

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 H_3O^+ catalysis. The water reaction proceeded by combination of 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-trichlorotriazocyclohexane¹⁰ then was formed; similarly the dinitro derivative of X in nitric acid gave 1,3,5-trinitrotriazocyclohexane.¹¹ 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).

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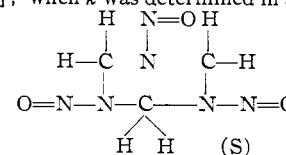
[CONTRIBUTION FROM TOKYO INSTITUTE OF TECHNOLOGY]

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 ROH_2^+ . With dioxane, the sudden increase in k occurred at a higher water concentration.

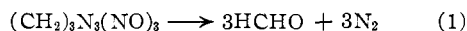


Experimental

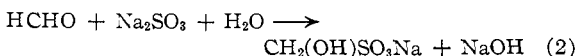
C.P. materials were used; solvents were purified by distillation. Care was taken to avoid reaction between the solvent and hydrochloric acid and to prevent crystal formation or turbidity in the reaction mixture.

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

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 method²; *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. $\times 10^3$	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. $\times 10^2$	HCl, mole/l. $\times 10^2$	V^a	E , kcal./mole	$\log C$	$\Delta S^*_{25^\circ}$, 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

^a 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

TABLE IV
DECOMPOSITION OF S CATALYZED BY HYDROCHLORIC ACID
[A] = 7.92×10^{-2} mole/l., [S] = 6.15×10^{-3} mole/l.,
 $t = 30^\circ$

T (sec.) $\times 10^3$	% S decomp.	$k \times 10^4$
1.08	15.8	1.59
2.58	34.6	1.64
4.08	54.7	1.94
6.72	68.6	1.73

other hand, a comparison of sodium chloride and bromide solutions shows that the larger anion, Br^- , caused a more marked depression of E than the smaller ion, Cl^- , a decrease in E which was accompanied by a considerable change in ΔS^* . That anion causes a greater decrease in E than cation in the neutral salt effect catalyzed by H^+ is reported here for the first time.

From equations 3 and 4 is obtained a linear

TABLE V
NEUTRAL SALT EFFECT
[A] = 3.59×10^{-2} mole/l.; [S] = 8.57×10^{-3} mole/l.; [methanol] = 10.7 vol. %

Salt	μ	$k \times 10^4$						E , kcal./ mole	log C	$\Delta F^* 25^\circ$, kcal./ mole	$\Delta S^* 25^\circ$, cal./ deg.
		15°	20°	25°	30°	35°	40°				
..	0.0359	0.0679	0.153	0.274	0.563	1.10	1.94	23.6	12.73	23.67	- 2.37
NaI	1.32			5.06							
	2.61			10.8							
NaBr	1.32			3.00							
	2.61	1.86	3.60	6.46	9.68	17.3	28.6	19.1	10.76	21.80	- 11.2
	4.32	4.40	8.49	15.3	25.6	43.2	62.2	18.8	10.96	21.29	- 10.3
LiCl	1.32			2.14							
	2.61			5.40							
NaCl	1.32			1.79							
	2.61	0.683	1.28	2.78	4.82	9.58	14.8	22.1	12.65	22.30	- 2.53
	3.25	.865	1.83	3.58	6.21	11.0	20.2	21.9	12.60	22.15	- 2.75
KCl	1.32	.272	0.634	1.23	2.27	4.04	7.92	22.9	12.88	22.78	- 1.53
	2.61	.492	0.930	1.93	3.59	6.00	11.2	22.4	12.67	22.52	- 2.44
CaCl_2^a	1.32			0.845							
	2.61			1.34							
SrCl_2^a	1.32			0.801							
	2.61			1.15							
BaCl_2^a	1.32			0.998							
	2.61			1.38							

^a Prior to titration, the alkaline earth ions were precipitated with sodium sulfate.

increases linearly with the ionic strength, according to equation 3.³

$$k = k_0(1 + b\mu) \quad (3)$$

Measurements were made in the presence of various salts at several concentrations; the effects of these variables on k are shown in Table V.

In the neutral salt effect, k increased linearly with μ in agreement with equation 3, with the exception that in the case of sodium bromide ($\mu = 4.32$), the increase in k was enormous.⁴ At a given ionic strength, the order of effectiveness of the cations was $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{M}^{++}$; the smaller the ion, the greater the effect. In the case of the anions, the order was $\text{I}^- > \text{Br}^- > \text{Cl}^-$; the larger the ion, the greater the effect. Several investigators⁵ have reported similar results but have not suggested an explanation. Table V shows that the effect of anions was much greater than that of cations.

The increase in k was due to a depression of E . In chloride solutions of the same ionic strength, the smaller cation, Na^+ , caused a slightly greater depression of E than the larger ion, K^+ ; on the

(3) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1941, p. 440.

