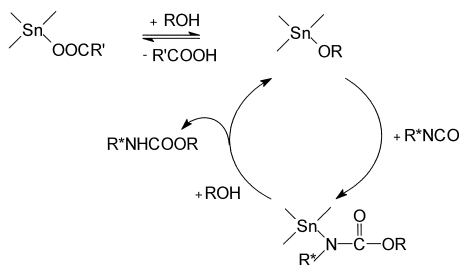
dependent presence of various nonproductive auto- and heteroassociates of alcohol and alkyltin carboxylate. However, in spite of a good agreement with experimental kinetics and though the presence of oligomers of alcohol is evident as well as that of small alcohol–organotin complexes [23], there are neither nonkinetic experimental evidences nor structural arguments to support the existence of high stoichiometry blocked organotin complexes.

(2) An ionic dissociation takes part in some rate determining step. This was considered by Borkent and Van Aartsen [9,10] and Borkent [11] and Wongkamolsesh and Kresta [14,15] and, in a somewhat different way, by Van der Weij [12,13]. Observing large rate lowerings in the presence of strong acids, this author expressed the idea that the increase of hydrogen lability in the ROH–Sn complex would be as large as to make it able to ionize into H^+ and an anionic pentavalent reactive intermediate later transformed and alcoholysed in a chain reaction. Although it algebraically fits numerous kinetic features, this interpretation is irrespective of the unlikelihood of an ionic reaction route in apolar media (cyclohexane, DBE) and must so be considered with wariness. The effect of weak acids should be explained in a different way and is suggested to be due to the formation of Sn–RCOOH complexes able to hinder the access of alcohol. In polar media (DMF), Borkent and Van Aartsen [9,10] and Borkent [11] observed a reaction order 1/2 with respect to organotin and deduced a reaction path involving an ionic dissociation of $R_3SnOOCR'$ into $R'COO^-$ and R_3Sn^+ . This cation would be able to complex with alcohol and isocyanate to form an urethane precursor. For Kresta, the reaction proceeds through the dissociation of $\equiv Sn-OOCR'$ bonds induced by an alcohol–Sn complexation [14,15], but the same unlikelihood remains about apolar media.

(3) Active intermediates are produced by alcoholysis of tin carboxylate bonds. Bloodworth and Davies [16,17] proposed a mechanism (Scheme 1) with a first step leading to an active Sn–OR intermediate (replacing eventually an internal carbonyl–Sn complex) so that organic acids would promote inactive Sn carboxylates and act as kinetic inhibitors in any solvent without being dissociated [18,19].

Generally speaking, agents able to share the catalyst should induce a reaction slowing down. This was investigated in the present work for strong and weak acids, some corresponding salts and carbonyl compounds added to the reaction of cyclopentanol with 1,6-diisocyanatohexane catalyzed by dibutyltin di(2-ethylhexanoate).

In polar and apolar media, acetic acid was already shown to lower the rate [12,13,20,21] while triethylamine increases it [6–8,20] but their relative effect is not related to the acido-basic strength. One may consider different ways of interpreting the acid-relevant kinetic alterations: (i) new blocking complexes could appear, i.e., mixed clusters of organotin, acid and alcohol constituting microheterogeneous regions isolating catalyst molecules from the reactants [21], (ii) acids could dissociate to a sufficient extent even in apolar media since alcohol acts as a proton acceptor and, as in Van der



Scheme 1.

Weij's scheme, induce a displacement towards some inactive species [12,13], or acids could inactivate the active intermediate by a parasitic complexation, (iii) acids could handicap the formation of active alkoxytin species by favouring the presence of new tin carboxylates or other salts.

2. Experimental

2.1. Reactants, solvents, added substances

Cyclopentanol (Acros Chimica 99%) dried according to Vogel [22] and distilled; 1,6-diisocyanatohexane (Acros Chimica 98%); di(*n*-butyl)tin di(2-ethylhexanoate) (Johnson-Matthey); toluene (Acros Chimica, spectrophotometric grade) dried over sodium, distilled and stocked over molecular sieve 5 Å.

