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SIDE REACTIONS IN THE FORMATION OF POLYURETHANES: MODEL REACTIONS BETWEEN PHENYLISOCYANATE AND 1-BUTANOL

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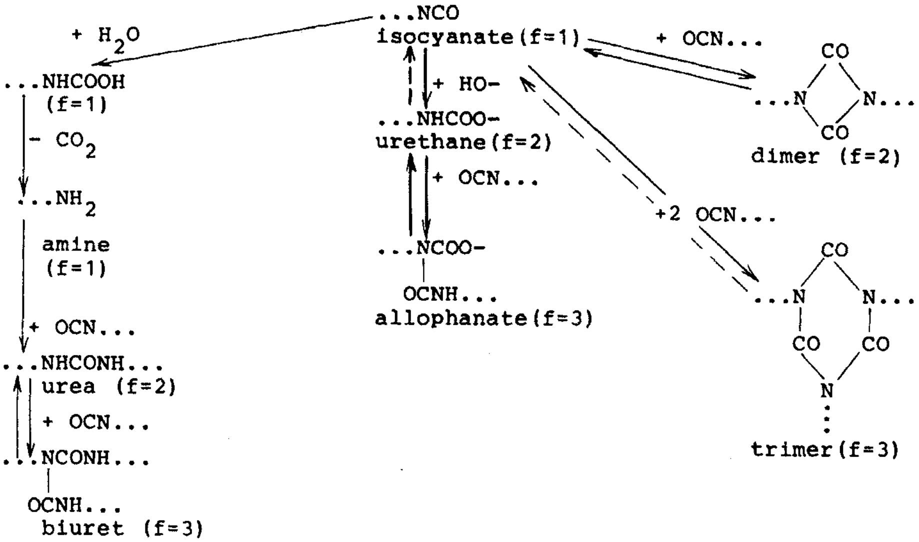
ABSTRACT

The following side reactions occurring in the formation of polyurethanes were modeled: a reaction of excess phenyl isocyanate either with 1-butanol in 1,4-dioxane and in bulk, or with *n*-butylphenyl urethane or water in dioxane catalyzed with dibutyltin dilaurate that leads to the formation of *n*-butyl-α,γ-diphenyl allophanate, *N,N'*-diphenylurea, and 1,3,5-triphenylbiuret. The reaction products were determined quantitatively by means of liquid chromatography. The rate and equilibrium constants were calculated at various temperatures and various initial ratios of functional groups. Biuret is formed from *N,N'*-diphenylurea much more quickly than allophanate from urethane, and the equilibrium constant of its formation is also higher.

INTRODUCTION

Side reactions play an important role in the formation of polyurethanes. They occur predominantly with an excess of isocyanate groups and with participation of water, which is usually present in small amounts in technical products. It cannot be said that these "side" reactions are undesirable from the point of view of achieving optimal properties of polyurethanes. Many of them



SCHEME 1.

are utilized, sometimes separately, in chain extension or crosslinking. The most important "side" reactions are listed in Scheme 1 (cf. also Ref. 1), which also indicates links present in a diisocyanate (. . .) and diol (-) unit, if these are used as the starting components. Thus, for example, a urea unit is bifunctional and plays the role of a chain extender in the polyurethane structure, while allophanate, biuret, or trimer units are trifunctional and lead to branching.

Although these "side" reactions are rather important in practice, relatively few quantitative data are available about their magnitude, not only in macromolecular systems but also in model reactions. The formation of products by "side" reactions depends predominantly on temperature and the type of catalyst used, and also on the molar ratio of functional groups. An example of the effect of the catalyst on the course of the reaction can be seen in the formation of allophanate from phenyl isocyanate (PhI) and ethylphenyl urethane (the main reaction product) even at room temperature, observed when some metal carboxylates are present as catalysts [2] ; without the catalyst, allophanates are generally formed only at temperatures above 100°C.

