

# JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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VOLUME 82

FEBRUARY 3, 1960

NUMBER 2

## PHYSICAL AND INORGANIC CHEMISTRY

[CONTRIBUTION FROM TOKYO INSTITUTE OF TECHNOLOGY]

### Decomposition Reaction of Hexamine by Acid

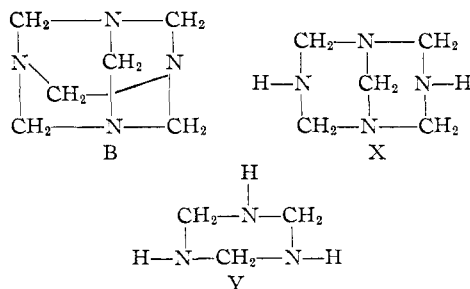
BY HIKOJI TADA

RECEIVED JULY 22, 1958

The decomposition reaction of hexamethylenetetramine (B) by acid can be expressed by  $k = k_w + k_b[H^+]$ . The effect of various cations and anions on  $k$  (neutral salt effect) was investigated. In buffer solution the decomposition is not an  $H^+$ -catalytic reaction; it depends upon the equilibrium concentration of  $BH^+$  and proceeds through a water reaction. In the solvent effect,  $E$  and  $\Delta S^\ddagger$  increased upon the addition of glycol or *t*-butyl alcohol, and  $E$  and  $\Delta S^\ddagger$  were proportional to the reciprocal of the dielectric constant in each solvent. The reaction was catalyzed by the conjugated acid of glycol and to greater extent by aldehydes. Sodium nitrite caused a marked increase in  $k$  which was attributable to the catalytic action of molecular nitrous acid. The mechanism of this reaction is discussed.

#### Introduction

Although several authors have reported<sup>1-4</sup> that the rate of the decomposition of hexamethylenetetramine (hexamine) increases with the hydrogen ion concentration, this reaction has not been studied theoretically. The author has investigated the kinetics of the reaction. In order to elucidate the reaction mechanism, the decomposition of derivatives of 1,5-endomethylene-3,7-tetrazocyclooctane (X) and of 1,3,5-triazo-cyclohexane (Y) by acid also was studied.



#### Experimental

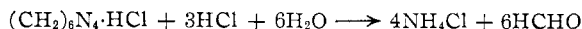
C.P. grade chemicals were used. Hexamine (B) was recrystallized from alcohol and the solvents were purified by distillation.

(1) C. Toffoli, *Rend. ist. super. sania*, **10**, 824 (1947); *C. A.*, **42**, 5611 (1948).

(2) C. Vassiliades, *Bodenkunde u. Pflanzenernähr*, **25**, 150 (1941); *C. A.*, **38**, 2151 (1944).

(3) E. Philippi and J. Löbering, *Biochem. Z.*, **277**, 365 (1935); *C. A.*, **29**, 4655 (1935).

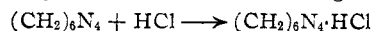
(4) P. Trendelenburg, *Vgl. Münch. Med. Wechschr.*, **66**, 653; *Chem. Zentr.*, **90**, III, 598 (1919).



The rate of the reaction was determined as will be described: aqueous solutions of hexamine were mixed with known amounts of aqueous hydrochloric acid. The reaction was stopped after various periods of time by the rapid addition of a large quantity of water, and the excess hydrochloric acid titrated with sodium hydroxide. Rosolic acid, phenolphthalein and *p*-nitrophenol were used, respectively, as indicators for reaction mixtures containing strong acid, buffer and aldehydes or ammonium chloride. The *pH* value was estimated with a glass electrode.

#### Results and Discussion

**Acid Effect.**—The hydrochloride salt was formed by the reaction of hexamine with an equivalent amount of hydrochloric acid according to



This was shown by the fact that a significant change appeared in the titration curve at the neutralization point; see Fig. 1.

In the present work, the ion  $(CH_2)_6N_4 \cdot H^+$  is represented by  $BH^+$  and the quantity of hydrochloric acid by  $A$ . Therefore, the hydrogen ion concentration is practically equal to the excess hydrochloric acid ( $A - B$ ). The rate can be expressed as a second-order reaction with respect to  $[A - B]$  and  $[BH^+]$ . Therefore, the rate constant  $k$  of the first order with respect to  $[B]$  increases linearly with  $[A - B]$ . At the same time a water reaction occurs, *i.e.*,  $BH^+$  reacts even in the absence of excess acid. The reaction is expressed by equations 1 and 2, and the  $k$ s for various hydrogen ion concentrations are given in Table I.

Since the rates were initial rates measured during the early stages of the reaction, the first-order equa-

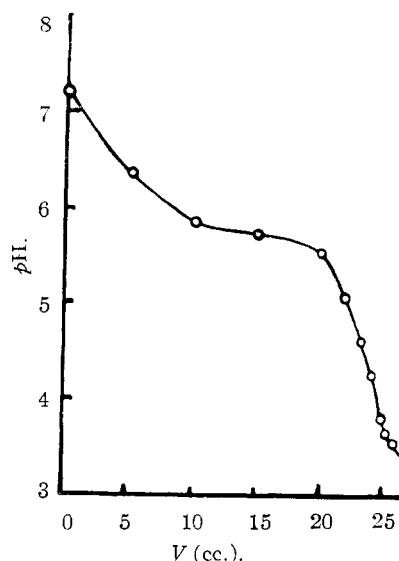


Fig. 1.—Neutralization of hexamine by hydrochloric acid (potentiometric titration).

tion with respect to B was used in experiments on the acid effect. The values of the energy of activation  $E$ , frequency factor  $C$  (p.z.), free energy of activation  $\Delta F^*$  and entropy of activation  $\Delta S^*$  are calculated in Table I.

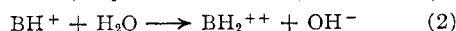
TABLE I

THE EFFECT OF ACID (A) ON THE RATE OF DECOMPOSITION OF HEXAMINE (B)

A, mole/l. $\times 10^2$	A - B, mole/l. $\times 10^2$	$k$ 1st $\times 10^3$ , $t = 30^\circ$	$E$ , kcal./mole	$\log C$	$\Delta F^*$ , 25°, kcal./mole	$\Delta S^*$ , 25°, cal./deg.
21.2	18.6	10.1	22.77	12.40	23.29	-3.73
19.9	17.4	9.27	22.50	12.19	23.33	-4.55
14.4	10.8	7.15				
6.29	4.73	3.51				
8.75	4.40	3.36	21.37	10.92	23.91	-10.52
4.75	3.10	2.46				
2.76	1.39	1.19				
9.52	0.00 <sup>a</sup>	0.605	19.55	8.91	24.84	-19.73

<sup>a</sup> Water reaction.

