# *On the Thermal Dissociation of Organic Compounds*[1]. *XIV.* *The Effects of the Solvents and of the Substituents on the Thermal Dissociation of Urethans in Amines*

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In previous papers[2,3] of this series the kinetic studies of the dissociation of *N*-phenyl-alkyl carbamates in basic solvents were described. *N*-phenyl-alkyl carbamates dissociate in the presence of 10 molar excess of an amine at above 120°C; however, *N*-phenyl-phenyl carbamates dissociate instantly under the same condition.

In the case of *N*-phenyl-phenyl carbamates, the addition reaction of isocyanates with phenols to form urethans, which is the reversal of the dissociations, reaction do not proceed under the experimental conditions. Therefore, the dissociation proceeds to essentially 100% completion in the presence of an equimolar amount of an amine.

$$\mathrm{RHNCOOR} \rightleftharpoons \mathrm{R{-}N{=}C{=}O + HO{-}R} \qquad (1)$$

$$\mathrm{R{-}N{=}C{=}O + HNR'R'} \rightleftharpoons \mathrm{RHNCONR'R'} \qquad (2)$$

As described in the previous papers, reaction 1 is the rate-determining step in the above

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

[2] T. Mukaiyama and Y. Hoshino, *J. Am. Chem. Soc.*, **78**, 1946 (1956).

[3] T. Mukaiyama and M. Iwanami, ibid., **79**, 73 (1957).

sequence and the rate constants for the dissociation of urethans can be measured by determining the amount of the remaining amine.

The kinetic order of the dissociation of urethans was studied by the effect of change of initial concentration of both urethan and amine and it was shown that the dissociation is of the first order with respect to urethan and to amine respectively.

In order to study the effects of amines and solvents on the rate of dissociation of urethans, eight amines such as di-*n*-butyl amine and benzyl amine and ten inert solvents such as nitrobenzene and cumene were used. It was observed that the rates of the dissociation increased as the base strength of amines increased and the rates increased also as the dielectric properties of solvents increased.

The rates of dissociation of *N*-phenyl-phenyl carbamates substituted with methyl, methoxyl, chloro and nitro groups in the ortho, meta and para positions were determined to clarify the effects of substituents on the dissociation of urethans in amines. The results show that meta and para substituted *N*-phenyl-tolyl carbamates, N-phenyl-anisyl carbamates and unsubstituted urethans follow the Hammett equation with a positive $\rho$ value, but *N*-phenyl-chlorophenyl carbamates and *N*-phenyl-nitrophenyl carbamates dissociate rapidly and deviate from the linear relationship of the Hammett equation. Except in the case of the methyl derivative, ortho-substituted urethans dissociate faster than the corresponding meta and para substituted urethans; this may be attributed to steric effects.

TABLE I. MELTING POINTS AND ANALYSES FOR $C_6H_5NHCOOC_6H_4R$

| R | M. p. °C | Nitrogen, % | |
|---|---|---|---|
| | | Calcd. | Found |
| *o*-Methoxy | 151~152 (136)[a] | 5.71 | 5.94 |
| *m*-Methoxy | 119 | 5.71 | 5.93 |
| *p*-Methoxy | 133 | 5.71 | 5.83 |
| *o*-Methyl | 143 (144)[b] | | |
| *m*-Methyl | 123~123.5 (125)[b] | | |
| *p*-Methyl | 114~115 (115)[b] | | |
| H | 126 (124)[c] | | |
| *o*-Chloro | 122~122.5 (120~121)[d] | | |
| *m*-Chloro | 124~125 | 5.65 | 5.95 |
| *p*-Chloro | 140~141 (138)[e] | | |
| *m*-Nitro | 129~129.5 (129)[f] | | |
| *p*-Nitro | 145~146 (147~148)[g] | | |

a) A. Morel, *Bull. soc. chim. France*, (3) **21**, 827 (1899).
b) E. Fromm and H. Eckhard, *Ber.*, **56**, 953 (1923).
c) R. Leuckart, *J. prakt. Chem.*, (2) **41**, 318 (1890).
d) A. Michael and P. Cobb, *Ann.*, **363**, 92 (1908).
e) A. Hantzsch and L. Mai, *Ber.*, **28**, 979(1895).
f) O. Brady and J. Harris, *J. Chem. Soc.*, **127**, 2176 (1925).
g) M. Busch, G. Blume and E. Pungs, *J. prakt. Chem.*, [2] **79**, 534 (1909).

