THE DECOMPOSITION OF α-NITROCARBOXYLIC ACIDS
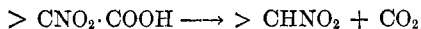
With Some Remarks on the Decomposition of β-Ketocarboxylic Acids

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The object of this paper is to contribute to our understanding of the tendency of α-nitrocarboxylic acids to split off carbon dioxide.

$$> CNO_2 \cdot COOH \longrightarrow > CHNO_2 + CO_2$$

The simplest acid of this type, nitroacetic acid, was studied kinetically by Heuberger (2, 3) and, independently, by the author of this paper (7). In the latter work, the rate of decomposition was determined on solutions of hydrochloric acid of various concentrations and in buffer solutions, mainly acetate buffers (pH = 4 to 5). The rate increases with decreasing hydrogen-ion concentration and reaches a maximum value in the acetate buffers. Here it is independent of the hydrogen-ion concentration. In sufficiently alkaline solution nitroacetic acid is stable.

While the free nitroacetic acid consists of two tautomers

$$O_2N \cdot CH_2 \cdot COOH \quad \text{and} \quad HOON:CH \cdot COOH$$
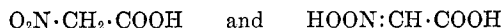
there are three possible forms of the univalent nitroacetate ion

$$O_2N \cdot CH_2 \cdot CO_2^-, \quad {}^-O_2N:CH \cdot COOH, \quad \text{and} \quad HOON:CH \cdot CO_2^-$$

and only one divalent ion

$$^-O_2N:CH \cdot CO_2^-$$
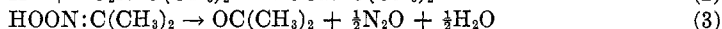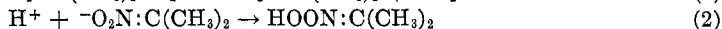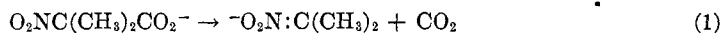
The experiments agree with the assumption that both the free acid and the divalent ion are stable, while one of the univalent ions is unstable. From the experiments the first dissociation constant of nitroacetic acid (about 0.02) was calculated. It could not be settled from the experiments on nitroacetic acid which of the three forms of the nitroacetate ion is unstable, or, in other words, whether the instability of the α-nitrocarboxylic acids is connected with the formation of an aci-form of the nitro compound. In order to solve this problem α-nitroisobutyric acid (dimethyl-

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nitroacetic acid) is studied in the present paper. This substance is not a pseudo acid. It forms only the ion $O_2NC(CH_3)_2CO_2^-$. It is found that it splits off carbon dioxide in the same way as nitroacetic acid and with a similar velocity. Consequently, the unstable form of the α-nitrocarboxylic acids is the ion $>CNO_2 \cdot CO_2^-$.

However, while nitroacetic acid gives carbon dioxide and nitromethane as final reaction products, the carbon dioxide cleavage of α-nitroisobutyric acid in hydrochloric acid is followed by a secondary reaction by which more gas is developed. From the experimental results given below the following mechanism is suggested

$$O_2NC(CH_3)_2CO_2^- \rightarrow {}^-O_2N{:}C(CH_3)_2 + CO_2 \tag{1}$$
$$H^+ + {}^-O_2N{:}C(CH_3)_2 \rightarrow HOON{:}C(CH_3)_2 \tag{2}$$
$$HOON{:}C(CH_3)_2 \rightarrow OC(CH_3)_2 + \tfrac{1}{2}N_2O + \tfrac{1}{2}H_2O \tag{3}$$

Reaction 1 is followed by the instantaneous reaction 2, and this by the decomposition 3. In not too weak hydrochloric acid, reaction 3 is so much quicker than reaction 1 that the carbon dioxide cleavage determines the velocity of the total reaction.

In acetate buffer solutions the production of gas in excess of one mole per mole of α-nitroisobutyric acid is extremely slow. Probably the aci-form produced by reaction 2 is transformed into the nitro compound

$$HOON{:}C(CH_3)_2 \rightarrow O_2N\dot{C}H(CH_3)_2 \tag{4}$$

sufficiently quickly to avoid the decomposition 3. This quick rearrangement in the acetate buffer is in conformity with earlier work (10) in which it was found that the prototropic isomerization of aliphatic nitro compounds is catalyzed by acetate ions and other bases.

