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Kinetic Studies of the Triethylenediamine-catalyzed Transamidation of 1,3-Diphenylurea with *n*-Butylamine in Dioxane

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The rates of the transamidation of 1,3-diphenylurea (abbreviated as DPU) with *n*-butylamine (BA) in dioxane in the presence of triethylenediamine (TED), forming *n*-butylphenylurea (BPU), aniline and carbon dioxide, were followed ultraviolet-spectrophotometrically. The rate of the reaction satisfied the following equation:

$$v = \{k_1'+k_2'[\mathrm{TED}]\}[\mathrm{DPU}] + \{k_2''+k_3[\mathrm{TED}]\}[\mathrm{BA}][\mathrm{DPU}] .$$

The first and second terms correspond to the non- and the TED-catalyzed hydrolysis of diphenylurea, while the third and fourth terms represent, respectively, the non- and the TED-catalyzed transamidation. In both the non- and the TED-catalyzed transamidation, a probable mechanism which involves the nucleophilic attack of the lone pair of the N-atom on the carbonyl C-atom of diphenylurea, followed by the formation of ion pairs of quaternary ammonium salt and of quaternary ammonium type salt, was discussed.

The transamidation of 1,3-diphenylurea with primary amines in the presence of tertiary amine in dioxane has been previously reported.[1] In the present paper, the TED-catalyzed transamidation of 1,3-diphenylurea with *n*-butylamine will be measured by means of ultraviolet spectrophotometry, and its probable mechanism discussed.

Experimental

Materials. 1,3-Diphenylurea (DPU) was recrystallized three times from aqueous methanol; mp 244°C. *n*-Butylamine (BA) was rectified; bp 182°C. *n*-Butylphenylurea (BPU) was prepared by the reaction of phenyl *N*-phenylcarbamate with BA[2] and recrystallized from aqueous methanol; mp 130—131°C (Found: N, 14.3%; Calcd: 14.6%). Triethylenediamine (TED) obtained from Meisei & Co., Ltd., was purified by sublimation under reduced pressure; mp 110°C. Dioxane was refluxed for 7 hr with 10% of its volume of 1 N aqueous hydrochloric acid, while a slow stream of air was passed through the condenser in order to remove the acetaldehyde formed. The organic layer was then separated after treating it with potassium hydroxide. It was then distilled from metal sodium; bp 102°C.

Ultraviolet Spectrophotometry and Chemical Analysis. The absorption maxima of DPU and BPU were 255 and 238 mμ, while the minima of DPU and BPU were 227 and 217 mμ, respectively (see Fig. 1). The absorptions of BA, TED, and aniline are negligible at these wavelengths. Mixtures of DPU, BA, TED, and BPU of known concentrations (corresponding to 0, 20, 40, 60, 80, and 100% conversion) were prepared at 90°C; a plot of the difference in extinctions, $(E_{255}-E_{227})$ *vs.* $(E_{255}-E_{238})$, gave a straight line,[3] and the conversions calculated from the values of $(E_{255}-E_{238})$ at 0 and 100% conversion agreed well with the conversions calculated from the composition of the mixture within a 1% error.

The aniline liberated from DPU in a reaction mixture was detected by paper chromatography[1] and by Anger's reaction.

A Typical Run for the Rate Measurements. A solution of 1.6 m*l* of 0.5 M BA in dioxane was added to a solution of 34.4 m*l* of 0.0233 M DPU in dioxane; then

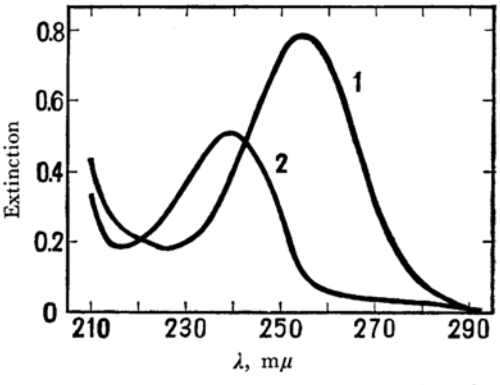

Fig. 1. Ultraviolet spectra of reactant and product in 2×10^{-5} M methanolic solution: 1, DPU; 2, BPU.

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[1] Y. Furuya and K. Itoho, *Chem. & Ind.*, **1967**, 359.

[2] Y. Furuya, S. Goto, K. Itoho, I. Urasaki and A. Morita, *Tetrahedron*, **24**, 2375 (1968).