It can be concluded that, in amine, the dissociation proceeds via the concerted mechanism involving both urethan and amine.

## Experimental

**Procedure.** — The experimental procedure was essentially that used in the earlier investigation[2,3]. The amount of the amine remaining was determined by titrating with 0.025 N hydrochloric acid, using Bromocresol Green as indicator.

**Materials.** — N-phenyl-phenly carbamates were prepared from phenyl isocyanate and the purified corresponding phenols according to the procedure of Leuckart[4]. Amines and solvents were purified by distillation. The boiling points for these substances are listed in Table I and II.

TABLE II

| Amines | B. p. °C/mmHg | Solvents | B. p. °C/mmHg |
|---|---|---|---|
| Di-benzyl | 187/18 | Anisole | 153~154 |
| Benzyl | 89~90/12 | Tetralin | 92/18 |
| Cyclohexyl | 130.5~131 | Decarlin | 192 |
| Di-isobutyl | 139 | Nitrobenzene | 93/11 |
| 2-Ethylhexyl | 165~165.5 | Phenetole | 167~168 |
| Di-*n*-butyl | 158~159 | Triethyl-benzene | 104~155/20 |
| Lauryl | 133~134/15 | Cumene | 150~151 |
| *n*-Hexyl | 129 | Cymene | 174~176 |
| | | *o*-Xylene | 141.5~142 |
| | | *p*-Xylene | 137.5 |

## Results

The second order rate constant $k_2$ was calculated by Eq. 3

$$k_2=1/t\cdot x/a\ (a-x) \tag{3}$$

where $t$, the time in second; $x$, the amount of reacted amine at time $t$; $a$, the initial concentration of both urethan and amine.

The values of the second order coefficient $k_2$ remained constant until the 60% of the dissociation with a tendency to drift upward in the later stage of the dissociation. It can be considered that the upward drift of $k_2$ might result from weak catalysis of the dissociation by urea or phenol produced. This was confirmed by the demonstration of the catalytic effect of added urea. The results are shown in Table III and Fig. 1. The addition of phenol to the reaction showed no effect on the rate of dissociation.

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[4] R. Leuckart, *J. prakt. Chem.*, [2] **41**, 318 (1890).

TABLE III. CATALYTIC EFFECT OF ADDED 1-PHENYL-3,3-DIBENZYLUREA ON THE DISSOCIATION OF *N*-PHENYL-PHENYL CARBAMATE IN BENZYL AMINE, BOTH 0.0535 mol./l. IN NITROBENZENE SOLVENT AT 94°C

| Urethan mol. | Urea mol. | $k_2\times10^3$ l. mol$^{-1}$ sec$^{-1}$ |
|---|---|---|
| 1 | 0 | 2.20 |
| 1 | 1 | 2.85 |
| 1 | 2 | 3.40 |

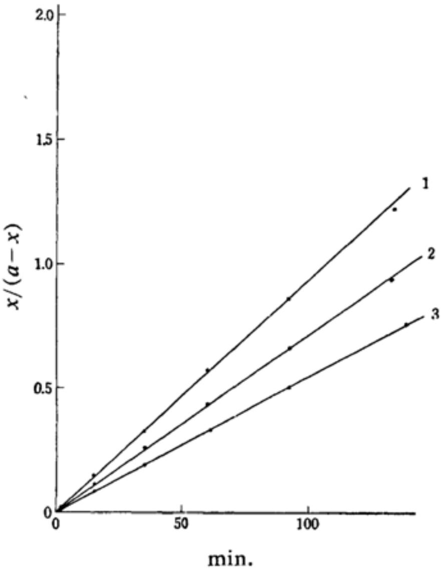


Fig. 1. Second-order plots of the thermal dissociation of *N*-phenyl-phenyl carbamate in benzyl amine and nitrobenzene in the presence or absence of 1-phenyl-3,3-dibenzylurea at 94°C.