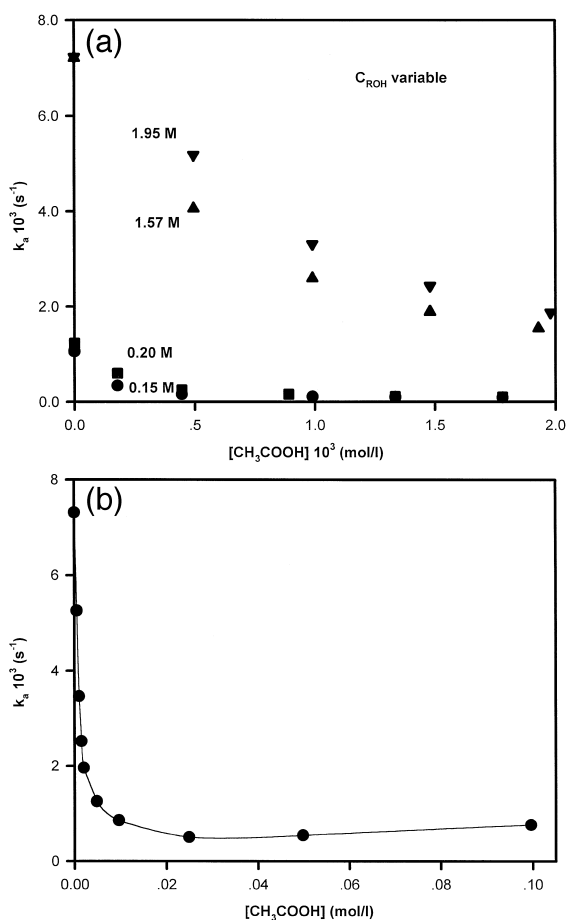


Fig. 1. Influence of acetic acid on the observed catalytic rate constant. (a) Small concentrations of acetic acid. Apparent rate constant k_a , as a function of $[\text{CH}_3\text{COOH}]$ for various alcohol concentrations. (b) Acetic acid up to 0.1 M. Apparent rate constant k_a , as a function of $[\text{CH}_3\text{COOH}]$ for cyclopentanol content 1.95 M. Cyclopentanol + $\text{OCN}-\text{C}_6\text{H}_{12}-\text{NCO}$ ($[\text{NCO}]_0 = 0.02 \text{ M}$)/dibutyltin di(2-ethylhexanoate) $8.74 \cdot 10^{-4} \text{ M}$; toluene, 55°C .

Acids: acetic (Acros Chimica, glacial); chloroacetic (Acros Chimica, p.a.) and formic (Merck, 98–100%) purified according to Weissberger [24] and distilled; HCl (Merck extra pure) dehydrated by sulphuric acid (Acros Chimica, p.a.) bubbled in purified cyclopentanol and titrated.

Salts: tetraethylammonium chloride (Chem. Fabrik., 90%), vacuum dried at 55°C, tetraethylammonium formiate, acetate and chloroacetate prepared by reacting the acids with tetraethylammonium hydroxide (Aldrich 35% solution), distilling with benzene and vacuum drying.

Others: ethyl acetate (Merck, synthesis); acetaldehyde (Merck, synthesis) purified according to Vogel [22] and distilled.

2.2. Procedure

Reaction mixtures: the observed rate constant k_a is determined from pseudo-first-order runs, i.e., with a stoichiometric excess of C_5H_9OH .

Infra-red spectroscopy: Perkin-Elmer model 1760 K FTIR fitted with a 1 mm optical path NaCl cell in a Specac model P/N 20710 jacket regulated by a thermocouple stuck against a window and connected to a Specac model P/N 20120 high stability automatic temperature controller. The maximum absorbance of the band related to the stretching of $Alk N=C=O$ at 2273 cm^{-1} was recorded as a function of time.

