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Kinetic Studies of the Triethylenediamine-catalyzed Hydrolysis of 1,3-Diphenylurea in Dioxane

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The rate of the hydrolysis of 1,3-diphenylurea (abbreviated as DPU) in dioxane in the presence of triethylenediamine (TED) was followed by ultraviolet spectrophotometry. The rate of the reaction satisfied the following equation:

$$\begin{aligned} v = {} & \{k_2-k_{3\text{h}}[\text{H}_2\text{O}]\}[\text{DPU}][\text{H}_2\text{O}] + \{k_{4\text{uh}}[\text{H}_2\text{O}]-k_{3\text{u}}\}[\text{DPU}]^2[\text{H}_2\text{O}] \\ & + \{k_{3\text{c}}-k_{4\text{ch}}[\text{H}_2\text{O}]\}[\text{TED}][\text{DPU}][\text{H}_2\text{O}] + \{k_{5\text{cuh}}[\text{H}_2\text{O}]-k_{4\text{cu}}\} \\ & \times [\text{TED}][\text{DPU}]^2[\text{H}_2\text{O}]. \end{aligned}$$

A probable mechanism which involves a nucleophilic attack of the lone pair of the O-atom of water and of the N-atom of TED on the carbonyl C-atom of DPU, passing through an ion pair of quaternary ammonium salt, is discussed.

In the kinetic studies of the TED-catalyzed transamidation of 1,3-diphenylurea with *n*-butylamine in dioxane which have been previously reported,[1] both non- and the TED-catalyzed hydrolyses were found. In the present paper, a probable mechanism of the hydrolysis, passing through an ion pair of quaternary ammonium salt, will be discussed.

Experimental

Materials. The 1,3-diphenylurea, the triethylenediamine, and the dioxane used as the reaction solvent were purified in a mannr similar to that described previously.[1]

Ultraviolet Spectrophotometry and Chemical Analyses. The absorption maxima of DPU and aniline were 255 and 234 mμ, while the minima were 227 and 214 mμ respectively. The absorption of TED is negligible at these wavelengths. Mixtures of DPU, aniline, and TED in known concentrations (corresponding to 0, 20, 40, 60, 80, and 100% conversion) were prepared at 90°C; plots of the extinction difference, ($E_{255}-E_{230}$) *vs.* ($E_{255}-E_{277}$), gave a straight line, and the cnoversions calculated from the values of ($E_{255}-E_{230}$) at 0 and 100% conversion agreed well with the conversions calculated from the mixtures within a 1% error.

Reaction-product Criterion. Aniline liberated from DPU in a reaction mixture was detected by paper chromatography in the manner described in a previous paper.[2]

A Typical Run for the Rate Measurements. A solution of 0.07 m*l* of 0.5M water in dioxane was added to a solution of 27.93 m*l* of 0.0143M DPU in dioxane; a solution of 12.00 m*l* of 0.05M TED in dioxane was poured into the solution of DPU in order to start the reaction after the three solutions had attained temperature equibrium at 90°C. Aliquots (0.2 m*l*, each) were pipetted out at appropriate intervals of time, and each one was diluted with methanol to a 2×10^{-5}M initial concentration of the reactant. The conversion was calculated graphically from the values of ($E_{255}-E_{230}$), and the value of the second-order rate constant, $k_{2\text{obs}}$, was calculated.

Determination of the Water. The water concentration in the reaction medium was determined by the Karl Fischer method.

Measurement of the Order of Self-association of DPU by the Cryoscopic Method. The order of the self-association of DPU in dioxane was measured by the cryoscopic method on solutions containing water ranging in concentration from 2×10^{-2} to 5×10^{-2}M.[3]

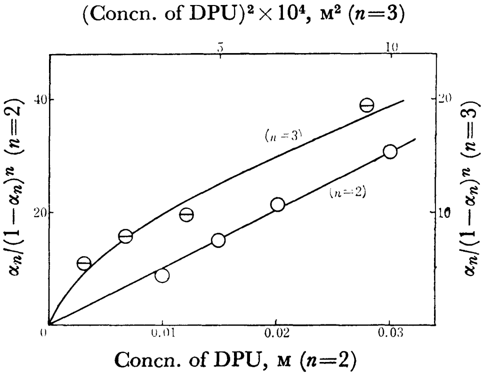

Fig. 1. Determination of the order of the self-association of DPU in dioxane.
Concn. of water: 0.02—0.05M

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[1] Y. Furuya, K. Itoho and H. Miyagi, This Bulletin, **42**, 2348 (1969).

