On the Thermal Dissociation of Organic Compounds[1]*. XV. Thermal Dissociation of Urethans in the Presence of Aromatic Amines*

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In the previous papers of this series[2,3] it was shown that, in the presence of amines, urethans dissociate into their component compounds via Eqs. 1 and 2.

$$\text{R-NHCOOR}' \rightleftharpoons \text{R-N=C=O} + \text{HO-R}' \quad (1)$$

$$\text{R-N=C=O} + \text{H}_2\text{N-R}'' \rightleftharpoons \text{R-NHCONH-R}'' \quad (2)$$

During the process of dissociation, the nitrogen atom of urethan donates a proton to form an isocyanate, and the oxygen atom accepts a proton to form an alcohol. Therefore, the dissociation reaction involves a double transfer of its protons, namely protonation and deprotonation of urethans by the action of a basic medium.

If Eq. 1 is the rate-determining step of the reactions, the dissociation rate can be followed by measuring the amount of amine remaining at various time intervals. In the case of the dissociation of *N*-phenyl-phenylurethan in the presence of aliphatic amines, such as di-*n*-butyl amine and benzyl amine, the plot for the second order reaction shows a straight line throughout a large portion of the reaction. However, the rate of the dissociation of urethan in weak basic medium, such as anilines, is much slower than in aliphatic amines and shows a tendency of increasing rate as the dissociation proceeds. In this case the rate deviates considerably from the true second-order kinetics.

It seems that the anomalous acceleration of the dissociation is due to the reaction products, urea and phenol. The acceleration of dissociation was therefore examined on the basis of the results obtained from experiments repeated with adding various amounts of urea and phenol in the initial process.

The acceleration of a reaction brought about by the products formed is called "products catalyzed reaction" and in the case of this dissociation, it was found that urea accelerates the dissociation much more than phenol. The products catalyzed reaction found in the thermal dissociation of urethan in aromatic amines makes the mechanism of dissociation of urethan in a weak base more complicated than that in a strong base, such as aliphatic amines.

On the other hand, under the present experimental condition, the dissociation of urethan could not be observed in the absence of anilines, even when urea or phenol is present. And it can be concluded that the coexistence of anilines is a necessary condition for urea or phenol to accelerate the dissociation.

In order to clarify the behavior of urea which accelerate the dissociation, the rates of dissociation of urethans in amine solution in the presence of ureas and analogous compounds, such as amide, were determined. The results can thus be explained by considering the acceptance of a proton by the accelerators from the urethan-amine complex in the transition state and to promote it to dissociate.

Experimental

Procedure.—The experimental procedure was essentially that used in the earlier investigation[2,3]. The amount of amine remaining was determined by titrating with 0.05 N perchloric acid in glacial acetic acid, using Crystal Violet as indicator. The perchloric acid glacial acetic acid solution was prepared according to the method of Markunas[4].

Materials.—*N*-Phenyl-phenylurethan, m. p. 122∼123°C, and *N*-phenyl-*p*-chlorophenyl urethan, m. p. 120∼121°C, were prepared from phenyl isocyanate and the corresponding phenols, and recrystallized from aqueous ethanol.

The physical properties for amines and accelerators are listed in Table I.

Determination of dissociation rate: As described in the introduction, the rates of the dissociation of urethan in the presence of aliphatic amines followed true second-order kinetics. However, the rates of the dissociation in aromatic amines showed anomalous acceleration of the dissociation, as shown in Fig. 1, which might have been caused by the reaction products, urea and phenol. Therfore, the rates of the dissociation, which are the initial

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[1] This investigation was performed at the Gakushuin University.

[2] T. Mukaiyama and M. Iwanami, *J. Am. Chem. Soc.*, 79, 73 (1957).

[3] T. Mukaiyama, T. Akiba and T. Asahi, This Bulletin, 33, 1137 (1960).

[4] P. C. Markunas and J. A. Riddick, *J. Ann. Chem.*, 23, 337 (1951).