So far, the rate and equilibrium constants for the formation of allophanates from phenyl isocyanate have been investigated by Kogon [3], Lipatova [4], and Šebenik [5]. Kogon [3] used IR spectroscopy in an investigation of the reaction between aryl isocyanates (I) and ethylaryl urethanes (U) and calculated the rate and equilibrium constants of ethyl-α,γ-diaryl allophanates (A). For a reaction of the type

$$U + I \overset{k_2}{\rightleftharpoons} A, \tag{1}$$

he found that at 100-140°C, k_2 increased from 1.0×10^{-6} to 6.0×10^{-6} $L \cdot mol^{-1} \cdot s^{-1}$, and the equilibrium constant of this reaction, K_{eq}, decreased from 0.4 to 0.2 L/mol.

Lipatova et al. [4] studied a reaction between excess PhI and 1-butanol and diethylene glycol in chlorobenzene, catalyzed with copper bis-(3-ethylacetylacetonate) at 50 and 70°C, by means of IR spectra and elemental analysis. From a model system consisting of *n*-butylphenyl urethane and PhI at a mole ratio of functional groups of 1:1 and 70°C, the rate and equilibrium constants were calculated as $k_2 = 0.021\ L \cdot mol^{-1} \cdot min^{-1}$ and $K_{eq} = 6.5$ L/mol.

Šebenik et al. [5] investigated the kinetics and mechanism of formation of urethane, biuret, allophanate, and isocyanurate in the synthesis of polyurethanes by using ^{13}C NMR and GPC. The rate constants of formation of allophanates from isocyanates and polyols (130°C, mole ratio 4:1) lie in the range $(40\text{-}70) \times 10^{-6}\ L \cdot mol^{-1} \cdot s^{-1}$.

The objective of this study was quantitative characterization of reactions taking place in model systems at concentrations of functional groups that correspond to typical polyol systems catalyzed with dibutyltin dilaurate (DBTDL) in the presence of trace (on a weight basis) amounts of water.

EXPERIMENTAL

Purification and Characterization of Raw Materials

Phenyl isocyanate (PhI) was distilled at reduced pressure (46°C/1330 Pa); GC purity was 99.8%. 1-Butanol (BuOH) was dried with anhydrous K_2CO_3 and distilled at 115°C; GC purity 99.4%; water content 0.05 wt% (Karl Fischer). 1,4-Dioxane was dried with Na and, after redistillation, was recirculated with Na and $LiAlH_4$ under an inert gas (N_2). Water content, determined coulometrically, was 0.0014 wt%; GC purity 99.5%. Methanol (MeOH) was dried with Na or CH_3ONa and redistilled at 64°C; water content was 0.05 wt% (Karl Fischer).

TABLE 1. Characterization of Model Compounds

Standard compound	Crystallization solvent	Melting point, °C	Elemental analysis,[a] wt%		
			C	H	N
MPU	Diethyl ether	46	63.92 (63.58)	6.01 (5.96)	9.50 (9.27)
BPU	*n*-Heptane	57-58	68.64 (68.39)	7.95 (7.77)	7.30 (7.25)
AL	*n*-Hexane	83-84	69.26 (69.23)	6.52 (6.41)	9.04 (8.97)
DPU	Ethanol	237	73.48 (73.58)	5.88 (5.66)	13.27 (13.21)
TPB	Cyclohexane + benzene	153-155	72.51 (72.54)	5.30 (5.14)	12.79 (12.72)

[a] Calculated value in parentheses.

Preparation and Characterization of Standard Compounds

n-Butylphenyl urethane (BPU) was prepared by reacting 6 mL PhI with 100 mL BuOH (4 h/80°C). The excess of BuOH was removed by distillation and BPU was recrystallized.

n-Butyl-α,γ-diphenyl allophanate (AL) was prepared by reacting 8.9 g BPU with 5 mL PhI (according to Kogon [2]; 6 h/35°C). Cobalt naphthenate (0.1 wt%) was used as the catalyst. The reaction mixture was then mixed with 50 mL boiling petroleum ether; the insoluble residue was filtered and removed while hot. Petroleum ether was evaporated from the filtrate and AL was recrystallized.

Methylphenyl urethane (MPU) was prepared by reacting 1 mL PhI with 10 mL MeOH (3 h/21°C). The excess of MeOH was removed by distillation, and MPU was recrystallized.