| | Urethan, mol. | Urea, mol. |
|---|---|---|
| 1) | 1 | 2 |
| 2) | 1 | 1 |
| 3) | 1 | 0 |

The kinetic order of the dissociation of urethans in amines were examined further by changing the initial concentration of both the urethan and the amine. The second order rate constants are nearly constant when the initial concentration of the reactants are changed from 1/2 : 1/2 to 2 : 2. When the molar ratio of the initial concentration of urethan to amine are changed from 1 : 1 to 1 : 10, the rates of dissociation increase as the amine concentration increases. When the molar ratio of urethan to amine is less than 2.5, the rate did not conform to the second order kinetics, but a first order plot fits the data well. The $k_2$ values calculated by dividing the $k_1$ value thus obtained by the concentration of the amine are nearly equal as shown in Table IV.

TABLE IV. EFFECT OF VARIATION OF THE RELATIVE CONCENTRATION OF *N*-PHENYL-PHENYL CARBAMATE AND DI-*n*-BUTYL AMINE, BOTH 0.0535 mol./l. IN NITROBENZENE SOLVENT AT 25°C AND 45°C

| Temp. °C | Urethan mol. | Amine mol. | $k_1\times10^6$ sec$^{-1}$ | $k_2\times10^4$ l. mol$^{-1}$ sec$^{-1}$ |
|---|---|---|---|---|
| 25 | 1 | 1 | | 5.93 |
| | 2 | 2 | | 6.80 |
| | 1 | 2.5 | 8.24 | 6.16 |
| | 1 | 5 | 16.3 | 6.09 |
| | 1 | 7.5 | 23.5 | 5.85 |
| | 1 | 10 | 27.4 | 5.12 |
| 45 | 1/2 | 1/2 | | 31.2 |
| | 1 | 1 | | 27.0 |
| | 2 | 2 | | 35.6 |

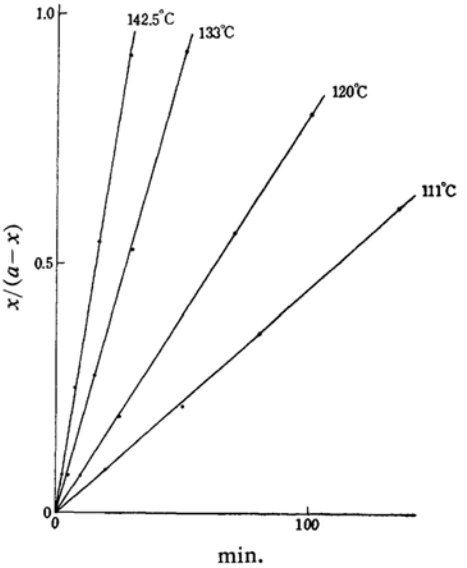


Fig. 2. Second-order plots of the thermal dissociation of N-phenyl-phenyl carbamate in dibenzyl amine and nitrobenzene.

The second order rate constants of various substituted urethans in amines and various inert solvents were obtained. As a typical run, the dissociation of *N*-phenyl-phenyl carbamate in dibenzyl amine and nitrobenzene at temperature betewen 111∼142.5°C is shown in Fig. 2. The rate constants of the dissociation of *N*-phenyl-phenyl carbamates in amines were calculated by the method of least squares and are shown in Tables V—VII.

The plot of the logarithm of the rate constants vs. reciprocal absolute temperature gave satisfactory straight lines from which the activation energies and the entropies of activation were calculated by the method of least squares (Tables V—VII).