The increase of  $k$  with acid was due to an increase of  $C$  or  $\Delta S^*$ ; the ion  $BH^+$  reacted, not hexamine in the molecular state. As the reaction proceeded by equations 1 and 2, the first-order  $k$



can be expressed by 3, where  $k_w$  is the constant for the water reaction and  $k_h$  is the  $H^+$  catalytic constant. Fig. 2b shows that  $E$  is proportional

$$k = k_w + k_h[H^+] \quad (3)$$

$$k = \frac{KT}{h} e^{-\Delta F^*/RT} = \frac{KT}{h} e^{-\Delta H^*/RT} e^{\Delta S^*/R} \quad (4)$$

to  $\Delta S^*$ , which in turn increased linearly with  $\log(1 + \alpha[H^+])$  as shown in Fig. 2a.

In experiments in which the ionic strength was kept constant by the addition of sodium chloride,  $k$  was obtained for various  $BH^+$  concentrations (Table II) and for various concentrations of an acetic acid-sodium acetate buffer solution (Table III).

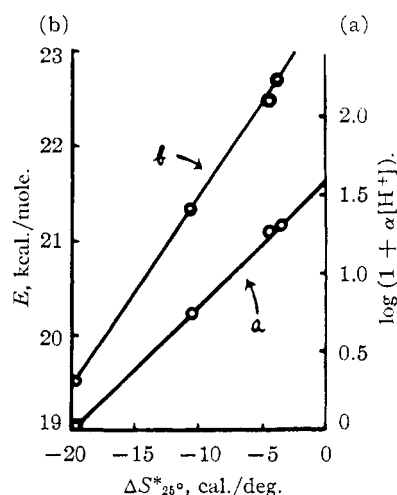


Fig. 2.—Acid effect: a,  $E \sim \Delta S^*$ ; b,  $\log(1 + \alpha[H^+]) \sim \Delta S^*$ .

The results indicate that general acid catalysis by  $BH^+$  (eq. 5) and molecular acetic acid (eq. 6) did not occur, since  $k$  of the first order with respect to B did not vary with either  $[BH^+]$  or  $[HAc]$ .



Let  $V$  be the reaction rate,  $V_1$  that of the  $H^+$  catalytic reaction and  $V_2$  that of the water reaction. Then

$$V = V_1 + V_2 \quad (7)$$

$$V_1 = k_h[BH^+][H^+]$$

$$V_2 = k_w[BH^+]$$

$$V = k_h[BH^+] \left\{ [H^+] + \frac{k_w}{k_h} \right\} \quad (8)$$

The values of  $k_w$  and  $k_h$  ( $t = 30^\circ$ ) were calculated from eq. 3 and the data in Table I:  $k_w = 6.05 \times 10^{-6}$ ;  $k_h = 6.33 \times 10^{-4}$ . Then from these values,

TABLE II

EFFECT OF  $BH^+$  CONCENTRATION

$\mu = 0.100$ ,  $t = 30^\circ$

A, mole/l.	B, mole/l.	$k$ 1st $\times 10^3$
0.100	0.100	5.93
.0500	.0500	5.89
.0200	.0200	6.07
.0100	.0100	6.11

TABLE III

EFFECT OF ACETIC ACID CONCENTRATION

$\mu = 0.0500$ ,  $t = 30^\circ$

HAc, mole/l.	B, mole/l.	NaAc, mole/l.	$k$ 1st $\times 10^3$
0.101	0.0500	0.0500	4.40
.0505	.0250	.0250	4.34
.0202	.0100	.0100	4.74
.0101	.00500	.00500	4.84

from the fact that  $[H^+]$  is practically  $[A-B]$ , and from an analysis of the experimental results, there is obtained an empirical equation of the second order

$$V = k(B - X)(A - 0.97B + 0.007 - 3.03X) \quad (9)$$

Since  $k$  computed by eq. 9 was comparatively constant for a wide range of  $A$  and  $B$ , eq. 9 was used for the calculation of the second-order reaction.

**Neutral Salt Effect.**—The effect of neutral salts<sup>5</sup> on interionic reactions in very dilute solution is expressed by eq. 11 which was derived from the first approximation of the Debye-Hückel equation 10, where  $\alpha$  is the activity coefficient and  $Z_A$  and  $Z_B$  the charge of each ion. The second-order  $k$  was

$$\ln \gamma = -aZi^2 \sqrt{\mu} \times \frac{1}{1 + Bai \sqrt{\mu}} + b\mu \quad (10)$$

$$\log k = \log k_0 + 2aZ_A Z_B \sqrt{\mu} \quad (11)$$

obtained from the neutral salt effect of various concentrations of sodium chloride in dilute solution as shown in Table IV.

TABLE IV  
NEUTRAL SALT EFFECT IN DILUTE SOLUTION  
[A] =  $6.17 \times 10^{-3}$  mole/l., [B] =  $3.07 \times 10^{-3}$  mole/l.,  
 $t = 30^\circ$

$\mu \times 10^2$	$k \times 10^4$
0.617	7.10
1.23	7.21
1.84	7.44
3.68	7.64
6.75	7.88
9.82	7.92

Since  $Z_A Z_B = 1$  (eq. 1),  $\log k$  vs.  $\sqrt{\mu}$  should give a straight line with a slope of  $45^\circ$  according to eq. 11, but the slope of the line obtained (Fig. 3a) is much lower.

In the reaction represented by eq. (1) and (2), the neutral salt effect occurs in (1) but not in (2). In dilute solution  $[H^+]$  is small and the ratio  $k_w/k$  is relatively large. Therefore, to obtain the relationship between  $\mu$  and  $k$  in the interionic reaction, it is necessary to subtract  $k_w$  from the  $k$  measured. From eq. (8), the water reaction  $k_a$  in the second-order  $k$  is given by (12)

$$k_a = k_b \times \frac{V_2}{V} = \frac{k_b k_w}{k_b [H^+] + k_w} \quad (12)$$

Then from (12) and the values calculated above for  $k_w$  and  $k_b$ ,  $k_a = 4.78 \times 10^{-4}$  ( $t = 30^\circ$ ). The plot of  $\log (k - k_a)$  vs.  $\sqrt{\mu}$  (Fig. 3b) gave a straight line with a slope of  $45^\circ$  when  $\mu$  was very small. However, when  $\mu$  was relatively large, the relationship between  $\mu$  and  $k$  is given by

$$k = k_0 (1 + b_1 \mu) \quad (13)$$

which was derived from the third approximation of the Debye-Hückel equation.<sup>6</sup>

The neutral salt effect did not occur in the absence of excess acid; see Table V.

TABLE V  
NEUTRAL SALT EFFECT IN THE PRESENCE OF EQUIVALENT AMOUNTS OF HEXAMINE AND HYDROCHLORIC ACID  
[A] =  $6.67 \times 10^{-2}$  mole/l., [B] =  $6.67 \times 10^{-2}$  mole/l.,  
 $t = 30^\circ$

Salt	$\mu$	$k \times 10^5$
...	0.0671	6.02
NaCl	0.234	5.67
NaCl	2.07	5.84
KCl	2.07	6.05
LiCl	4.07	5.87
NaBr	4.07	5.72
NaI	4.07	5.94

(5) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1941, p. 428.

(6) Ref. 5, p. 441.