N,N'-Diphenylurea (DPU) was prepared by reacting 1 mL PhI with 0.5 mL H_2O in 10 mL 1,4-dioxane (2 h/60°C). After evaporation of the solvent, DPU was recrystallized.

1,3,5-Triphenylbiuret (TPB) was prepared [6] by heating 200 mg 1,3-diphenyldiaza-2,4-cyclobutanedione (dimer of PhI) in 2 g aniline (6 h/95°C).

Characteristics of the standard compounds are given in Table 1.

Procedure Used in the Preparation and Determination of Reaction Products

A stock solution of BuOH, dioxane, and DBTDL was prepared. Weighed amounts of the mixture were transferred into ampules, PhI was added, air was removed by N_2, and the ampules were sealed. The reaction was terminated after the desired time intervals by adding an excess of MeOH, so that the amount of unreacted PhI corresponded to that of MPU determined in the product.

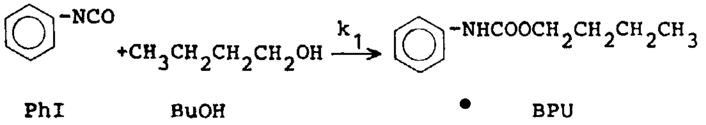
Reaction conditions: BuOH concentration 0.54-0.64 mol/L; mole ratio PhI:BuOH 1.5:1 and 3:1; reaction temperature 90°C and 120°C. The kinetics of the reaction between BuOH and PhI in bulk (mole ratio PhI:BuOH 1.5:1; reaction temperature 90°C) and of the reaction between BPU and PhI in dioxane (120°C, mole ratio PhI:BPU 2.16:1) was also investigated. The concentration of DBTDL was 0.01 wt% calculated as PhI in all cases.

Reaction products were determined by means of reverse-phase liquid chromatography (RP HPLC) using a Spectra Physics 8100 apparatus; 40°C; CGC column 0.3 × 150 mm (Laboratory Instruments, Prague) packed with SiO_2 (5 μm) with bound octadecyl groups; linear concentration gradient $MeOH:H_2O$ from 45:55 to 80:20 by volume; UV detection at $\lambda = 254$ nm.

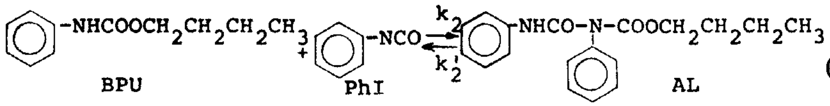
LC measurements carried out with the individual standard compounds and their calibration mixtures showed that, under the given conditions, the retention times are about 2 min (MPU), 5 min (DPU), 9 min (BPU), 12 min (TBP), and 14 min (AL). The individual components are fully resolved; thus liquid chromatography can be used for the quantification of reaction products.

RESULTS AND DISCUSSION

Results of chromatographic analyses allow the following reaction scheme to be assumed for the reaction of phenyl isocyanate with 1-butanol in dioxane in the presence of water and of an excess of –NCO groups:



(2)



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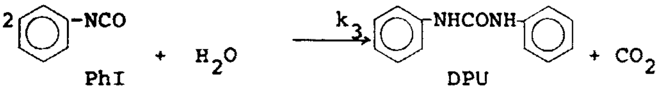

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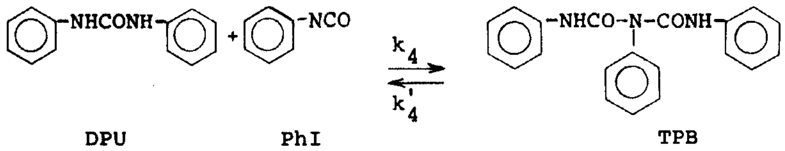
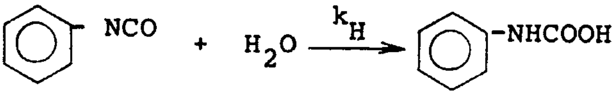


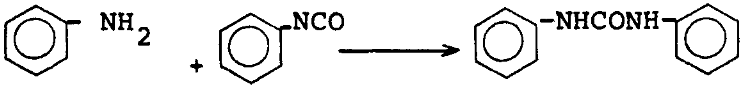
(5)

Equation (4) is the overall expression of the reaction between PhI and water. As mentioned in the Introduction (Scheme 1 and Ref. 1), the reaction proceeds in several steps:



(6a)

(6b)



(6c)

and it is assumed that Reaction (6a) is the rate-controlling process.

