however, since the isomerization requires 65 kcal./mole.[12]

All of the frequency factors are "normal," *i.e.*, around 10^{13} sec.$^{-1}$, implying little, if any, entropy of activation. Although the transition state involves a freezing of a single restricted internal rotation, with a consequent entropy decrease, the fact that there are three equivalent positions leading to reaction on a 360° rotation about the C–C bond of ethyl bromide leads effectively to an entropy increase which must nearly balance the aforementioned decrease. The frequency factor for the isopropyl bromide decomposition is, as expected, higher than for the other two. There are twice as many chances for reaction during internal rotation as there are for ethyl bromide. The numerical value of 5 is somewhat larger than predicted by this simple interpolation, but the conclusion is valid within the experimental error.

The lower activation energy observed for isopropyl bromide is in the direction to be expected on the basis of the known electron directing power of the methyl group. Whether the magnitude of this difference in activation energy between this and the other bromides is reasonable, is a question which we are unable to answer.

We are indebted to Professor F. Daniels and Dr. A. Goldberg for stimulating discussions. Dr. Goldberg also collaborated with us on some of the HBr analyses. Mr. D. Johnson performed the infrared analyses. This work received financial support by the University Research Committee from funds supplied by the Wisconsin Alumni Research Foundation.

MADISON, WISCONSIN

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[12] T. S. Chambers and G. B. Kistiakowsky, THIS JOURNAL, **56**, 399 (1934).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF NEW YORK UNIVERSITY]

Kinetics and Mechanism of the Acid-Catalyzed Decomposition of Diazoacetone[1]

BY CHARLES E. MCCAULEY AND CECIL V. KING

RECEIVED MARCH 21, 1952

In dilute aqueous acids the conversion of diazoacetone to hydroxyacetone is catalyzed by hydronium ion but not by other acids. Neutral salts increase the rate, the effect of each salt being somewhat specific and showing little or no influence of the charge type of the cation. With halides present, considerable amounts of haloacetone are formed; with nitrates, a small amount of nitric acid enters the product. The mechanism of reaction with water and halogen acids is similar to that of diazoacetic ester; the rate-determining steps are subsequent to an equilibrium reaction with hydrogen ion, prior to or simultaneous with nitrogen expulsion.

The convenient synthesis of diazoketones discovered by Arndt and Eistert in 1927 has made these compounds useful intermediates in organic preparative chemistry.[2] Since no kinetic studies have been published, it was decided to examine the decomposition rate of diazoacetone in aqueous acid solutions. It was proposed to determine (a) the general level of rates as compared to other aliphatic diazo compounds, (b) the order of reaction with respect to diazoacetone and acid, (c) whether there is general acid or only specific hydronium ion catalysis, (d) the nature and magnitude of neutral salt effects, (e) whether the reaction can be used to measure unknown hydrogen ion concentrations, (f) whether any acid anions enter the product or act as specific catalysts, and (g) whether the kinetic results might elucidate the reaction mechanism. More or less satisfactory information has been obtained on all these points.

Materials and Method

Diazoacetone was prepared by the reaction of freshly distilled acetyl chloride with a sevenfold excess of diazomethane in dry ether.[3] After removing all ether, it was distilled through a short helix-packed column at 11.5 mm. Starting with 25 ml. (28 g.) of acetyl chloride, about 20 g. of diazoacetone could be collected at 46.0–46.8°. The specific gravity $^{28}/_{28}$ was 1.058, $n^{21}\mathrm{D}$ was 1.488. Arndt and Amende report a boiling point of 49° at 13 mm. The compound gave 98% of the theoretical nitrogen from dilute acid, as determined in the rate measuring apparatus by careful comparison with hydrogen evolution from zinc and acid. There was no deterioration over a period of 16 months.

Stock sodium hydroxide solution (carbonate-free) was prepared with especial care and standardized with a precision of two parts in 1500; this was used to standardize the various acids. Monochloroacetic acid was recrystallized from water, then from benzene.