[2] Y. Furuya and K. Itoho, *Chem. & Ind.* (London), **1967**, 359.

It became evident that DPU existed in the dimer form, as is shown in Fig. 1.

However, DPU exists in the monomer form when the dioxane solution contains *n*-butylamine in the range from 1×10^{-2} to 5×10^{-2}M. Thus, the molecular weight of DPU gave the values of the monomer form, as is shown in Table 1.

Table 1. The values of the molecular weight of DPU in dioxane containing *n*-butylamine

Concn. of *n*-butylamine (M)	Molecular weight of DPU	
	Obsd*	Calcd
0.01	223.95	212.25
0.015	209.95	212.25
0.02	213.29	212.25
0.03	216.73	212.25

* They were obtained by cryoscopic method.

Results and Discussion

The reaction followed the second-order kinetics with DPU and H_2O. The plots of the observed second-order rate constant *vs.* the concentration of TED gave a straight line which does not pass through the point of origin, as is shown in Fig. 2.

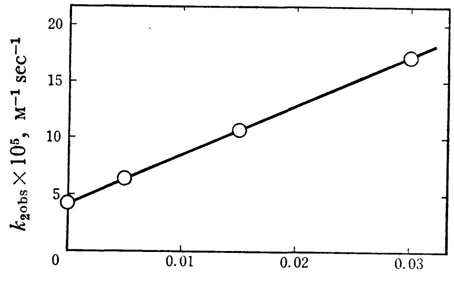

Fig. 2. The plots of k_{2obs} *vs.* the concentration of TED for the TED-catalyzed hydrolysis of DPU in dioxane at 90°C.
Initial concn. of DPU: 0.01M
Initial concn. of water: 0.02M

Therefore, the observed second-order rate constant is given by the following equation:

$$k_{2obs} = k_2'' + k_{3c}''[\mathrm{TED}]. \tag{1}$$

The plots of k_2'' and k_{3c}'' *vs.* the concentration of DPU gave straight lines which have minus signs, as is shown in Figs. 3 and 4.

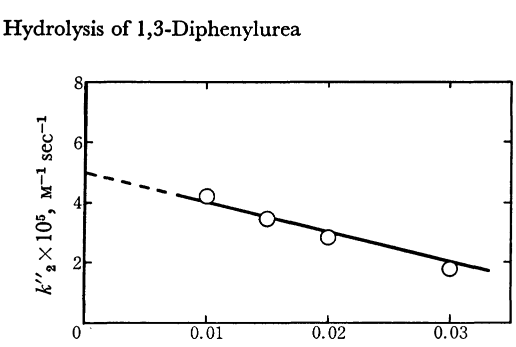

Fig. 3. The plots of k_2'' *vs.* the concentration of DPU for the TED-catalyzed hydrolysis of DPU in dioxane at 90°C.
Initial Concn. of water: 0.02M

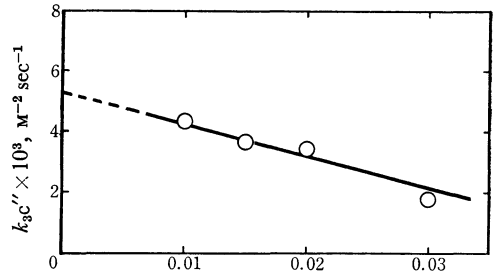

Fig. 4. The plots of k_{3c}'' *vs.* the concentration of DPU for the TED-catalyzed hydrolysis of DPU in dioxane at 90°C.
Initial concn. of water: 0.02M