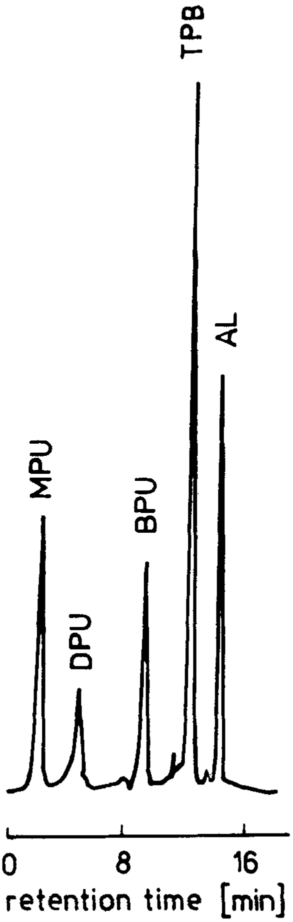


FIG. 1. Example of a chromatogram of reaction products (Series 2, reaction time 144 h).

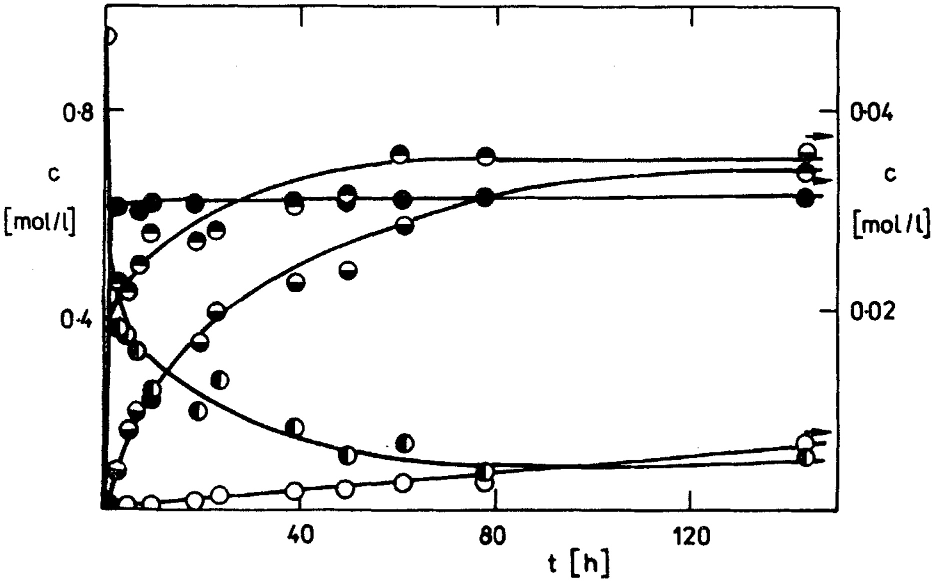


FIG. 2. Time dependence of the concentration of products of the reaction between PhI and BuOH. Starting conditions for Series 1: $(C_0)_{\mathrm{PhI}} = 0.96$ mol/L, $(C_0)_{\mathrm{BuOH}} = 0.64$ mol/L, $C_{\mathrm{DBTDL}} = 93\ \mu$mol/L, 90°C. Reaction products denoted as (◐) MPU, (●) BPU, (⊖) DPU, (⊖) TPB, (○) AL.

The time dependences of concentrations of the starting components and products under various reaction conditions are given in Figs. 1-7.

