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The Decomposition Rate of Diazomalonate Ions in Dilute Aqueous Solutions

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The diethyl ester of diazomalonic acid has been known for many years, but apparently salts of this acid have not been previously isolated or studied. We have found it possible to hydrolyze the ester and obtain both the mono- and dipotassium (or sodium) salts, nearly 100% pure. These salts are fairly stable in dilute solutions of strong bases, but in dilute acids they decompose rapidly with evolution of nitrogen and carbon dioxide. We have studied the rates quantitatively in dilute strong acid and in buffer solutions.

The purpose of this investigation was primarily to compare these compounds with other aliphatic diazo compounds, the study of whose reaction rates has provided much useful information. Diazoacetic ethyl ester was the first such compound to be studied quantitatively.[1] Its decomposition is subject to specific hydrogen ion catalysis, and Bredig proposed use of the rate to measure hydrogen ion concentration. When proper allowance is made for primary salt effects, the measurement is reasonably accurate.[2] The decomposition of diazoacetate and azodicarbonate has been studied in this laboratory.[3] Both reactions have been found exceedingly sensitive to general acid catalysis. There is, as yet, little basis upon which to predict any relation between structure and reactivity of such compounds. The salt ions are much more sensitive to acids than the neutral esters, which is partly at least due to their negative charge. Greater distance to the diazo group from a carboxyl group should lead to greater stability. Study of other aliphatic diazo compounds and the mechanism of their decomposition should thus prove interesting and useful.

Experimental

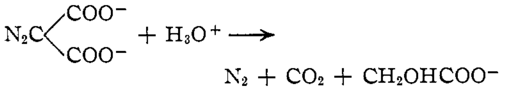
Preparation of the Compounds.—As the first step, diethyl mesoxalate was prepared by oxidation of diethyl malonate by the use of nitrogen tetroxide.[4] The corresponding hydrazone was then made by reaction with hydrazine in acetic acid solution.[5] The hydrazone was oxidized to the diazo-ester by employing mercuric acetate in a pyridine–ethanol mixture, with addition of triethylamine. These reagents permit homogeneous reaction and the method is superior to the previous use of suspended mercuric oxide.[6]

The monopotassium salt was prepared by hydrolyzing the ester with one mole of potassium hydroxide in absolute ethanol; the dipotassium salt by further hydrolysis in 25% ethanol. Both salts were isolated as crystalline solids which evolved between 95 and 100% of the theoretical amount of nitrogen on treatment with strong acid and absorption of the carbon dioxide. The above preparations have been described in detail by Mebane.[7]

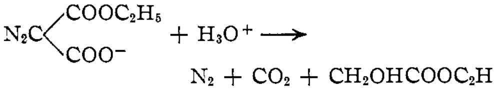
Reagents and Experimental Method.—Solutions were prepared from reagents of the best commercial grade and standardized by customary procedures. Decomposition rates were measured by following the pressure of nitrogen and carbon dioxde evolved in a modification of the apparatus first used by Brönsted and Duus.[8] The flasks were of 100 ml. capacity, and 50 ml. of solution was introduced; after sealing and evacuating, a 65-mg. sample of diazo-salt was dropped, in a capsule, from a glass hook in the upper part of the flask. All experiments were carried out at 25 ± 0.02°.

The pressure measurements give satisfactory rate constants since the nitrogen and carbon dioxide are evolved simultaneously, or nearly so. Most of the rates were of first order over the whole range, and the constants were evaluated by plotting log ($p_\infty - p$) *vs.* time or by the Guggenheim modification of this method.[9]

Nature of the Reactions.—Diethyl diazomalonate does not hydrolyze or decompose appreciably in dilute hydrochloric or perchloric acid solution in twenty-four hours. The evolution of nitrogen and carbon dioxide suggests the following reactions of the di- and monopotassium salts



$$\mathrm{N_2C}\left\langle\begin{matrix}\mathrm{COO^-}\\ \mathrm{COO^-}\end{matrix}\right. + \mathrm{H_3O^+} \longrightarrow \mathrm{N_2} + \mathrm{CO_2} + \mathrm{CH_2OHCOO^-} \quad (1)$$



$$\mathrm{N_2C}\left\langle\begin{matrix}\mathrm{COOC_2H_5}\\ \mathrm{COO^-}\end{matrix}\right. + \mathrm{H_3O^+} \longrightarrow \mathrm{N_2} + \mathrm{CO_2} + \mathrm{CH_2OHCOOC_2H_5} \quad (2)$$

A separate water molecule may be involved in each case, and (2) may be followed by hydrolysis of the ester.

