On the Thermal Dissociation of Organic Compounds. II. The Dissociation of the Urea Linkage in Sym-dimethylurea, Asym-dimethylurea and Asym-phenylethylurea in Butyric Acid

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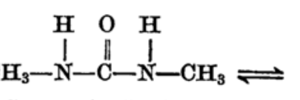
Introduction

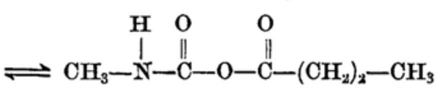
The results of measurements of the rate constants and the activation energy of the thermal dissociation of aryl urea have already been shown in the preceeding report.⑴ Then we tried to determine the same constants in alkyl urea.

On heating, alkyl urea dissociates to isocyanate and amine by the same mechanism as in sym-diphenylurea which was shown in the preceeding report. The dissociated isocyanate reacts instantaneously with butyric acid which was used as solvent and forms carbaminic acid-butyric acid-anhydride and then easily decomposes to butyrated amine and carbon dioxide.

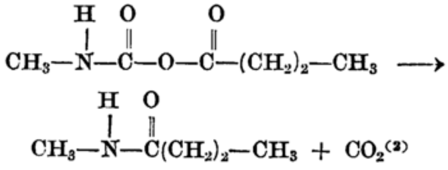
The thermal dissociation of sym-dimethylurea in butyric acid involves the following reactions:

(1)


$$CH_3-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-CH_3 \rightleftharpoons CH_3-N{=}C{=}O + CH_3-NH_2$$

(2)


$$CH_3-N{=}C{=}O + CH_3-(CH_2)_2-COOH \rightleftharpoons CH_3-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-(CH_2)_2-CH_3$$

(3)


$$CH_3-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-(CH_2)_2-CH_3 \longrightarrow CH_3-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}(CH_2)_2-CH_3 + CO_2{}^{(2)}$$

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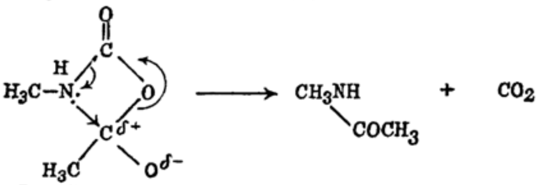
(1) T. Hoshino, T. Mukaiyama and H. Hoshino, *J. Am. Chem. Soc.*, **74**, 3097 (1952).

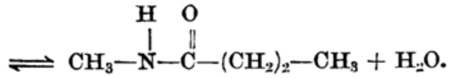
(2) The mechanism of process (3) can be considered as follows;. Conceivably it will proceed by way of an intramolecular nucleophilic displacement as sketched below. The use of isotropic carbon should be serviceable to demonstrate that the carbon dioxide which was evolved originated from the urea molecule.



Recently, as we have assumed on the mechanism of the decarboxylation of anhydride of carbamic and fatty acids, it was proved(2)′ by using C13 atom that carbon dioxide which was evolved originated from the urea molecule.

(2)′ H. R. V. Arnstein and Ronald Bentley, *J. Chem. Soc.*, **1951**, 3509.

(4) $CH_3-NH_2 + CH_3-(CH_2)_2-COOH$



$$\rightleftharpoons CH_3-\overset{\overset{\displaystyle H}{|}}{N}-\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_2-CH_3 + H_2O.$$

If reaction (1) is rate-determining, the rate of dissociation becomes measurable if one determines the amount of carbon dioxide evolved according to (3).

Unlike the case of sym-diphenylurea described in the previous report, sym-dimethylurea could not be dissociated in acetic acid even at the boiling point (118°C), so butyric acid was adopted as the solvent and the reaction was carried above 130°C·

Asym-dimethylurea and asym-phenylethylurea dissociate, respectively, to dimethylamine and isocyanic acid, phenylethylamin and isocyanic acid in acetic acid. It was found that the reactions are similar to the case of sym-diphenylurea in acetic acid as shown in the first report. The dissociation reaction and the reaction of isocyanic acid with acetic acid proceed at comparable rate.

The rate constants and the activation energy of thermal dissociation in butyric acid were deremined.