(4) H. Tada, THIS JOURNAL, **82**, 255 (1960).

(5) E. A. Guggenheim and L. A. Wiseman, Proc. Roy. Soc. (London), **A203**, 17 (1950); A. R. Olson and L. K. J. Tong, THIS JOURNAL, **66**, 1555 (1944); F. A. Long and D. McIntyre, *ibid.*, **76**, 3243 (1954); J. N. Pearce and M. E. Thomas, J. Phys. Chem., **42**, 455 (1938); L. C. Riesch and M. Kilpatrick, *ibid.*, **39**, 561 (1935).

TABLE VI

THE SOLVENT EFFECT

[S] = 1.33×10^{-2} mole/l., [A] = 1.28×10^{-1} mole/l.,
 $t = 30^\circ$

Solvent	Vol. %	$k \times 10^5$	Solvent	Vol. %	$k \times 10^5$
Methanol	16.7	24.6	1-Propanol	44.4	6.04
Methanol	44.4	9.74	1-Propanol	72.2	3.37
Methanol	72.2	3.31	1-Propanol	94.4	3.35
Methanol	94.4	4.73	1-Propanol	100.0	60.8
Methanol	98.3	19.5	<i>t</i> -Butyl alc.	44.4	2.98
Methanol	100.0	82.5	<i>t</i> -Butyl alc.	72.2	1.87
Ethanol	16.7	16.2	Dioxane	16.7	11.0
Ethanol	44.4	4.84	Dioxane	44.4	3.72
Ethanol	72.2	1.94	Dioxane	72.2	3.45
Ethanol	94.4	2.28	Dioxane	88.9	17.9
Ethanol	97.8	3.16	Dioxane	92.4	30.6
Ethanol	99.1	4.22	Dioxane	94.4	67.8
Ethanol	100.0	18.5	Dioxane	100.0	209

relation between ΔF^* and $\log(1 + b\mu)$, where b represents a specific coefficient for each salt. E

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

is inversely proportional to $\log(1 + b\mu)$ (Fig. 1) because the differences in ΔS^* were comparatively small for the various cations and for different concentrations of the same ion.

These results concerning the relative effectiveness of various ions in the neutral salt effect are in agreement with the activity coefficients, α , of these ions

TABLE VII

[S] = 1.33×10^{-2} mole/l.; [A] = 1.28×10^{-1} mole/l.

Solvent	Vol. %	$k \times 10^6$						E , kcal./ mole	log C	$\Delta F^* 25^\circ$, kcal./ mole	$\Delta S^* 25^\circ$, cal./ deg.
		20°	25°	30°	35°	40°	45°				
Methanol	16.7	6.58	13.2	24.6	46.4	81.3	22.9	12.90	22.74	- 1.50	
Methanol	72.2		1.71	3.31	5.22	11.7	23.9	12.73	23.95	- 2.28	
Ethanol	72.2		0.97	1.94	3.64	6.99	24.6	13.00	24.29	- 1.06	
Dioxane	100.0 ^a	77.0	125	209			14.4	7.64	21.41	-25.6	

^a $k = 40.8$ and 54.0×10^{-1} at 10 and 15°, respectively.

estimated from the Debye-Hückel expression for α .⁶

This is reasonable since the coefficient b in equation 3 is derived from the correction term $b\mu$ in the Debye-Hückel equation 5, and in concentrated

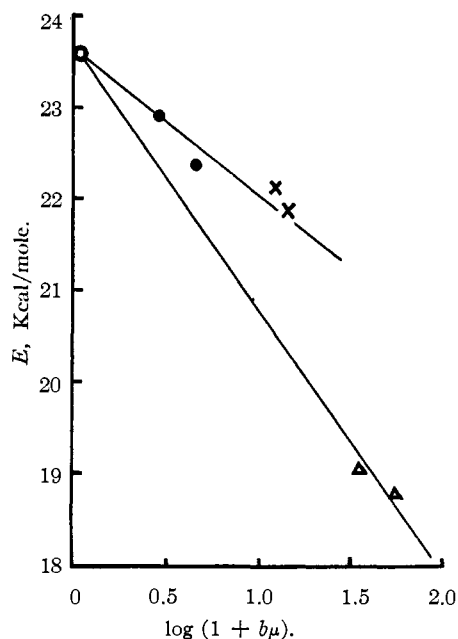


Fig. 1.—Relation between energy of activation and ionic strength: [A] = 3.59×10^{-2} mole/l., [S] = 8.57×10^{-3} mole/l., [methanol] = 10.7 vol %; O, blank; ●, KCl; ×, NaCl; Δ NaBr.

solution b and α are dependent on the character of the ion. In this type of neutral salt effect, b would be greater the smaller the cation and the larger the anion.

$$\ln \alpha = -aZi^2 \sqrt{\mu} \times \frac{1}{1 + Ba_1\sqrt{\mu}} + b\mu \quad (5)$$

The finding that anion exerted a greater influence on k than cation can be explained as follows: the appearance probability of anion in the vicinity of the positively charged, activated complex, SH^+ , would be higher than that of cation. Therefore, if it assumed that SH^+ is the center ion surrounded by an ionic atmosphere, anion would be more effective in the stabilization of SH^+ , *i.e.*, anions would cause a greater depression of E .