TABLE I. BOILING POINTS AND pK_b VALUES FOR AMINES

Amines	B. p., °C/mmHg	pK_b	Amines	B. p., °C/mmHg	pK_b
Aniline	184.4	9.30	*m*-Chloroaniline	230.5	10.40
o-Toluidine	200	9.47	*p*-Chloroaniline	232	12.00
m-Toluidine	203	9.30	*N*-Methylaniline	195.5	9.60
p-Toluidine	200.5	9.70	*N*-Ethylaniline	204	9.38
o-Anisidine	225	9.70	*N*-*n*-Butylaniline	240	
m-Anisidine	250~1		*N*-Benzylaniline	201~3/37	
p-Anisidine	244	8.82			

Melting points and boiling points for accelerators.

$RC_6H_4NHCOOCH_2C_6H_5$ R	M. p. °C
H	78
m-Nitro	115.5~116
p-Nitro	155
p-Methoxy	98.5~ 99
o-Chloro	110
p-Methyl	82.5~ 83
Acetanilide	113~4
Benzsulfoamide	156
Benzamide	130
Phthalimide	238
Diphenylbenzamide	177

	M. p. (b. p.) °C
Diethylbenzamide	(280~2)
Benzanilide	163
Benz-*p*-toluidide	157~8
sym-Diphenylurea	234
Triphenylurea	136
Tetraphenylurea	183
N,*N*-Diphenyl-*N'*,*N'*-diethylurea	41~41.5

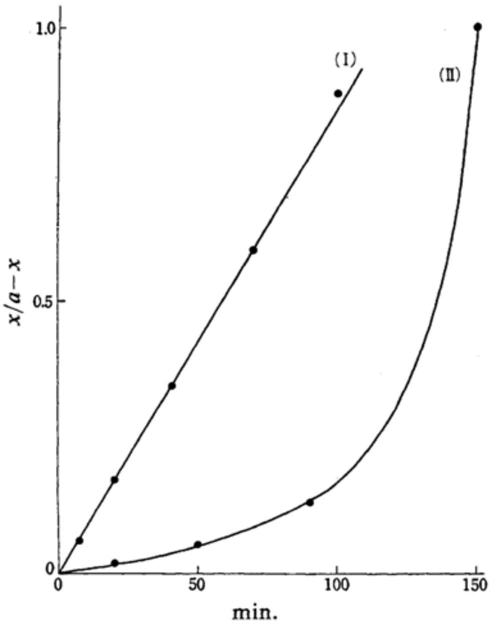

Fig. 1. Second-order plots of the thermal dissociation of *N*-phenyl phenylurethan in di-*n*-butyl amine—nitrobenzene solution at 45°C (I) and that in *p*-chloroaniline—nitrobenzene solution at 165°C (II).

gradiencies, obtained from the titration curve of the residual amine, were measured before appreciable quantities of products, urea and phenol, are formed. The initial rates show substantial variations in their dependence upon the concentration of the amines, or the accelerators, as shown in Tables IV—VI.

Results and Discussion

As reported in earlier papers⁵⁾, the rates of the dissociation of urethan in the presence of amines increased with the basicity of the medium. As shown in Table II, the rates of the dissociation using aliphatic amines are much faster than those with aromatic ones.

TABLE II. THE INITIAL RATES OF THE THERMAL DISSOCIATION OF *N*-PHENYL PHENYLURETHAN IN ALIPHATIC AND AROMATIC AMINES—NITROBENZENE SOLUTION

Amines	°C	Initial rate $V_0\times10^5$ mol./min.
Aniline	165	0.0303
p-Toluidine	165	0.0161
N-Methylaniline	165	0.261
N-Ethylaniline	165	0.381
Diisobutylamine	89	1.25
Cyclohexylamine	89	3.03
n-Hexylamine	89	4.26
2-Ethylhexylamine	89	1.87

The dissociation rates of urethan in the presence of aromatic amines with electron-donating substituents, such as anisidine and *N*-alkyl aniline, are much greater than those

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5) T. Mukaiyama and Y. Hoshino, *J. Am. Chem. Soc.*, **78**, 1756 (1956).

in aromatic amines with electron-withdrawing substituents, such as *m*- and *p*-chloroanilines, as tabulated in Table III.