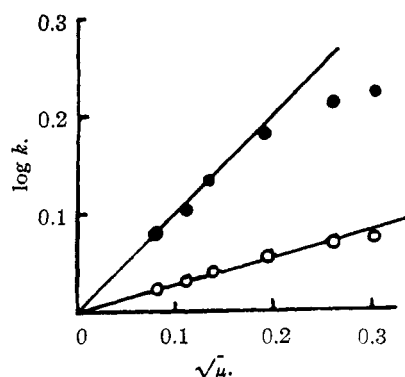


Fig. 3.—Neutral salt effect: [A] =  $6.17 \times 10^{-3}$  mole/l., [B] =  $3.07 \times 10^{-3}$  mole/l.,  $t = 30^\circ$ : a, O; b, ●.

Measurements were made on hexamine solutions containing excess acid; the salt added, the salt concentration and the temperature were varied. The effect of these variables on  $k$  is shown in Table VI.

In general  $k$  increased linearly with  $\mu$  in agreement with eq. 13 for values of  $\mu$  below about 3 to 4. This is true also when the salt added was ammonium chloride, a product of the decomposition reaction which might be expected to retard the reaction. However, in the case of LiCl, NaBr and CaCl<sub>2</sub>, when  $\mu$  was very large,  $k$  increased remarkably and  $\log k$  vs.  $\mu$  gives a straight line. Only in the case of potassium sulfate did  $k$  decrease with increasing  $\mu$ , probably due to the decrease in  $[H^+]$  by the reaction  $SO_4^{--} + H^+ \rightleftharpoons HSO_4^-$ .

A comparison of the  $k$  values obtained in the presence of various salts at a given ionic strength shows the order of effectiveness of the cations (in chloride or bromide salts) to be  $Li^+ > Na^+ > K^+ > M^{++}$  ( $M^{++}$  represents the alkaline earths); the smaller the cation, the greater the effect. For the anions (sodium or potassium salts) the order is  $I^- > Br^- > Cl^-$ ; the larger the anion, the greater the effect. The increase of  $k$  (or decrease of  $\Delta F^*$ ) was due to an increase of  $\Delta S^*$  or p.z. At given ionic strength, the order of effectiveness of the anions and cations in increasing  $\Delta S^*$  was the same as that given above. In the case of the cations, the differences in  $\Delta S^*$  are small.

Using  $b_1$  values calculated from Table VI, it is found that  $\Delta S^*$  increased linearly with  $\log (1 + b_1 \mu)$  as shown in Fig. 4b, because  $E$  increased with  $\Delta S^*$  (Fig. 4a).

In general in the reaction depicted in eq. 1 and 2, relationship 11 was obtained if the water reaction was deducted from the  $k$  value determined. The effect of neutral salts on the interionic reaction catalyzed by hydrogen ion is in accord with (11) when  $\mu$  was extremely small, but in more concentrated solution  $k$  increased linearly with  $\mu$  according to eq. 13.

The fact that anions exerted a greater influence on  $k$  than cations may be explained by the assumption that the positively charged, activated complex  $(BH_2^{++})$  would be surrounded by a shell of anions. The order of effectiveness of the ions was interpreted on the basis of the fact that  $b_1$  in eq. 13 was derived from the correction term  $b$  of eq. 10; and it was greatly affected by small ions

TABLE VI  
NEUTRAL SALT EFFECT

Salt	$\mu$	$[A] = 8.27 \times 10^{-3}$ , mole/l.; $[B] = 2.08 \times 10^{-2}$ , mole/l.					$E_a$ kcal./mole	log p.z.	$\Delta F^* 25^\circ$ , kcal./mole	$\Delta S^* 25^\circ$ , cal./degree
		20°	25°	$k \times 10^4$ 30°	35°	40°				
..	0.0827	0.173	0.329	0.606	1.07	1.85	21.63	12.37	22.20	-3.90
NaI	1.58			1.59						
	3.08	0.802	1.57	3.15	5.98	10.9	23.89	14.72	21.28	+6.78
NaBr	1.58			1.52						
	3.08	0.678	1.37	2.74	5.02	9.25	23.57	14.42	21.36	+5.44
	5.92 <sup>a</sup>	2.07	4.08	7.78	14.7		23.36	14.74	20.71	+6.91
NaCl	1.58			1.41						
	3.08	0.594	1.18	2.28	4.27	7.77	23.29	14.15	21.45	+4.20
	3.83	0.720	1.42	2.74	5.27	9.35	23.62	14.46	21.34	+5.66
KI	1.58			1.54						
	3.08			2.82						
KBr	1.58			1.43						
	3.08			2.35						
KCl	1.58			1.34						
	3.08	0.519	1.06	2.04	3.73	6.78	23.29	14.09	21.51	+3.99
LiCl	1.58			1.52						
	3.08	0.658	1.34	2.62	4.65	8.51	23.25	14.17	21.37	+4.30
	9.19 <sup>b</sup>	7.25	14.2	26.3			23.04	15.04	19.97	+8.32
BaCl <sub>2</sub>	1.58			1.18						
	3.08			1.64						
SrCl <sub>2</sub>	1.58			1.20						
	3.08			1.63						
CaCl <sub>2</sub>	1.58			1.17						
	3.08			1.68						
	11.51 <sup>c</sup>	3.53	7.48	13.9			23.63	15.19	20.35	+9.01
NH <sub>4</sub> Cl	1.58			1.33						
	3.08			2.01						
NaClO <sub>4</sub>	1.58			1.45						
	3.08	0.596	1.17	2.45	4.40	7.92	23.55	14.35	21.45	+5.05
NaNO <sub>3</sub>	1.58			1.22						
	3.08			1.79						
	6.08	0.865	1.64	3.19	5.73	9.66	22.49	13.71	21.25	+2.17
K <sub>2</sub> SO <sub>4</sub>	0.708			0.547						
	1.33			0.544						

<sup>a</sup> 15°,  $k = 1.04 \times 10^{-3}$ . <sup>b</sup> 10°,  $k = 1.80 \times 10^{-3}$ ; 15°,  $k = 3.64 \times 10^{-3}$ . <sup>c</sup> 10°,  $k = 0.917 \times 10^{-3}$ ; 15°,  $k = 1.80 \times 10^{-3}$ .

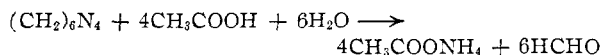
in the case of cations and by large ions in the case of anions. An example of this reaction calculated from equation 9 of the second order is given in Table VII.

TABLE VII  
DECOMPOSITION OF B CATALYZED BY HYDROCHLORIC ACID

$[A] = 8.27 \times 10^{-2}$  mole/l.,  $[B] = 2.08 \times 10^{-2}$  mole/l.,  
 $t = 30^\circ$

$T$ (sec.) $\times 10^{-2}$	% B dec.	$k$ 2nd order $\times 10^4$
1.8	6.02	5.87
3.6	13.0	6.00
5.4	18.7	6.06
7.2	23.6	6.08
9.0	27.8	6.01
10.8	31.9	6.07
12.6	35.0	6.02
14.4	38.9	6.12

**Reaction in Buffer Solution.**—Since the decomposition reaction in acetic acid-sodium acetate buffer solution was measured during the early stages of reaction, the first-order equation with respect to B was used.