Barium perchlorate stock solutions were made from pure barium carbonate and standard perchloric acid; zinc perchlorate from C.P. metal; lanthanum perchlorate from the commercial nitrate *via* oxalate ignited to oxide, followed by dissolution in standard perchloric acid. Sodium perchlorate solutions were prepared both from pure sodium carbonate and from the commercial salt after recrystallization and dehydration. Sodium benzenesulfonate was decolorized with charcoal and recrystallized from ethanol. A titration curve showed no weak acid anions present. Other salts were of analytical grade and were dried at 125° for weighing, or the solutions were standardized.

Rates were measured by following nitrogen pressure in an apparatus similar to that described by Brönsted and Duus.[4] The solution volume was 50 ml. and the diazoacetone sample was normally 0.04 ml. Since in some solutions the reaction was quite rapid (half-time 3 to 5 min.) it was necessary to maintain an optimum shaking rate[5] (200 per minute with the apparatus used). Ordinarily first-order rate constants were evaluated by the Guggenheim method in the most rapid experiments by using the final pressure readings. There was always sufficient excess reagent to make the rates essentially first order.

The bath thermometer was compared with one calibrated at the National Bureau of Standards. It is believed that the error in computing each rate constant k is less than 1%. Rates were nearly always reproducible within 3%, usually

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[1] Manuscript prepared from a thesis submitted by Charles E. McCauley in partial fulfillment of the requirements for the Ph.D. degree at New York University, February, 1952.

[2] W. E. Bachman and W. S. Struve, "Organic Reactions," Vol. I, John Wiley and Sons, New York, N. Y., 1942, Chap. 2.

[3] F. Arndt and J. Amende, *Ber.*, **61**, 1124 (1928).

[4] J. N. Brönsted and H. Duus, *Z. physik. Chem.*, **117**, 229 (1925).

[5] K. J. Pedersen, THIS JOURNAL, **49**, 2681 (1927).

2%. Critical experiments were always repeated several times.

Experimental Results

1. **Perchloric Acid.**—Titration of solutions after reaction showed that this acid does not enter the product, nor is any weak acid formed, *i.e.*, there is no rearrangement. The reaction is therefore assumed to be

$$CH_3COCHN_2 + H_2O \longrightarrow CH_3COCH_2OH + N_2 \quad (1)$$

The product hydroxyacetone or acetol was identified by its isolation as the 2,4-dinitrophenylosazone (m.p. 298°); comparison was made with an authentic sample of acetol.

The rate was found to be strictly first order with respect to diazoacetone, not quite first order with respect to acid unless total ionic concentration was kept constant by suitable salt additions. The initial concentration of diazoacetone was varied fourfold in a few experiments with no variation in rate constant. Successive runs in the same solution showed that the acetol produced had no effect on the rate.

Tables I and II show the rate constants obtained in perchloric acid alone and with sodium perchlorate added to maintain constant total ionic concentration. The data of Table I for 25° may be expressed by the equation

$$k = 1.275\ C_{H^+}\ (1 + 0.863\ C_{HClO_4}) \quad (2)$$

with an average deviation of 0.93%, maximum deviation 2.6%. The data of Table II are linear in acid at each ionic strength and are best represented by similar equations with slightly different constants. The salt effect is linear in total concentration, which is characteristic for this type of reaction, in this concentration range

TABLE I

RATE CONSTANTS IN PERCHLORIC ACID ALONE

t, °C.	C_{HClO_4}, M	No. expts.	Av. k, min.$^{-1}$	Av. dev.
25.06	0.02	7	0.0257	0.0003
	.03	1	.0393	....
	.04	19	.0527	.0005
	.05	1	.0660	....
	.06	4	.0810	.0009
	.07	2	.0959	.0004
	.08	3	.1119	.0005
	.09	3	.1245	.0012
	.10	7	.1369	.0010
19.98	.04	4	.0292	.0001
29.98	.04	4	.0894	.0006