Solvent Effect.—The data on the solvent effect are listed in Table VI. In the case of the alcohols, k at first decreased with decreasing water concentration and then increased suddenly when the water concentration was very low or when water

was absent. On the other hand, k first decreased with increasing dioxane and then suddenly increased when the dioxane concentration was over about 80 vol. %. Braude obtained similar results.⁷

The rate constants determined at various temperatures and the values for E , etc., are given in Table VII.

The decrease of k in the solvent effect was due to an increase of E , and there was hardly any change in ΔS^* . The sudden increase of k in the absence of water was due to depression of E , which was accompanied by a marked change in ΔS^* .

Rate constants were determined in benzene-methanol solutions containing 27.8–88.9 vol. % benzene; a minute quantity of the surface-active agent, Triton, was added prior to the titration. The rate constant increased markedly with benzene concentration, and $\log k$ was proportional to $1/D^3$ (Fig. 2).

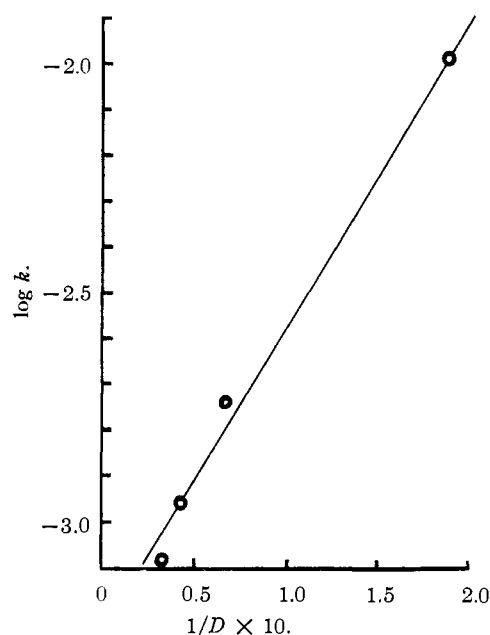
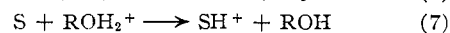
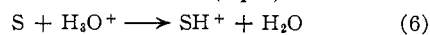


Fig. 2.—Effect of D and k in methanol-benzene system; [A] = 1.28×10^{-1} mole/l., [S] = 1.33×10^{-2} mole/l., $t = 30^\circ$.

The sudden increase of k in alcohol solution in the presence of very little or no water was due to the catalytic action of ROH_2^+ (eq. 7). In the com-



petitive reactions shown in eq. 6 and 7, 6 proceeded

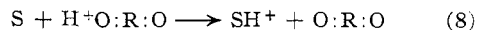
(7) E. A. Braude and E. S. Stern, *J. Chem. Soc.*, 1982 (1948).

(8) Ref. 3, p. 430.

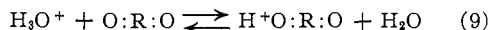
(6) Landolt-Börnstein, "Physikalische-Chemische Tabellen," Zweiter Ergänzungs Band, J. Springer, Berlin, 1931, p. 1114.

even when the water concentration was small as the oxonium salt of alcohol is very unstable; *i.e.*, $[\text{ROH}_2^+]$ was very low under these conditions.

In dioxane (O:R:O) solution, reactions 6 and 8 compete



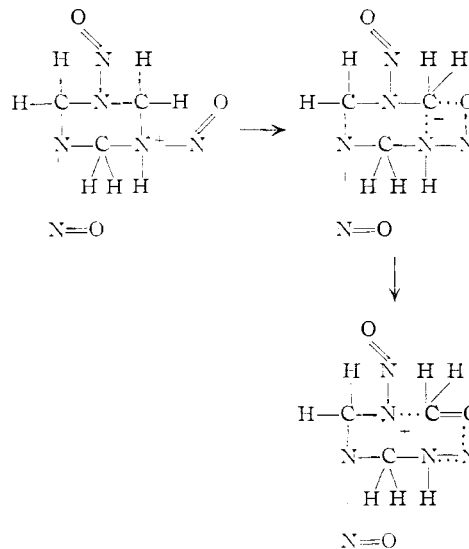
When $[\text{H}_2\text{O}]$ was large, $[\text{H}^+\text{O}:\text{R}:\text{O}]$ was practically negligible and (6) proceeded. When $[\text{H}_2\text{O}]$ was small, $[\text{H}^+\text{O}:\text{R}:\text{O}]$ in the equilibrium state of reaction 9 was appreciable as ethers, unlike alcohols, readily form oxonium salts.