As mentioned previously, the rate of this decomposition increases with  $[\text{H}^+]$ , so the relationship between  $k$  and  $[\text{H}^+]$  in acetate buffer-hexamine solutions was studied.  $[\text{H}^+]$  was varied in one series by the addition of various amounts of sodium acetate (Fig. 5a); in another by the addition of various amounts of acetic acid (Fig. 6a).

As Fig. 5a and 6a show, a linear relationship between  $k$  and  $[\text{H}^+]$  was not obtained.  $\text{BH}^+$  was not produced quantitatively by the neutralization of a weak base (B), by a weak acid (HAc) but  $[\text{BH}^+]$  was maintained at an equilibrium value depending on the quantity of hexamine, acetic acid (HAc) and sodium acetate (NaAc). It had been found that molecular hexamine does not react. Also in buffer solution, the  $\text{H}^+$  catalytic reaction is extremely small and, therefore, the water reaction becomes dominant. Consequently the rate is proportional to  $[\text{BH}^+]$  in the equilibrium state.

At equilibrium

$$[\text{BH}^+] = \frac{K([\text{B}] + [\text{HAc}]) + [\text{NaAc}]}{\sqrt{K([\text{B}] + [\text{HAc}]) + [\text{NaAc}]^2 - 4K(K-1)[\text{B}][\text{HAc}]}} / \frac{2(K-1)}$$

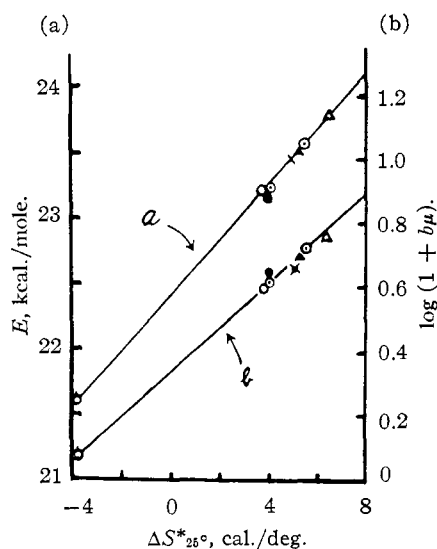


Fig. 4.—Relation between entropy of activation and ionic strength:  $[A] = 8.27 \times 10^{-2}$  mole/l.,  $[B] = 2.08 \times 10^{-2}$  mole/l.;  $\circ$ , blank;  $\bullet$ , LiCl;  $\odot$ , NaCl;  $\bigcirc$ , KCl;  $\blacktriangle$ , NaBr;  $\triangle$ , NaI;  $\bullet$ , NaClO<sub>4</sub>;  $\times$ , NaNO<sub>3</sub>; a,  $E \sim \Delta S^*$ ; b,  $\Delta S \sim \log(1 + b\mu)$ .

$$K[\text{HAc}] - \sqrt{\{K([\text{B}] + [\text{HAc}] + [\text{NaAc}])^2 - 4K(K-1)[\text{B}][\text{HAc}]\}}$$

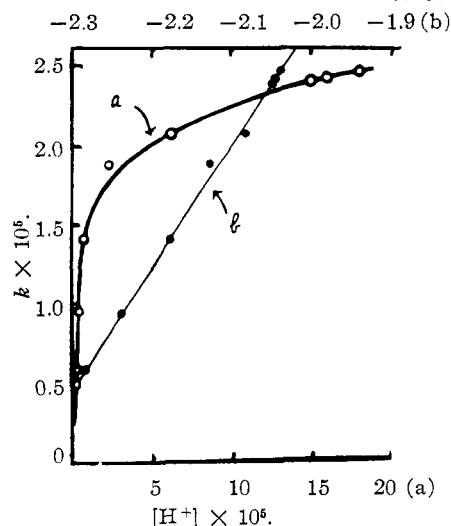


Fig. 5.—Decomposition reaction of hexamine in buffer solution (various quantities of sodium acetate were used):  $[\text{HAc}] = 8.33 \times 10^{-2}$  mole/l.,  $[\text{NaAc}] = 1.67 \sim 0$  mole/l.,  $[B] = 1.04 \times 10^{-2}$  mole/l.,  $t = 45^\circ$ .

where  $K$  is the equilibrium constant of the reaction

$$K = [\text{BH}^+][\text{Ac}^-]/[\text{HAc}][\text{BH}\cdot\text{OH}]$$

$B$  is given for convenience as a base  $\text{BH}\cdot\text{OH}$ .  $K$  can be evaluated from the dissociation constants, since

$$K = K_a K_b / K_w = 2.5$$

where  $K_a$ ,  $K_b$  and  $K_w$  are the dissociation constants of acetic acid, hexamine and water, respectively.

Then from the above equation, with sodium acetate as the variable,  $k$  is proportional to

$$[\text{NaAc}] - \sqrt{\{K([\text{B}] + [\text{HAc}]) + [\text{NaAc}]\}^2 - 4K(K-1)[\text{B}][\text{HAc}]}$$

which is presented in Fig. 5b.

$$K[\text{HAc}] - \sqrt{\{K([\text{B}] + [\text{HAc}] + [\text{NaAc}])^2 - 4K(K-1)[\text{B}][\text{HAc}]\}}$$

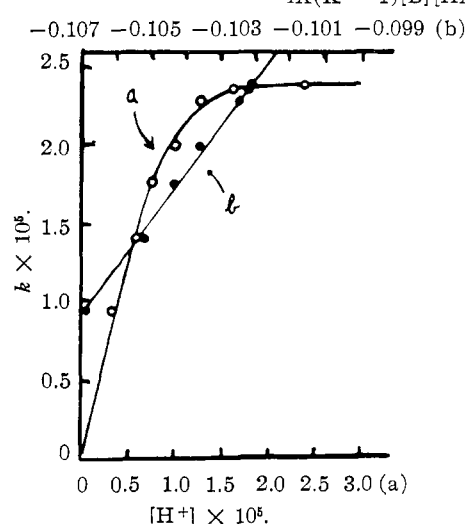


Fig. 6.—Decomposition reaction of hexamine in buffer solution (various quantities of acetic acid were used):  $[\text{HAc}] = 4.17 \sim 29.2 \times 10^{-2}$  mole/l.,  $[\text{NaAc}] = 2.50 \times 10^{-1}$  mole/l.,  $[B] = 1.04 \times 10^{-2}$  mole/l.,  $t = 45^\circ$ .

With acetic acid as the variable, the relationship is

$$k \sim K[\text{HAc}] -$$

$$\sqrt{\{K([\text{B}] + [\text{HAc}]) + [\text{NaAc}]\}^2 - 4K(K-1)[\text{B}][\text{HAc}]}$$

which is given in Fig. 6b. In both cases a good linear relation was obtained between  $k$  and the expression derived for  $[\text{BH}^+]$ .

