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SIDE REACTIONS IN THE FORMATION OF POLYURETHANES: STABILITY OF REACTION PRODUCTS OF PHENYL ISOCYANATE

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ABSTRACT

The thermal and hydrolytic stabilities at 90 and 120°C of butyl *N*-phenyl urethane, *N,N'*-diphenylurea, butyl-α,γ-diphenyl allophanate, and 1,3,5-triphenylbiuret in 1,4-dioxane containing traces of water were investigated in the presence of dibutyltin dilaurate by HPLC. The stabilities decrease with increasing temperature and are also affected by the presence of water in the system. The rate and equilibrium constants of allophanate and biuret were calculated.

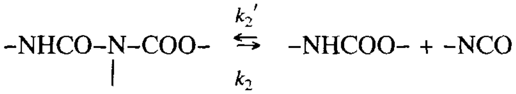
INTRODUCTION

During the formation and processing of polyurethanes, side reactions may occur, especially at elevated temperatures, with isocyanate groups in excess and in the presence of some catalysts. Water present in small quantities in the raw materials also usually participates in the side reactions. For this reason, urea, allophanate, biuret, and isocyanurate groups which influence the final structure and properties of polyurethanes may also be present in polyurethanes, along with urethane groups. Hence, it is important to know not only conditions favoring the side reactions but also data regarding the stability of the reaction products, predominantly thermal and hydrolytic stabilities.

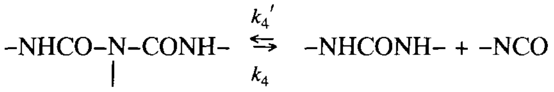
The stability of allophanate and biuret groups depends on the type of structure and on temperature. By using model aliphatic, cycloaliphatic, and aromatic compounds, it was shown [1–3] that aromatic allophanates and biurets are the least stable compounds, and that the same applies to polyurethanes. Aromatic allophanate and biuret groups dissociate to a considerable extent, even if heated for a short time only (10 min at 165–210°C) [4].

The stability of allophanate and biuret groups is also affected by the reaction medium. Investigation of the stability of ethyl-α,γ-diphenyl allophanate has revealed [5] that oxygen and some catalysts (zinc diethylcaprylate, triethylamine) virtually do not reduce the thermal stability; water and 1,4-diazabicyclo-(2,2,2)-octane accelerate the dissociation of allophanate. The fact that aromatic allophanate and biuret groups in polyurethanes are hydrolyzable sites has been confirmed by HPLC [6].

In the dissociation of allophanate or biuret, urethane and isocyanate, or substituted urea and isocyanate are respectively formed:



$$\text{-NHCO-}\underset{|}{\text{N}}\text{-COO-} \underset{k_2}{\overset{k_2'}{\leftrightarrows}} \text{-NHCOO-} + \text{-NCO} \qquad (1)$$



$$\text{-NHCO-}\underset{|}{\text{N}}\text{-CONH-} \underset{k_4}{\overset{k_4'}{\leftrightarrows}} \text{-NHCONH-} + \text{-NCO} \qquad (2)$$

The rate constants of dissociation of ethyl-α,γ-diphenyl allophanate (k_2') and of some arylalkylbiurets (k_4') at 130–150°C were determined by Kogon [7]. The rate constant k_2' increases from 3.9×10^{-5} s^{-1} (132°C) to 1.65×10^{-4} s^{-1} (150°C). The rate constant k_4' for biurets of the type $C_6H_5NHCON(R)COR'$, where R = C_6H_5– or C_2H_5– and R' = $-N(CH_3)C_6H_5$, increases from 2×10^{-5} s^{-1} (131°C) to 1.5×10^{-3} s^{-1} (145°C).

In an earlier paper [8], side reactions occurring in the formation of polyurethanes were modeled using the system 1-butanol–phenyl isocyanate in excess in the presence of dibutyltin dilaurate (DBTDL) in 1,4-dioxane containing trace quantities of water. The reactions were investigated at 90 and 120°C in sealed ampules in an inert nitrogen atmosphere and terminated by adding methanol in excess. The reaction products detected by HPLC were butyl-*N*-phenyl urethane (BPU), *N,N'*-diphenylurea (DPU), butyl-α,γ-diphenyl allophanate (AL), 1,3,5-triphenylbiuret (TBP), and unreacted phenyl isocyanate in the form of methyl-*N*-phenyl urethane (MPU).