3. Results

3.1. Addition of acids

Acetic acid [12,13,20,21] added to the catalyzed reaction medium provides an appreciable lowering of the rate even at concentrations much smaller than that of catalyst. However, it acts itself as a weak catalyst [21] so that a slight increase of the relative rate constant occurs at large concentrations (Fig. 1b). That means that k_a is an overall constant resulting from the simultaneous progress of the

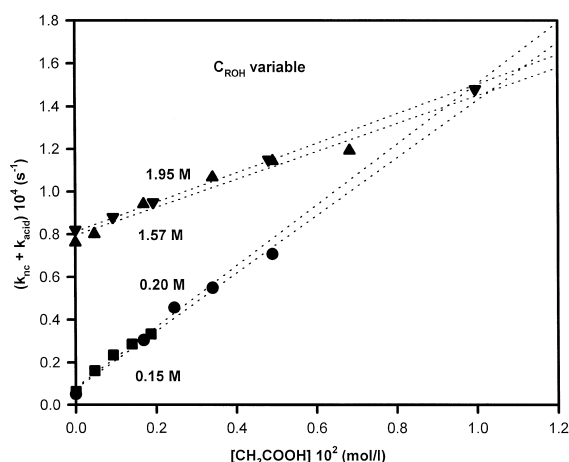


Fig. 2. Influence of acetic acid on the rate constant. $OCN-C_6H_{12}-NCO + C_5H_9OH$ without dibutyltin di(2-ethylhexanoate). Pseudo-first-order rate constant ($k_{nc} + k_{acid}$) as a function of $[CH_3COOH]$ for various concentrations of cyclopentanol; $OCN-C_6H_{12}-NCO$ ($[NCO]_0 = 0.02\text{ M}$); toluene, 55°C. (C_{ROH} , slope $\cdot 10^5$, intercept $\cdot 10^2$: 0.15, 0.70, 1.40; 0.20, 0.83, 1.42; 1.57, 7.96, 0.66; 1.95, 7.79, 0.69).

Table 1

Influence of acetic acid on the observed rate constant k_a and on the catalyzed rate constant $k_c = k_a - (k_{nc} + k_{acid})$

[acid] 10^4 (mol/l)	C_{ROH} (mol/l)									
	0.15		0.20	1.57	1.95	0.15		0.20	1.57	1.95
	$k_a \cdot 10^3$ (s^{-1})				$k_c \cdot 10^3$ (s^{-1})					
0	1.06	1.23	7.21	7.31	1.05	1.22	7.13	7.23		
1.78	0.34	0.60			0.33	0.59				
4.45	0.16	0.25			0.15	0.23				
4.95			4.06	5.26			3.98	5.18		
8.90		0.16				0.14				
9.90	0.11		2.59	3.46	0.09		2.50	3.31		
13.35	0.10	0.11			0.07	0.08				
14.80			1.89	2.52			1.80	2.43		
17.80	0.09	0.10			0.06	0.07				
19.80			1.54	1.96			1.45	1.87		
48.0				1.25				1.14		
96.0				0.75				0.60		
249				0.50				0.24		
498				0.54				0.12		
996				0.76				0		

$C_5H_9OH + OCN-C_6H_{12}-NCO$ ($[NCO]_0 = 0.02$ M)/dibutyltin di(2-ethylhexanoate) $8.74 \cdot 10^{-4}$ M; toluene, $55^\circ C$.

uncatalyzed reaction (k_{nc}), the acid-catalyzed one (k_{acid}) and the reaction catalyzed by dibutyltin di(2-ethylhexanoate) (k_c), this latter being strongly decelerated by acids so that it should vanish at sufficiently high acid contents (Fig. 1b), at which only k_{nc} and k_{acid} remain.

The sum ($k_{nc} + k_{acid}$) was determined for runs performed in the absence of tin catalyst and was shown to be linearly dependent on the acid molarity so that its interpolated values could be subtracted from k_a , to obtain the organotin-catalyzed pseudo first-order constant k_c (Fig. 2, Table 1).

Acids stronger than acetic ($pK_a = 4.75$), i.e., formic (3.75) and chloroacetic (2.85) are poorer inhibitors but the dependence of k_a on acid molarity is not fundamentally different, which suggests that they probably act in the same way (Fig. 3).