Thus, the rate constants, k_2'' and k_{3c}'', can be expressed by the following equations:

$$k_2'' = k_2' - k_{3u}'[\mathrm{DPU}] \tag{2}$$

and

$$k_{3c}'' = k_{3c}' - k_{4cu}'[\mathrm{DPU}]. \tag{3}$$

Moreover, k_2', k_{3u}', k'_{3c}, and k_{4cu}' are variables for the concentration of water, as is illustrated in Figs. 5, 6, 7, and 8. Therefore, the following relationships are given:

$$k_2' = k_2 - k_{3h}[H_2O]$$
$$-k_{3u}' = -k_{3u} + k_{4uh}[H_2O]$$

and

$$k_{3c}' = k_{3c} - k_{4ch}[H_2O]$$
$$-k_{4cu}' = -k_{4cu} + k_{5cuh}[H_2O].$$

Consequently, the total kinetics may be given by the following equation:

$$\begin{aligned} v = &\{k_2-k_{3h}[H_2O]\}[\mathrm{DPU}][H_2O] \\ &+\{k_{4uh}[H_2O]-k_{3u}\}[\mathrm{DPU}]^2[H_2O] \\ &+\{k_{3c}-k_{4ch}[H_2O]\}[\mathrm{TED}][\mathrm{DPU}][H_2O] \\ &+\{k_{5cuh}[H_2O]-k_{4cu}\}[\mathrm{TED}][\mathrm{DPU}]^2[H_2O] \end{aligned} \tag{4}$$

The values of $k_2\times10^5\mathrm{M}^{-1}\,\mathrm{sec}^{-1}$, $-k_{3h}\times10^3\mathrm{M}^{-2}\,\mathrm{sec}^{-1}$, $k_{4uh}\times10^2\mathrm{M}^{-3}\,\mathrm{sec}^{-1}$, $-k_{3u}\times10^3\mathrm{M}^{-2}\,\mathrm{sec}^{-1}$, $k_{3c}\times10^3\mathrm{M}^{-2}$

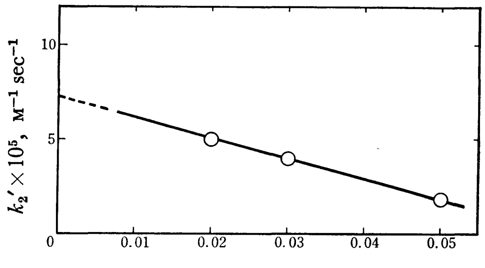

Fig. 5. The plots of k_2' *vs.* the concentration of water for the TED-catalyzed hydrolysis of DPU in dioxane at 90°C.

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3) Cf. T. Tonomura, K. Okamoto, T. Fujishima and H. Yamamura, *Nippon Kagaku Zasshi*, **88**, 707 (1967).

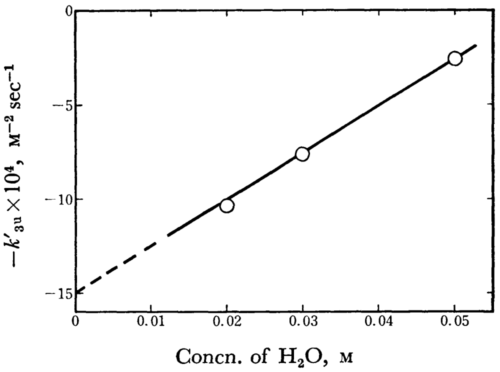


Fig. 6. The plots of $-k'_{3u}$ *vs.* the concentration of water for the TED-catalyzed hydrolysis of DPU in dioxane at 90°C.

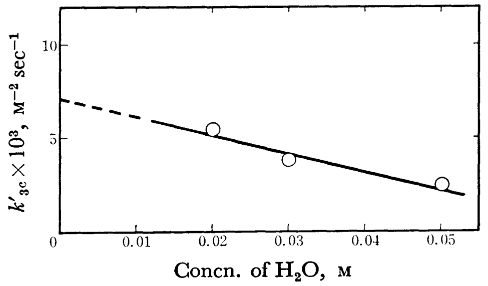


Fig. 7. The plots of k'_{3c} *vs.* the concentration of water for the TED-catalyzed hydrolysis of DPU in dioxane at 90°C.

sec^{-1}, $-k_{4ch}\times10^2$M^{-3} sec^{-1}, k_{5cuh}M^{-4} sec^{-1}, and $-k_{4cu}\times10^{-3}$ sec^{-1} were 7.28, −1.12, 2.49, −1.50, 7.10, −9.82, 2.39, and −1.54 respectively. The values of the rates of steps (5a) and (9) in non-catalyzed reactions and/or of steps (8c) and (10) in the TED-catalyzed hydrolyses are both comparable under these concentration conditions.