Experimental Part

A 35 ml. long-necked, round-bottomed flask was connected to a gas buret by means of a capillary tube. Halfway along the capillary tube, a 10 ml. bulb was inserted which was maintained at 0°C. to condense reaction products less volatile than carbon dioxide. The reaction vessel was maintained at a desired, constant temperature by immersion into the vapors above a suitable boiling liquid contained in a three-necked flask equipped with condenser and thermometer; the reaction vessel was inserted in the centre neck of the flask. Vapors of the following liquid were used as heating agents: water, isoamylalcohol, xylene and anisole. The liquid was distilled prior to each run; during the course of an experiment (one to two hours) the temperature remained satisfactorily constant as long as the atmospheric pressure did not fluctuate.

Sym-dimethylurea (m. p. 108.5°C.), asym-dimethylurea (m. p. 181.0°C.) and asym-phenylethylurea (m. p. 60∼61°C.) were used. Acetic acid was distilled after prolonged boiling with acetic anhydride. Butyric acid was carefully purified by vacuum distillation.

The ratio of urea to fatty acid was 1 mole: 100 moles.

To compute the rate constant of the reaction of the thermal dissociation of urea, we have used the following treatment. The first order rate law can be expressed as

$$Y=A(1-e^{-kt}), \qquad (1)$$

in which A is initial concentration of urea and Y is the amount of dissociated urea at any time. Therefore

$$\ln \varDelta Y=[\ln A+\ln(1-e^{-k\varDelta t})]-kt. \qquad (2)$$

As $[\ln A+\ln(1-e^{-k\varDelta t})]$ is considered as independent term with respect to t, equation (2) can be expressed as follows;

$$\ln \varDelta Y=\text{Constant}-kt$$

For the reaction of the first order, it requires the plot of $\ln \varDelta Y$ against t to be a straight line. The rate constant is given by the gradient of the $t-\ln \varDelta Y$ diagram shown in the Fig. 1, 3, and 5. For example, the experiment gave the following results. (Table 1, 2 and 3) Thermal dissociation of sym-dimethylurea in butyric acid.

Table 1

Sym-dimethylurea in Butyric Acid at 409.0°K.'
Calculated with the Value of $\varDelta t=60$ min.

time (min.)	CO_2 evolved(cc.)	time (min.)	CO_2 evolved(cc.)	$\varDelta Y$
10	4.2	70	24.0	19.8
15	6.1	75	25.3	19.2
20	8.1	80	26.7	18.6
25	9.9	85	27.9	18.0
30	11.6	90	29.3	17.7
35	13.3	95	30.5	17.2
40	15.0	100	31.7	16.7
45	16.6	105	32.9	16.3
50	18.2	110	34.0	15.8
55	19.7	115	35.0	15.3
60	21.2	120	36.1	14.9
65	22.6	125	37.2	14.6

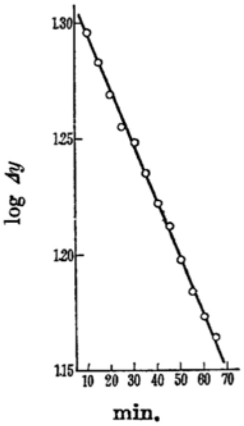


Fig. 1.—The plot of t against $\log \varDelta Y$. Sym-dimethylurea in butyric acid at 409.0°K.

First order kinetics with respect to sym-dimethylurea was observed.

The rate constant (min.$^{-1}$)

$T=409.0$°K. $k=5.64\times10^{-3}$
$T=413.2$°K. $k=8.42\times10^{-3}$
$T=421.5$°K. $k=1.62\times10^{-2}$

The activation energy

$E=34.3$ kcal.

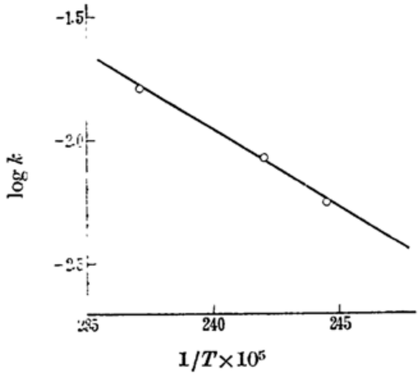


Fig. 2.—Thermal dissociation of sym-dimethylurea in butyric acid: the plot of $1/T$ against $\log k$.