TABLE II

AVERAGE RATE CONSTANTS WITH SODIUM PERCHLORATE TO MAINTAIN CONSTANT IONIC STRENGTH, 25.06°

C_{HClO_4}, M	k, $\mu = 0.1$	k, $\mu = 0.2$
0.02	0.0279	0.0306
.04	.0550	.0607
.06	.0832	.0909
.08	....	.1209
.10	.1369	.1516

2. **Monochloroacetic Acid.**—Since there is no perceptible decomposition of diazoacetone in dilute base or pure water, and the hydrogen ion catalysis is comparatively small, general acid catalysis seemed unlikely. To test this point further a few experiments were run in monochloroacetic acid, since the molecular acid is a powerful catalyst in favorable cases.

In Table III, values of the ionization constant K_A are from the precision data of Shedlovsky, Brown and MacInnes,[6] and hydrogen ion concentrations (third column) are taken from these. Values in the last column are calculated from the rate constants using equation (2), assuming that the salt effect is the same as in perchloric acid. The close agreement gives no indication of molecular acid catalysis, and shows that the diazoacetone reaction may be used to measure unknown hydrogen ion concentrations in solutions of suitable salt content.

TABLE III

RATE CONSTANTS AND HYDROGEN ION CONCENTRATIONS IN MONOCHLOROACETIC ACID SOLUTIONS AT 25.06°

C_{Acid}, M	$K_A \times 10^3$	C_{H^+}	Av. k	C_{H^+}, calcd.
0.0683	1.716	0.0100	0.0130	0.0101
.200	1.745	.0178	.0231	.0178

3. **Salt Effects.**—Starting with 0.04 M perchloric acid the effect of the following salts was determined: sodium, zinc, barium and lanthanum perchlorates and sodium benzenesulfonate. For lithium, sodium and potassium nitrates the starting solution was 0.04 M nitric acid, and since a linear effect was expected four or five duplicate runs were made at only one salt concentration. A small amount of nitric acid disappears during the reaction but the correction for this was less than 1%. Silver nitrate could not be used; it is reduced rapidly to metallic silver.

These rates are plotted in Fig. 1 using equivalent concentration as the abscissa. The data agree well with equations of the type

$$k = 1.275C_{H^+}(1 + \alpha_\xi\ \xi) \quad (3)$$

where ξ is the equivalent concentration or total charge density. There is equally good agreement with similar equations involving ionic strength, which for each salt is proportional to equivalent concentration

$$k = 1.275C_{H^+}(1 + \alpha_\mu\ \mu) \quad (4)$$

Equation (4) resembles the dilute solution form of the relation usually invoked for this type of reaction[7]

$$\log k = \log k_0 + B\mu \quad (5)$$

In all salts studied in detail here, the linear form is definitely superior to the logarithmic, in spite of the wide concentration range.

Values of α_ξ and α_μ are compared in Table IV. While for salts of the same or similar anion the former are much closer together than the latter, the effect of each salt is seen to be specific in nature. The behavior of sodium benzenesulfonate[8] is in accord with the effect of salts of this type on the solubility of weak or non-electrolytes.[9] It is unfortunate that no common salts with anions of higher charge are suitable for these experiments.

TABLE IV

LINEAR SALT EFFECT PARAMETERS, 25.06°

Salt	α_μ	α_ξ	Salt	α
$HClO_4$	0.863	0.63	$NaNO_3$	1.04
$NaClO_4$	1.16	1.16	KNO_3	.96
$Zn(ClO_4)_2$	.665	1.00	$NaBzSO_3$	.3[a]
$Ba(ClO_4)_2$	.656	.98	NaCl	(5.0)[a]
$La(ClO_4)_3$	.480	.96	NaBr	(12.1)[a]
$LiNO_3$	1.04	1.04	NaI	(24.8)[a]

[a] Equation 3 becomes: $k = 0.0528 + 0.0510\ \alpha\ C$salt.