A number of titrations were carried out to determine the exact amount of hydrogen ion disappearing in the course of the reaction. The average was close to three-fourths mole per mole of diazo-salt in both cases. This suggests that part of the product is glycoylglycolate ion, which would require one-half mole hydrogen ion per mole diazo-salt. This product suggests that the initial reaction may be loss of carbon dioxide; the diazoacetate formed would decompose instantly with formation of some glycoylglycolate.[3]

Rates in Perchloric Acid.—Perchloric acid was used in preference to other acids which might replace nitrogen as they do with diazoacetic ethyl ester. Rate constants with the dipotassium salt are summarized in Table I, and with the monopotassium salt in Table II. Each value is the average of at least two measurements which generally agreed within 5% or less. A few measurements which disagreed by much larger amounts were discarded.

The behavior of these salts is similar to that of potassium ethyl and methyl xanthates, which were studied by v. Halban and Hecht.[10] It indicates that the diazo-acid (or intermediate ion in the case of the dipotassium salt) is not fully ionized and the reaction is either (a) a first order decomposition of the undissociated acid or (b)

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[1] Bredig and Frankel, *Z. Elektrochem.*, **11**, 525 (1905).

[2] Brönsted and Teeter, *J. Phys. Chem.*, **28**, 579 (1924). Brönsted and King, *Z. physik. Chem.*, **130**, 699 (1927). Brönsted and Volquartz, *ibid.*, **134**, 97 (1928).

[3] King and Bolinger, THIS JOURNAL, **58**, 1533 (1936). King. *ibid.*, **62**, 379 (1940).

[4] Gilman and Johnson, *ibid.*, **50**, 3341 (1928).

[5] Staudinger and Hammet, *Helv. Chim. Acta*, **4**, 217 (1921).

[6] Neresheimer, Beilstein, Vol. XXV, p. 157; Ergw. Vol. III, p. 268.

[7] Mebane, Master's Thesis, New York University, 1948.

[8] Brönsted and Duus, *Z. physik. Chem.*, **117**, 299 (1925).

[9] Guggenheim, *Phil. Mag.*, [7] **2**, 538 (1926).

[10] v. Halban and Hecht, *Z. Elektrochem.*, **24**, 65 (1918).

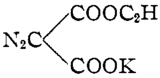
TABLE I

RATE CONSTANTS FOR THE DECOMPOSITION OF $N_2C(COOK)_2$ (0.0063 *M*) IN DILUTE $HClO_4$, AT 25°

C_{HClO_4}, *M*	k', min.$^{-1}$	k'/C_{H^+}	Salt effect C_{HClO_4}, *M*	 C_{NaClO_4}, *M*	 k', min.$^{-1}$
0.01	0.0198	1.98	0.01	0.06	0.0188
.02	.0319	1.60		.08	.0188
.04	.0462	1.16	.02	.04	.0309
.06	.0590	0.98		.08	.0305
.08	.0698	.87		.12	.0287
.10	.0751	.75	.06	.06	.0587
.12	.0787	.66		C_{HAc}	
.16	.0909	.57	.02	.06	.0321
.20	.0916	.46		.12	.0311

TABLE II

RATE CONSTANTS FOR THE DECOMPOSITION OF



$N_2C(COOC_2H_5)(COOK)$ (0.0066 *M*) IN DILUTE $HClO_4$, 25°

C_{HClO_4}, *M*	k', min.$^{-1}$	k'/C_{H^+}	Salt effect C_{HClO_4}, *M*	 C_{NaClO_4}, *M*	 k', min.$^{-1}$
0.01	0.024	2.4	0.02	0.04	0.0429
.02	.0449	2.25		.08	.0428
.04	.0474	1.19		.12	.0436
.06	.0495	0.83		.16	.0424
.08	.0513	.64	.06	.04	.0489
.10	.0505	.51		.08	.0516
.15	.0523	.35		.12	.0500
.20	.0526	.26		C_{HAc}	
.30	.0588	.20	.02	.04	.0439
.40	.0600	.15		.08	.0460
.50	.0632	.13		.12	.0433

a second order reaction of the anion with hydrogen ion. The rate and ionization constants can be evaluated as shown below.