TABLE V. THE RATE CONSTANTS AND THE THERMODYNAMIC QUANTITIES FOR THE DISSOCIATION OF *N*-PHENYL-PHENYL CARBAMATE AND VARIOUS AMINES, BOTH 0.0535 mol./l. IN NITROBENZENE SOLVENT

| Amines | Temp. °C | $k_2 \times 10^3$ l. mol$^{-1}$ sec$^{-1}$ | $E$ kcal. | $\Delta S^{\ddagger}$ e. u. |
|---|---|---|---|---|
| Dibenzyl | 111 | 1.45 ±0.01 | 21.0±0.2 | −17.3±1.2 |
| | 120 | 2.52 ±0.02 | | |
| | 133 | 5.89 ±0.09 | | |
| | 142.5 | 11.2 ±0.03 | | |
| Benzyl | 94 | 2.21 ±0.03 | 19.2±0.4 | −18.6±2.5 |
| | 103 | 4.33 ±0.11 | | |
| | 113 | 8.04 ±0.00 | | |
| | 133 | 23.7 ±0.09 | | |
| *n*-Hexyl | 61 | 2.83 ±0.07 | 13.8±0.08 | −29.5±0.5 |
| | 70 | 5.08 ±0.01 | | |
| | 80 | 8.61 ±0.05 | | |
| | 89 | 14.3 ±0.13 | | |
| Cyclohexyl | 61 | 1.99 ±0.04 | 15.3±0.45 | −25.4±2.5 |
| | 70 | 3.53 ±0.01 | | |
| | 80 | 6.28 ±0.06 | | |
| | 89 | 12.1 ±0.09 | | |
| 2-Ethylhexyl | 61 | 1.37 ±0.03 | 15.2±0.16 | −26.6±0.9 |
| | 70 | 2.28 ±0.02 | | |
| | 80 | 4.30 ±0.06 | | |
| | 89 | 7.36 ±0.09 | | |
| Di-isobutyl | 61 | 1.05 ±0.00 | 15.6±0.33 | −25.6±1.9 |
| | 70 | 2.06 ±0.00 | | |
| | 80 | 4.04 ±0.02 | | |
| | 89 | 6.86 ±0.05 | | |
| Lauryl | 35 | 0.611±0.00 | 14.6±0.7 | −26.2±4.0 |
| | 45 | 1.05 ±0.08 | | |
| | 55 | 2.92 ±0.00 | | |
| | 80 | 12.2 ±0.00 | | |
| Di-*n*-butyl | 25 | 0.593±0.00 | 15.1±0.3 | −20.6±1.4 |
| | 35 | 1.36 ±0.00 | | |
| | 45 | 2.73 ±0.00 | | |
| | 60 | 8.75 ±0.00 | | |

## Discussion

The rate constants of the dissociation of urethans in various amines increase in the following order,

di-*n*-butyl ≫ lauryl > *n*-hexyl,
cyclohexyl > 2-ethylhexyl,
di-isobutyl > benzyl ≫ dibenzyl.

As noted in the above sequence, urethans dissociate rapidly in di-*n*-butyl amine ($K_b = 2.05 \times 10^3$, at 25°C), moderately in cyclohexyl amine ($K_b = 4.39 \times 10^4$, at 25°C) and slowly in benzyl amine ($K_b = 2.4 \times 10^5$, at 25°C).

The activation energies of the dissociation of urethans in weak bases such as benzyl amine and dibenzyl amine are greater than those in strong bases such as di-*n*-butyl amine.

The results show that, in amines the rates of dissociation increase as the basicities of the amines increase and it can be concluded that the dissociation proceeds via the base catalyzed mechanism in which the process of deprotonation of urethans by a base is a predominant factor.

The rates of dissociation are also affected by the nature of inert solvents. The rate constant of dissociation in a polar solvent such as nitrobenzene is much larger than that in a non-polar solvent such as tetralin and *m*-xylene. As shown in the following sequence, the rates increase as the dielectric properties of solvent increase.