By using the graphic differentiation method, the apparent rate constants of formation and dissociation of allophanate and biuret were calculated. The equilibrium constants of formation of allophanate and biuret were calculated from the rate constants and also from equilibrium concentrations. Biuret was found to be formed from urea and isocyanate much more quickly than allophanate from urethane and isocyanate. Also, the equilibrium constant of formation of biuret is higher by an order of magnitude at a given temperature than the equilibrium constant of formation of allophanate.

Thus, in reactions of excess phenyl isocyanate with 1-butanol in the presence of water, several reaction products are formed by parallel and consecutive reactions. To check the thermal and hydrolytic behavior of the individual products, in this study the stabilities of butyl-*N*-phenyl urethane, *N,N'*-diphenylurea, bu tyl-α,γ-diphenyl allophanate, and 1,3,5-triphenylbiuret were investigated at the same temperatures and at approximately the same concentrations of compounds and of the catalyst as those used in paper [8]. The rate and equilibrium constants thus obtained are compared with those determined earlier [8].

EXPERIMENTAL

Materials

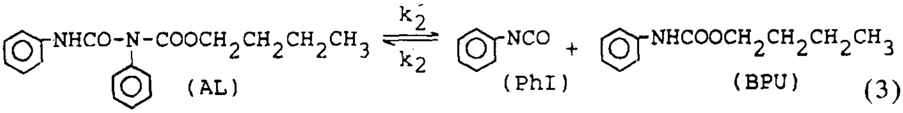
The preparation, characterization, and purification of the starting compounds were reported in Ref. 8. Aniline (ANI) was distilled at reduced pressure (68°C/1330 Pa). The procedure used in sample preparation and the termination of reactions with methanol are the same as in Ref. 8.

The concentration of reaction products was determined by using reversed-phase liquid chromatography (RP HPLC) with a Spectra Physics 8100 apparatus (40°C; CGC column 0.3 × 150 mm, Laboratory Instruments Prague, packed with SiO_2 ($d_p = 5$ μm) with bounded octadecyl groups; a linear concentration gradient methanol:water 45:55–80:20 by volume; UV detection at $\lambda = 254$ nm). Under these conditions the retention times lay around 1.5 min (ANI), 2 min (MPU), 5 min (DPU), 9 min (BPU), 12 min (TPB), and 14 min (AL).

RESULTS AND DISCUSSION

I. Determination of the Reaction Products of Dissociation

Under the reaction conditions used, all products formed from phenyl isocyanate were found to undergo thermal or hydrolytic dissociation. The time dependences of concentrations of the starting compounds and reaction products are given in Figs. 1 through 9. The following reactions are assumed to occur as indicated by the results of chromatographic analyses:



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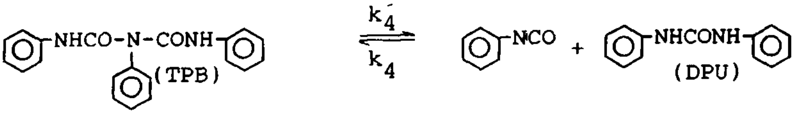

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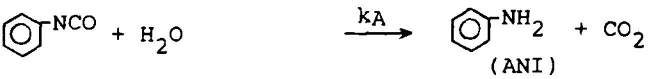

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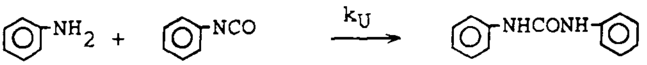

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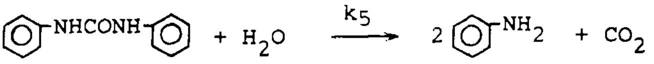
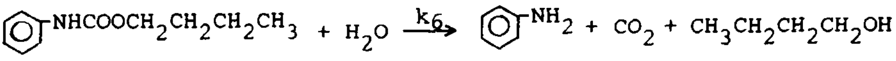
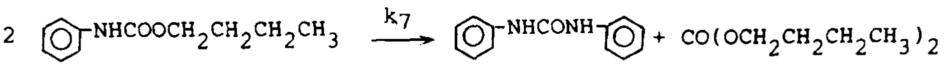


(7)



(8)



(9)

It has been proved that in a solution of *N,N'*-diphenylurea in 1,4-dioxane containing traces of water (Fig. 1), partial hydrolysis of urea should be considered, i.e., the reaction described by Eq. (7).