α-Nitroisobutyric acid was prepared by the method of Steinkopf and Supan (14). The beautiful white crystals obtained were used for the kinetic experiments without purification. The acid could only be recrystallized with very great loss. When an experiment was repeated with different preparations (m.p., 93–95°C.) concordant results were obtained.

The decomposition was investigated at 17.84 and at 9.78°C. Experiments were carried out in hydrochloric acid and acetate buffer solution by observing the increase in pressure above the solution during reaction by means of an apparatus described in an earlier paper (9).

For comparison some experiments on nitroacetic acid were carried out under the same circumstances. The substance was prepared as described in the paper on nitroacetic acid (7).

When a little nitroisobutyric acid was dissolved in barium hydroxide the solution kept clear for some seconds. Then a precipitate of barium carbonate began to be formed. This shows that the nitroisobutyrate ion is unstable.

EXPERIMENTS IN ACETATE BUFFER SOLUTIONS

Here

c = the initial concentration of the reacting acid.

$c - x$ = its concentration t minutes after the start.

P = the difference between the final pressure readings and the reading at the time t.

P_0 = the value of P, when $t = 0$.

ϕ = the proportionality factor $P_0/c = P/(c - x)$ (cm. of mercury per mole per liter).

k^* = unimolecular velocity constant. By an asterisk we denote that the constant has been calculated by means of decadic logarithms. k^* is computed in the usual way by plotting log P against t.

The agreement with the unimolecular law is good. The carbon dioxide cleavage was finished a few hours after the start. After that time a very slow pressure increase was noticed. This secondary reaction was sufficiently slow to allow an accurate determination of the end point of the primary reaction. When the primary reaction was near its end the solution assumed a greenish color.

The results of experiments in different acetate buffer solutions are given in table 1. Each experiment was carried out with 60 cc. of solution and enough nitroisobutyric acid to make it 8 to 10 $\times$ $10^{-3}M$. The total pressure increase (about 6 cm. of mercury) corresponds to an average value of φ = P_0/c = 643 for the experiments at 17.84°C. This is only 3.4 per cent more than the value $\varphi = 622$ found by adding a known amount of sodium carbonate to 60 cc. of the acetate buffer. The discrepancy may be due to a small vapor pressure of the other reaction product. Hence, one mole of carbon dioxide is produced per mole of nitroisobutyric acid in the acetate buffers.

As seen from table 1 the velocity of decomposition is not affected by a considerable variation of the ratio between the concentrations of acetic acid and sodium acetate. In the last experiment at 17.84°C. the final pressure was not determined as accurately as usual. It was therefore omitted when taking the mean values. The fourth column gives the number of the preparation of nitroisobutyric acid. It is seen that different preparations decompose with the same velocity.

In table 2 are given the results of experiments on the decomposition of nitroacetic acid carried out under the same experimental conditions.

EXPERIMENTS IN HYDROCHLORIC ACID

Here the pressure increase was approximately one and a half times as great as would be expected from the experiments in acetate buffer solutions. According to the mechanism suggested in the schemes 1 to 3, one

mole of carbon dioxide and half a mole of nitrous oxide should be produced per mole of nitroisobutyric acid. In order to test this assumption the following calculations were carried out.

First the total volume, v cc., of the reaction vessel was determined by adding a known amount of sodium carbonate to the flask which contained a known volume, u cc., of 0.1 M hydrochloric acid at 17.84°C. If we denote by p_0 (cm. of mercury) the pressure increase per mole of sodium car-

TABLE 1

Decomposition of α-nitroisobutyric acid in acetate buffer solutions

TEMPERATURE	(CH₃COOH)	(CH₃CO₂Na)	PREPARATION	φ	k^*
degrees C.					
	0.100	0.100	1	646	0.0449
	0.100	0.100	1	641	0.0446
17.84	0.050	0.050†	1	643	0.0449
	0.050	0.100	1	642	0.0448
	0.180	0.100	1	(652)	(0.0440)
Average values....................................				643	0.0448
9.78	0.100	0.100	1	570	0.01396
	0.100	0.100	3	575	0.01394
Average values....................................				572	0.01395

