even when the water concentration was small as the oxonium salt of alcohol is very unstable; *i.e.*, $[ROH_2^+]$ was very low under these conditions.

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

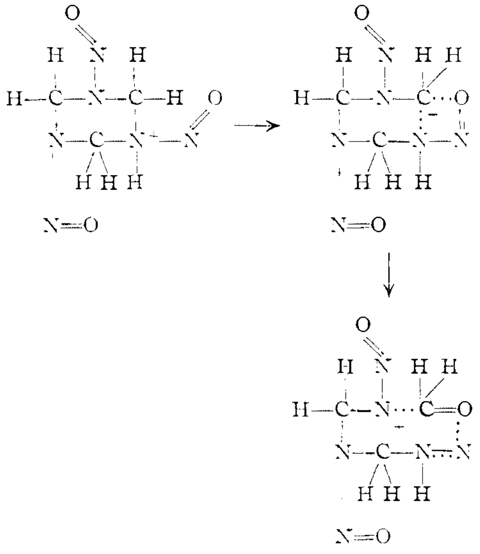
$$S + H^+O{:}R{:}O \longrightarrow SH^+ + O{:}R{:}O \qquad (8)$$

When $[H_2O]$ was large, $[H^+O{:}R{:}O]$ was practically negligible and (6) proceeded. When $[H_2O]$ was small, $[H^+O{:}R{:}O]$ in the equilibrium state of reaction 9 was appreciable as ethers, unlike alcohols, readily form oxonium salts.

$$H_3O^+ + O{:}R{:}O \rightleftarrows H^+O{:}R{:}O + H_2O \qquad (9)$$

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.



MEGURO, TOKYO, JAPAN

[CONTRIBUTION FROM TOKYO INSTITUTE OF TECHNOLOGY]

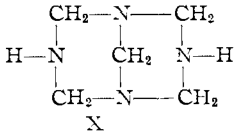
Decomposition Reaction of 1,3,5-Trimethyltriazocyclohexane and 1,5-Endomethylene-3,7-tetrazocyclooctane Derivatives by Acid

BY HIKOJI TADA

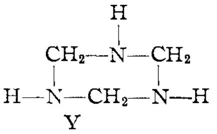
RECEIVED JULY 22, 1958

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.



X



Y

Experimental

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

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]

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

[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. Domikiowicz, *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).

Determination of Reaction Rate.—The reaction rate was determined by the procedure described in the preceding paper[1] with some modifications. An aqueous solution of M was mixed with a known amount of aqueous hydrochloric acid (A), the reaction was stopped after various periods of time by the rapid addition of a large quantity of water and the unconsumed hydrochloric acid titrated with sodium hydroxide with methyl orange as the indicator. P was dissolved in acetone and the reaction mixture contained 80 vol. % acetone; the unconsumed hydrochloric acid was determined by a potentiometric titration. In the case of N and E, the reaction was stopped by the rapid addition of sodium hydroxide solution, and the hydrochloric acid consumed determined by titration of the excess sodium hydroxide with hydrochloric acid using methyl orange as the indicator; in the experiments in acetic acid–sodium acetate buffer, the acetic acid consumed was determined, using phenolphthalein as the indicator. An aqueous solution of E was used; N was dissolved in acetone and the reaction mixture contained 7.69 vol. % acetone. An ethanolic solution of C was mixed with an aqueous solution of acetic acid and silver nitrate; the reaction mixture contained 45.5 vol. % ethanol. The reaction was stopped by the addition of sodium chloride, silver chloride was removed and the unconsumed acetic acid titrated with sodium hydroxide with phenolphthalein as the indicator; ClO^- which would have interfered with the titration was removed by the silver ion[7]

$$3ClO^- + 2Ag^+ \longrightarrow 2AgCl + ClO_3^-$$

In the experiments with N, P and C, care was taken to prevent turbidity or crystal formation by sample. In studies of the neutral salt effect, the ionic strength μ was varied by the addition of sodium chloride.

1,3,5-Trimethyl-triazocyclohexane (M).—

$$(CH_3NCH_2)_3{\cdot}HCl + 2HCl + 3H_2O \longrightarrow 3CH_3NH_2{\cdot}HCl + 3HCHO$$

In the titration of M with acid, a significant *p*H change occurred at the neutralization point, as M is a weak monoacidic base; *i.e.*, it exists quantitatively as MH^+ in the presence of sufficient acid. The reaction rate did not increase with an increase in the amount of excess hydrochloric acid (A–M), and it is a first-order reaction with respect to $[MH^+]$; see Table I. The half-life τ is independent of the initial concentration as shown in Table II.