This decomposition is a  $\text{H}^+$  catalytic reaction accompanied by a water reaction of  $\text{BH}^+$ ; general acid catalysis does not occur. Since in buffer solution  $[\text{H}^+]$  is very small, hexamine did not decompose via the  $\text{H}^+$  catalytic reaction and the water reaction was dominant;  $k$ , therefore, is proportional to  $[\text{BH}^+]$  and can be expressed approximately by the expression  $k = k_w \times [\text{BH}^+]/[\text{B}]$ . This proportionality confirms the conclusion that molecular hexamine does not react as such and that  $\text{BH}^+$  is the reacting species.

**Solvent Effect.**—The measurements made in the presence of various concentrations of different solvents are presented in Fig. 7. It has been reported that for interionic reactions  $\log k$  is proportional to the reciprocal of the dielectric constant ( $D$ ), but the results in general showed no such relationship. The second-order  $k$  increased with increasing concentrations of glycerol, glycol, methanol and dioxane and decreased with increasing  $t$ -butyl alcohol, isopropyl alcohol and acetone; with low concentrations of 1-propanol and ethanol,  $k$  decreased, but with high concentrations it increased. The rate constants determined at various temperatures and the values calculated for  $E$ , etc., are given in Table VIII.

Glycol and  $t$ -butyl alcohol brought about an increase of  $E$  and  $\Delta S^*$  changes which were not dependent upon the tendency of the rate to increase or decrease. The change of  $E$  due to the solvent effect interionic reactions is related to  $D$  (when

TABLE VIII  
SOLVENT EFFECT[A] =  $8.75 \times 10^{-2}$  mole/l., [B] =  $4.35 \times 10^{-2}$  mole/l.

Solvent	Mole/l.	20°	25°	$k \times 10^4$ 30°	35°	40°	$E$ , kcal./mole	log p.z.	$\Delta F^*$ 25°, kcal./mole	$\Delta S^*$ 25°, cal./deg.
....	...	1.82	3.69	6.52	11.7	19.8	21.52	12.32	22.13	-4.06
Glycol	7.81	2.08	4.15	7.72	14.1	24.8	22.41	13.04	22.06	-0.83
	15.6	3.22	6.60	12.5	22.6	43.6	23.22	13.84	21.79	+2.81
<i>t</i> -Butyl alc.	4.63	1.39	2.53	4.60	8.55	15.6	22.25	12.96	22.36	-2.34
	9.26	1.13	2.46	4.08	8.93	17.0	24.65	14.46	22.37	+5.63

 $\mu \rightarrow 0$ ) as<sup>8</sup>

$$\Delta H^* - \Delta H^*_D = -\frac{\epsilon^2 Z_A Z_B}{r} (1 - 1/D) \quad (14)$$

where  $\epsilon$  is the unit change and  $r$  the interionic distance. In agreement with this relationship, it is found  $E$  and  $\Delta S^*$  to be proportional to  $1/D$  for both solvents (Fig. 8).

As water molecules took part in this reaction, the effect of the water concentration was studied. Since hexamine hydrochloride precipitates in high concentrations of the organic solvents other than glycol, measurements were made in glycol solutions containing small amounts of water; see Table IX and Fig. 7.

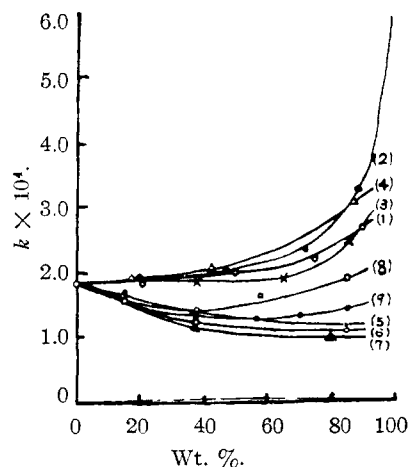


Fig. 7.—Solvent effect: [A] =  $8.75 \times 10^{-2}$  mole/l., [B] =  $4.35 \times 10^{-2}$  mole/l.,  $t = 20^\circ$ : 1, glycerol; 2, glycol; 3, methanol; 4, dioxane; 5, *t*-butyl alcohol; 6, isopropyl alcohol; 7, acetone; 8, 1-propanol; 9, ethanol.

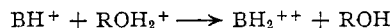
When A and B were equivalent,  $k$  decreased with decreasing  $[H_2O]$  but, in the presence of excess acid,  $k$  increased suddenly when  $[H_2O]$  was decreased.

The rate constants determined at various temperatures and the values for  $E$ , etc., are listed in Table X.

The increase of  $E$  and  $\Delta S^*$  in the solvent effect was associated with a decrease of  $D$  as shown in eq. 14, because the reaction is an interionic reaction of the same type of ion that participates in eq. 1.

The rate constant increased slightly with increasing glycol due to the solvent effect on (1), but the sudden increase in  $k$ , which occurred when  $[H_2O]$  was very small, is attributable to the catalytic action of the conjugated acid of glycol which is formed from hydrochloric acid and glycol and

which reacts with  $BH^+$  as



and thus competes for  $BH^+$  with reaction 1. That the sudden increase in  $k$  is due to a mechanism different from that of the solvent effect on eq. 1 is supported by the fact that this increase did not occur in the absence of excess acid and that it was associated with low values of  $E$  and  $\Delta S^*$ ; whereas with the solvent effect  $E$  and  $\Delta S^*$  increased markedly.

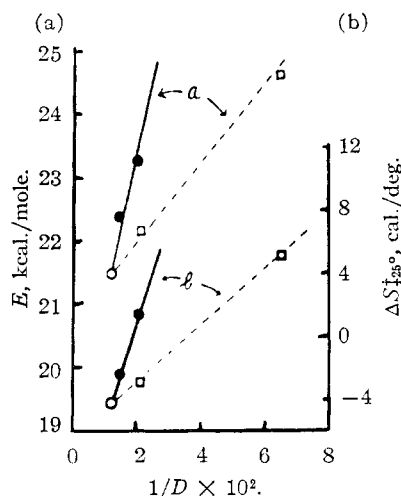


Fig. 8.—[A] =  $8.75 \times 10^{-2}$  mole/l., [B] =  $4.35 \times 10^{-2}$  mole/l.: O, blank; ●, glycol; □, *t*-butyl alcohol.

**Effects of Aldehydes.**—In the presence of excess acid,  $k$  of the second order was determined for reaction mixtures containing various concentrations of aldehydes; the first-order  $k$  was used when A and B were equivalent.

In the presence of excess acid, acetaldehyde, propionaldehyde and butyraldehyde exerted a marked catalytic effect; the increase in  $k$  with the aldehyde concentration was almost linear and of about the same magnitude for the three aldehydes. With minute quantities of formaldehyde,  $k$  decreased slightly but increased with the formaldehyde concentration when it became large; this effect, however, was much smaller than that of the other aldehydes studied. The aldehyde effect was much greater than that of the solvent effect. With equivalents amounts of A and B,  $k$  decreased markedly with the addition of formaldehyde; propionaldehyde, however, exerted a slight catalytic effect.