4. **Chloride, Bromide and Iodide.**—These salts introduce a complication in that halogen acid enters the product to a certain extent and the reaction is not strictly first order.

$$CH_3COCHN_2 + H^+ + X^- \longrightarrow CH_3COCH_2X + N_2 \quad (6)$$

With iodide, some iodine is formed, since the iodination of acetone is reversible.[10]

$$CH_3COCH_2I + HI \rightleftarrows CH_3COCH_3 + I_2 \quad (7)$$

In addition, hydroxyacetone reacts very slowly with hydrogen iodide

$$CH_3COCH_2OH + HI \longrightarrow CH_3COCH_2I + H_2O \quad (8)$$

The last reaction, as well as air oxidation of iodide, was negligible in the experiments described below.

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[6] T. Shedlovsky, A. S. Brown and D. A. MacInnes, *Trans. Electrochem. Soc.*, **66**, 165 (1934).

[7] R. P. Bell, "Acid-Base Catalysis," Oxford Press, 1941, p. 34.

[8] Measurements with this salt were far less precise than with other salts, possibly because the solutions tend to foam.

[9] A. Osol and M. Kilpatrick, THIS JOURNAL, **55** 4430, 4440 (1933).

[10] H. M. Dawson and M. S. Leslie, *J. Chem. Soc.*, **95**, 1860 (1909).

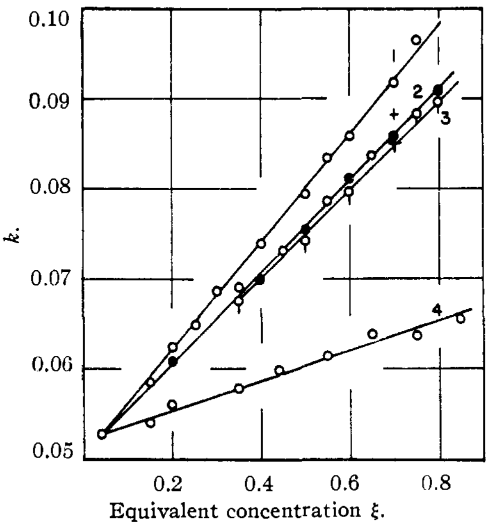

Fig. 1.—Salt effects on the rate in 0.04 M acid: 1, sodium perchlorate; 2, barium (●) and zinc (O) perchlorates; 3, lanthanum perchlorate; 4, sodium benzene sulfonate; upper $^+$, lithium and sodium nitrates; lower +, potassium nitrate, lanthanum perchlorate.

Nitrogen evolution becomes very rapid in 0.04 M perchloric acid with added halogen salts, but since it is complete and considerable excess acid was present, sufficiently accurate rate constants were obtained. Twelve to fourteen pressure readings were taken at 30 second intervals, and the first six or seven used to evaluate the constant. The resulting values of k were considered to correspond to the average hydrogen ion concentration during the readings used, as determined by the titration experiments described below. The values can then be corrected to 0.04 M hydrogen ion by means of equation (3). The results are shown in Fig. 2 and expressed in the α-values of Table IV. Addition of as much as 0.1 ml. of chloroacetone to some of the reacting solutions showed that this product does not change the rate.

To determine the amount of haloacetone formed, 50-ml. samples of hydrochloric and hydrobromic acids, containing the sodium salt in various concentrations up to 0.66 M, were prepared. With sodium iodide, perchloric acid was used. The acid concentration was varied from 0.02 to 0.06 M but was usually 0.04 M. To each solution a measured amount of diazoacetone was added, usually 0.49 millimole but in some cases as much as 0.123 millimole. After 1–20 hours the chloride and bromide solutions were titrated with standard base. The iodide solutions were titrated with standard thiosulfate until the end-point persisted several minutes. This required addition of thiosulfate for 10–15 minutes with fleeting end-points, but ensured the titration of one mole of iodine per equivalent of hydrogen ion absorbed initially.