[3] Y. Ogata, Y. Furuya and M. Ito, *J. Am. Chem. Soc.*, **85**, 3649 (1963).

a solution of 4.0 m*l* of 0.05 M TED in dioxane was poured into this mixture in order to start the reaction after the three solutions had attained temperature equilibrium at 90°C. Aliquots (0.2 m*l* each) were pipetted out at appropriate time intervals; for spectrophotometry each one was diluted with methanol to a 2×10^{-5} M initial concentration of the reactant. Then, the extinctions at 255, 238, and 227 mμ were measured. The conversion was calculated graphically from the observed value of $(E_{255}-E_{238})$, and the value of the first-order rate constant, $k_{1\,\mathrm{obs}}$, was calculated.

Determination of the Water in the Reaction Medium. The remaining water in the dioxane was determined to be 0.047 M by the Karl Fischer method.

A Typical Procedure for the Conductivity Measurement. A 20 m*l* portion of the dioxane solution of DPU (0.02 M), BA (0.02 M), and TED (0.005 M) was heated at 90°C for 40 hr, after which the solution was diluted with 20 m*l* of conductivity water. The precipitate thus formed was filtered off by a glass filter. Then the conductivity of the solution was measured by means of a Yokogawa-Hewlett-Packard universal bridge 4255A(BV-Z-13C) at 25±0.2°C. The values of the conductivity of each member and couple for the reaction of DPU with BA in the presence of TED are indicated in Table 1.

TABLE 1. SPECIFIC CONDUCTIVITIES OF THE REACTANTS AND PRODUCTS AT 25±0.2°C

Reaction concn. of DPU, BA and aniline: 0.02 M
concn. of TED: 0.005 M
Measurement concn.: half of the values described above

Substance or couple of substances	Specific conductivity $\kappa\times10^6\ \Omega^{-1}\,\mathrm{cm}^{-1}$ at 0 hr		at 40hr	at 90 hr
Cond. water	1.553			
Dioxane	2.848			
DPU	5.180			
BA	21.41			
TED	3.023			
Aniline	3.075			
DPU+TED	10.87	(1.33)*	(1.56)	(1.36)
DPU+BA	69.64	(2.62)	(0.88)	(0.46)
BA+TED	21.95	(0.90)	(0.56)	(0.89)
Aniline+TED	7.880	(1.29)	(2.95)	(2.75)
DPU+BA+TED	33.69	(1.14)	(0.40)	(0.40)

* The values in parentheses are the ratios of an actual value of each couple by the sum of the components.

Results and Discussion

The reaction follows the first-order kinetics with DPU, as is shown in Fig. 2. The plots of the first-order rate constant *vs.* the concentration of BA gives a straight line which does not pass through the point of origin, as is illustrated in Fig. 3. Therefore, the observed first-order rate constant is given by the following equation:

$$k_{1\,\mathrm{obs}} = k_1 + k_2[\mathrm{BA}] \qquad (1)$$

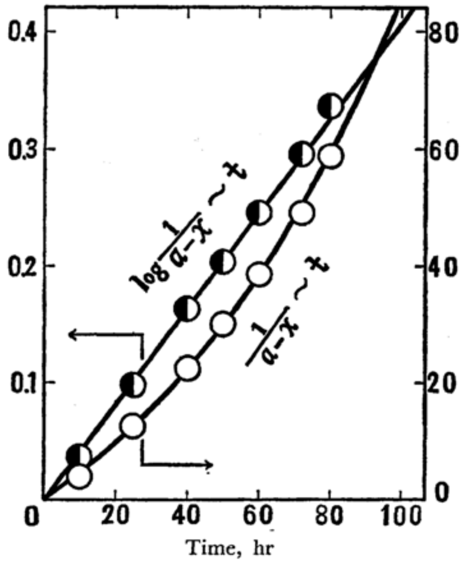


Fig. 2. Determination of reaction order in dioxane at 90°C.
Initial concn. of DPU and BA: 0.02 M,
concn. of TED: 0.005 M

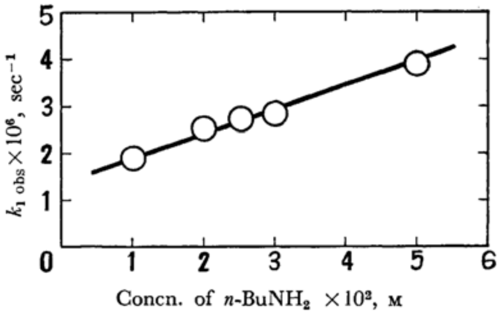


Fig. 3. The plots of $k_{1\,\mathrm{obs}}$ *vs.* concentration of BA for the TED-catalyzed transamidation of DPU with BA in dioxane at 90°C.
Initial concn. of DPU: 0.02 M,
concn. of TED: 0.005 M