Rate constants determined at various temperatures and the values of  $E$ , etc., are given in Table XII. Unlike the solvent effect, the increase of  $k$

(8) Ref. 5, p. 438.

TABLE IX  
RATE CONSTANTS OF GLYCOL SOLUTIONS CONTAINING SMALL AMOUNTS OF WATER

[A] =  $8.75 \times 10^{-2}$  mole/l., [B] =  $4.35 \times 10^{-2}$  mole/l.  
 $t = 30^\circ$

H <sub>2</sub> O, mole/l.	$k \text{ 2nd} \times 10^3$
Aqueous sol.	0.652
5.39	1.44
2.97	2.07
1.78	2.88
1.06	4.31
0.817	5.05
.578	5.55
.483	6.57
.278	7.78
.111	8.56

[A] =  $1.05 \times 10^{-1}$  mole/l., [B] =  $1.05 \times 10^{-1}$  mole/l.

H <sub>2</sub> O mole/l.	$k \text{ 1st} \times 10^4$
Aqueous sol.	5.93
3.54	4.49
2.09	4.21
0.644	4.06
.292	3.73
.173	3.69
.111	3.52

TABLE X  
[A] =  $8.75 \times 10^{-2}$  mole/l., [B] =  $4.35 \times 10^{-2}$  mole/l.,  
[H<sub>2</sub>O] =  $2.78 \times 10^{-1}$  mole/l., glycol solution

$t$ (°C.)	20	25	30	35	40
$k \times 10^3$	2.40	4.46	7.78	14.2	22.6
$E$ , kcal./mole					
20.47		12.66	20.66		$\Delta S^* 25^\circ$ , cal./deg.
					-2.61

TABLE XI  
EFFECT OF ALDEHYDES

A, mole/l. $\times 10^2$	B, mole/l. $\times 10^2$	Aldehyde	Aldehyde, mole/l.	$t = 30^\circ$ $k \text{ 2nd} \times 10^4$
8.10	2.46	.....	.....	6.09
8.10	2.46	Formaldehyde	0.0529	5.86
8.10	2.46	Formaldehyde	.211	5.62
8.10	2.46	Formaldehyde	.529	5.91
8.10	2.46	Formaldehyde	1.06	7.03
8.10	2.46	Formaldehyde	2.11	9.68
8.10	2.46	Formaldehyde	5.29	15.4
8.10	2.46	Formaldehyde	10.6	21.2
8.33	2.08	.....	.....	6.06
8.33	2.08	Propionaldehyde	0.227	40.7
8.33	2.08	Propionaldehyde	0.567	67.4
8.33	2.08	Propionaldehyde	1.13	104
8.33	2.08	Propionaldehyde	1.70	126
8.33	2.08	Isobutyraldehyde	0.0911	27.9
8.33	2.08	Isobutyraldehyde	.183	34.7
8.33	2.08	Isobutyraldehyde	.456	61.2
8.40	2.17	.....	.....	1.80 ( $t = 20^\circ$ )
8.40	2.17	Acetaldehyde	.236	7.71 ( $t = 20^\circ$ )
8.40	2.17	Acetaldehyde	.589	14.3 ( $t = 20^\circ$ )
8.40	2.17	Acetaldehyde	1.18	25.2 ( $t = 20^\circ$ )
8.40	2.17	Acetaldehyde	2.95	51.9 ( $t = 20^\circ$ )
8.40	2.17	Acetaldehyde	5.89	74.3 ( $t = 20^\circ$ )
				$t = 30^\circ$ $k \text{ 1st} \times 10^4$
8.00	8.00	.....	.....	6.02
8.00	8.00	Formaldehyde	0.122	3.11
8.00	8.00	Formaldehyde	0.490	1.32
8.00	8.00	Formaldehyde	1.22	1.17
8.00	8.00	Formaldehyde	4.90	1.88
8.00	8.00	Formaldehyde	9.79	2.21
10.00	10.00	Propionaldehyde	0.272	7.46
10.00	10.00	Propionaldehyde	0.680	9.82
10.00	10.00	Propionaldehyde	1.36	12.2

was due to a decrease in  $E$  which was accompanied by a large decrease in  $\Delta S^*$ . The aldehyde effect

TABLE XII

A, mole/l. $\times 10^2$	B, mole/l. $\times 10^2$	Aldehyde, mole/l.	15°	20°	$k \times 10^3$	25°	30°	35°
16.1	4.00	F, <sup>a</sup> 9.79	0.483	0.842	1.45	2.48	4.22	
8.33	2.08	P, <sup>b</sup> 1.13	2.24	3.85	6.16	10.4	17.2	
			$E$ , kcal./mole	log p.z	$\Delta F^* 25^\circ$ , kcal./mole	$\Delta S^* 25^\circ$ , cal./deg.		
8.75	4.35	.....	21.52	12.32	22.13	-4.06		
16.1	4.00	F, <sup>a</sup> 9.79	19.16	11.21	21.32	-9.24		
8.33	2.08	P, <sup>b</sup> 1.33	18.01	11.01	20.47	-10.22		

<sup>a</sup> Formaldehyde. <sup>b</sup> Propionaldehyde.

was first order with respect to the aldehyde concentration ( $k$  increased linearly with the aldehyde concentration); the solvent effect was not of the first order. The comparatively small catalytic effect of formaldehyde is attributable to the fact that it is a decomposition product. From these results the catalytic action of the aldehydes was explained as follows: aldehydes reacted with the C-N bond of BH<sup>+</sup> and promoted cleavage of the bond by the reaction of aldehyde with secondary amine.

**Effect of Nitrous Acid.**—In this work care was taken to prevent the decomposition of nitrous acid and the precipitation of 1,5-dinitroso-3,7-endomethylenetetrazocyclooctane (D.N.T.). The effect of sodium nitrite on the reaction is shown in Table XIII; the second-order  $k$  was determined for reaction mixtures containing excess acid and the first-order  $k$  with respect to B was used for mixtures in which A and B were equivalent. The addition of sodium nitrite caused a marked increase in  $k$  in both the presence and absence of excess acid.

TABLE XIII

THE EFFECT OF SODIUM NITRITE ON THE DECOMPOSITION OF HEXAMINE

[A] =  $8.33 \times 10^{-2}$  mole/l., [B] =  $2.08 \times 10^{-2}$  mole/l.  
 $t = 30^\circ$

NaNO <sub>2</sub> , mole/l. $\times 10^2$	$k \times 10^3$
...	0.606
0.833	63.0
1.67	157
4.17	347
8.33	402
20.8	327
41.7	274
[A] = [B] = $6.67 \times 10^{-2}$ mole/l.	
...	0.00602
1.33	.355
3.33	.644
6.67	.707

[A] =  $8.33 \times 10^{-2}$  mole/l., [B] =  $2.08 \times 10^{-2}$  mole/l.,  
[NaNO<sub>2</sub>] =  $4.17 \times 10^{-2}$  mole/l.