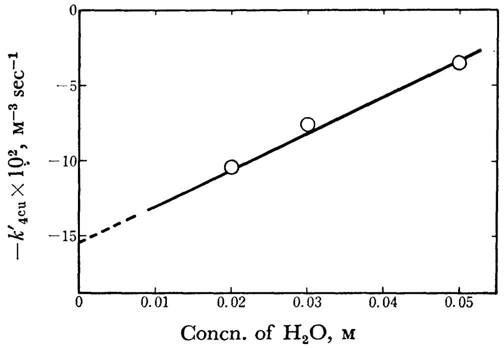
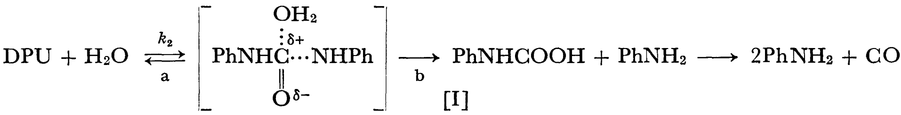


Fig. 8. The plots of $-k'_{4cu}$ *vs.* the concentration of water for the TED-catalyzed hydrolysis of DPU in dioxane at 90°C.

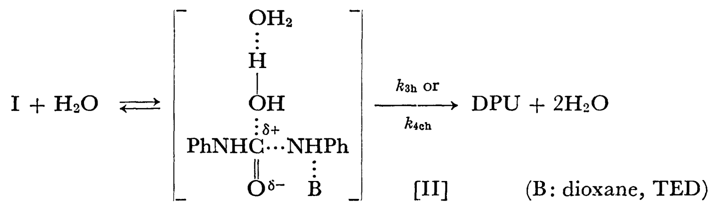
Here, four terms of both the non- and the TED-catalyzed hydrolyses of DPU contain the second-order terms with the concentration of DPU, though each term in the non- and the TED-catalyzed hydrolyses in the presence of *n*-butylamine contains only the first-order term with the concentration of DPU, as has been described in a previous paper.[1] The reasons for this are evident in view of the measurements of the order of the self-association of DPU in dioxanes containing water only and/or containing also *n*-butylamine, as has been described above.

As has been described in a previous paper,[1] the conductivity of the couple (DPU+TED) ($10.87\times10^{-6}\ \Omega^{-1}\ \mathrm{cm}^{-1}$) is larger than the sum of the conductivities of the components ($8.20\times10^{-6}\ \Omega^{-1}\ \mathrm{cm}^{-1}$); in that couple, the existence of quaternary ammonium salt was detected by Wagner's and Dragendorff's reagents.

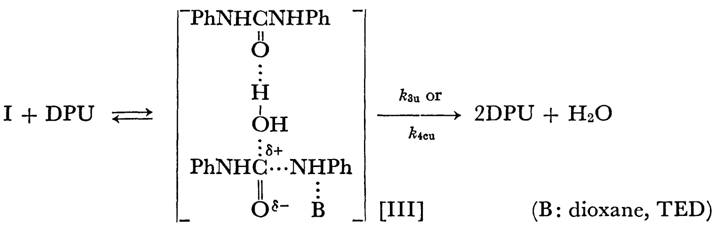
From these findings, the following probable mechanism, one which involves a nucleophilic attack by the lone pairs of the N-atom of TED and the O-atom of water on the carbonyl C-atom of DPU, may be suggested:



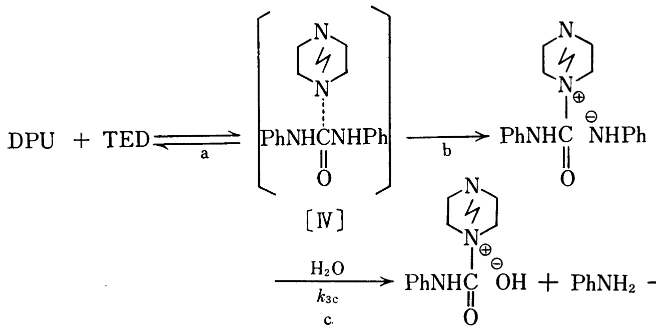
$$\mathrm{DPU + H_2O} \underset{a}{\overset{k_2}{\rightleftarrows}} \left[\begin{array}{c} \mathrm{OH_2}\\ \vdots\,\delta+\\ \mathrm{PhNHC\cdots NHPh}\\ \|\\ \mathrm{O}^{\delta-}\end{array}\right] \underset{[\mathrm{I}]}{\xrightarrow[b]{}} \mathrm{PhNHCOOH + PhNH_2} \longrightarrow \mathrm{2PhNH_2 + CO_2} \tag{5}$$



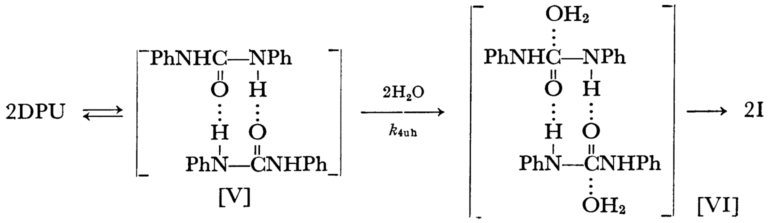
$$\mathrm{I + H_2O} \rightleftarrows \left[\begin{array}{c} \mathrm{OH_2}\\ \vdots\\ \mathrm{H}\\ |\\ \mathrm{OH}\\ \vdots\,\delta+\\ \mathrm{PhNHC\cdots NHPh}\\ \|\quad\ \ \vdots\\ \mathrm{O}^{\delta-}\ \ \mathrm{B}\end{array}\right] \underset{[\mathrm{II}]}{\xrightarrow[k_{4ch}]{k_{3h}\text{ or}}} \mathrm{DPU + 2H_2O} \qquad (\mathrm{B}\text{: dioxane, TED}) \tag{6}$$



$$\mathrm{I + DPU} \rightleftarrows \left[\begin{array}{c} \mathrm{PhNHCNHPh}\\ \|\\ \mathrm{O}\\ \vdots\\ \mathrm{H}\\ |\\ \mathrm{OH}\\ \vdots\,\delta+\\ \mathrm{PhNHC\cdots NHPh}\\ \|\quad\ \ \vdots\\ \mathrm{O}^{\delta-}\ \ \mathrm{B}\end{array}\right] \underset{[\mathrm{III}]}{\xrightarrow[k_{4cu}]{k_{3u}\text{ or}}} \mathrm{2DPU + H_2O} \qquad (\mathrm{B}\text{: dioxane, TED}) \tag{7}$$



(8)



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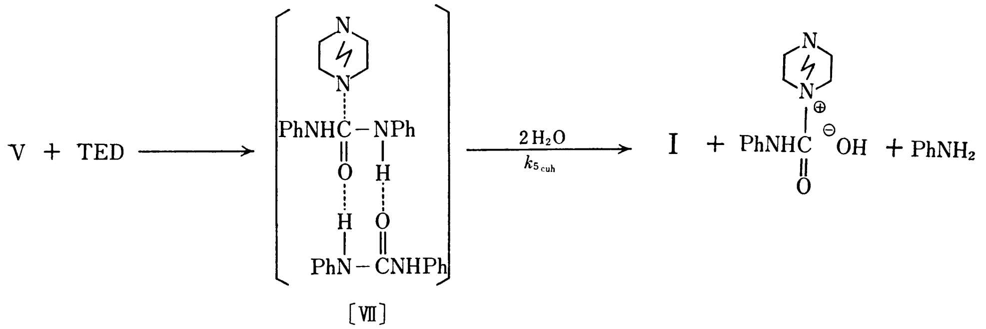

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