In the investigation of the stability of butyl-*N*-phenyl urethane at 120°C in 1,4-dioxane (Fig. 2), the partial dissociation of urethane according to Eq. (9) giving rise to *N,N'*-diphenylurea and dibutyl carbonate was considered, along with the partial hydrolysis of urethane, i.e., Eq. (8). This reaction is also operative in the dissociation of butyl-*N*-phenyl urethane at the same temperature in bulk (Fig. 3).

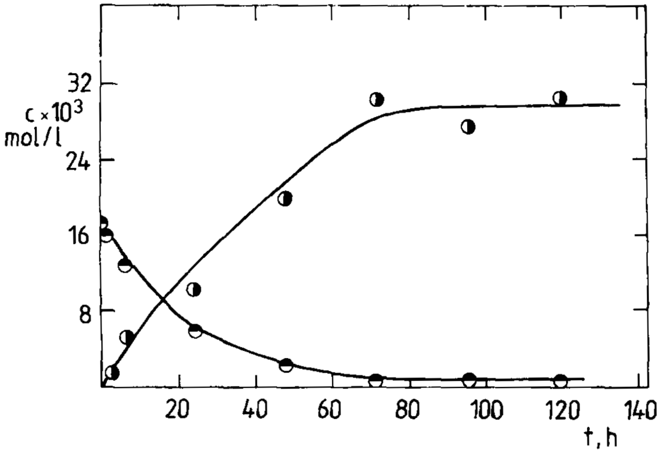


FIG. 1. Time dependence of the concentration of products in the dissociation of *N,N′*-diphenylurea in dioxane. Starting conditions: $(c_0)_{DPU}$ = 0.017 mol/L, c_{DBTDL} = 0.1 mmol/L, 120°C. Reaction products in Figs. 1–9 are denoted as (◐) MPU, (●) BPU, (◓) DPU, (◒) TPB, (○) AL, (◑) ANI.

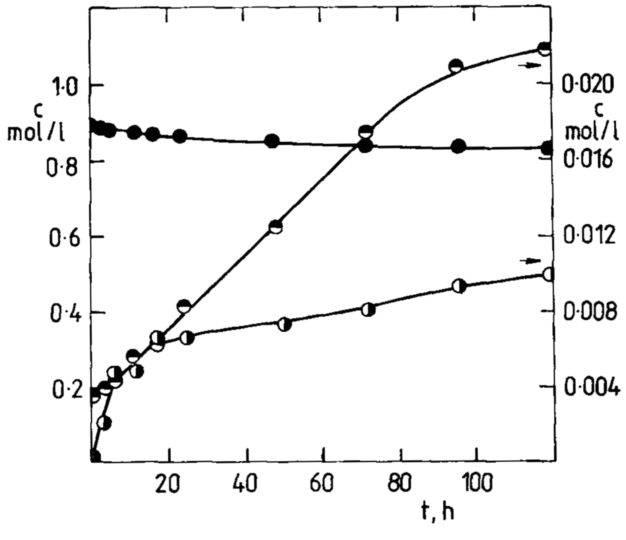


FIG. 2. Time dependence of the concentration of products in the dissociation of butyl-*N*-phenyl urethane in dioxane. Starting conditions: $(c_0)_{BPU}$ = 0.89 mol/L, $(c_0)_{DPU}$ = 0.0036 mol/L, c_{DBTDL} = 0.17 mmol/L, 120°C. Symbols as in Fig. 1.

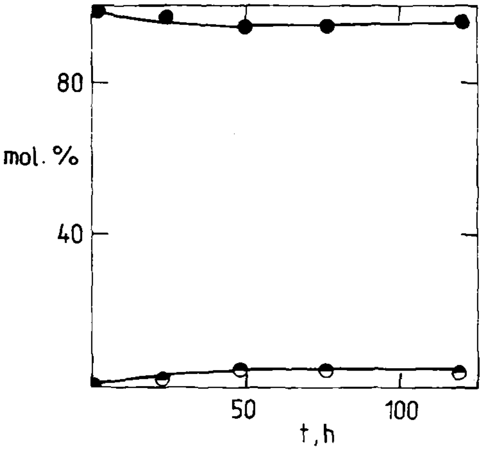


FIG. 3. Time dependence of the concentration of products in the dissociation of butyl-*N*-phenyl urethane in bulk. Starting conditions: c_{DBTDL} = 0.1 mol% (related to BPU), 120°C. Symbols as in Fig. 1.