TABLE III. THE INITIAL RATES OF THE THERMAL DISSOCIATION OF *N*-PHENYL-*m*-CHLOROPHENYL-URETHAN IN AN AMINE—NITROBENZENE SOLUTIONS

Amines	°C	$V_0\times 10^6$ mol./min.
Aniline	145	0.52
o-Anisidine	145	0.91
p-Anisidine	145	1.79
m-Chloroaniline	145	0.05
p-Chloroaniline	165	0.25
o-Toluidine	145	0.208
m-Toluidine	145	0.406
p-Toluidine	145	0.659
N-Methylaniline	145	1.87
N-Ethylaniline	145	2.22
p-Aminophenol	115	6.25
m-Aminophenol	165	2.54

As shown in Fig. 1, an anomalous acceleration of dissociation occurs after about 20% of the urethan dissociated in the presence of aromatic amines. This phenomenon was not observed, when urethan is dissociated in the presence of aliphatic amines, which are stronger bases than aromatic ones. Assuming that the acceleration might be caused by urea and phenol, which are produced during the dissociation, 2.5 equimolecular proportions of *sym*-diphenylurea and phenol were added to the reaction system in advance. Consequently the amount of amines remaining decreased remarkably by the addition of both urea and phenol, as shown in Fig. 2. The acceleration of the reaction aided by the products is generally called " products catalyzed reaction ".

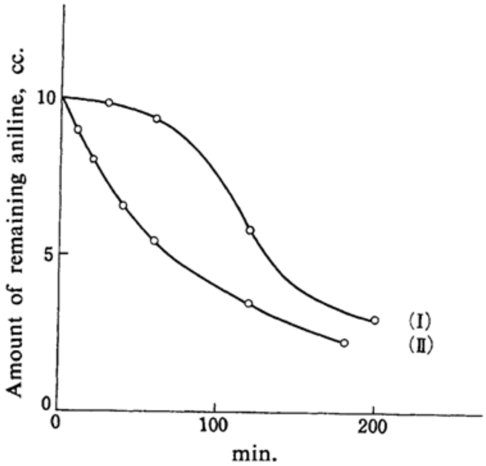

Fig. 2. Catalyzed thermal dissociation of *N*-phenyl *m*-chlorophenyl urethan with additional accelerators in aniline—nitrobenzene solution at 165°C.

	N-Phenyl *m*-chlorophenyl urethan	Aniline	*m*-Chlorophenol	*sym*-Diphenylurea
(I)	1 mol.	1 mol.	0	0
(II)	1 mol.	1 mol.	2.5 mol.	2.5 mol.

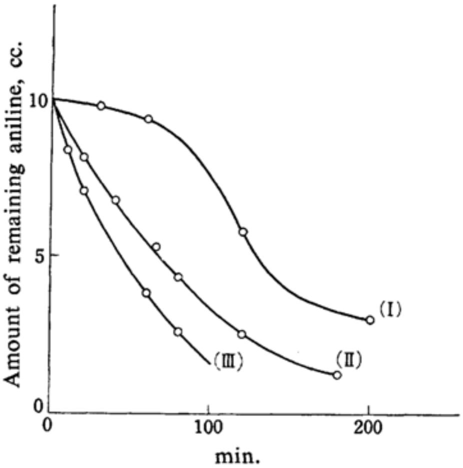

Fig. 3a. Catalyzed thermal dissociation of *N*-phenyl *m*-chlorophenyl urethan with additional accelerator in aniline—nitrobenzene solution at 165°C.

	N-Phenyl *m*-chlorophenyl urethan	Aniline	*sym*-Diphenylurea
(I)	1 mol.	1 mol.	0
(II)	1 mol.	1 mol.	1 mol.
(III)	1 mol.	1 mol.	2 mol.