Nitrobenzene ≫ anisole, phenetole >
tetralin, decalin, *o*-xylene, cumene,
triethylbenzene, *m*-xylene, cymene

The results suggest an important solvent interaction in the dissociation process which may stabilize the forming phenoxyl ion and facilitate the cleavage of the carbon-oxygen bond in the activated state.

The results of the rate measurement given in Table VII show that for substitution in the *meta* and *para* position, the greater the electron-attracting power of the substituents, the greater

TABLE VI. THE RATE CONSTANTS AND THE THERMODYNAMIC QUANTITIES FOR THE DISSOCIATION OF *N*-PHENYL-PHENYL CARBAMATE AND DI-*n*-BUTYL AMINE, BOTH 0.0535 mol./l. IN VARIOUS SOLVENTS

| Solvent | Temp. °C | $k_2 \times 10^3$ l. mol$^{-1}$ sec$^{-1}$ | $E$ kcal. | $\Delta S^{\neq}$ e. u. |
|---|---|---|---|---|
| Decalin | 70 | 0.767±0.06 | 14.6±0.5 | −30.5±2.61 |
| | 80 | 1.30 ±0.01 | | |
| | 90 | 1.86 ±0.02 | | |
| | 100 | 4.24 ±0.01 | | |
| Tetralin | 70 | 0.900±0.00 | 15.2±0.1 | −28.5±0.53 |
| | 80 | 1.67 ±0.01 | | |
| | 90 | 3.06 ±0.76 | | |
| | 100 | 5.85 ±0.03 | | |
| Anisole | 70 | 1.96 ±0.01 | 15.0±0.5 | −27.6±2.95 |
| | 80 | 3.27 ±0.00 | | |
| | 90 | 6.01 ±0.00 | | |
| | 100 | 11.4 ±0.27 | | |
| Nitrobenzene | 25 | 0.593±0.00 | 15.1±0.25 | −20.6±1.4 |
| | 45 | 1.36 ±0.00 | | |
| | 60 | 2.73 ±0.00 | | |
| | 80 | 8.75 ±0.00 | | |
| Cumene | 80 | 1.31 ±0.06 | 17.4±1.6 | −22.6±8.8 |
| | 90 | 2.61 ±0.01 | | |
| | 100 | 5.09 ±0.00 | | |
| | 110 | 8.88 ±0.24 | | |
| Cymene | 80 | 1.01 ±0.01 | 17.3±0.3 | −23.5±1.0 |
| | 90 | 2.03 ±0.00 | | |
| | 100 | 3.93 ±0.06 | | |
| | 110 | 7.09 ±0.02 | | |
| Phenetole | 80 | 2.09 ±0.00 | 19.0±0.2 | −17.3±1.1 |
| | 90 | 4.28 ±0.02 | | |
| | 100 | 9.45 ±0.12 | | |
| | 110 | 17.3 ±0.27 | | |
| Triethylbenzene | 80 | 1.24 ±0.02 | 17.1±0.1 | −23.7±0.3 |
| | 90 | 2.45 ±0.02 | | |
| | 100 | 4.60 ±0.16 | | |
| | 110 | 8.42 ±0.19 | | |
| *o*-Xylene | 80 | 1.34 ±0.01 | 16.7±0.3 | −24.7±0.5 |
| | 90 | 2.62 ±0.04 | | |
| | 100 | 4.81 ±0.07 | | |
| | 110 | 8.36 ±0.12 | | |
| *m*-Xylene | 80 | 1.13 ±0.01 | 17.2±0.7 | −23.6±1.9 |
| | 90 | 2.17 ±0.02 | | |
| | 110 | 7.71 ±0.07 | | |

are the rate constants and the lower the activation energy; the greater the electron-donating power of the substituents, the lower are the rate constants and the greater the activation energy. The logarithm of the $k$ of the dissociation of methyl and methoxy substituted urethans and unsubstituted urethan is a linear function of the substituent constants given by Hammett and the gradient of the plot gave values for the reaction constant, $\rho$, of 1.72 in di-*n*-butyl amine and of 1.90 in benzyl amine, respectively. *N*-phenyl-chlorophenyl carbamate and *N*-phenyl-nitrophenyl carbamate dissociate very rapidly and deviate from the linear relationship of the Hammett equation.