These titrations showed the amount of halogen acid absorbed to be (a) independent of hydrogen ion concentration, (b) directly proportional to the initial concentration of diazoacetone, and (c) highly dependent on the halide ion concentration. Agreement of the titrations at various time intervals showed that the haloacetones, once formed, do not hydrolyze appreciably in the course of several hours.

TABLE V

FRACTION F OF DIAZOACETONE CONVERTED TO HALOACETONE

0.04 M HCl		0.04 M HBr		0.04 M HClO$_4$	
C_{Cl^-}*	F_{Cl}	C_{Br^-}*	F_{Br}	C_{I^-}*	F_I
0.04	0.17	0.04	0.22	0.05	0.46
.15	.37	.10	.38	.10	.61
.35	.52	.15	.42	.15	.69
.50	.58	.20	.48	.20	.73
.70	.64	.40	.55	.25	.77
		.60	.60		

* Initial concentrations.

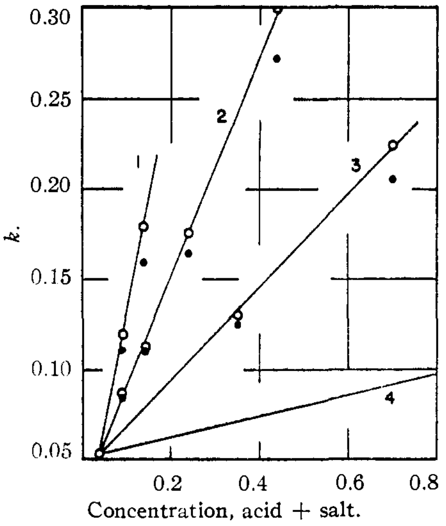

Fig. 2.—Rates in 0.04 M perchloric acid with added sodium halide: 1, iodide; 2, bromide; 3, chloride; 4, sodium perchlorate; measured rate constant ●, corrected to 0.04 M H^+ O.

The results may be summarized briefly in terms of the fraction of diazoacetone converted to haloacetone, and this is done in Table V.

Discussion

1. Salt Effects.—For reaction (1), the Brönsted principle requires a salt effect equation of the type

$$k = k_0 \frac{\gamma_{AN_2}\ \gamma_{H^+}\ \gamma_{H_2O}}{\gamma_{X^+}} \qquad (9)$$

In this equation k_0 is the rate constant extrapolated to zero ion concentration, AN_2 and X^+ refer to the diazoacetone molecule and a "critical complex," respectively. (If H_2O does not enter the rate-controlling step, γ_{H_2O} is omitted, but this is not important.) It is generally assumed that the activity coefficient ratio (γ) ought to be expressed by terms linear in ionic strength in the extended Debye–Hückel equation

$$\log \gamma = (\beta_{AN_2} + \beta_{H^+} + \beta_{X^+})\mu \qquad (10)$$

(omitting γ_{H_2O}). Equation (5) follows.

In certain reactions of this type, notably the hydrolysis of acetal and related compounds, salt effects are so large that the validity of equation (9) has been questioned.[11] In particular, Olson and his co-workers[12] have questioned the application of the Brönsted medium effect factors either with or without combination with the Debye–Hückel equations, to reactions of this or other ionic types. On the other hand, in a detailed study of the hydrolysis of γ-butyrolactone Long, McDevit and Dunkle[13] decide that equation (9) is probably valid and criticize the estimation of activity coefficients by Olson and Tong.

The value of γ_{X^+} can neither be measured nor calculated, and no measurements for salts with ions of similar structure are available. Long and

[11] L. C. Riesch and M. Kilpatrick, *J. Phys. Chem.*, **39**, 561 (1935).

[12] A. R. Olson and L. K. J. Tong, THIS JOURNAL, **66**, 1555 (1944); A. R. Olson and T. R. Simonson, *J. Chem. Phys.*, **17**, 1167 (1949).