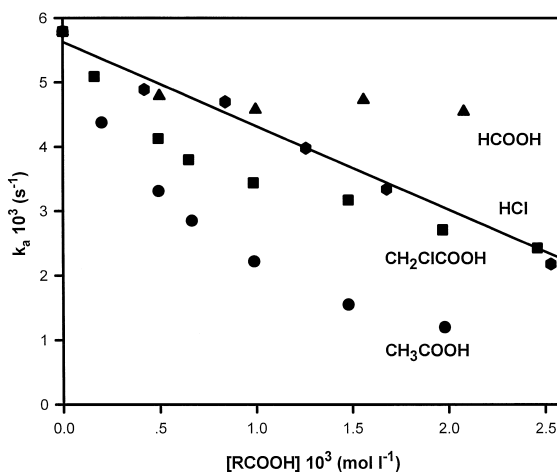


Fig. 3. Influence of formic, chloroacetic and hydrochloric acids on the observed catalytic rate constant. C_5H_9OH 1.39 M + $OCN-C_6H_{12}-NCO$ ($[NCO]_0 = 0.18$ M)/dibutyltin di(2-ethylhexanoate) $8.74 \cdot 10^{-4}$ M; toluene, $55^\circ C$.

Table 2

Influence of carbonyl compounds and of quaternary ammonium salts on the relative rate constant

Ethyl acetate		Acetaldehyde	
Molarity (mmol/l)	k_{rel}	Molarity (mmol/l)	k_{rel}
0	1.00	0	1.00
1.14	1.00	2.0	1.03
2.25	1.04		

Tetraethylammonium salts					
Chloride		Formiate		Acetate	
Molarity (mmol/l)	k_{rel}	Molarity (mmol/l)	k_{rel}	Molarity (mmol/l)	k_{rel}
0	1	0	1	0	1
0.74	1.06	2.53	1.08	2.18	0.91
1.20	1.02	13.2	0.99	21.8	0.98
2.50	0.97	25.3	0.94		

C₅H₉OH 1.39 M + OCN-C₆H₁₂-NCO ([NCO]₀ = 0.18 M)/dibutyltin di(2-ethylhexanoate) 8.74 10⁻⁴ M; toluene, 55°C. Relative rate constant $k_{rel} = k_a$ (with addition)/ k_a (without addition). TEA chloroacetate showed to be insoluble.

On the other hand, hydrogen chloride also slows down the reaction but likely acts according to a different scheme since it influences k_a in a different pattern (Fig. 3).

3.2. Influence of carbonyl compounds

Up to 2.25 mM, ethyl acetate and acetaldehyde exert no significant kinetic effect (Table 2). One can so conclude that possible interactions of C=O with Sn are kinetically negligible, contrarily to Van der Weij's statements [12,13].

3.3. Influence of quaternary ammonium salts

Tetraethylammonium formiate, acetate and chloride do not influence the reaction rate in a significant manner (Table 2). A tentative determination showed the conductance of solutions of these salts to be as small as for pure toluene, which supports a non-electrolyte or ion-pair behaviour. So this result is unable to bring any evidence about a kinetic effect of free carboxylate or Cl⁻ anions.

4. Discussion

4.1. Effect of carboxylic acids

4.1.1. Hypothesis of catalyst complexation

A distinction was made earlier [12,13] between the decelerative effect of strong and weak acids. The former were considered to dissociate to H⁺ and to shift an equilibrium between reactants and ionized [alkoxy-Sn]⁻, H⁺ active intermediates. On the contrary, weak acids were regarded as undissociated molecules able to inhibit either by a simple carbonyl-Sn complexation [12,13] or through the formation of inactive reactant-catalyst-acid aggregates [2–5]. However, non-acidic C=O

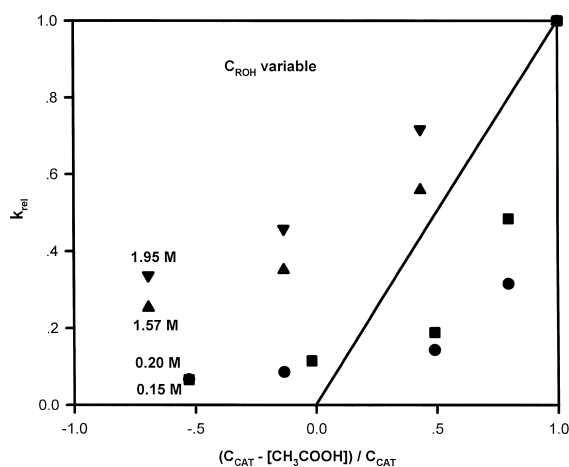


Fig. 4. Experimental points and straight lines corresponding to the hypothesis of an acetic acid–catalyst 1:1 blocked complex. $C_5H_9OH + OCN-C_6H_{12}-NCO$ ($[NCO]_0 = 0.02$ M)/dibutyltin di(2-ethylhexanoate) $8.74 \cdot 10^{-4}$ M; toluene, 55°C . Relative rate constant $k_{rel} = k_a$ (with addition)/ k_a (without addition). C_{ROH} overall alcohol concentration.