The rates of dissociation of various substituted urethans in di-*n*-butyl amine are greater than those in benzyl amine and the activation energies and the entropies of activation in di-*n*-butyl amine are lower than those in benzyl amine. As mentioned above, the rates of dissociation depend on the basic strength of amine and the results might be attributed to the basicity of the amines which participate in the deprotonation of urethans in the dissociation process.

The higher rates with lower activation energies for the dissociation of urethans with electron-attracting substituents such as chloro and nitro groups may be ascribed to the stability of the phenoxyl ion dissociated. The phenoxyl ion with electron-attracting groups is

TABLE VII. THE RATE CONSTANTS AND THE THERMODYNAMIC QUANTITIES FOR THE DISSOCIATION OF *N*-PHENYL-PHENYL CARBAMATES AND AMINES, BOTH 0.044 mol./l. IN NITROBENZENE SOLVENT

a) In di-*n*-butyl amine:

| Substituents | Temp. °C | $k_2 \times 10^3$ l. mol$^{-1}$ sec$^{-1}$ | $E$ kcal. | $\Delta S^{\neq}$ e. u. |
|---|---|---|---|---|
| *o*-Methyl | 60 | 1.50 ±0.13 | 16.6±0.4 | −21.5±2.7 |
| | 70 | 3.48 ±0.18 | | |
| | 80 | 6.26 ±0.21 | | |
| | 90 | 12.2 ±0.53 | | |
| *m*-Methyl | 50 | 2.07 ±0.20 | 16.4±0.3 | −20.2±1.8 |
| | 60 | 3.48 ±0.17 | | |
| | 70 | 8.07 ±0.24 | | |
| | 80 | 17.7 ±0.00 | | |
| *p*-Methyl | 60 | 2.64 ±0.01 | 16.2±0.1 | −23.2±0.4 |
| | 70 | 6.42 ±0.13 | | |
| | 80 | 10.6 ±0.29 | | |
| | 90 | 20.1 ±0.92 | | |
| *o*-Methoxy | 40 | 5.27 ±0.14 | 13.1±0.2 | −21.1±1.1 |
| | 50 | 10.64 ±0.00 | | |
| | 60 | 19.3 ±0.51 | | |
| *m*-Methoxy | 70 | 1.95 ±0.20 | 15.8±0.2 | −20.3±1.4 |
| | 80 | 4.1 ±0.96 | | |
| | 90 | 6.76 ±0.43 | | |
| | 100 | 12.4 ±0.12 | | |
| *p*-Methoxy | 60 | 1.90 ±0.00 | 14.5±0.0 | −27.4±0.2 |
| | 70 | 3.60 ±0.15 | | |
| | 80 | 7.51 ±0.26 | | |
| | 90 | 11.65 ±0.28 | | |
| *o*-Chloro | 0 | 3.62 ±0.27 | 11.6±0.0 | −26.4±0.1 |
| | 15 | 17.8 ±1.3 | | |
| | 25 | 36.1 ±0.0 | | |
| | 35 | 66.0 ±0.22 | | |
| *m*-Chloro | 0 | 1.47 ±0.02 | 12.4±0.3 | −26.1±1.6 |
| | 15 | 4.50 ±0.82 | | |
| | 25 | 12.8 ±0.82 | | |
| | 35 | 19.6 ±0.02 | | |
| *p*-Chloro | 0 | 0.455±0.01 | 13.3±0.2 | −25.2±1.4 |
| | 15 | 1.02 ±0.08 | | |
| | 25 | 3.37 ±0.00 | | |
| | 35 | 7.45 ±0.07 | | |
| *m*-Nitro | | fast | | |
| *p*-Nitro | | very fast | | |