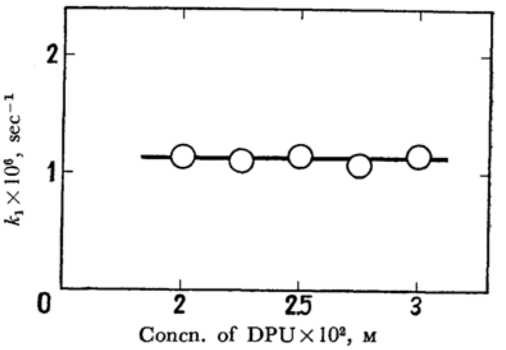


Fig. 4. The plots of k_1 *vs.* concentration of DPU for the TED-catalyzed transamidation of DPU with BA in dioxane at 90°C.
Initial concn. of BA: 0.02 M,
concn. of TED: 0.005 M

The values of k_1 and k_2 did not vary with the concentration of DPU (Figs. 4 and 5). However, these values contain the concentration of TED, as is obvious in Figs. 6 and 7.

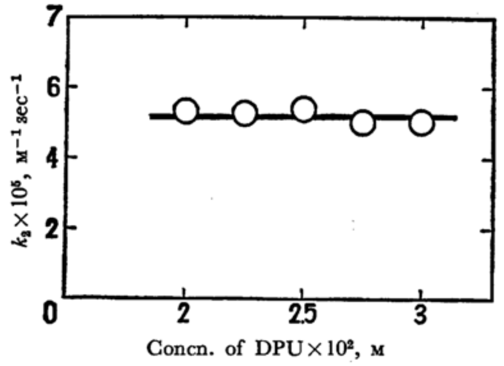


Fig. 5. The plots of k_2 *vs.* concentration of DPU for the TED-catalyzed transamidation of DPU with BA in dioxane at 90°C.
Initial concn. of BA: 0.02 M,
concn. of TED: 0.005 M

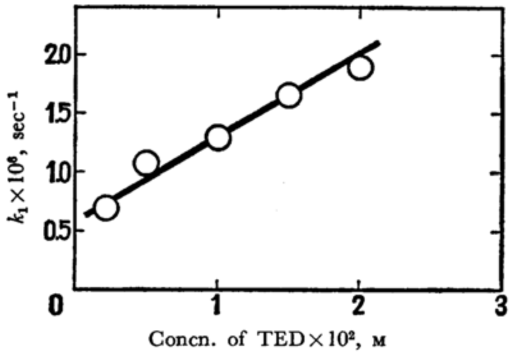


Fig. 6. The plots of k_1 *vs.* concentration of TED for the TED-catalyzed transamidation of DPU with BA in dioxane at 90°C.
Initial concn. of DPU and BA: 0.02 M

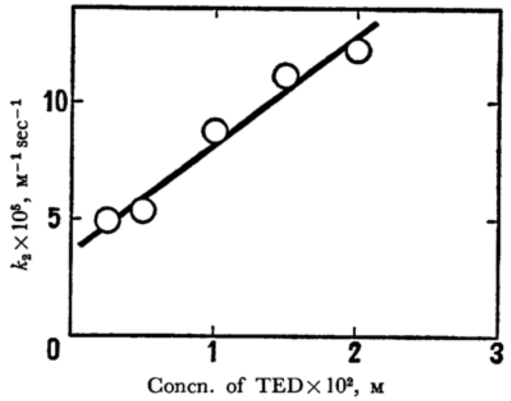


Fig. 7. The plots of k_2 *vs.* concentration of TED for the TED-catalyzed transamidation of DPU with BA in dioxane at 90°C.
Initial concn. of DPU and BA: 0.02 M

Hence, the k_1 and k_2 rate constants should be expressed as follows:

$$k_1 = k_1' + k_2'[\mathrm{TED}] \tag{2}$$

$$k_2 = k_2'' + k_3[\mathrm{TED}] \tag{3}$$

The total kinetics is, therefore, given by following equation:

$$v = \{k_1'+k_2'[\mathrm{TED}]\}[\mathrm{DPU}] + \{k_2''+k_3[\mathrm{TED}]\}[\mathrm{BA}][\mathrm{DPU}] \tag{4}$$

The values of $k_1'\times10^6$ sec^{-1}, $k_2'\times10^5$ M^{-1} sec^{-1}, $k_2''\times10^5$ M^{-1} sec^{-1}, and $k_3\times10^3$ M^{-2} sec^{-1} were 0.57, 7.00, 3.50, and 4.69 respectively. The first and second rate constants are those of the hydrolysis of DPU in the absence and in the presence of TED as a catalyst. The values agree well with the experimental values of 0.56×10^{-6} sec^{-1} and 6.85×10^{-5} M^{-1} sec^{-1} obtained by the non- and the TED-catalyzed hydrolysis of DPU respectively (see Fig. 8). The conversions of the non- and the TED-catalyzed hydrolysis were *ca.* 6 and 30% respectively in the reaction heated at 90°C for 90 hr.