[13] F. A. Long, W. F. McDevit and F. B. Dunkle, *J. Phys. Colloid Chem.*, **55**, 813, 829 (1951).

his co-workers have suggested that $\gamma_{H^+}/\gamma_{X^+}$ might be taken approximately equal to $\gamma_{HCl}/\gamma_{CsCl}$.

The use of ionic strength in equation (10) has never been satisfactory, and is of no aid in interpreting the data reported here. For non-electrolytes, the activity coefficient or its logarithm changes linearly with ionic concentration, but β varies widely even with salts of the same valence type.[9,13,14] The Debye–McAulay equation, which involves ionic radii and ionic strength, is of no help in this concentration range.

The effect of ions on non-electrolytes is no doubt related to their size and polarizability,[15] and this is true of the ratio γ_{H+}/γ_{X+} as well, outside the Debye–Hückel range. It would be in accordance with Brönsted's principle of specific interaction of ions[16] if the latter ratio is specifically sensitive to the influence of anions, with particular cations playing a minor role.

A rough calculation of the salt effect to be expected in reaction (1) can be made. We have used $\gamma_{acetone}$ in 0.7 M sodium chloride[17] for γ_{AN_2}, γ_{HCl} (0.01 M in 0.7 M sodium chloride)[18] for γ_{H^+}, and the mean activity coefficient of trimethylammonium chloride[19] at 0.7 M as a plausible approximation for γ_{X^+} in equation (9).

$$\frac{\gamma_{acetone}\,\gamma_{HCl}\,\gamma_{H_2O}}{\gamma_{Me_3NHCl}} = \frac{1.20 \times 0.74 \times 0.98}{0.51} = 1.71$$

In sodium perchlorate at $\xi = 0.7$, $k/k_0 = 0.0924/0.0510 = 1.81$, in the other perchlorates and the nitrates k/k_0 is somewhat smaller. Equation 9 is apparently satisfactory if the activity coefficients can be estimated properly. The much smaller effect of sodium benzenesulfonate implies that this compound would "salt in" diazoacetone, *i.e.*, reduce γ_{AN_2} below unity.

2. Halogen Absorption and Reaction Mechanism.—If a reaction is subject to general acid catalysis, proton transfer must be the rate-determining step.[20] When only hydronium catalysis is detectable, further information is needed, and in the present case this is provided by the halogen absorption. The effect of halides is far too large to be ascribed to a simple salt effect, and reaction with halide ion must be a rate-controlling step. This suggests an initial equilibrium between substrate and hydrogen ion, as has been proposed for diazoacetic ester[21]

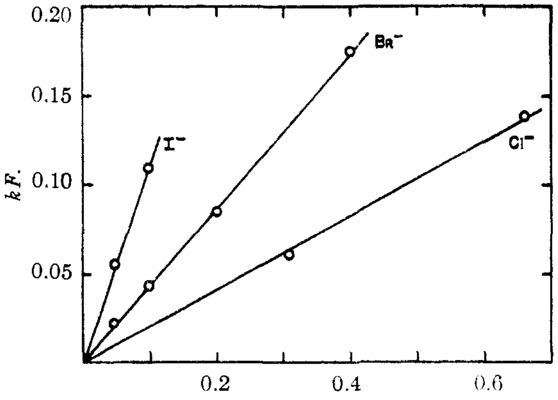

Fig. 3.—Rate of halogen acid absorption in 0.04 M $HClO_4$ with added NaCl, NaBr, NaI.

$$CH_3COCHN_2 + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH_3COCH_2N_2^+ \quad (11)$$

followed by competitive reactions with water and halide

$$CH_3COCH_2N_2^+ + H_2O \xrightarrow{k_3} CH_3COCH_2OH + N_2 + H^+ \quad (12)$$

$$CH_3COCH_2N_2^+ + X^- \xrightarrow{k_4} CH_3COCH_2X + N_2 \quad (13)$$

The constant k_{-1} must be much larger than k_1, since the rate does not become independent of acid concentration; both must be large compared to k_3 and k_4. Nitrogen may be expelled simultaneously with water and halide absorption or after a brief delay, but not in advance of these steps. A free radical mechanism is excluded, at least from the rate-determining steps.