compounds (Table 2) show to be inactive, so making inconsistent an inhibition by a carbonyl–catalyst complexation. More, at low alcohol and acid contents, the values of k_{rel} are smaller than if they resulted from a blocking by an acid–catalyst 1:1 complex (Fig. 4). This excludes that inhibition by acetic acid solely results from a complexation on the tin atom. Moreover, such an effect due to so small quantities of added acid involves an action at the level of scarce species, i.e., labile intermediates.

4.1.2. Hypothesis of an inhibition due to H^+ or to $RCOO^-$ ions

This hypothesis is not completely unlikely since, at high alcohol contents, $RO^-ROH_2^+$ ion pairs could be produced even as minor amounts of H^+ since the aromatic cycle may be regarded as a slight proton acceptor. However, it should be discarded, because (a) the carboxylic acids inhibiting power does not follow the sequence of pK_a (see Section 3.1); (b) hydrochloric acid added in the same proportion as acetic acid (Fig. 3) can produce a smaller effect, (c) an increased alcohol concentration leads to a smaller effect of acetic acid when it should assist its electrolytic dissociation (Fig. 1a).

The insensibility of the system to tetraalkylammonium (TAA) carboxylates (Table 2) is unfortunately non-conclusive about the complexability of Sn by $RCOO^-$ which in toluene could be released only in insignificant quantities from TAA^+RCOO^- ion pairs. However, this non-evidence allows to exclude mechanisms involving a catalyst dissociation to $\equiv Sn^+$ and $RCOO^-$ [9–11,14,15] since this shows that inhibition occurs in the absence of significant amounts of free carboxylate.

4.1.3. Hypothesis of an inhibition by COOH groups

The only remaining possibility would be that the observed effect results from the presence of the whole COOH function. This is in agreement with Davies' first step [16,17] of alcoholysis of tin dicarboxylate into tin alkoxide and acid (Scheme 1). In such a scheme, organic acids added to the medium would reverse the alcoholysis and lead to a new inactive carboxylated catalyst. This also adapts to a smaller effect of acids at increased alcohol contents since a larger quantity of alcohol would be able to displace the first reaction step towards the active alkoxy form (Fig. 1a).

4.2. Inhibition by hydrochloric acid

At a rough guess, the effect of HCl (Fig. 3) seems to be in agreement with a determining step of dissociation of an alcohol–catalyst complex into $(\text{Sn-OR})^-$ and H^+ [12,13] but this scheme is unlikely in apolar solvents such as toluene.

On the other hand, Davies' reaction sequence [16,17] contains no proton sensitive step and, more, a possible inactivation of alcohol or isocyanate by proton acceptance is insignificant since at least a 50 times excess of alcohol and isocyanate to HCl was used in kinetic runs. Consequently, a remaining possibility is that the observed effect result from an inactivating nucleophilic complexation of the 5d orbitals of tin by Cl^- [25].

5. Rate law

A formerly observed linear dependence [12,13] of k_a vs. $1/[\text{RCOOH}]$ does not fit our results, except for the higher acid contents. The reverse correlation $1/k_a$ vs. $[\text{RCOOH}]$ holds only at small acid concentration but if the increased influence of the acid catalyzed channel is taken into account the calculated Sn catalyzed contribution $1/k_c$ correlates over the whole range of concentration (Fig. 5) and also for the other added acids (HCOOH and CH_2ClCOOH). So, the rate lowering does not result from the formation of acid–catalyst blocking complexes since, in this case, Sn would be fully complexed at large acid contents so that a ceiling of the inhibiting effect and thus of the function $1/k_c$ vs. $[\text{acid}]$ would be observed. Consequently, carboxylic acids likely disrupt the formation of urethane by reducing the production of the active alkoxy form of the catalyst (Scheme 2, step i). This alkoxide is able to react thereafter with isocyanate to yield an urethane precursor which in turn reacts easily with one more alcohol molecule to produce carbamate and restore the alkoxide (Scheme 2).