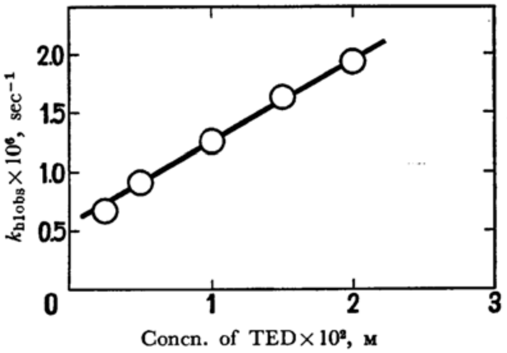
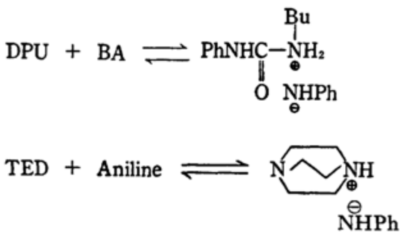


Fig. 8. The plots of k_{h1obs} *vs.* concentration of TED for the TED-catalyzed hydrolysis of DPU in dioxane at 90°C.
Initial concn. of DPU: 0.02 M.

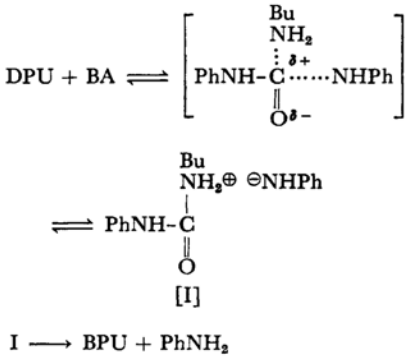
The reaction is accelerated by a tertiary amine, especially TED. The conductivities of the couples of (DPU+TED) and (DPU+BA) are larger than the sum of the conductivities of the components, as is shown in Table 1. In the couples of (DPU+TED) heated at 90°C for 0 and 90 hr, the existence of quaternary ammonium salt was indicated by Wagner's and Dragendorff's reagents. The couple of (BPU+TED) heated for 0 hr indicates weakly the formation of quaternary ammonium salt by Dragendorff's reagent. No positive results were obtained in the couple of (DPU+BA) and/or (Aniline+TED) by Wagner's, Mayer's, and Dragendorff's reagents, for these couples do not form the quaternary ammonium salt. The conductivities of these couples probably depend on the formation of the ion pairs like a quaternary ammonium salt.



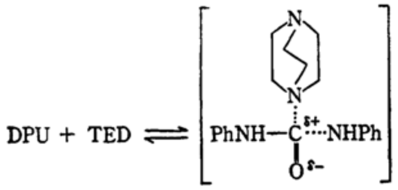
From these findings, a probable mechanism, which involves the nucleophilic attack by the lone pair of the N-atom of amine on the carbonyl C-atom of DPU, followed by the formation of a quaternary ammonium-type ion pair, may be suggested as follows:

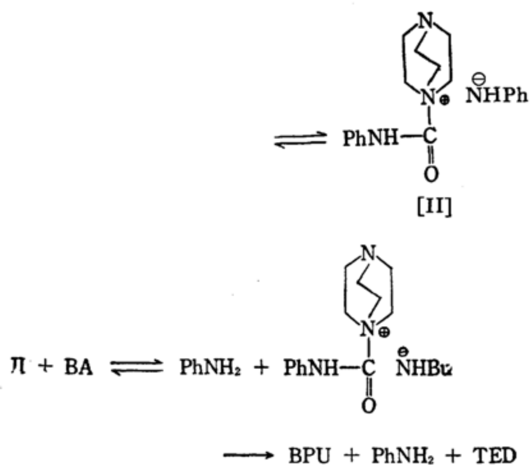
Transamidation

Non-catalyzed



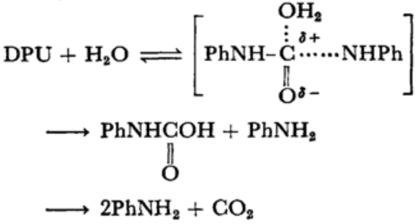
TED-catalyzed



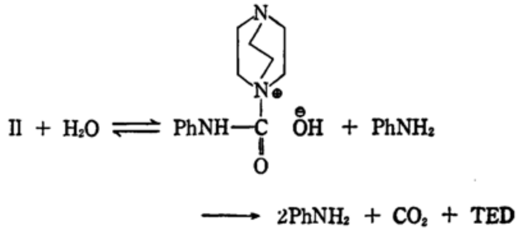


Hydrolysis

non-catalyzed



TED-catalyzed



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