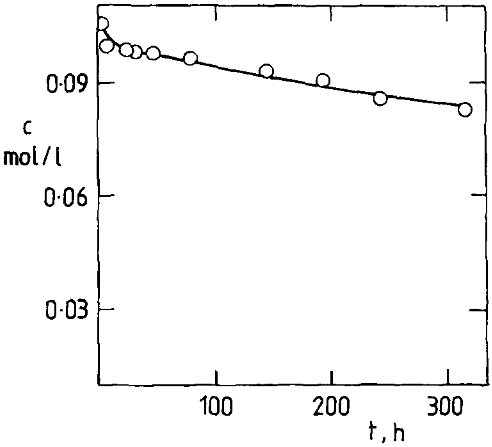


FIG. 4. Time dependence of the concentration of the starting compound in the dissociation of butyl-α,γ-diphenyl allophanate in dioxane. Starting conditions: $(c_0)_{AL}$ = 0.11 mol/L, c_{DBTDL} = 0.38 mmol/L, 90°C. Symbols as in Fig. 1.

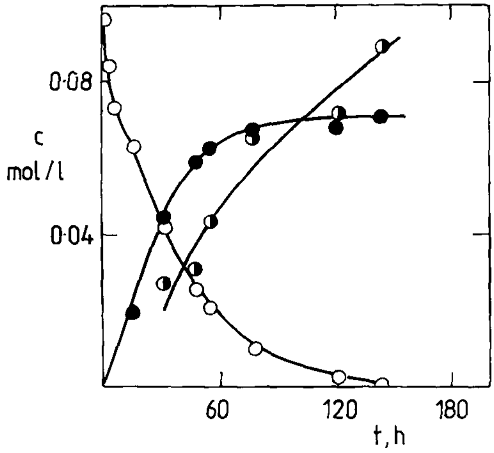


FIG. 5. Time dependence of the concentration of products in the dissociation of butyl-α,γ-diphenyl allophanate in dioxane. Starting conditions: $(c_0)_{AL}$ = 0.097 mol/L, c_{DBTDL} = 0.38 mmol/L, 90°C. Symbols as in Fig. 1.

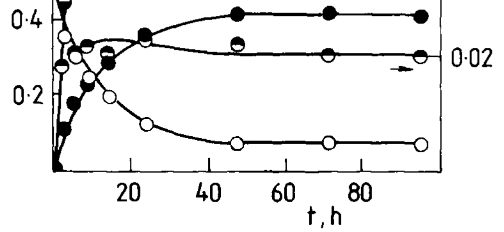


FIG. 6. Time dependence of the concentration of products in the dissociation of butyl-α,γ-diphenyl allophanate in dioxane. Starting conditions: $(c_0)_{AL}$ = 0.48 mol/L, $(c_0)_{PhI}$ = 0.83 mol/L, c_{DBTDL} = 0.34 mmol/L, 120°C. Symbols as in Fig. 1.

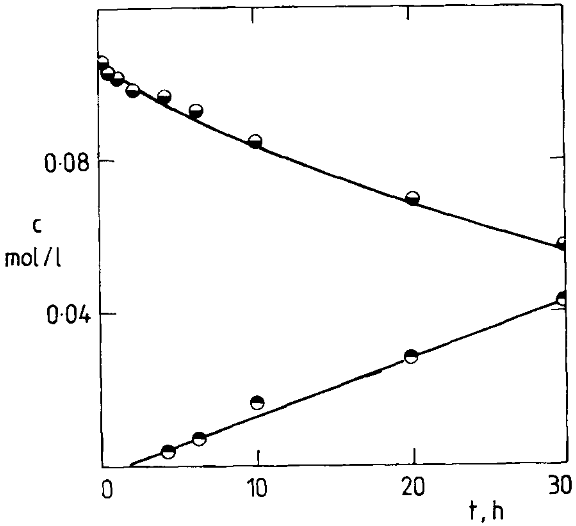


FIG. 7. Time dependence of the concentration of products in the dissociation of 1,3,5-triphenylbiuret in dioxane. Starting conditions: $(c_0)_{TPB}$ = 0.10 mmol/L, c_{DBTDL} = 0.39 mmol/L, 90°C. Symbols as in Fig. 1.

