On the Thermal Dissociation of Organic Compounds. III. The Dissociation of Ester Linkage in Phenylcarbaminic acid phenylester in Butyric acid.

By Toshio HOSHINO, Teruaki MUKAIYAMA and Hiroko HOSHINO

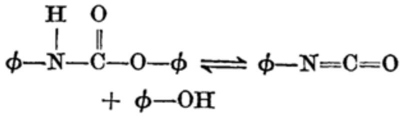
(Received April 28, 1952)

Introduction

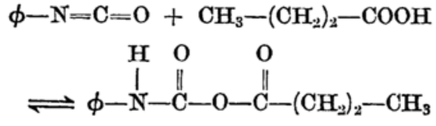
That phenylcarbaminic acid phenylester decomposes to phenyisocyanate and phenol on heating has already been reported.(1) It can be considered that the carbaminic acid ester linkage of phenylcarbaminic acid phenylester dissociates to phenylisocyanate and phenol by the same mechanism as described in the preceding report(2)(3) in the urea linkage which showed that it dissociates to isocyanate and amine.

In the present work, we tried to determine the rate constant and the activation energy of dissociation by the same method used in the thermal dissociation of urea linkage.

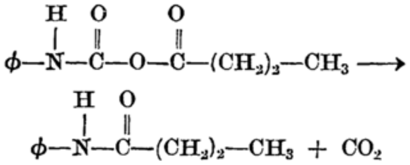
The thermal dissociation of phenylcarbaminic acid phenylester in butyric acid involves the following reactions:

(1) 

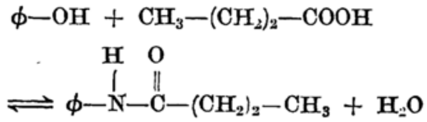
$$\phi\text{—}\overset{\displaystyle H}{\overset{|}{N}}\text{—}\overset{\displaystyle O}{\overset{\|}{C}}\text{—}O\text{—}\phi \rightleftharpoons \phi\text{—}N{=}C{=}O + \phi\text{—}OH$$

(2) 

$$\phi\text{—}N{=}C{=}O + CH_3\text{—}(CH_2)_2\text{—}COOH \rightleftharpoons \phi\text{—}\overset{\displaystyle H}{\overset{|}{N}}\text{—}\overset{\displaystyle O}{\overset{\|}{C}}\text{—}O\text{—}\overset{\displaystyle O}{\overset{\|}{C}}\text{—}(CH_2)_2\text{—}CH_3$$

(3) 

$$\phi\text{—}\overset{\displaystyle H}{\overset{|}{N}}\text{—}\overset{\displaystyle O}{\overset{\|}{C}}\text{—}O\text{—}\overset{\displaystyle O}{\overset{\|}{C}}\text{—}(CH_2)_2\text{—}CH_3 \longrightarrow \phi\text{—}\overset{\displaystyle H}{\overset{|}{N}}\text{—}\overset{\displaystyle O}{\overset{\|}{C}}\text{—}(CH_2)_2\text{—}CH_3 + CO_2$$

(4) 

$$\phi\text{—}OH + CH_3\text{—}(CH_2)_2\text{—}COOH \rightleftharpoons \phi\text{—}\overset{\displaystyle H}{\overset{|}{N}}\text{—}\overset{\displaystyle O}{\overset{\|}{C}}\text{—}(CH_2)_2\text{—}CH_3 + H_2O$$

Even at the boiling point of acetic acid, the thermal dissociation of ester linkage of phenylester could not be observed. Then ester was heated in butyric acid and the dissociation reaction was observed above 130°.

As the rate of reaction of the isocyanate dissociated with butyric acid is thirty times faster than that of dissociation as it was observed by our previous experiment, we were able to determine the rate constant and the activation energy of dissociation of ester by measuring the volume of carbon dioxide evolved throughout the reaction.

Experiment Part

The apparatus was the same as that described in the first report and the volume of carbon dioxide evolved during the reaction was measured.

The sample was prepared from phenylisocyanate and phenol, recrystallized from alcohol. (m. p. 127.0°C.) Butyric acid was carefully purified by vacuum distillation.

The reaction was carried out with the ratios of 1mole of ester to 100 moles of butyric acid.

The rate of reaction was computed using the same procedure as described in the previous report.

Table 1

Phenylcarbaminic acid phenylester in butyric acid at 409.1°K, calculated with the value of $\Delta t = 50$ min.

time (min.)	CO_2 evolved (cc.)	time (min.)	CO_2 evolved (cc.)	ΔY
10	6.2	60	28.7	22.5
15	9.3	65	30.5	21.2
20	12.0	70	32.0	20.0
25	14.2	75	33.7	19.5
30	16.5	80	35.2	18.7
35	18.7	85	36.4	17.7
40	20.7	90	37.6	16.9
45	22.9	95	38.8	15.9
50	24.9	100	39.7	14.8
55	26.7	105	40.6	13.9

The rate satisfied the requirement for first order kinetics with respect to the ester.

---

(1) R. Leuckart, *J. prakt. Chem.*, **41**, 318 (1890).

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

(3) T. Hoshino, T. Mukaiyama and H. Hoshino, This Bulletin, **25**, 392 (1952).

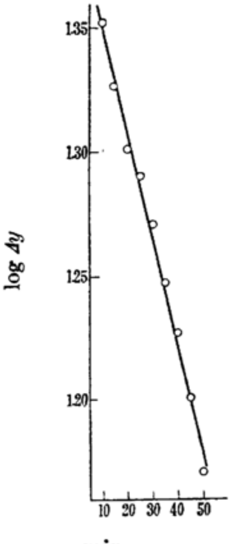


Fig. 1.—The plot of t against log ΔY. Phenylcarbaminic acid phenylester in butyric acid at 409.1°K.