$t$ , °C.	10	15	20	25	30
$k \times 10^2$	4.94	7.70	13.7	22.7	34.7
NaNO <sub>2</sub> , mole/l. $\times 10^2$					
...					
$E$ , kcal./mole	21.52	12.32	22.13	-4.06	
log p.z.	4.17	16.72	11.60	18.33	-7.37

<sup>a</sup> [A] =  $8.75 \times 10^{-2}$  mole/l.; [B] =  $4.35 \times 10^{-2}$  mole/l.

Measurements also were made on reaction mixtures containing a constant amount of sodium nitrite and various amounts of sodium chloride;

these results given in Table XIV show that the neutral salt effect was slight.

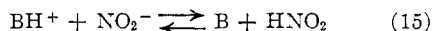
TABLE XIV

NEUTRAL SALT EFFECT WHEN SODIUM NITRITE WAS ADDED  
 $[A] = 8.33 \times 10^{-2}$  mole/l.,  $[B] = 2.08 \times 10^{-2}$  mole/l.,  
 $[\text{NaNO}_2] = 4.17 \times 10^{-2}$  mole/l.,  $t = 30^\circ$

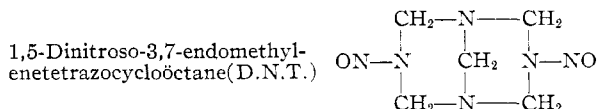
$\mu$	$k$
0.0833	0.347
1.08	.350
2.33	.443

In the presence of excess acid (Table XIII) there was a rapid and linear increase in rate with the sodium nitrite concentration up to about  $4 \times 10^{-2}$  mole  $\text{NaNO}_2$ /l.; between about  $4 \times 10^{-2}$  and  $8 \times 10^{-2}$  mole/l., the increase in rate was less rapid; a maximum was reached at about  $8.33 \times 10^{-2}$  mole/l., and at higher concentrations the rate fell off.

These findings can be interpreted as follows: in acid solution the nitrite was present almost completely as molecular nitrous acid which exerted a marked catalytic effect on  $\text{BH}^+$ . When  $[\text{NaNO}_2]$  exceeded  $[A-B]$ , equilibrium (15) was established involving the weak base B and weak acid  $\text{HNO}_2$



Therefore, in the presence of a large amount of sodium nitrite,  $[\text{BH}^+]$  was reduced due to the increase in  $[\text{NO}_2^-]$ , and since molecular hexamine does not react as such, the decomposition rate fell off. The fact that a large amount of sodium nitrite caused a decrease in  $k$  indicates that the catalysis was due to molecular  $\text{HNO}_2$  and not to  $\text{NO}_2^-$ . Even in the absence of excess acid, sodium nitrite exerted a pronounced catalytic effect in spite of the decrease in  $[\text{BH}^+]$  by (15). The neutral salt effect in the presence of nitrite was very small. All this suggests that the catalytic action of nitrous acid is due to its reaction with the C-N bond of  $\text{BH}^+$  and cleavage of the bond by the reaction of nitrous acid with secondary amines. This explanation is supported by the fact that the rate of the acid decomposition of D.N.T.,<sup>9</sup> a stable compound in which the  $>\text{N}-\text{CH}_2-\text{N}<$  bond of hexamine is perfectly broken is 2,000 times greater than that of B.



Like the catalytic effect of aldehydes and glycol, the increase of  $k$  by the catalytic action of nitrous acid was due to a depression of  $E$ . This suggests that the mechanism differs essentially from the  $\text{H}^+$  catalytic reaction of (1) since  $E$  and  $\Delta S^*$  increased with  $k$  in the case of the neutral salt, acid and solvent effects, which are  $\text{H}^+$  catalytic reactions of (1). These results indicate, therefore, that sodium nitrite catalysis is due to reaction between  $\text{HNO}_2$  and  $\text{BH}^+$ .

**Reaction Mechanism.**—From the results these several conclusions can be drawn: (1) in acid solution B becomes  $\text{BH}^+$ . The decomposition reaction in buffer solution did not proceed with

molecular B but with  $\text{BH}^+$  which was decomposed by the water reaction. (2) In experiments catalyzed by strong acid,  $\text{BH}^+$  decomposed by the  $\text{H}^+$  catalytic reaction which accompanied the water reaction. The neutral salt effect by  $\text{H}^+$  catalysis took place and general acid catalysis did not occur. (3) The results suggest that the same ions were involved in the neutral salt and solvent effects; *i.e.*, reaction occurred between  $\text{BH}^+$  and  $\text{H}^+$ . (4) The catalytic effect of the conjugated acid of glycol, aldehydes and nitrous acid was accompanied by a decrease in  $E$  and  $\Delta S^*$ . This indicates that the mechanism differs from the  $\text{H}^+$  catalysis of (1) produced by acid, solvent and neutral salt effects, all of which caused an increase in  $E$ . (5) In strong alkali, neutral and very weak acid solution, B gave mainly derivatives of 1,5-endomethylene-3,7-tetrazocyclooctane (X). As Table XV shows, the derivatives of X were decomposed by acid at rates much faster than that of B. (6) In acid solution B gave mainly derivatives of 1,3,5-triazocyclohexane (Y). The acid decomposition of the 1,3,5-trimethyl derivative of Y was much faster than the decomposition rates of B and the derivatives of X; Table XV.

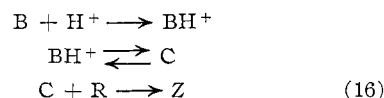
TABLE XV

RELATIVE RATES OF DECOMPOSITION OF HEXAMINE AND RELATED COMPOUNDS

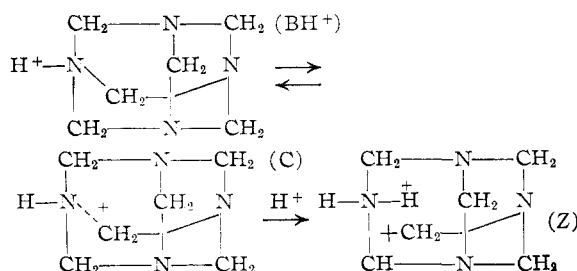
	$V'^a$	$E$ , kcal./mole	$\Delta S^*$ 25°, cal./deg.
Hexamine	1	21.5	-4.06
Derivative of X, biacetyl	10	23.0	+3.98
Derivative of X, bisazo-phenyl	500	19.9	-4.79
Derivative of X, dinitroso	2,000	20.2	+5.57
Derivative of X, dichloro	2,000	15.0	-2.77
1,3,5-Trimethyltriazocyclohexane	20,000	19.1	-1.53 (0.6°)

<sup>a</sup>  $V'$  is the relative rate of decomposition.