Similarly to earlier papers [3-5], the addition reactions were taken to be bimolecular. Hence, the suggested reaction scheme can be described by a system of differential rate equations (Eqs. 7-12):

$$\frac{d[\mathrm{PhI}]}{dt} = -k_1[\mathrm{BuOH}][\mathrm{PhI}] - k_2[\mathrm{BPU}][\mathrm{PhI}] + k_2'[\mathrm{AL}] - 2k_H[\mathrm{PhI}][\mathrm{H_2O}] - k_4[\mathrm{PhI}][\mathrm{DPU}] + k_4'[\mathrm{TPB}], \quad (7)$$

$$\frac{d[\mathrm{BPU}]}{dt} = k_1[\mathrm{BuOH}][\mathrm{PhI}] - k_2[\mathrm{BPU}]\mathrm{PhI}] + k_2'[\mathrm{AL}], \quad (8)$$

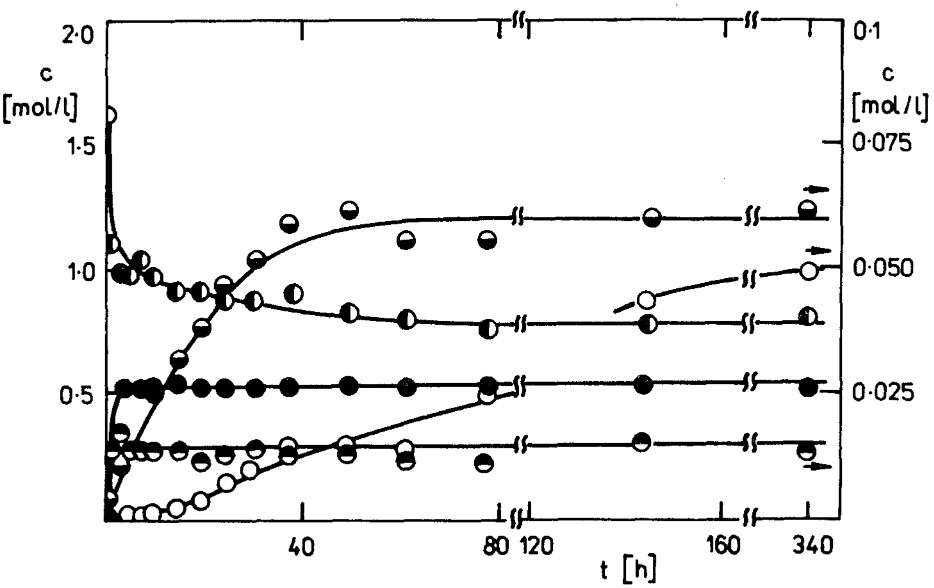


FIG. 3. Time dependence of the concentration of products of the reaction between PhI and BuOH. Starting conditions for Series 2: $(C_0)_{\mathrm{PhI}} = 1.64$ mol/L, $(C_0)_{\mathrm{BuOH}} = 0.54$ mol/L, $C_{\mathrm{DBTDL}} = 160$ µmol/L, 90°C. Symbols as in Fig. 2.

$$\frac{d[\mathrm{H_2O}]}{dt} = -\,2k_H\,[\mathrm{PhI}]\,[\mathrm{H_2O}]\,, \tag{9}$$

$$\frac{d[\mathrm{DPU}]}{dt} = 2k_H\,[\mathrm{H_2O}]\,[\mathrm{PhI}] - k_4\,[\mathrm{PhI}]\,[\mathrm{DPU}] + k_4'\,[\mathrm{TPB}]\,, \tag{10}$$

$$\frac{d[\mathrm{TPB}]}{dt} = k_4\,[\mathrm{PhI}]\,[\mathrm{DPU}] - k_4'\,[\mathrm{TPB}]\,, \tag{11}$$

$$\frac{d[\mathrm{AL}]}{dt} = k_2\,[\mathrm{BPU}]\,[\mathrm{PhI}] - k_2'\,[\mathrm{AL}]\,. \tag{12}$$