In the diazoacetic ester reaction halogen acids are absorbed in the same order as here, HI > HBr > HCl.[22] The amount of absorption was found to be independent of the cation, with ten salts including different valence types. Absorption of hydrogen chloride in 50% ethanol solution was studied, using a conductance method, by Lachs,[23] who found the rate of formation of chloroester to be roughly proportional to the 4/5 power of the chloride concentration (in the range 0.013 to 0.066 M).

In the present case, the rate of formation of haloacetone can be found by multiplying the over-all rate constants of Fig. 2 by the fractions F of Table V. The resulting values are plotted in Fig. 3, and are apparently linear with salt concentration. The salt effect factor in reaction (13) is expected to be negative, and non-linear at low concentrations

$$\gamma_{AN_2}\gamma_{H^+}\gamma_{X^-}/\gamma_{AN_2HX}$$

The variation would be small in the concentration range employed here; for instance, from 0.09 to 0.7 M, γ^2_{HCl} varies between 0.64 and 0.58, going through a minimum.[18] (Since perchloric acid was present, 0.09 M was the lowest experimental concentration with halide present.) Salt effect probably accounts for the fractional order found by Lachs.

The remainder of the rate, $k(1 - F)$, is to be ascribed to acetol formation. Equation (3) may be expanded to

$$k = 0.0510(1.0018 + \alpha' C_{X^-} + \alpha'' C_{X^-}) \quad (14)$$

where the first term is due to perchloric acid alone, α' represents salt effect of halide on reaction (12),

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(14) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1943, pp. 398–399.

(15) See F. A. Long and W. F. McDevit, *Chem. Rev.*, **51**, 119 (1952).

(16) J. N. Brönsted, THIS JOURNAL, **44**, 877 (1922).

(17) P. Gross and M. Iser, *Monatsh.*, **55**, 329 (1930). Values are given for 15°; the temperature coefficient is small.

(18) Reference 15, Appendix.

(19) J. H. Jones, F. J. Spuhler and W. A. Felsing, THIS JOURNAL, **64**, 965 (1942). From freezing point measurements.

(20) Reference 8, p. 125.

(21) L. H. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 288.

(22) G. Bredig and P. F. Ripley, *Ber.*, **40**, 4015 (1907).

(23) H. Lachs, *Z. physik. Chem.*, **72**, 291 (1910).

and α'' represents halogen acid absorption (reaction 13). Values of α' are 0.94, 3.6 and 3.4 for chloride, bromide and iodide, respectively; α'' is obtained by subtracting α' from the values of α in Table IV.

The effect of chloride on acetol formation is similar to that of perchlorates and nitrates, and appears to be a true kinetic salt effect. The values for bromide and iodide are so large as to suggest a specific catalysis by these ions; this might result if the intermediate complex of reaction (13) partly reacts with water to form acetol instead of decomposing to haloacetone.

Olson and Tong[12] found potassium bromide and iodide to have much larger effects than the chloride on the rate of hydrolysis of dipropylformal in dilute hydrochloric acid. This is not an effect on the activity of the neutral molecules, which is expected to go in the opposite direction.

There is no explanation for the selective absorption of certain acids. It might be thought that other acids would catalyze reaction (1) by entering the product temporarily, then being replaced by water. This process is excluded by the demonstration that salt effects are normal.