These results can be interpreted mechanistically as



where ( $\text{R} = \text{H}_3\text{O}^+$ ,  $\text{HNO}_2$ ,  $\text{R}\cdot\text{CHO}$ ,  $\text{CH}_2\text{OH}\cdot\text{CH}_2\text{OH}_2^+$ ,  $\text{H}_2\text{O}$ ), and Z is an activated complex, which is produced by the reaction between C and R. Namely, weakening of the C-N bond of  $\text{BH}^+$  produced the carbonium ion C. With the attachment of  $\text{H}^+$  to  $\text{NH}$  in  $>\text{NH}\dots\text{C}^+\text{H}_2-$  of C, the C-N bond was broken completely by the reaction of like charge. As this compound Z was a derivative of X, it decomposed much faster than B. In other words, (16) was the rate-determining step of this reaction



(9) H. Tada *J. Chem. Soc. Japan, Ind. Chem. Sect.*, **56**, 506 (1953).



The catalytic action of the conjugated acid of glycol can also be accounted for by this means. The aldehydes and nitrous acid reacted with the NH of  $\text{NH} \dots \text{CH}_2^+$ , and this resulted in cleavage of the C-N bond. Thus, reaction (16) is the rate-determining step just as in  $\text{H}_3\text{O}^+$  catalysis. The water reaction proceeded by combination of  $\text{H}^+$  from a water molecule with the NH of C. Therefore, the experimental results can all be accounted for on the basis of reaction 16 as the rate-determining step.

When the dichloro derivative of X, 1,5-dichloro-3,7-endomethylenetetrazocyclooctane, was dis-

solved in acetic acid and the solution diluted with water, 1,3,5-trichlorotriazocyclohexane<sup>10</sup> then was formed; similarly the dinitro derivative of X in nitric acid gave 1,3,5-trinitrotriacyclohexane.<sup>11</sup> Therefore, the decomposition after the rate-determining step 16 probably proceeds thusly: since Z is derivative of X, Z decomposes through Y by reactions involving the elimination of methylene and amino groups.

(10) M. Delépine, *Bull. soc. chim.*, **9**, 1025 (1911).

(11) A. F. McKay, H. H. Richmond and G. F. Wright, *Can. J. Research*, **27**, 462 (1949).

MEGURO, TOKYO, JAPAN

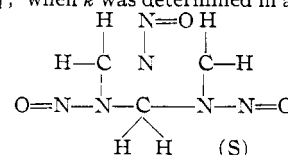
[CONTRIBUTION FROM TOKYO INSTITUTE OF TECHNOLOGY]

## Decomposition Reaction of 1,3,5-Trinitrosotriazocyclohexane by Acid

BY HIKOJI TADA

RECEIVED JULY 22, 1958

A kinetic study was made of the acid decomposition reaction of 1,3,5-trinitrosotriazocyclohexane (S). When the reaction was catalyzed by hydrochloric acid, the first-order rate constant was proportional to  $[\text{HCl}]$ ; when  $k$  was determined in a potassium biphthalate-hydrochloric acid buffer solution, it increased linearly with  $[\text{H}^+]$ . In the experiments on the neutral salt effect, the relative effectiveness of various anions and cations was determined:  $\text{I}^- > \text{Br}^- > \text{Cl}^-$ ;  $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{M}^{++}$ . The effect of anion on  $k$  and  $E$  was much greater than that of cation. In regard to the solvent effect: at first  $k$  decreased with the alcohol concentration, but suddenly increased when the water concentration was very small, due to the catalytic action of  $\text{ROH}_2^+$ . With dioxane, the sudden increase in  $k$  occurred at a higher water concentration.

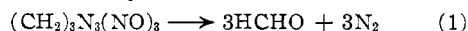


### Experimental

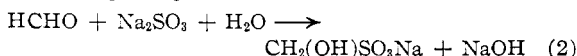
C.P. materials were used; solvents were purified by distillation. Care was taken to avoid reaction between the solvent and hydrochloric acid and to prevent crystal formation or turbidity in the reaction mixture.

1,3,5-Trinitrosotriazocyclohexane (S), m.p. 106°, was prepared by the method of Richmond, *et al.*<sup>1</sup>

The acid-catalyzed decomposition of S, eq. 1, is a first-order reaction with respect to S



Reaction rates were measured by mixing a methanolic solution of S with aqueous hydrochloric acid (A), the reaction was stopped after various periods of time by the rapid addition of sodium hydroxide solution, and the amount of formaldehyde formed measured by the sodium sulfite method<sup>2</sup>; *i.e.*, the resultant solutions were mixed with aqueous sodium sulfite solution, and the sodium hydroxide formed by reaction 2 was titrated with 0.1 *N* hydrochloric acid with phenolphthalein as the indicator



### Results and Discussion

**Acid Effect.**—The first-order rate constant, which was measured in a potassium biphthalate (K.H.P.)-hydrochloric acid (A) buffer solution increased linearly with  $[\text{H}^+]$ , as shown in Table I.

Since a water reaction did not accompany the hydrogen ion-catalyzed reaction,  $k$  is given by the equation:  $k = 8.3 \times 10^{-3} [\text{H}^+]$ .

The first-order rate constant increased linearly with  $[\text{HCl}]$ , when the reaction was catalyzed by hydrochloric acid (Table II).

The increase of  $k$  by the acid effect was due to a depression of  $E$  as shown in Table III.

(1) H. H. Richmond, G. S. Meyers and G. Wright, *THIS JOURNAL*, **70**, 3659 (1948); F. Mayer, *Ber.*, **21**, 2883 (1888).

(2) G. Lemme, *Chem. Ztg.*, **27**, 896 (1903).

TABLE I

THE EFFECT OF HYDROGEN ION CONCENTRATION ON THE RATE CONSTANT

$[\text{S}] = 1.33 \times 10^{-2}$  mole/l.,  $[\text{Methanol}] = 16.7$  vol. %,  $t = 45^\circ$

A, mole/l. $\times 10^2$	K.H.P., mole/l. $\times 10^2$	$[\text{H}^+] \times 10^3$	$k \times 10^3$
4.11	4.31	6.4	5.23
3.74	4.67	3.8	2.92
2.46	5.93	1.0	1.14
0.425	7.92	0.16	0.240

TABLE II

THE EFFECT OF HYDROCHLORIC ACID ON THE RATE CONSTANT

$t = 30^\circ$

S, mole/l. $\times 10^4$	A, mole/l. $\times 10^2$	$k \times 10^3$
6.15	0.792	1.32
6.15	3.18	5.69
6.15	7.92	17.3
3.69	3.18	5.93

TABLE III

ACID EFFECT

Methanol, vol. %	S, mole/l. $\times 10^3$	HCl, mole/l. $\times 10^2$	$V^a$	$E$ , kcal./mole	$\log C$	$\Delta S^*$ , cal./deg.
10.7	8.57	3.59	1.00	23.6	12.73	-2.28
16.7	13.3	12.8	4.82	22.9	12.90	-1.50

<sup>a</sup>  $V$  is the relative reaction rate.

The results in Table IV are typical for this acid-catalyzed decomposition.

**Neutral Salt Effect.**—In the case of a hydrogen ion-catalyzed reaction of a neutral molecule,  $k$