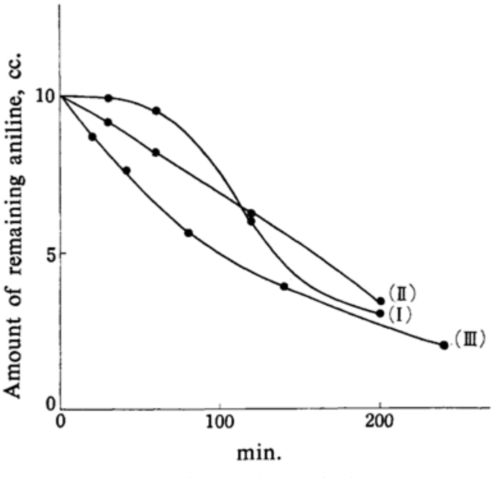

Fig. 3b. Catalyzed thermal dissociation of *N*-phenyl *m*-chlorophenyl urethan with additional accelerator in aniline—nitrobenzene solution at 165°C.

	N-Phenyl *m*-chlorophenyl urethan	Aniline	*m*-Chlorophenol
(I)	1 mol.	1 mol.	0
(II)	1 mol.	1 mol.	0.5 mol.
(III)	1 mol.	1 mol.	1.0 mol.

Similar results are shown by Baker[6] in the addition reaction of isocyanate with alcohol, a reversal of the present type of dissociation.

On the other hand, under the present experimental conditions, the dissociation of urethan could not be observed in the absence of anilines even when urea or phenol is present. It can be concluded that the coexistence of anilines is a necessary condition for urea or phenol to accelerate the dissociation.

In the present experiment, the catalytic activities of products or urea and phenol, adding them individually, were demonstrated by varying molar ratios of urethan, 0.5 to 2.5, as shown in Fig. 3 and Table IV.

TABLE IV. THE INITIAL RATES OF THE CATALYZED DISSOCIATION OF *N*-PHENYL *m*-CHLOROPHENYL URETHAN (1 MOL.) WITH ADDED ACCELERATORS IN AN AMINE (1 MOL.)—NITROBENZENE SOLUTION

$V_0 \times 10^6$ mol./min.

Added accelerators	Mol.	Aniline 165°C	*p*-Chloro aniline 165°C	*p*-Toluidine 145°C
None		0.902	0.24	0.66
m-Chlorophenol	0.5	2.61	1.5	6.3
	1.0	5.42	1.25	3.13
	1.5	1.63	1.5	4.10
	2.0	2.19	1.67	3.58
	2.5		2.40	13.0
sym-diphenylurea	0.5	1.97	0.28	3.57
	1.0	10.38	5.06	4.60
	1.5	14.5	3.16	7.92
	2.0	13.32	13.7	21.4
	2.5	17.65	21.5	22.4
sym-Diphenylurea and *m*-chlorophenol	0.5	6.88	3.2	11.7
	1.0	12.5	3.7	4.73
	1.5	9.07	9.9	24.17
	2.0	9.38	21.0	14.5
	2.5		33.3	35.0

As shown in Table IV, the rate of the catalyzed dissociation is much greater in the presence of urea than of phenol, and it increases concomitantly with increasing concentrations of urea. However, the increase of rate by varying the initial concentration of phenol could be scarcely observed. Therefore, the acceleration of reaction due to the products is caused chiefly by urea. In aromatic amine series, the accelerating action of urea becomes more effective, when a weak base is used. For example, the ratio of the rates in the presence and in the absence of urea in *p*-chloroaniline is 110 : 1, while that in *p*-toluidine, the stronger base, is 40 : 1.

In order to investigate the catalytic activity of ureas, urethans and acid amides, having both an active hydrogen atom and a basic nitrogen atom and exhibiting the same amphoteric character as urea, were used as accelerators.