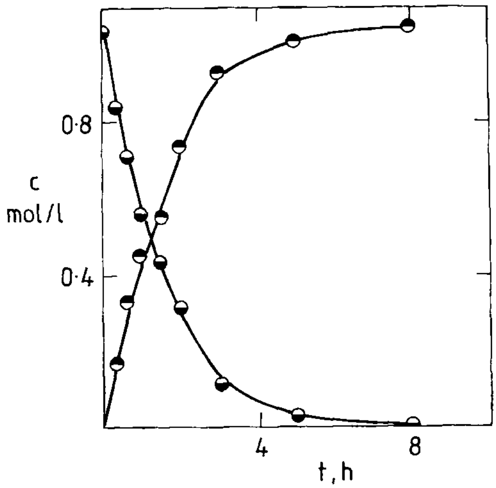


FIG. 8. Time dependence of the concentration of products in the dissociation of 1,3,5-triphenylbiuret in dioxane. Starting conditions: $(c_0)_{TPB}$ = 0.45 mmol/L, $(c_0)_{PhI}$ = 1.01 mmol/L, c_{DBTDL} = 0.28 120°C. Symbols as in Fig. 1.

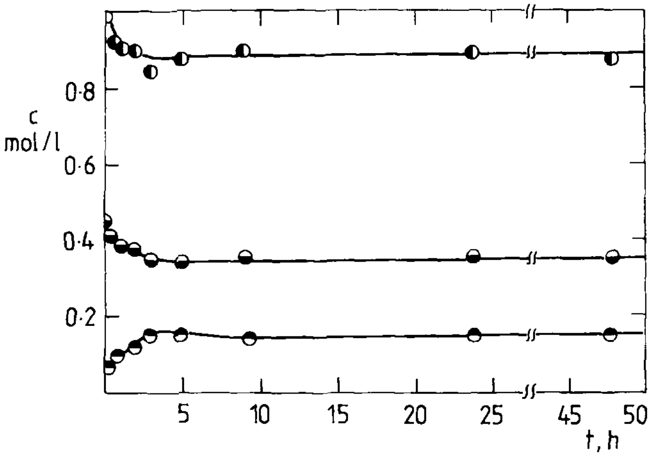


FIG. 9. Time dependence of the concentration of products in the dissociation of 1,3,5-triphenylbiuret in dioxane. *Starting conditions*: $(c_0)_{TPB}$ = 0.45 mol/L, $(c_0)_{PhI}$ = 1.01 mol/L, c_{DBTDL} = 0.28 mmol/L, 120°C. Symbols as in Fig. 1.

In the investigation of reactions between phenyl isocyanate and 1-butanol, Reactions (7)–(9) were not considered in our earlier paper [8] because under the given conditions they either did not take place at all (Eqs. 7 and 8) or were not observed (Eq. 9).

The dissociation of butyl-α,γ-diphenyl allophanate (Figs. 4–6) gives rise to butyl-*N*-phenyl urethane and phenyl isocyanate. The system contains water, which immediately reacts with the formed isocyanate; this is the reason why in the series shown in Figs. 4 and 5 the concentration of phenyl isocyanate during the reaction is zero or cannot be detected. If phenyl isocyanate is present in the system only as the dissociation product of butyl-α,γ-diphenyl allophanate and if $[Al]_0 \leq [H_2O]_0$, aniline is formed according to Eq. (5). This shifts the equilibrium of Reaction (3). After a sufficiently long time and with a sufficient amount of water $[H_2O]_0$, allophanate may dissociate completely. If in the system $[PhI] >> [H_2O]_0$ (Fig. 6), *N*,*N*′-diphenylurea or 1,3,5-triphenylbiuret are the reaction products (Eqs. 4–6), and an equilibrium is established in the system between allophanate, urethane, and isocyanate, and between biuret, urea, and isocyanate.

Similar results were obtained in the investigation of the stability of 1,3,5-triphenylbiuret (Figs. 7–9), where a gradual or even a complete decomposition of biuret takes place if the concentration of the isocyanate formed is comparable with the concentration of water in the system (Figs. 7 and 8), or an equilibrium is established between biuret, urea, and isocyanate if isocyanate is present in the system in excess (Fig. 9).