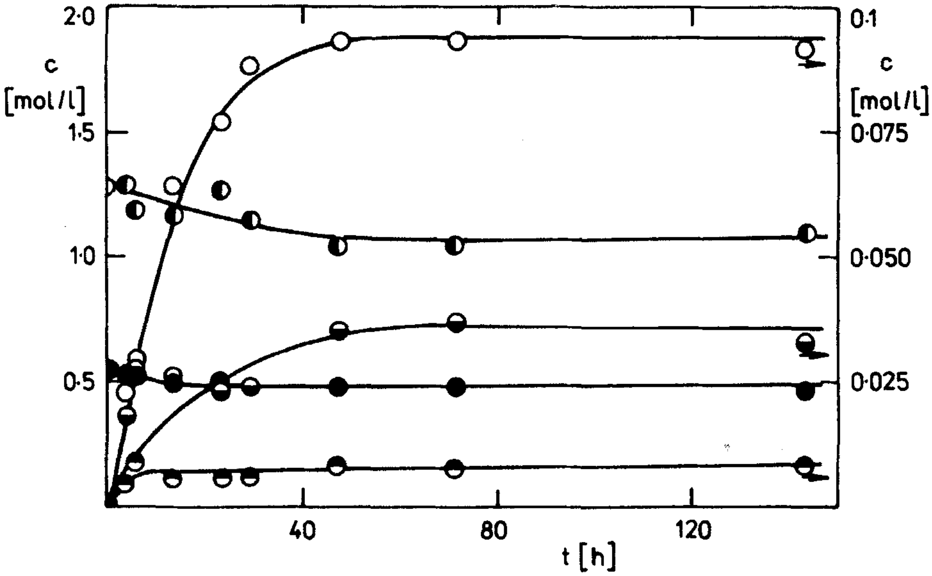


FIG. 4. Time dependence of the concentration of products of the reaction between PhI and BPU. Starting conditions for Series 6: $(C_0)_{\mathrm{PhI}} = 1.24$ mol/L, $(C_0)_{\mathrm{BPU}} = 0.57$ mol/L, $C_{\mathrm{DBTDL}} = 110\,\mu$mol/L, 120°C. Symbols as in Fig. 2.

The urethane formation is too fast under the given conditions for the rate constant k_1 to be determined. The rate constants k_2, k_2', k_H, k_4, and k_4' were calculated by a graphic differentiation method. The rate constants k_2 and k_2' were determined from a linearized plot according to Eq. (12) rearranged as

$$\frac{\dfrac{d[\mathrm{AL}]}{dt}}{[\mathrm{AL}]} = k_2 \frac{[\mathrm{BPU}]\,[\mathrm{PhI}]}{[\mathrm{AL}]} - k_2'. \tag{13}$$

A similar rearrangement of Eq. (11) yields the rate constants k_4 and k_4'. The rate constant k_H is obtained from Eq. (10) by the following rearrangement:

$$\frac{\dfrac{d[\mathrm{DPU}]}{dt} - k_4'[\mathrm{TPB}]}{[\mathrm{PhI}]\,[\mathrm{DPU}]} = \frac{2k_H[\mathrm{H_2O}]}{[\mathrm{DPU}]} - k_4. \tag{14}$$

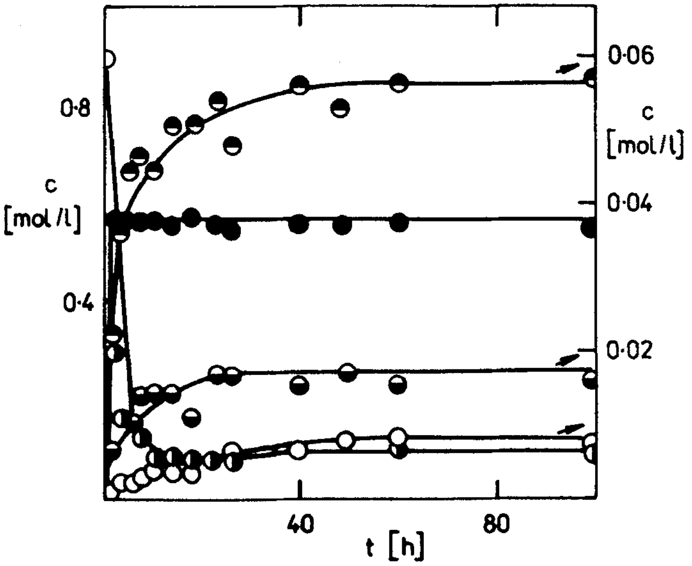


FIG. 5. Time dependence of the concentration of products of the reaction between PhI and BuOH. Starting conditions for Series 3: $(C_0)_{\mathrm{PhI}} = 0.90$ mol/L, $(C_0)_{\mathrm{BuOH}} = 0.59$ mol/L, $C_{\mathrm{DBTDL}} = 93$ μmol/L, 120°C. Symbols as in Fig. 2.