TABLE V. THE INITIAL RATES OF THE CATALYZED DISSOCIATION OF *N*-PHENYL PHENYLURETHAN WITH ADDED ACCELERATOR IN A *p*-TOLUIDINE —NITROBENZENE SOLUTION

	Urethan	*p*-Toluidine	*m*-Chlorophenol	Accelerator
mol.	1	1	2.5	2.5

Accelerator	°C	$V_0 \times 10^6$ mol./min.
R-$C_6H_4NHCOOCH_2C_6H_5$		
R: H	145	1.43
m-Nitro	145	0.25
p-Nitro	145	1.63
p-Methoxy	145	2.12
p-Chloro	145	2.08
p-Methyl	145	5.16
Acetanilide	165	9.00
Benzenesulfonamide	165	5.9
Benzamide	115	2.72
Phthalimide	145	4.98

The initial rates of dissociation in the presence of these accelerators (Tables IV—VI) represent the relative catalytic activities and the order of the acceleration ability is as follows;

benzamide≫ *sym*-diphenylurea≫ phthalimide
> *N*-phenyl benzyl urethans>acetanilide
> benzenesulfonamide.

From this observation, benzamide and *sym*-diphenylurea appear to have greater activity of acceleration as compared to phthalimide and sulfonamide. It can be shown that sulfonamide and phthalimide, having more acidic hydrogen atoms, are less effective than benzamide and urea.

The thermal dissociation of urethan was carried out in various anilines by adding ureas or benzamides substituted with alkyl or aryl groups for hydrogen atom, in equimolecular proportion, as shown in Table VI. Table VI shows that benzamide and *N*, *N*-diphenyl-*N'*, *N'*-diethylurea possess remarkable catalytic activities, while diphenylbenzamide is hardly effective. Accordingly, the relative order of activity of the accelerators is as follows;

benzamide≫ *N*, *N*-diphenyl-*N'*, *N'*-diethylurea
> *sym*-diphenylurea> triphenylurea
≧tetraphenylurea≧diethylbenzamide
> benz-*p*-toluidide> benzanilide
> diphenylbenzamide≧none

As presented in the above order, benzamide accelerates the reaction very remarkably. The

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[6] J. W. Baker and J. B. Holdsworth, *J. Chem. Soc.*, 1943, 713.

TABLE VIa. THE INITIAL RATES OF THE CATALYZED DISSOCIATION OF *N*-PHENYL *o*-CHLOROPHENYL URETHAN WITH ADDED ACCELERATORS IN AN ANILINE—NITROBENZENE SOLUTION

$V_0 \times 10^5$ mol./min. at 145°C

Accelerators	Anilines							
	Aniline	*p*-Methyl	*p*-Methoxy	*p*-Chloro	*N*-Methyl	*N*-Ethyl	*N*-*n*-Butyl	*N*-Benzyl
None	0.02	0.035	0.12	0.019	0.019	0.110	0.107	0.005
sym-Diphenylurea	0.21	0.681	0.707	0.022	0.711	1.06	0.57	0.078
Triphenylurea	0.213	0.142	0.024	0.025				
Tetraphenylurea	3.43	0.073	0.243	0.018	0.184	7.37	0.326	0.109
N, *N*-Diphenyl-*N'*, *N'*-diethylurea	6.14	0.078	0.922	0.066	1.32			0.306
Benzamide	1.51	2.00	2.07	0.598	1.10	2.11	1.08	0.415
Benzanilide	0.026	0.065	0.128	0.007	1.58	2.00	0.025	0.015
Benz-*p*-toluidide	0.060	0.067	0.245	0.012	0.052	6.84	0.078	0.050
Diphenylbenzamide	0.021	0.063	0.148	0.008	0.039	0.113	0.097	0.012
Diethylbenzamide	0.033	0.130	0.259	0.038	0.148	0.116	0.096	0.020

TABLE VIb. THE INITIAL RATES OF THE CATALYZED DISSOCIATION OF *N*-PHENYL PHENYLURETHAN WITH ADDED ACCELERATORS IN AN ANILINE—NITROBENZENE SOLUTION