II. Rate and Equilibrium Constants

A total reaction scheme described by Eqs. (3) through (9) has been suggested for the dissociation of reaction products arising from phenyl isocyanate. The reaction scheme is rather complicated, predominantly due to the formation of the individual products (aniline, *N,N'*-diphenylurea) and to their subsequent reactions proceeding in several ways. This is why this study is restricted to the determination of apparent rate constants of decomposition of allophanate and biuret, i.e., to the determination of k_2' and k_4' For systems with phenyl isocyanate in excess (Figs. 6 and 9), the rate constants k_2 and k_4 and the equilibrium constants (K_{eq}) were also calculated.

In water-containing systems, where the reaction with water gradually consumes all isocyanate due to the dissociation of allophanate (biuret), the dissociation reaction is slower than that between isocyanate and water. This is why the concentration of isocyanate during the dissociation is very low, and the dissociation of allophanate (biuret) can be regarded as a first-order reaction. Indeed, the time-dependent decrease of allophanate or biuret concentrations satisfy the first-order kinetic equation

$$\ln [X] = k_i't, \tag{10}$$

where $k_i' = k_2'$ or k_4', [X] is the concentration of allophanate or biuret, and t is the time.

For systems with phenyl isocyanate in excess (Figs. 6 and 9), the rate constants were obtained by a graphic differentiation of the kinetic differential equation rearranged as

$$\frac{\frac{-d[X]}{dt}}{[X]} = k_i' - k_i \frac{[Y][PhI]}{[X]} \qquad (i = 2 \text{ or } 4), \tag{11}$$

where for $i = 2$, [X] is the concentration of allophanate and [Y] is the concentration of urethane, and for $i = 4$, [X] is the concentration of biuret and [Y] is the concentration of urea.

Moreover, equilibrium constants were calculated for these two series by using the ratio of rate constants,

$$(K_{eq}) = k_i/k_i' \qquad (i = 2 \text{ or } 4), \tag{12}$$

and also from equilibrium concentrations,

$$(K_{eq})_{\mathrm{AL}}{}^{*} = \frac{[\mathrm{AL}]_{eq}}{[\mathrm{BPU}]_{eq}[\mathrm{PhI}]_{eq}} \; ; \qquad (K_{eq})_{\mathrm{TPB}}{}^{*} = \frac{[\mathrm{TPB}]_{eq}}{[\mathrm{DPU}]_{eq}[\mathrm{PhI}]_{eq}} . \tag{13}$$

Values of the rate and equilibrium constants obtained by measuring the stability of allophanate and biuret are summarized in Tables 1 and 2, together with some values of these constants obtained by the investigation of model reactions between phenyl isocyanate and 1-butanol in the presence of water [8].

The agreement between the rate and equilibrium constants obtained in the investigation of reactions between phenyl isocyanate and 1-butanol in the presence of water and by following the stability of allophanate and biuret can be regarded as satisfactory, with the exception of the rate constants k_4 and k_4' at 120°C. In this instance, k_4' calculated from the dissociation of biuret is as much as 10 times higher than k_4' determined for the reaction of water with phenyl isocyanate in excess [8]. Such a discrepancy could be explained either by a considerable dependence of the rate constants k_4 and k_4' on the concentration of DBTDL, c_{DBTDL}, or by a lower reliability of the earlier k_4 and k_4' values.

A number of measurements were therefore carried out in which, for $c_{\mathrm{TPB}} = 0.1$ mol/L, c_{DBTDL} was varied between 0 and 3×10^{-3} mol/L. It was found (cf. Table 2) that DBTDL catalyzes the dissociation of biuret only very weakly: the rate constant of dissociation increases from 1.1×10^{-4} s^{-1} for the noncatalyzed reaction to $(1.4–1.5) \times 10^{-4}$ s^{-1} for the catalyzed reactions. The concentration of DBTDL in the range 1×10^{-4} to 3×10^{-3} mol/L has no effect on the rate of biuret dissociation.

Time intervals in the reactions between phenyl isocyanate and 1-butanol in the presence of water were chosen in Ref. 8 so as to follow closely the formation of allophanate, which proceeds much more slowly than the formation of biuret. Time dependences of the concentration of urea, biuret, and isocyanate showed a larger scatter of values than the other time dependences. In such case there was a danger of incorrect plotting of curves through experimental points, and thus also of an incorrect determination of k_4 and k_4', particularly in the case of faster reactions. Indeed, at 90°C the number of experimental points was sufficient for correctly plotting the curves also in the range of short times, but this was not so at 120°C. Accordingly, slower and incorrect rate constants k_4 and k_4' were determined at 120°C in the preceding paper [8].