Therefore, k increased with the dioxane concentration even when some water was present, because the activation energy of reaction 8 is low. This interpretation is supported by the values obtained for ΔS^* . No pronounced change in ΔS^* occurred in the acid effect or in the solvent effect when some water was present; this suggests that the reaction with H_3O^+ (6) proceeded. The pronounced decrease in ΔS^* in dioxane suggests that reaction 8 occurred and that the degree of freedom of the activated complex in this case was considerably less than that of the activated complex of the reaction with H_3O^+ .

The addition of benzene caused a remarkable increase in k in the methanol reaction mixture. When the reaction mixture contained 100 vol. % benzene (no contained alcohols), the decomposition did not proceed according to (1), but a brown gelatinous mass appeared which subsequently dissolved with the evolution of a gas, giving a brown

solution. Therefore catalytic action by molecular hydrochloric acid did not take place. The solvent effect in the case of methanol-benzene solution was due to the catalytic action of CH_3OH_2^+ as shown by the linear relation between $\log k$ and $1/D$. These results indicate that water is unnecessary for the reaction and suggest this reaction mechanism: after the addition of a proton to S, the carbonium ion was formed which reacted with the nitroso group to split off formaldehyde; nitrogen was produced and the molecule decomposed.



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[CONTRIBUTION FROM TOKYO INSTITUTE OF TECHNOLOGY]

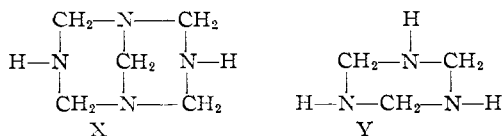
Decomposition Reaction of 1,3,5-Trimethyltriazocyclohexane and 1,5-Endomethylene-3,7-tetrazocyclooctane Derivatives by Acid

BY HIKOJI TADA

RECEIVED JULY 22, 1958

A kinetic study was made of the acid decomposition reaction of 1,3,5-trimethyl-triazocyclohexane and of 1,5-endomethylene-3,7-tetrazocyclooctane derivatives.

In the preceding paper,¹ the rates of the acid decomposition of derivatives of 1,5-endomethylene-3,7-tetrazocyclooctane (X) and of the trimethyl derivative of 1,3,5-triazocyclohexane (Y) were found to be much faster than that of hexamine, a result which was useful for the elucidation of the mechanism of the hexamine decomposition. In this study a detailed kinetic study is reported of the acid decomposition of derivatives of X and Y.



Experimental

C.P. grade chemicals were used; the solvents were purified by distillation.

(1) H. Tada, *THIS JOURNAL*, **82**, 263 (1960).

1,3,5-Trimethyl-triazocyclohexane (M) was prepared from an aqueous solution of methylamine and formalin; b.p. 162–163°.²

The 3,7-disubstituted derivatives of X were prepared as follows: The dinitroso compound (N) was obtained by the addition of dilute nitric acid to an ice-cooled aqueous solution of sodium nitrite and hexamine; m.p. 207°.³ The diacetyl derivative (E) was prepared from hexamine by the addition of acetic anhydride and ether; m.p. 188°.⁴ The 3,7-bis-azophenyl compound (P) was synthesized from hexamine and phenyldiazonium salt; m.p. 228°.⁵ The dichloro derivative (C) was prepared by the addition of sodium hypochlorite solution to an aqueous solution of hexamine; it decomposed at 78°.⁶

(2) "Beilstein," Bd. XXVI, J. Springer, Berlin, 1937, p. 1.

(3) H. H. Richmond, G. S. Meyers and G. Wright, *THIS JOURNAL*, **70**, 3659 (1948); P. Griess and G. Harrow, *Ber.*, **21**, 2737 (1888); F. Mayer, *ibid.*, **21**, 2883 (1888).

(4) M. Domikowicz, *Arch. Chem. Farm.*, **2**, 78 (1935); *Chem. Zentr.*, **106**, 1884 (1935).

(5) H. H. Richmond, G. S. Meyers and G. Wright, *THIS JOURNAL*, **70**, 3659 (1948); P. Duden and M. Scharff, *Ann.*, **287**, 241 (1895).

(6) M. Delépine, *Bull. soc. chim.*, **9**, 1025 (1911); *J. Chem. Soc.*, **97**, 2404 (1911).