TABLE I

THE EFFECT OF EXCESS HYDROCHLORIC ACID ON THE RATE CONSTANT; $t = 0.6°$

A,[a] mole/l. × 10²	M, mole/l. × 10²	*k* 1st × 10³
3.65	1.07	4.68
4.38	1.07	4.70
5.12	1.07	4.63
3.65	1.50	4.96
3.65	1.93	4.41
5.12	1.50	4.92

[a] A represents hydrochloric acid.

TABLE II

HALF-LIFE OF THE DECOMPOSITION

$M \sim A$ is $0.3 \sim 1$, $t = 0.6°$

M, mole/l. × 10²	τsec (1st-order)	$1/M\tau$ (2nd-order)	$1/M^2\tau$ (3rd-order)
1.50	135	0.413	27.5
1.07	140	.667	62.3
0.75	155	.860	115
0.50	160	1.25	250

It was expected that the neutral salt effect would not occur because this reaction is not catalyzed by an increase in the amount of excess acid;. as Table III shows, the rate constant was independent of the ionic strength.

TABLE III

NEUTRAL SALT EFFECT

$[A] = 2.56 \times 10^{-2}$ mole/l., $[M] = 7.50 \times 10^{-3}$ mole/l $t = 0.6°$

μ	$k \times 10^3$
0.0256	4.36
.0856	4.37
.176	4.50
.326	4.25
.776	4.05
1.53	4.05

TABLE IV

DECOMPOSITION OF M

$[A] = 3.65 \times 10^{-2}$ mole/l., $[M] = 1.07 \times 10^{-2}$ mole/l., $t = 0.6°$

T (sec.)	% M dec.	$k \times 10^3$
40	17.3	4.73
65	27.4	4.89
90	33.8	4.56
135	48.7	4.94
200	62.8	4.92
255	68.4	4.64
305	74.4	4.46
360	80.9	4.58

TABLE V

$[A] = 2.56 \times 10^{-2}$ mole/l., $[M] = 7.50 \times 10^{-3}$ mole/l.

Temp., °C.	$k \times 10^3$
0.6	4.28
2.5	5.93
5.0	7.98
9.5	10.9
10.0	15.0

The results of a typical experiment are given in Table IV. From the rate constants determined at various temperatures (Table V), these values were calculated: activation energy E = 19,100 cal./mole, frequency factor C (p.z.) = 7.17 × 10,[12] and entropy of activation $\Delta S^* = -1.53$ cal./deg., 0.6°.

1,5-Dinitroso-3,7-endomethylenetetrazocycloöctane (N).—The relationship between the reaction rate and hydrogen ion concentration was investigated by determining *k* in buffered solutions; see Table VI. The rate constant of 1st order increased linearly with $[H^+]$ according to the equation: $k = 6.00 \times 10^{-6} + 4.04 \times 10^{-1} [H^+]$, $t = 30°$. The H^+ catalyzed reaction was accompanied by a water reaction, *i.e.*, the N reacted with water even in the absence of acid as shown in Table VII.

TABLE VI

THE EFFECT OF HYDROGEN ION CONCENTRATION ON THE RATE CONSTANT

$[N] = 6.15 \times 10^{-3}$ mole/l., $[CH_3COOH] = 1.54 \times 10^{-2}$ mole/l., $t = 30°$

$[H^+] \times 10^5$	$k \times 10^5$	CH_3COONa, mole/l. × 10³
39.9	16.8	0.769
23.5	9.78	1.54
9.34	4.56	3.85
5.02	2.45	7.69
2.14	1.55	15.4
1.00	1.12	30.8
0.08	0.206[a]	....

[a] Water reaction (in the absence of acetic acid).

A second-order reaction took place when the reaction was catalyzed by hydrochloric acid

$$(CH_2)_5N_4(NO)_2 + 2HCl + 3H_2O \longrightarrow 5HCHO + 2N_2 + 2NH_4Cl$$

and the neutral salt effect occurred as shown in Table VIII.

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[7] J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. II, Longmans, Green and Co., New York, N. Y., 1952, p. 256.

TABLE VII

DECOMPOSITION OF N BY THE WATER REACTION

[N] = 6.15 × 10^{-3} mole/l., *t* = 30°

T (sec.)	% N dec.	*k* × 10^6
5.4 × 10^3	2.40	2.48
10.8 × 10^3	3.20	2.00
16.2 × 10^3	4.27	2.00
21.6 × 10^3	5.74	2.16
31.2 × 10^3	7.34	2.08

TABLE VIII

NEUTRAL SALT EFFECT

[A] = 1.82 × 10^{-2} mole/l., [N] = 6.15 × 10^{-3} mole/l., *t* = 30°

μ	*k*
0.018	1.08
.0797	1.09
.172	1.08
.326	1.14
.787	1.34
1.25	1.50
1.56	1.42

TABLE IX

DECOMPOSITION OF N CATALYZED BY HYDROCHLORIC ACID

[A] = 1.82 × 10^{-2} mole/l., [N] = 6.15 × 10^{-3} mole/l., *t* = 20°

T (sec.)	% N dec.	*k*
33	17.3	0.345
75	32.8	.336
136	48.4	.336
176	58.7	.369
262	73.5	.320
634	86.1	.293
894	94.2	.354

From the rate constant determined at various temperatures (Table X), these values were calculated: *E* = 20,200 cal./mole, p.z. = 2.79 × 10^{14}, Δ*S** = +5.57 cal./deg., 25°.