3. **Temperature Coefficients.**—Table I gives measurements from which activation energies and entropy can be calculated. While the temperature range is small, great care was taken to be sure that the accuracy was sufficient for the present purpose. Rates at the three temperatures are represented within less than 1% by the equation

$$k_2 = 6.79 \times 10^{12} e^{-19800/RT} \text{ liters mole}^{-1} \text{ sec.}^{-1} \quad (15)$$

where k_2 is the specific second-order rate constant.

The entropy, enthalpy and free energy of activation have been calculated[24] and are compared in Table VI with corresponding values for diazoacetic ester[25] and azodicarbonate ion.[26] No data for other diazo compounds are available. The maximum error in E for diazoacetone is estimated as 400 cal., corresponding to 1.3 units in $\Delta S.^*$

TABLE VI

ENERGIES AND ENTROPY OF ACTIVATION

Substrate	E, kcal.	ΔS^*, e.u.	ΔH^*	ΔF^*
Diazoacetone	19.8	− 2.1	19.2	19.8
Diazoacetic ester	17.5	− 2.7	16.9	17.7
Azodicarbonate	10.2	+12.9	9.6	5.7

There is strong indication in the values of Table VI that the reactions of diazoacetone and diazoacetic ester are similar in mechanism. The ester is more sensitive to hydronium ion catalysis, and since the entropies are similar most of the difference is due to the smaller enthalpy and free energy of activation. These energies include the effect of temperature on equilibrium (11). The greater sensitivity of the ester probably indicates that it is more basic than diazoacetone and a higher concentration of the acid ion is available for the rate-determining reaction.

(24) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, pp. 197–199.

(25) W. Fraenkel, *Z. physik. Chem.*, **60**, 202 (1907).

(26) C. V. King and J. J. Josephs, THIS JOURNAL, **66**, 767 (1944).

NEW YORK, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

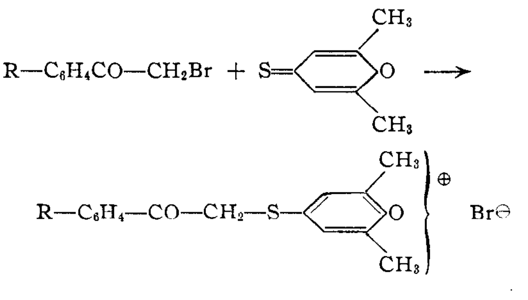
Formation and Kinetics of Formation of Substituted Mercaptopyrylium Salts[1]

BY FRANCIS J. OZOG, VIVIANE COMTE AND L. CARROLL KING

RECEIVED JULY 17, 1952

Substituted phenacyl bromides react with 2,6-dimethyl-4-thiopyrone to give pyrylium salts. In benzene or in acetone solution the reaction is first order with respect to each of the reacting species. The effect on the reaction rate of meta and para substituents in the phenacyl bromide was determined. These results can be described by the Hammett equation where ρ has the value 1.0 at 14.8° and 0.98 at 25.4°.

A recent paper from this Laboratory reported the reaction of 2,6-dimethyl-4-thiopyrone with active alkylating agents to give substituted mercaptopyrylium salts.[2] In the present paper the reactions of a number of substituted phenacyl bromides with 3,6-dimethyl-4-thiopyrone are reported. The results of the preparative experiments are summarized in Table I. The structures of the pyrylium salts described in Table I will be evident from a consideration of the method of preparation (equation 1). In each case the structure of the expected pyrylium salt was verified by analytical data.[3]



(1)

The kinetics of the reaction between phenacyl bromide and 2,6-dimethyl-4-thiopyrone (DMTP) was studied in detail. Some typical results are given in Table II and in Figs. 1 and 2. The reaction is a second-order process. In benzene solution the second-order rate constants show a drift, becoming significantly smaller when the reaction is

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(1) Paper No. 102, Division of Organic Chemistry of the American Chemical Society, Chicago Meeting, September, 1950.

(2) L. C. King, F. J. Ozog and J. Moffat, THIS JOURNAL, **73**, 300 (1951).

(3) A further discussion of the structural assignment is given in reference 2.