Davies assumes that X is very reactive towards alcohol, which suggests the limiting step to be the addition of isocyanate to tin alkoxide. This hypothesis is moreover supported by another work [26] which points out that electron donating substituents slow down the reaction of phenylisocyanate with alcohol while electrons accepting ones accelerate it. So, one can apply to X the stationary approxima-

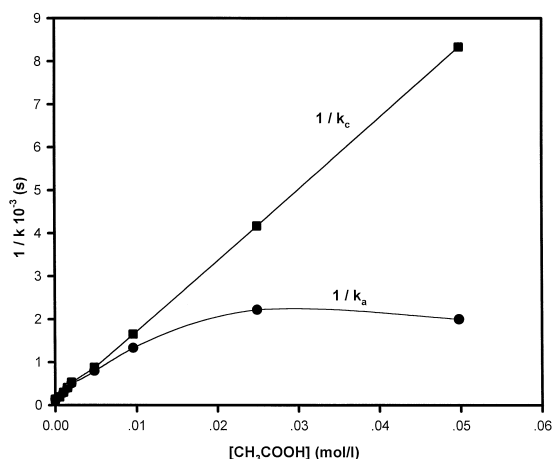
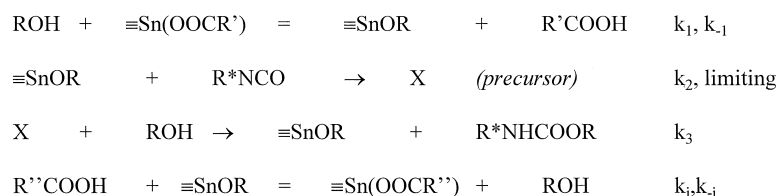


Fig. 5. Influence of acetic acid on the inverse catalytic rate constant $1/k_c$. $\text{C}_5\text{H}_9\text{OH}$ 1.95 M + $\text{OCN-C}_6\text{H}_{12}\text{-NCO}$ ($[\text{NCO}]_0 = 0.02$ M); dibutyltin di(2-ethylhexanoate) $8.74 \cdot 10^{-4}$ M; toluene, 55°C .



Scheme 2.

tion so that the catalytic rate constant k_c becomes equal to $k_2 [\text{R}^* \text{NCO}]$. Since step 2 is determining, it should not perturb alcoholysis equilibria in a significant manner and the tin alkoxide content can be written as:

$$[\text{SnOR}] = \frac{K_1 [\text{Sn}(\text{OOCR}')][\text{ROH}]_0}{[\text{R}'\text{COOH}]} = \frac{[\text{Sn}(\text{OOCR}'')][\text{ROH}]_0}{K_i [\text{R}''\text{COOH}]} \quad (1)$$

Expressing $[\text{SnOR}]$ and $[\text{Sn}(\text{OOCR}'')]$ as a function of $[\text{Sn}(\text{OOCR}')]_0$, putting it in the balance equation of the catalyst and neglecting the stationary concentration of X, one gets (C_{CAT} is the overall catalyst concentration):

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

The catalytic rate constant is obtained by combining Eqs. (1) and (2):

$$k_c = k_2 [\text{SnOR}] = \frac{k_2 K_1 [\text{ROH}]_0 C_{\text{CAT}}}{[\text{R}'\text{COOH}] + K_1 K_i [\text{R}''\text{COOH}] + K_1 [\text{ROH}]_0} \quad (3)$$

This relation is in agreement with the experimental linear dependence of $1/k_c$ on the added acid concentration $[\text{R}''\text{COOH}]$.

Moreover, let us notice that this equation also fits the former results [12,13] since, for large values of $[\text{R}''\text{COOH}]$, the terms $([\text{R}'\text{COOH}] + K_1 [\text{ROH}]_0)$ become negligible, making k_c proportional to $1/[\text{R}''\text{COOH}]$.