The equilibrium constants of Reactions (3) and (5) were calculated from the rate constants k_i and k_i' ($i = 2$ or 4) according to

$$K_{eq} = k_i/k_i', \tag{15}$$

and also from the equilibrium concentrations by

$$(K_{eq})_{\mathrm{AL}}{}^* = \frac{[\mathrm{AL}]_{eq}}{[\mathrm{BPU}]_{eq}[\mathrm{PhI}]_{eq}}; \qquad (K_{eq})_{\mathrm{TPB}}{}^* = \frac{[\mathrm{TPB}]_{eq}}{[\mathrm{DPU}]_{eq}[\mathrm{PhI}]_{eq}}. \tag{16}$$

Values of the rate constants are summarized in Table 2; those of the equilibrium constants in Table 3.

From the results obtained, the following conclusions may be drawn: It follows from the mass balance that 95% of the PhI participates in the reac-

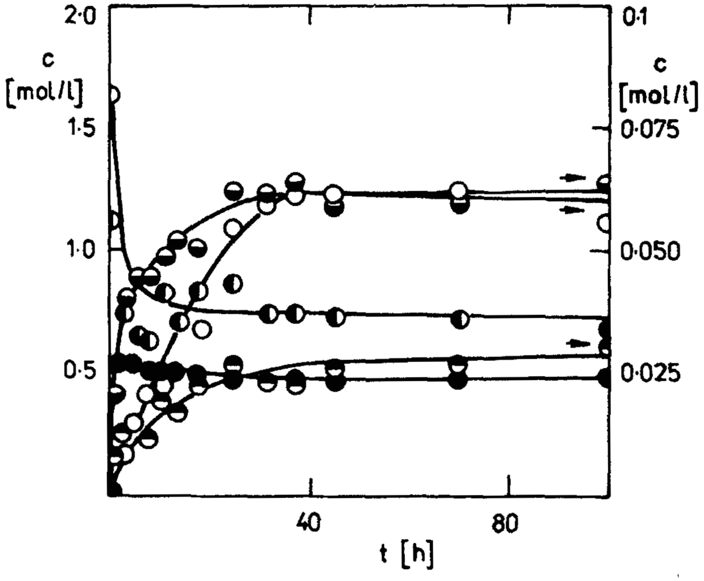


FIG. 6. Time dependence of the concentration of products of the reaction between *PhI and BuOH. Starting conditions for Series 4:* $(C_0)_{\mathrm{PhI}} = 1.64$ mol/L, $(C_0)_{\mathrm{BuOH}} = 0.55$ mol/L, $C_{\mathrm{DBTDL}} = 160\ \mu$mol/L, 120°C. Symbols as in Fig. 2.

tions described by Eqs. (2)-(5), while less than 5% is consumed by the formation of other unidentified products. However, under the given conditions, the comparatively stable cyclic trimer was not found among the reaction products. The formation of allophanate is comparatively slow. The equilibrium constants are also comparatively small. This means, for example, that at the initial mole ratio of PhI:BuOH 1.5:1, only 1% BPU reacts to allophanate at equilibrium and 120°C, while the allophanate content is 10% at the mole ratio 3:1. There is comparatively good agreement between the equilibrium constants calculated from the equilibrium concentrations and from the ratio of the rate constants.

The rate constants of allophanate formation are difficult to compare with the results obtained by other authors in view of the different catalysis of the reaction. The equilibrium constants of allophanate formation are close to the values reported by Kogon [3] and differ by an order of magnitude from the data reported by Lipatova [4].