Assume the following equilibrium to exist

$$HN^- \rightleftarrows H^+ + N^= \qquad (3)$$

where $N^=$ represents the diazo anion. Also

$$C_{HN} + C_{N^=} = (a - x) \qquad (4)$$

i.e., the total concentration of diazo-salt is a initially, $(a - x)$ at time t. Then

$$\frac{dx}{dt} = kC_{HN^-} = \frac{kC_{H^+}f_2}{K + C_{H^+}f_2}(a - x) \qquad (5)$$

or

$$\frac{dx}{dt} = kC_{H^+}C_{N^=}f_2 = \frac{kKC_{H^+}f_2}{K + C_{H^+}f_2}(a - x) \qquad (6)$$

where K represents the equilibrium constant of reaction (3) at zero ionic strength and f_2 is the activity coefficient of a bivalent ion; other activity coefficients cancel. In most of the experiments the hydrogen ion concentration can be considered constant throughout the reaction, and the rate to be first order with respect to total diazo-salt concentration; exceptions will be discussed later. If $K >> C_{H^+}$, equations (5) and (6) predict a large salt effect; if $K << C_{H^+}$, the f_2 terms cancel. As seen in Tables I and II, salt effects are negligible except with 0.01 and 0.02 *M* perchloric acid.

The constants k' of Tables I and II correspond to the rate equation

$$dx/dt = k'(a - x) \qquad (7)$$

Adopting the mechanism of equation (6), and neglecting activity coefficients

$$k' = \frac{kKC_{H^+}}{K + C_{H^+}} \qquad (8)$$

This may be written in the form

$$k'/C_{H^+} = -k'/K + k \qquad (9)$$

which should be linear in k/C_{H^+} and k.

Figures 1 and 2 show plots of equation (9) for the di- and monopotassium salts, respectively, with values of K and k, determined from the slopes and intercepts, given in the legend. In Fig. 1, the points at $k' < 0.04$ are in doubt because the

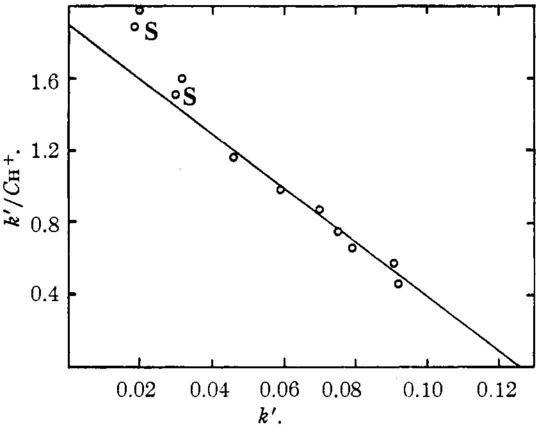


Fig. 1.—Plot of equation 9 for $N_2C(COOK)_2$: k = 1.90, K = 0.066. Points marked S are with added sodium perchlorate.

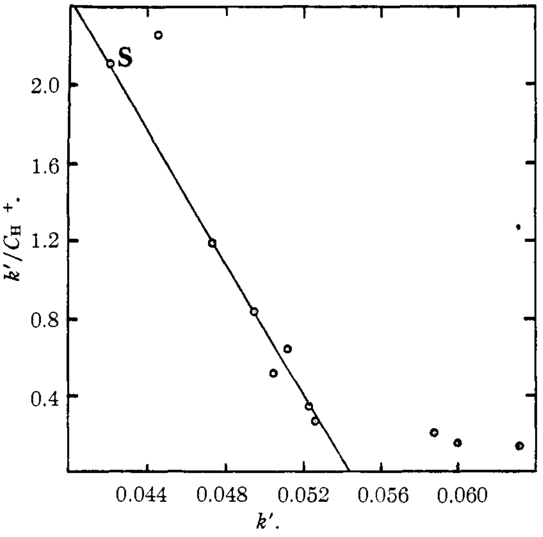


Fig. 2.—Plot of equation 9 for $N_2C(COOC_2H_5)(COOK)$: k = 9.22, K = 0.0059. Point marked S is with added sodium perchlorate.

effects of ionic strength, of changing hydrogen ion concentration and of catalysis by glycolate ion produced during the reaction are uncertain. The results in Fig. 2, most of which conform to equation (9), are less satisfactory because the acid is much weaker and less than 20% ionized when $C_{H^+} > 0.02$ *M*. The points at $k' > 0.056$ are high, probably because hydrolysis of the ester becomes rapid enough to influence the rate.