TABLE X

[A] = 1.82 × 10^{-2} mole/l., [N] = 6.15 × 10^{-3} mole/l.

Temp., °C.	*k*
20	0.336
25	.586
30	1.08
35	1.70
40	2.99

1,5-Diacetyl-3,7-endomethylenetetrazocycloöctane (E).—The first-order rate constants were determined in buffered solutions (Table XI); *k* increased linearly with [H⁺], *k* = 5.0 × 10^{-3} [H⁺].

$$(CH_2)_5N_4(CH_3CO)_2 + 2HCl + 7H_2O = 2NH_4Cl + 2CH_3COONH_4 + 5HCHO$$

TABLE XI

THE EFFECT OF HYDROGEN ION CONCENTRATION ON THE RATE CONSTANT

[E] = 4.71 × 10^{-2} mole/l., [CH_3COOH] = 1.02 × 10^{-1} mole/l., *t* = 45°

[H⁺] × 10^4	*k* × 10^6	CH_3COONa, mole/l. × 10^3
9.8	4.09	2.50
5.7	2.73	5.00
3.6	2.28	7.50
2.8	1.43	10.0
2.2	1.03	12.5

A second-order reaction took place when the reaction was catalyzed by hydrochloric acid, and the second-order *k* increased linearly with respect to μ (Table XII).

TABLE XII

NEUTRAL SALT EFFECT

[A] = 9.34 × 10^{-2} mole/l., [E] = 4.71 × 10^{-2} mole/l., *t* = 30°

μ	*k* × 10^3
0.0934	2.71
.293	3.11
.493	3.34
1.09	4.16
1.89	5.10

TABLE XIII

DECOMPOSITION OF E CATALYZED BY HYDROCHLORIC ACID

[A] = 4.67 × 10^{-2} mole/l., [E] = 2.36 × 10^{-2} mole/l., *t* = 30°

T (sec.) × 10^{-2}	% E dec.	*k* × 10^3
9.3	13.0	3.47
18.0	23.3	3.65
27.0	31.2	3.62
36.0	36.4	3.44
54.0	47.5	3.64
72.0	54.6	3.63

From the rate constants determined at various temperatures (Table XIV), these values were calculated: *E* = 23,000 cal./mole, p.z. = 1.25 × 10^{14}, Δ*S** = +3.98 cal./deg., 25°.

TABLE XIV

[A] = 9.34 × 10^{-2} mole/l., [E] = 4.71 × 10^{-2} mole/l.

Temp., °C.	*k* × 10^3
25	1.32
30	2.71
35	5.14
40	9.22
45	17.0

1,5-Bis-azophenyl-3,7-endomethylenetetrazocycloöctane (P).—

$$(CH_2)_5N_4(N_2C_6H_5)_2 + 2HCl + 5H_2O \longrightarrow 5HCHO + 2N_2 + 2NH_4Cl + 2C_6H_5NH_2$$

Since the reaction mixture contained a large quantity of hydrochloric acid, the first-order equation with respect to P was used.

TABLE XV

DECOMPOSITION OF P

[A] = 1.89 × 10^{-2} mole/l., [P] = 2.14 × 10^{-3} mole/l. *t* = 20°

T (sec.)	% P dec.	*k* × 10^3
113	22.3	2.24
276	44.6	2.22
365	56.2	2.27
590	74.1	2.29

The rate constants determined at various temperatures are listed in Table XVI.

TABLE XVI

[A] = 1.89 × 10^{-2} mole/l., [P] = 2.14 × 10^{-3} mole/l., *E* = 19,900 cal./mole, *C* = 1.52 × 10^{12}, Δ*S** = −4.79 cal./deg., 25°

Temp., °C.	*k* × 10^3
20	2.25
30	6.80
35	12.2

1,5-Dichloro-3,7-endomethylenetetrazocycloöctane (**C**).—

$$(CH_2)_5N_4Cl_2 + 4CH_3COOH + 7H_2O \longrightarrow 5HCHO + 4CH_3COONH_4 + 2HClO$$

Since the rates are initial rates measured during the early stages of the reaction, the first-order equation with respect to C was used.