† Containing 0.050 M sodium chloride

TABLE 2

Decomposition of nitroacetic acid in acetate buffer solutions

TEMPERATURE	(CH₃COOH)	(CH₃CO₂Na)	k^*	AVERAGE VALUE OF k^*
degrees C.				
	0.100	0.100	0.02464	
17.84	0.100	0.100	0.02456	0.02460
	0.050	0.050	0.02460	
9.78	0.100	0.100	0.00772	0.00774
	0.100	0.100	0.00776	

bonate and by f the Ostwald absorption coefficient (the ratio between the concentrations of a gas in liquid and gaseous phase at equilibrium), the following formula holds

$$p_0 (v - u + fu) = RT$$

where $RT = 1.815 \times 10^6$. From the investigation of Geffcken (1) we find for carbon dioxide at 17.84°C. $f = 0.988$. The results are given in table 3. The average value of the volume is $v = 173.6$ cc.

The molar pressure increase p_2 for nitroisobutyric acid added to hydrochloric acid is given in the fifth line of table 3.   By subtraction of p_0, the molar pressure increase for sodium carbonate added to hydrochloric acid, we find the partial pressure p_3 (per mole of nitroisobutyric acid) of the gas which is produced in addition to the carbon dioxide.   If we assume that n moles of a gas with the absorption coefficient f is produced per mole of the acid, we have

$$p_3(v - u + fu) = nRT$$

or

$$173.6p_3 = 1.815 \times 10^6 \, n + (1 - f) \, p_3 u$$

When the experimental values of u and p_3 are introduced we get as result $n = 0.538$ mole of a gas with the absorption coefficient $f = 0.728$ (compare

TABLE 3

u, volume of solution	20	60	100
p_0, pressure increase per mole of Na_2-CO_3 in 0.1 M HCl	1.042×10^4	1.046×10^4	1.061×10^4
v, total volume of vessel	174.3	174.2	172.2
p_1, pressure increase per mole of nitroisobutyric acid in acetate buffers	(1.068×10^4)	$1.072 \times 10^{4*}$	(1.088×10^4)
p_2, pressure increase per mole of nitroisobutyric acid in 0.03–0.3 M HCl	1.623×10^4	$1.667 \times 10^{4\dagger}$	1.729×10^4
$p_3 = p_2 - p_0$ (observed)	0.581×10^4	0.621×10^4	0.668×10^4
p_3 (calculated from $f = 0.728$ and $n = 0.538$)	0.581×10^4	0.621×10^4	0.667×10^4
$p_4 = p_2 - p_1$ (observed)	0.555×10^4	0.595×10^4	0.641×10^4
p_4 (calculated from $f = 0.716$ and $n = 0.513$)	0.554×10^4	0.594×10^4	0.641×10^4

* Average of four experiments (table 1).

† Average of six experiments (table 4).

the sixth and seventh line of table 3).   From Geffcken's paper we get for nitrous oxide at 17.84°C. $f = 0.718$.

If instead of subtracting the molar pressure increase for sodium carbonate in hydrochloric acid we subtract that for nitroisobutyric acid in acetate buffers (p_1), we get an even better agreement.   Only the value of p_1 for 60 cc. of buffer solution has been determined by experiment.   For the calculation of the values in parentheses we have used the assumption that the ratio p_1/p_0 is independent of the volume u.   We find (compare the last two lines of the table) $n = 0.513$ and $f = 0.716$.

In order to show that one mole of acetone is formed per mole of nitro-

isobutyric acid (scheme 3), samples were taken from the reaction vessel after some of the experiments. Acetone was determined by the method of Messinger (6) in the form suggested by Ljunggren (5). By addition of sodium hydroxide and an excess of iodine solution iodoform was precipitated. The excess of iodine was titrated with thiosulfate after the solution had been acidified with sulfuric acid. The analysis gave as result that 0.96 to 1.00 moles of acetone had been formed per mole of nitroisobutyric acid. After the iodine set free by the addition of the acid had been titrated, more iodine was slowly liberated. The solution seemed to contain a substance which catalyzes the oxidation of hydriodic acid by the air. The deviation from 1.00 found in the analysis may have its origin in this source of error.

Shortly after the start of the reaction the solution assumed a light green color which vanished when the reaction was finished.