That the diazo-acids are somewhat weak was shown directly as follows: to 1 ml. of 0.001 *M* perchloric acid containing a trace of methyl orange and phenolphthalein, 0.1 g. of the mono- or dipotassium salt was rapidly added. The solutions became yellow instantly; after some time (quickly on warming) the pink color of phenolphthalein appeared.

Rates in Acetic Acid–Sodium Acetate Buffers.—As shown in Tables I and II, experiments with acetic acid added to 0.02 *M* perchloric acid gave no appreciable effect. In buffers with $C_{H^+} \sim 10^{-5}$ *M*, decomposition should be very slow according to the preceding explanation. Experiments in buffer solutions gave most unexpected results, and showed that the reaction is subject to general base catalysis.

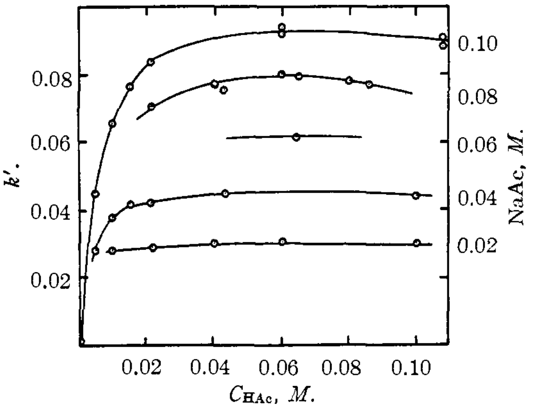


Fig. 3.—The effect of acid concentration on acetate ion catalysis.

Figure 3 is a plot of rate constants obtained in acetic acid–sodium acetate mixtures. The decomposition is evidently catalyzed by acetate ion, and this catalysis is influenced by the hydrogen ion concentration. As shown in Fig. 3, the effect of hydrogen ion reaches a maximum at about 0.06 *M* acetic acid, or 1 to 5 × 10^{-5} *M* hydrogen ion. Figure 4 is a plot of rate constants in 0.06 *M* acetic acid *vs.* acetate ion concentration. The slope of the straight line is 0.82, which is then the molar catalytic constant for acetate ion, although for precise comparison with other catalytic constants the value should be corrected for salt effect. The intercept (0.013) is presumably to be ascribed to catalysis by water and hydroxyl ion.

Several solutions originally containing 0.01 *M* diazomalonate, 0.0216 *M* acetic acid and 0.02 *M* sodium acetate were titrated at completion of the reaction (after heating to expel carbon dioxide), and again showed the loss of approximately three-fourths mole of acid per mole of diazo-salt. Apparently the same products are formed as in solutions of strong acid.

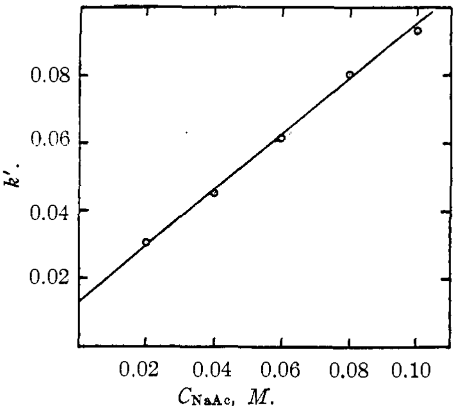


Fig 4.—Maximum catalysis by acetate ion (at $C_{HAc} = 0.06$ *M*), $k_M = 0.82$.

Aniline–Anilinium Perchlorate Buffers.—Very similar results were obtained with these solutions, as shown in Fig. 5. No detailed study was made of the effect of hydrogen ion, but the values given are probably near the maximum ones. The molar catalytic constant for aniline is 0.47, and the intercept (0.018) is similar to the value found with acetate ion.

The neutral salt effect in these buffers is almost negligible, while the acetic acid–sodium acetate buffers show a considerable positive salt effect.