6. Conclusions

This work points out that the deceleration of isocyanate–alcohol reactions due to added acids (a) cannot be due to a simple immobilization of the organotin catalyst in RCOOH-Sn complexes since it cannot be kinetically supported and since other carbonyl compounds exert no effect; (b) is not due to the acidic character of RCOOH (compare RCOOH and HCl); (c) is not the result of the presence of RCOO^- . Consequently, the whole COOH group is responsible for the observed kinetic inhibition. This is in agreement with the assumption of an active alkoxide form of the catalyst resulting from tin carboxylate alcoholysis. A rate law is worked out on the basis of the proposed mechanism and fits the accessible experimental data.

Acknowledgements

A.-C. Draye was financed for four years by Fonds National de la Recherche Scientifique.

References

- [1] J.-J. Tondeur, G. Vandendunghen, M. Watelet, *J. Chem. Res.* (1992) (S) 262–263 (M) 2024–2034.
- [2] S.G. Entelis, P.A. Berlin, R.P. Tiger, S.P. Bondarenko, *Materials of IV International Symposium on Homogeneous Catalysis*, Leningrad, 1985.
- [3] P.A. Berlin, R.P. Tiger, Yu.N. Chirkov, S.G. Entelis, *Kinet. Katal.* 28 (1987) 1354.
- [4] P.A. Berlin, R.P. Tiger, S.G. Entelis, S.V. Zaporozhskaya, *Zh. Fiz. Khim.* 59 (1985) 262.
- [5] S.P. Bondarenko, P.A. Berlin, Yu.N. Chirkov, R.P. Tiger, S.G. Entelis, *Zh. Fiz. Khim.* 59 (1985) 1644.
- [6] K.C. Frish, S.L. Reegen, W.V. Floutz, J.P. Oliver, *J. Polym. Sci. A 1* (5) (1967) 135.
- [7] K.C. Frish, S.L. Reegen, B. Thir, *J. Polym. Sci. C 16* (1967) 2191.
- [8] S.L. Reegen, K.C. Frish, *J. Polym. Sci. A 1* (8) (1970) 2883.
- [9] G. Borkent, J.J. Van Aartsen, *Rec. Trav. Chim. Pays-Bas* 91 (1972) 1079.
- [10] G. Borkent, J.J. Van Aartsen, *Adv. Chem. Ser.* 128 (1973) 274.
- [11] G. Borkent, *Adv. Urethane Sci. Technol.* 3 (1974) 1.
- [12] F.W. Van der Weij, *J. Polym. Sci.* 19 (1981) 381.
- [13] F.W. Van der Weij, *J. Polym. Sci.* 19 (1981) 3063.
- [14] K. Wongkamolsesh, J.E. Kresta, *Polym. Mater. Sci. Eng.* 49 (1983) 465.
- [15] K. Wongkamolsesh, J.E. Kresta, *ACS Symp. Ser.* 270 (1985) 111.
- [16] A.J. Bloodworth, A.G. Davies, *Proc. Chem. Soc.* (1963) 264.
- [17] A.J. Bloodworth, A.G. Davies, *J. Chem. Soc.* (1965) 5238.
- [18] R.P. Houghton, A.W. Mulvaney, *J. Organometal. Chem.* 517 (1996) 107–113.
- [19] R.P. Houghton, A.W. Mulvaney, *J. Organometal. Chem.* 518 (1996) 21–27.
- [20] M. Watelet, Thesis, Université de Mons-Hainaut, Belgium, 1991.
- [21] P.A. Berlin, M.A. Levina, Yu.N. Chirkov, R.P. Tiger, S.G. Entelis, *Kinetics and Catalysis* 34 (4) (1993) 641.
- [22] A.I. Vogel, in: *Practical Organic Chemistry*, 3rd edn., Longman, London, 1967.
- [23] J.-J. Tondeur, G. Vandendunghen, M. Watelet, *J. Chem. Res.* (1992) (S) 398–399 (M) 3039–3055.
- [24] A. Weissberger, in: *Technique of Organic Chemistry*, 2nd edn., Wiley, New York, 1967.
- [25] N.N. Greenwood, A. Earnshaw, in: *Chemistry of the Elements*, Pergamon, Oxford, 1984.
- [26] A. Petrus, *Int. Chem. Eng.* 11 (1971) 314.