$V_0 \times 10^6$ mol./min. at 165°C

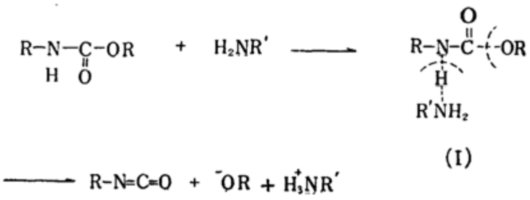
Accelerators	Anilines			
	Aniline	*p*-Methyl	*N*-Methyl	*N*-Ethyl
None	0.303	0.161	2.60	3.81
sym-Diphenylurea	1.59	1.51	3.02	9.17
Benzaniline	0.098	0.232	0.553	0.917
Benz-*p*-toluidide	0.419	0.446	0.473	
Benzamide	7.14	0.758	5.41	9.63
Diphenylbenzamide	0.071	0.589	0.330	10.6
Diethylbenzamide	0.58	0.107	0.91	0.089

order [*N*, *N*-diphenyl-*N'*-*N'*-diethylurea> tetraphenylurea and diethylbenzamide>diphenylbenzamide] indicates that in similar compounds such as urea and benzamide, diethyl derivatives catalyze more strongly than diphenyl derivatives. Furthermore, the order of urea compounds, *N*, *N*-diphenyl-*N'*-*N'*-diethylurea>*sym*-diphenylurea>tetraphenylurea, indicates that the hydrogen atom attached to the nitrogen atom is not effective in accelerating the dissociation, but the character of the nitrogen atom is the responsible factor. It is considered that the ability of a compound to accelerate the dissociation is attributed to the electrical and structural character of nitrogen atom which is capable of receiving a proton.

In view of the above discussion, it has been observed that the rate of dissociation of urethan, including a double transfer of its proton, in a strong basic or acidic medium is faster than that in a weak basic or acidic medium. This indicates that the rate of dissociation is dependent on the acidic or basic strength of the medium. However, the rate of dissociation is enhanced in a medium containing a mixture of weak base and acid, such as aniline and phenol, rather than in a medium containing the individual compounds.

Reaction Mechanism

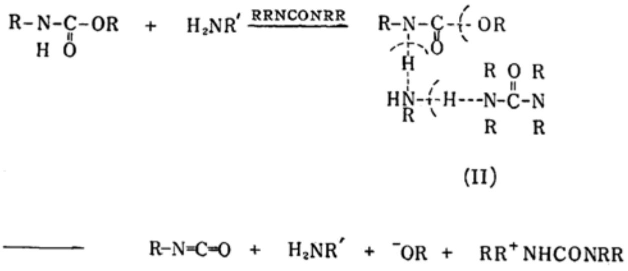
The scheme of the uncatalyzed dissociation of urethan in the presence of an organic base is illustrated as follows;



(I)

In state I, amine behaves as such as to accept a proton which results in the formation of a complex with urethan. State I then dissociates through a shift of a pair of electrons. The catalytic activity of an amine, which assists in the proton transfer of urethan at state I is affected by the basicity of amine as shown in Table II.

The scheme of the dissociation of urethan in an aromatic amine medium in the presence of an accelerator is illustrated as follows;



(II)

$$\longrightarrow R{-}N{=}C{=}O + H_2NR' + {}^{-}OR + RR^{+}NHCONRR$$

In state II, the amine behaves in such a manner as to accept a proton, and the accelerator encourages the deprotonation of the amine to proceed. That is, an accelerator accepts a hydrogen atom from the amine–urethan complex (state II) and induces the amine to take up the hydrogen atom from urethan, hence the dissociation proceeds more readily. Therefore, the accelerator plays an important role in promoting the dissociation of the amine-urethan complex by participating in the proton transfer.

Summary

N-Phenyl phenylurethans dissociate readily into their component compounds in the presence of aliphatic amines and the plot for the second order reaction shows a straight line throughout a large portion of the dissociation. However, the rate of the dissociation of urethans in aromatic amines is much slower than in aliphatic ones and shows a tendency of increasing rate as the dissociation proceeds. The anomalous acceleration of the dissociation is due to the reaction products, urea and phenol.

In order to clarify the behavior of urea which accelerates the dissociation effectively, the rates of the dissociation of urethans in the presence of ureas and analogous compounds, such as urethans and amides, were determined.

The mechanism of the dissociation of urethans in aromatic amines which involve the product catalyzed reaction was discussed.

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