It may be noted again that the thermal dissociation of sym-dimethylurea does not occur in acetic acid.

Thermal dissociation of asym-dimethylurea in butyric acid.

Table 2

Asym-dimethylurea in Butyric Acid at 402.8°K.' Calculated with Value of $\Delta t=60$ min.

time (min.)	CO_2 evolved (c.c.)	time (min.)	CO_2 evolved (c.c.)	ΔY
10	1.4	70	8.7	7.3
15	2.0	75	9.2	7.2
20	2.8	80	9.8	7.0
25	3.4	85	10.3	6.9
30	4.1	90	10.8	6.7
35	4.7	95	11.2	6.5
40	5.2	100	11.7	6.5
45	5.8	105	12.2	6.4
50	6.4	110	12.6	6.2
55	7.0	115	13.1	6.1
60	7.5	120	13.5	6.0
65	8.2	125	13.9	5.7

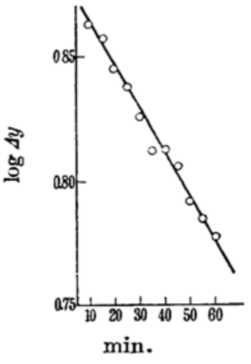


Fig. 3.—The plot of t against $\log \Delta Y$. Asym-dimetylurea in butyric acid. at 402.8°K.

First order kinetics with respect to asym-dimethylurea was observed.

The rate constant (min.$^{-1}$)

$T=402.8°K.$ $k=3.98\times10^{-3}$
$T=409.0°K.$ $k=5.94\times10^{-3}$
$T=422.0°K.$ $k=1.70\times10^{-2}$

The activation energy

$E=26.7$ kcal.

When asym-dimethylurea is heated in acetic acid, the result does not satisfy the requirement for first order kinetics. As shown in Fig. 4, the reaction belongs to the successive one.

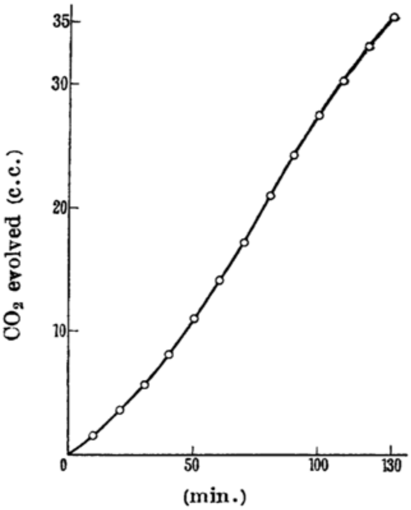


Fig. 4.—Thermal dissociation of asym-dimethylurea in acetic acid at 372.1°K.

The thermal dissociation of asym-phenylethylurea in butyric acid.

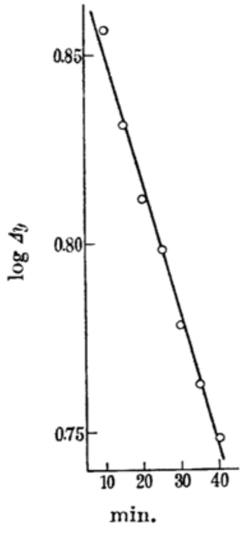


Fig. 5.—The plot of t against $\log \Delta Y$. Asym-phenylethylurea in butyric acid at 409.8°K.

Table 3

Asym-phenylethylurea in Butyric Acid at 409.8°K., Calculated with the Value of $\Delta t = 35$ min.

time (min.)	CO_2 evolved (c.c.)	time (min.)	CO_2 evolved (c.c.)	ΔY
10	1.4	45	8.6	7.2
15	2.7	50	9.5	6.8
20	3.9	55	10.4	6.5
25	4.9	60	11.2	6.3
30	5.9	65	11.9	6.0
35	6.9	70	12.7	5.8
40	7.8	75	13.4	5.6

First order kinetics with respect to asym-phenylethylurea were observed.