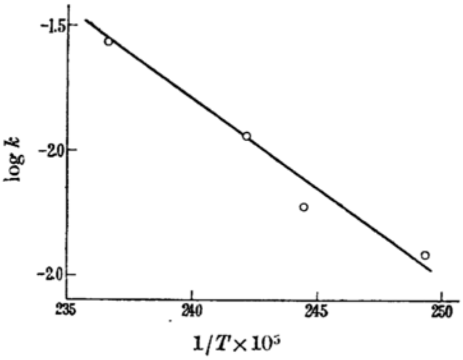


Fig. 2.—Thermal dissociation of phenylcarbaminic acid phenylester in butyric acid: the plot of $1/T$ against log k.

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

$T=401.1$°K. $k=3.98\times10^{-3}$
$T=409.1$°K. $k=5.94\times10^{-3}$
$T=413.0$°K. $k=1.23\times10^{-2}$
$T=422.6$°K. $k=2.71\times10^{-2}$

The activation energy

$E=33.3$ kcal.

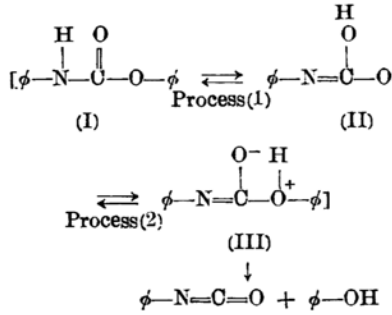
It may be noted again that the thermal dissociation of ester does not occur in acetic acid even at the boiling point.

Discussion

As the result of the experiment, the activation energy of thermal dissociation of ester is shown to be larger than that of urea. This explains the fact that the dissociation of ester does not occur even at the boiling point of acetic acid.

The activation energy of dissociation of diphenylurea in butyric acid is 28.0 kcal. and that of phenylcarbaminic acid phenylester is 33.3 kcal.. This difference between the two substances can be explained by the following considerations.

In phenylcarbaminic acid phenylester, it may be shown that the equilibrium will take place between (II) and (III) by a intramolecular proton transfer. The equilibrium shifts in the direction of (II) and (III) on heating. The (III) dissociates to phenol and phenylisocyanate.



$$[\phi-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-O-\phi \underset{\text{Process(1)}}{\rightleftarrows} \phi-N=\overset{\overset{H}{O}}{\overset{|}{C}}-O-\phi$$

(I) (II)

$$\underset{\text{Process(2)}}{\rightleftarrows} \phi-N=\overset{O^-}{\overset{|}{C}}-\overset{H}{\overset{|}{O^+}}-\phi]$$

(III)

$$\downarrow$$

$$\phi-N=C=O + \phi-OH$$

The urea, as shown in the first report, dissociates by the same mechanism.

The difference of the activation energies required for dissociation between urea and ester will be explained by using the terms, "chemical driving force" and "chemical inertia," introduced by Evans and Polanyi(4). In the tautomerization above mentioned, (III) may be considered as activated state, which is ready to dissociate into isocyanate and alcohol. The difference between urea and ester may depend on process (2), because no appreciable difference can be found in process (1).

With the aid of this consideration, the energy required for dissociation depends on the following factors.

The chemical inertia may be attributed to the work in overcoming the interference action against the dissociating proton from $\overset{O-H}{\overset{|}{-C-}}$ to $\overset{O^-}{\overset{|}{-C-}}$ $+H^+$ and to that breaking the C—O linkage or C—N linkage. These two compounds may have a similar tendency for the former factor. According to Pauling(5) the bond energy of C—N linkage is smaller than that of C—O linkage as shown in Table 2. In this case, however, instead of neutral atoms, they should be considered as $C-N^+ \rightarrow C^+:N$ or $C-O^+ \rightarrow C^+:O$, and the numerical values can not be designated exactly. These considerations suggest that the chemical inertia of ester is larger than that of urea.

The chemical driving force necessary for the rupture of the ester or urea linkages may be

---

(4) Reviewed by Evans and Polanyi, *Trans. Fard. Soc.*, **34**, 11. (1938).

(5) L. Pauling, "The nature of the Chemical Bond", Cornell University Press, 1939, p. 57.

attributed to the formation of alcohol or amine. The heat of formation of aniline from $H^+ + -\overset{H}{\underset{\cdot\cdot}{N}}-\phi$ or phenol from $H^+ + -\underset{\cdot\cdot}{\ddot{O}}\phi$ and the proton acceptability of nitrogen of urea or oxygen of ester are considered as the chemical driving force in these reactions. The basity of aniline is much larger than that of phenol and this suggests that the chemical driving force is larger in urea than in ester.

The difference of the chemical inertia and the chemical driving force is the necessary potential energy of activation. On these considerations, it can be concluded that ester requires more activation energy than urea.

Table 2

Single bond energy for neutral atoms as shown by Pauling(5)

N—C	48.6 kcal.
O—C	70.0 kcal.

Summary

(1) The rate constant and the activation energy of thermal dissociation of phenylcarbaminic acid phenylester in butyric acid are determined.

(2) It has been made clear on the basis of reaction mechanism that dissociation of ester linkage requires larger activation energy than that of urea linkage.

Laboratory of Organic Chemistry,
Tokyo Institute of Technology, Tokyo