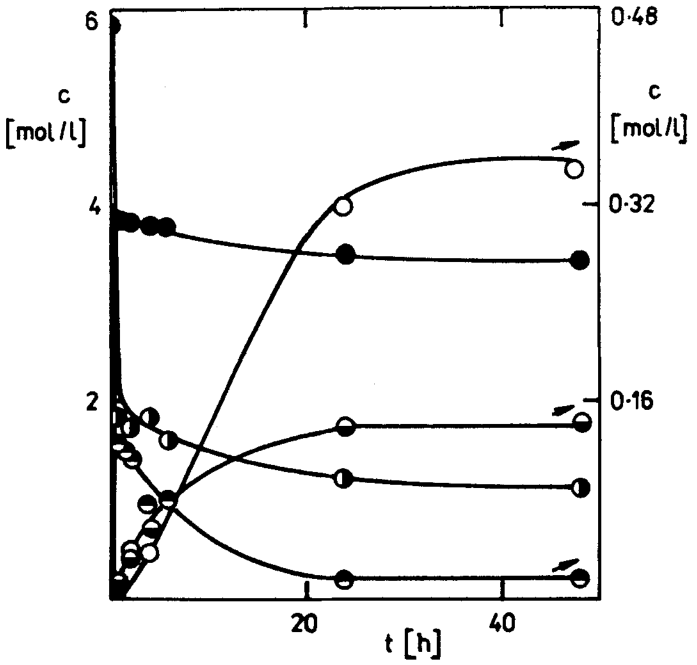


FIG. 7. Time dependence of the concentration of products of the reaction between PhI and BuOH in bulk. Starting conditions for Series 5: $(C_0)_{PhI}$ = 5.84 mol/L, $(C_0)_{BuOH}$ = 3.89 mol/L, C_{DBTDL} = 710 μmol/L, 90°C. Symbols as in Fig. 2.

A remarkable finding is the considerably higher rate of formation of biuret from diphenylurea and PhI, and also the higher stability of biuret compared with allophanate. This means that traces of water may participate in "side" reactions leading to crosslinking to a more important degree than do reactions between urethane and isocyanate, which give rise to the allophanate group.

These model reactions serve as a prerequisite for the treatment of the effect of additional crosslinking in both linear and crosslinked polyurethanes and may be used as input data for description of the network build-up in terms of branching theories. Recently, the effect of allophanate formation on gelatin and gel properties has been treated theoretically [7].

TABLE 2. Rate Constants

	C_0, mol/L					Rate constant × 10^6				
Series	[PhI]	[BuOH]	[DBTDL] × 10^5	$\frac{[NCO]}{[OH]}$	Temperature, °C	k_2[a]	k_2'[b]	k_4[a]	k_4'[b]	k_H[a]
1	0.96	0.64	9.3	1.50	90	0.09	0.28	23	1.94	13.0
2	1.64	0.54	16	3.04	90	0.21	0.56	47	7.5	5.6
3	0.90	0.59	9.3	1.54	120	1.75	11.1	58	18.0	9.2
4	1.64	0.55	16	2.99	120	2.22	11.1	53	15.3	7.2
5	5.84	3.89	71	1.50	90	0.94	10.3	19	2.22	—
6	1.24	0.57[c]	11	2.16[d]	120	2.08	11.4	47	12.5	6.4

[a] Value in $L \cdot mol^{-1} \cdot s^{-1}$.

[b] Value in s^{-1}.

[c] $(C_0)_{BPU}$.

[d] [NCO]/[NH].

TABLE 3. Equilibrium Constants

	Equilibrium constants, L/mol			
Series	$(K_{eq})_{AL}$[a]	$(K_{eq})_{AL}{}^*$[b]	$(K_{eq})_{TPB}$[a]	$(K_{eq})_{TPB}{}^*$[b]
1	0.32	–	11.9	11.9
2	0.34	0.2	6.3	6.6
3	0.16	0.13	3.2	2.7
4	0.20	0.17	3.5	3.1
5	0.09	0.09	8.6	8.8
6	0.18	0.19	3.8	3.8

[a] Calculated from the ratio of rate constants.
[b] Calculated from equilibrium concentrations.

ABBREVIATIONS

PhI	phenyl isocyanate
BuOH	1-butanol
MeOH	methanol
MPU	methylphenyl urethane
BPU	*n*-butylphenyl urethane
DPU	*N,N'*-diphenylurea
TPB	1,3,5-triphenylbiuret
AL	*n*-butyl-α,γ-diphenyl allophanate
DBTDL	dibutyltin dilaurate
GC	gas chromatography
LC	liquid chromatography

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