The rate constant (min.$^{-1}$)

$T=400.5$°K. $k=1.47\times10^{-3}$
$T=409.8$°K. $k=4.07\times10^{-3}$
$T=411.8$°K. $k=4.93\times10^{-2}$

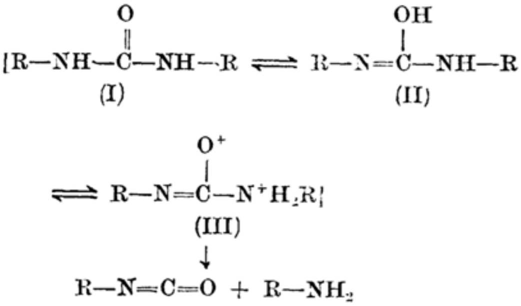
The activation energy

$E=30.2$ kcal.

When asym-phenylethylurea is heated in acetic acid, the result was similar to that described in the case of asym-dimethylurea in acetic acid.

Discussion

The dissociation of urea may be considered to proceed over tautomerizations:



$$[\mathrm{R{-}NH{-}\overset{\overset{O}{\|}}{C}{-}NH{-}R} \rightleftharpoons \mathrm{R{-}N{=}\overset{\overset{OH}{|}}{C}{-}NH{-}R}$$

(I) (II)

$$\rightleftharpoons \mathrm{R{-}N{=}\overset{\overset{O^{+}}{|}}{C}{-}N^{+}H_2R}]$$

(III)

$$\downarrow$$

$$\mathrm{R{-}N{=}C{=}O + R{-}NH_2}$$

As the tautomerization occurs by an intramolecular proton transfer, the ability of proton-donors or proton-acceptors of nitrogen of urea is considered as one of the important factors for the reaction to proceed. In the tautomerization above mentioned, the tautomer (III) may be considered as activated state, which ready to dissociate into isocyanate and amine.

Experiment shows that the activation energy of sym-dimethylurea (34.3 kcal.) is larger than that of sym-diphenylurea (28.0 kcal.). By resonance effect of phenyl group, the basic strength of aromatic amine is less than that of alkyl amine as shown in Table 4 by pKh values. The tautomer (II) formed in sym-diphenylurea has more tendency to dissociate proton than in sym-dimethylurea which will be proportional to the basic charactor of corresponding amines. Also, when the tautomer (III) is formed the stability of dissociated products in arylurea introduced by resonance energy will promote the reaction more than in alkylurea. Consequently, the dissociation reaction of alkylurea needs more energy than that of arylurea.

Table 4

The pKh value for amines reported by Hall and Sprinkle(3)

ammonia	9.27	dimethylamine	10.71
methylamine	10.64	phenylethylamine	5.11
aniline	4.62		

The activation energy of asym-dimethylurea (26.7 kcal.) is smaller than that of sym-dimethylurea. In case of asym-dimethylurea, one nitrogen of urea is the primary and the other is the tertiary. In asym-dimethylurea, the tautomer (II) has more tendency to dissociate proton and to accept proton in the tautomer (III). These considerations are deduced from the basic strength of the corresponding amines. By these two effects, the reason for the lower activation energy of dissociation can be explained.

The activation energy of asym-phenylethylurea (30.2 kcal.) is larger than that of asym-dimethylurea. In these ureas, the ability of dissociating proton from the tautomer (II) is the same and that of accepting proton in the tautomer (III) is different. The tertiary nitrogen of asym-phenylethylurea has aliphatic- and phenyl-groups. By the resonance effect of the phenyl-group, the basic strength decreased as compared with that in asym-dimethylurea. Consequently, it is clear that the larger activation energy will be required.

Summary

(1) The rate constants and the activation energies of the thermal dissociation of sym-dimethylurea, asym-dimethylurea and asym-phenylethylurea were determined.

(2) It was demonstrated that the substituents have great influence on the dissociation reaction.

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(3) Norris F. Hall and Marshall R. Sprinkle, *J. Am. Chem. Soc.*, **54**, 3469 (1932).