Model reactions, in which the stability of butyl-*N*-phenyl urethane, *N,N*′-diphenylurea, butyl-α,γ-diphenyl allophanate, and 1,3,5-triphenylbiuret was investigated, led to the following conclusions.

At temperatures above 100°C, partial hydrolysis of both urea and urethane occurs at sufficiently long times in the presence of even a small quantity of water.

TABLE 1. Rate and Equilibrium Constants Obtained in the Investigation of Butyl-α,γ-diphenyl Allophanate (Figs. 4–6) and in Reactions between Phenyl Isocyanate and 1-Butanol[a]

c_0, mol/L				Temperature, °C	Rate constant × 10^6		Equilibrium constant, L/mol	
PhI	BuOH	AL	DBTDL × 10^5		k_2 L/mol·s	k_2', 1/s	$(K_{eq})_{AL}$	$(K_{eq})_{AL}^*$
0	0	0.11	38	90	—	0.14 ± 0.03	—	—
0.96	0.64	0	9.3	90	0.09[a]	0.28[a]	0.32[a]	—
1.64	0.54	0	16	90	0.21[a]	0.56[a]	0.34[a]	0.20[a]
	0	0.097	38	120	—	8.0 ± 1.2	—	—
0								
0.83	0	0.48	34	120	2.90	15.0	0.19	0.18
0.90	0.59	0	9.3	120	1.75[a]	11.1[a]	0.16[a]	0.13[a]
1.64	0.55	0	16	120	2.22[a]	11.1[a]	0.20[a]	0.17[a]

[a] From Ref. 8.

TABLE 2. Rate and Equilibrium Constants Obtained in the Investigation of the Stability of 1,3,5-Triphenylbiuret (Figs. 7–9) and in Reactions between Phenyl Isocyanate and 1-Butanol in the Presence of Water[a]

c_0, mol/L				Temperature, °C	Rate constant × 10^6		Equilibrium constant, L/mol	
PhI	BuOH	TPB	DBTDL × 10^5		k_4 L/mol·s	k_4', 1/s	$(K_{eq})_{TPB}$	$(K_{eq})_{TPB}^*$
0	0	0.10	39	90	—	5.9 ± 0.8	—	—
0.96	0.64	0	9.3	90	23[a]	1.94[a]	11.9[a]	11.9[a]
1.64	0.54	0	16	90	47[a]	7.5[a]	7.5[a]	6.6[a]
0	0	0.10	0	120	—	107 ± 22	—	—
0	0	0.10	10	120	—	143 ± 13	—	—
0	0	0.10	36	120	—	145 ± 18	—	—
0	0	0.10	54	120	—	146 ± 9	—	—
0	0	0.10	111	120	—	146 ± 14	—	—
0	0	0.10	303	120	—	141 ± 15	—	—
1.01	0	0.45	28	120	190	76	2.6	2.7
0.90	0.59	0	9.3	120	58[a]	18.0[a]	3.2[a]	2.7[a]
1.64	0.55	0	16	120	53[a]	15.3[a]	3.5[a]	3.1[a]

[a] From Ref. 8.

If the concentration of water present in the system is comparable with the concentration of allophanate or biuret, the dissociation after some time may be quantitative. If a sufficient amount of phenyl isocyanate is present in the system, an equilibrium is established between the concentrations of isocyanate, urethane, and allophanate, or between the concentrations of isocyanate, biuret, and urea.

Dibutyltin dilaurate accelerates the dissociation of 1,3,5-triphenylbiuret only to a small extent, and in the range of c_{DBTDL} 1×10^{-4} to 3×10^{-3} mol/L, the rate of dissociation of biuret is independent of the catalyst concentration.

At 120°C the rate constant of dissociation of 1,3,5-triphenylbiuret assumes values of the order of magnitude 10^{-4} s^{-1}.

Model reactions of phenyl isocyanate at elevated temperatures indicate that traces of water not only participate in side reactions leading to the crosslinking in polymer systems [8], but also have a considerable effect on the stability of reaction products of phenyl isocyanate (urethane, urea, allophanate, and biuret).

ABBREVIATIONS

AL	butyl-α,γ-diphenyl allophanate
ANI	aniline
BPU	butyl-*N*-phenyl urethane
DBTDL	dibutyltin dilaurate
DPU	*N,N'*-diphenylurea
MPU	methyl-*N*-phenyl urethane
PhI	phenyl isocyanate
TPB	1,3,5-triphenylbiuret

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