TABLE XVII

DECOMPOSITION OF C

[C] = 9.23×10^{-3} mole/l., [CH_3COOH] = 4.55×10^{-2} mole/l., [$AgNO_3$] = 2.28×10^{-2} mole/l., t = 20°

T (sec.)	% C dec.	$k \times 10^4$
510	8.6	1.68
720	11.5	1.69
1200	17.2	1.57
1400	22.3	1.82

The rate constants determined at various temperatures are listed in Table XVIII.

TABLE XVIII

[C] = 9.23×10^{-3} mole/l., [CH_3COOH] = 4.55×10^{-2} mole/l., [$AgNO_3$] = 2.28×10^{-2} mole/l., E = 15,000 cal./mole, C = 1.52×10^7, ΔS^* = -2.77 cal./deg., 25°.

Temp., °C.	$k \times 10^4$
20	1.6
23	1.8
25	2.5
30	3.0

MEGURO, TOKYO, JAPAN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, DAVIS]

The Kinetics of Ozonization of Polyalkylbenzenes

BY T. W. NAKAGAWA, L. J. ANDREWS AND R. M. KEEFER

RECEIVED JUNE 8, 1959

A spectrophotometric method has been employed in studying the kinetics of the reactions of a series of polyalkylbenzenes with ozone in carbon tetrachloride and in acetic acid at 25°. Rate constants have been calculated on the assumption that the reactions are first order in ozone and in aromatic hydrocarbon and that three molecules of ozone are consumed per mole of aromatic substance. For reaction in a particular solvent the logarithms of the constants for the polymethylbenzenes increase linearly with the number of methyl substituents on the aromatic nucleus. The rate constants for the polyethyl- and polyisopropylbenzenes are similar in magnitude to those for the polymethylbenzenes with the exception of that for hexaethylbenzene. The logarithms of rate constants for this compound and for *t*-butyl substituted benzenes fall far short of the line which best accommodates the data for their methyl analogs, a fact which is explained on steric grounds. The products of ozonization of the aromatic hydrocarbons at 25° are similar to those formed at much lower temperatures.

Because of the favorable electronic influences of alkyl substituents on π electron availability, the stabilities of donor–acceptor complexes of polymethylbenzenes with iodine and with iodine monochloride increase as the donor ring becomes more extensively alkylated.[1,2,3] With the exception that hexaethylbenzene is a very weak donor the polyethylbenzene–halogen complexes also become more stable as the number of ring substituents is increased. Presumably the six large alkyl groups in the hexaethylbenzene molecule inhibit the coördination of an acceptor by forming a protective screen about the electrons of the aromatic nucleus.

It may be anticipated, if the steric interpretation of its low donor strength is correct, that hexaethylbenzene will also be unusually resistant to attack by electrophilic reagents. Two such reagents which are appropriate for use in studying hexaalkylbenzenes are perbenzoic acid[4] and ozone.[5] It has been shown previously[4] that perbenzoic acid reacts somewhat less rapidly with hexaethylbenzene than with hexamethylbenzene in chloroform, although it oxidizes mesitylene and 1,3,5-triethylbenzene at comparable rates. The differences in reactivity of the two hexaalkylbenzenes are not, however, sufficiently large to support strongly the argument that the hexaethyl derivative is, for steric reasons, resistant to electrophilic attack.

In earlier investigations of the kinetics of ozonization of aromatic hydrocarbons in solution, the reaction mixtures were continuously saturated with ozone, and the concentrations of the benzene derivatives were relatively high initially.[5–7] Even at temperatures below 0° the more highly alkylated benzenes proved to be so reactive that they were susceptible only to qualitative investigation when this procedure was used. A spectrophotometric method for studying aromatic ozonization kinetics has now been developed which is applicable to solutions of the reactants at high dilution at room temperature. This method has been successfully applied in demonstrating that hexaethylbenzene is indeed much less reactive than hexamethylbenzene in both carbon tetrachloride and acetic acid. Ozonization rate constants for a large number of other alkyl substituted benzenes in these solvents also have been determined. In general the effects of alkyl substituents on alkylbenzene reactivity (with respect to ozone) are parallel to those encountered in investigating halogen complex stabilities.

Experimental

Materials.—With certain exceptions the sources and methods of purification of the alkylbenzenes already have been described.[3] Hemimellitene, pseudocumene and *t*-butylbenzene of purissima grade were obtained from the Aldrich Chemical Co. and were used without further treatment.

Acetic acid was purified for use as a solvent in rate work by the procedure of Orton and Bradfield.[8] It was established by spectrophotometric methods that ozone decomposed in this solution at the approximate rate of 8% per hour at 25°.

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[2] R. M. Keefer and L. J. Andrews, *ibid.*, **77**, 2164 (1955).

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[5] J. P. Wibaut and F. L. J. Sixma, *Rec. trav. chim.*, **71**, 761 (1952).

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