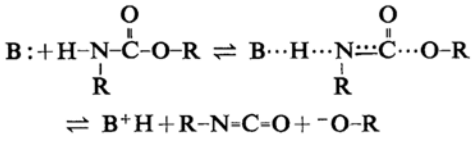
b) In benzyl amine:

| | | | | |
|---|---|---|---|---|
| *o*-Methyl | 110 | 2.40 ±0.32 | 21.4±0.91 | −15.4±4.5 |
| | 120 | 5.10 ±0.14 | | |
| | 140 | 21.5 ±1.03 | | |
| *m*-Methyl | 110 | 4.33 ±0.03 | 17.1±0.3 | −25.3±1.6 |
| | 120 | 7.97 ±0.02 | | |
| | 130 | 12.9 ±0.00 | | |
| | 140 | 22.7 ±0.01 | | |
| *p*-Methyl | 110 | 2.56 ±0.01 | 17.7±0.6 | −24.7±0.0 |
| | 120 | 4.20 ±0.02 | | |
| | 130 | 8.39 ±0.00 | | |
| | 140 | 13.2 ±0.02 | | |
| *o*-Methoxy | 100 | 8.70 ±0.06 | 19.1±1.4 | −15.5±7.2 |
| | 110 | 14.9 ±0.71 | | |
| | 120 | 37.5 ±0.85 | | |
| | 130 | 55.2 ±0.50 | | |

TABLE VII (continued)

| Substituents | Temp. °C | $k_2\times10^3$ l. mol$^{-1}$ sec$^{-1}$ | $E$ kcal. | $\Delta S^{\ddagger}$ e. u. |
|---|---|---|---|---|
| *m*-Methoxy | 100 | 7.3 ±0.64 | 16.8±0.5 | −24.2±2.3 |
| | 110 | 11.0 ±0.29 | | |
| | 120 | 18.5 ±0.65 | | |
| *p*-Methoxy | 110 | 2.72 ±0.17 | 20.7±0.7 | −16.8±3.8 |
| | 120 | 4.73 ±0.36 | | |
| | 130 | 9.60 ±0.28 | | |
| *o*-Chloro | 50 | 5.43 ±0.07 | 14.0±1.3 | −24.7±6.7 |
| | 60 | 12.7 ±0.41 | | |
| | 70 | 21.8 ±1.31 | | |
| | 80 | 49.8 ±0.98 | | |
| *m*-Chloro | 60 | 7.67 ±0.00 | 15.3±0.0 | −22.6±0.2 |
| | 70 | 15.2 ±0.00 | | |
| | 80 | 28.5 ±0.03 | | |
| | 90 | 71.9 ±1.11 | | |

more stable than that with electron-donating groups and this ion stabilizing effect may be the chemical driving force in the following dissociation mechanism.



$$B:+H-\underset{\displaystyle R}{\underset{|}{N}}-\overset{\displaystyle O}{\overset{\|}{C}}-O-R \rightleftharpoons B\cdots H\cdots\underset{\displaystyle R}{\underset{|}{N}}\overset{\cdots}{=}\overset{\displaystyle O}{\overset{\|}{C}}\cdots O-R$$

$$\rightleftharpoons B^{+}H+R-N=C=O+{}^{-}O-R$$

The above one step mechanism involving urethan and amine can be confirmed by the rate dependency on both factors. In the strong bases, such as aliphatic amines, the dissociation proceeds by bimolecular concerted mechanism and not by termolecular mechanism as proposed in the previous reports[2,3].

## Summary

*N*-phenyl-phenyl carbamates dissociate into their component compounds very readily in the presence of a base. Unlike the case of *N*-phenyl-alkyl carbamates, *N*-phenyl-phenyl carbamates dissociate in the presence of an equimolar amount of an amine at lower temperature. The kinetics of the dissociation of *N*-phenyl-phenyl carbamates were of the first order with respect to carbamates and of the first order with respect to base.

The rate constants, the activation energies and the entropies of activation of the dissociation of *N*-phenyl-phenyl carbamates in various amines and solvents were measured throughout temperature interval 0～140°C.

The effects of amines, solvents and substituents on the dissociation of urethans in amines were studied.

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