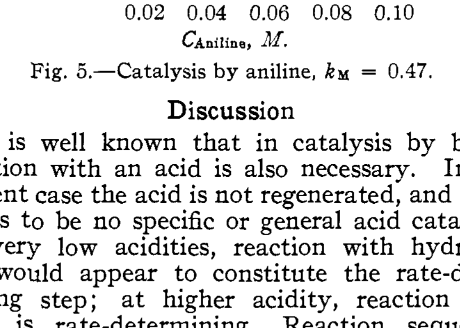


Fig. 5.—Catalysis by aniline, $k_M = 0.47$.

Discussion

It is well known that in catalysis by bases, reaction with an acid is also necessary. In the present case the acid is not regenerated, and there seems to be no specific or general acid catalysis. At very low acidities, reaction with hydrogen ion would appear to constitute the rate-determining step; at higher acidity, reaction with base is rate-determining. Reaction sequences which lead to such behavior have been discussed by several authors.[11]

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[11] For a résumé see Bell, "Acid-Base Catalysis," Oxford Press New York, N. Y., 1941, pp. 123-127.

Assume the base B to form a complex with the diazo-ion

$$N_2C(COO)_2^{=} + B \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} BN_2C(COO)_2^{=} \qquad (10)$$

This is followed by reaction with hydrogen ion

$$BN_2C(COO)_2^{=} + H_3O^+ \xrightarrow{k_2} N_2 + CO_2 + CH_2OHCOO^- + B \qquad (11)$$

The rate constant k_{-1} is much larger than k_1, while k_2 is comparable in value to k_{-1}. At very low acidity, equilibrium is maintained in reaction (10), the measured rate is determined by k_2 and is proportional to C_{H^+}. At sufficiently high acidity the complex is virtually all removed as fast as formed, by reaction (11), and the observed rate is entirely dependent on k_1.

This mechanism explains the nature of the curves of Fig. 4, and is in qualitative agreement with the salt effects observed in the buffers. Neutral salts increase the hydrogen ion concentration of dilute acetic acid buffers, have little effect on the aniline–anilinium type. However, the increase in hydrogen ion is not important here, and the salt effect is a primary one on the rate constant k_1 of equation (10).

The reaction in perchloric acid probably has a similar mechanism: that is, formation of a complex between water acting as a base and diazo-ion is followed by reaction with hydrogen ion. Since water is a much weaker base than acetate ion or aniline, a far higher hydrogen ion concentration is necessary to obtain maximum catalysis. A further complication is the attachment of hydrogen ion to the carboxyl groups.

It was mentioned previously that nearly all the observed rates were first order throughout. The exceptions were in solutions of the lowest initial hydrogen ion concentration. In general deviations from the first order equation were positive in these cases; even though hydrogen ion was disappearing with time, this was more than compensated for by the catalytic effect of the glycolate and glycoylglycolate ions produced. While initial slopes of the log $(p_\infty - p)$ *vs.* time curves were used, this effect probably accounts for the fact that the two upper left points of Fig. 1 are above the straight line even when salt effect is considered. The points below $C_{HAc} = 0.02$ *M* in Fig. 3 must also be considered as approximate values, since the buffer capacity of the solutions is low. With 0.005 *M* acetic acid the divergence from the first order law was in the negative direction. Also the total pressure rise in the experimental apparatus was smaller than in more acid solutions, since bicarbonate ion was no doubt retained in solution to a greater extent.

Further detailed study of the decomposition rates of both salts in these and other buffers is in progress, and we expect to report the results in a later paper.

Summary

The diethyl ester of diazomalonic acid has been prepared, and the mono- and dipotassium salts have been made by hydrolysis of the ester and isolated as pure crystalline solids.

The decomposition rate of the two salts in dilute perchloric acid has been studied at 25°. Assuming that the acids are not fully ionized, the ionization constant of the ester-acid and the second constant of the diazomalonic acid have been determined from the rates.

The decomposition rate of the dipotassium salt has been studied in acetic acid–sodium acetate and in aniline–anilinium perchlorate buffers. The basic components of these solutions catalyze the reaction, which is thus subject to general base catalysis in the Brönsted sense.

Catalysis by these bases has been found to be highly dependent on the hydrogen ion concentration, and a reaction mechanism has been proposed to account for this.

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