We shall now see that a comparison of the experiments in hydrochloric acid and acetate buffers leads to the following explanation. In the acetate buffers the acid is completely ionized and the velocity constant k found here is that for the decomposition of the nitroisobutyrate ion. In hydrochloric acid the fraction α which is ionized decomposes with the velocity constant k, while the unionized acid is stable. This is formally equivalent to saying that all the nitroisobutyric acid (free and ionized) decomposes with the velocity constant αk. We test the explanation by calculating the dissociation constant K of the nitroisobutyric acid from the degree of dissociation α found as the ratio between the velocity constants in hydrochloric acid and in acetate buffers.

We first assume that reaction 3 is so rapid compared with reaction 1 that the latter determines the velocity of the total reaction.

In computing the velocity constant we must take into account that the hydrogen-ion concentration of the solution of the acid in hydrochloric acid is diminished a little when the acid decomposes. We denote by a the concentration of hydrochloric acid, by $\alpha_0, \alpha,$ and α_∞ the degrees of dissociation of the nitroisobutyric acid at the times $0, t,$ and ∞. According to the mass action law we have

$$\frac{\alpha}{1 - \alpha}\,[a + \alpha\,(c - x)] = K$$

From this we obtain

$$\alpha = \frac{K}{a + \alpha(c - x) + K} \qquad \text{and} \qquad \alpha_\infty = \frac{K}{a + K} \tag{5}$$

The velocity is given by

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k\alpha(c - x) \tag{6}$$

When equation 5 is introduced equation 6 may be written

$$k\alpha_{\infty}dt = \left(\frac{1}{c-x} + \frac{\alpha_{\infty}}{a+K} - \frac{\alpha_{\infty}-\alpha}{a+K} \right) dx$$

By integration we get

$$- k\alpha_{\infty}t = \text{const.} + l(c-x) + \frac{\alpha_{\infty}}{a+K}(c-x) - \int_{c}^{c-x} \frac{\alpha_{\infty}-\alpha}{a+K}\, d(c-x)$$

If we introduce $P = \varphi\,(c - x)$, equation 5, and $k^* = 0.4343k$, we may write the expression as follows

$$- k^*\alpha_{x}t = \text{const.} + \log P + \beta P + \Delta \tag{7}$$

where

$$\beta \equiv \frac{0.4343K}{\varphi(a+K^2)}$$

and

$$\Delta \equiv \beta \int_{P_0-P=0}^{P_0-P} \frac{\alpha_{\infty}-\alpha}{\alpha_{\infty}}\, d\,(P_0 - P) < \beta P_0 \frac{\alpha_{\infty}-\alpha_0}{\alpha_{\infty}}$$

For the calculation of the correction βP we must know K. This is found sufficiently accurately by calculating α_{∞} from a preliminary value of the velocity constant $\alpha_{\infty}k$. The correction Δ is of no importance except in the most dilute solutions of hydrochloric acid. Here we may compute it by rough graphical integration.

The results of the experiments on nitroisobutyric acid are given in tables 4 and 5. The velocity constant $k^*\alpha_{\infty}$ is found by plotting the sum of $\log P$ and βP and, if necessary, the correction Δ against t. For the most concentrated solutions of hydrochloric acid we get points that fall well on a straight line. For 0.1 M and less concentrated acid the points fall on a curve which approaches more quickly to a straight line the more concentrated the acid. This result is what one would expect when a part of the gas is developed by a consecutive reaction whose velocity is less predominating the smaller the hydrogen-ion concentration. For the velocity constant $\alpha_{\infty}k^*$ of the primary reaction we take the numerical value of the slope of the straight line. While the approach to the straight line was sufficiently quick in 0.1 M hydrochloric acid to allow a good determination of $\alpha_{\infty}k^*$, this was uncertain even in 0.05 and 0.033 M, and in 0.02 and 0.01 M hydrochloric acid the straight line could not be drawn accurately enough. However, if we calculate $\alpha_{\infty}k^*$ for the experiment in 0.02 M HCl + 0.08 M NaCl according to the interpretation given above, using the dissociation constant K found for the same salt concentration in more acid solution, a line with the slope $-\alpha_{\infty}k^*$ fits well as an asymptote to the curve.

For the calculation of α_∞ from $\alpha_\infty k^*$ we use the value of k^* found in the experiments in acetate buffer solutions. It is seen from the tables that $K = a\dfrac{\alpha_\infty}{1 - \alpha_\infty}$ is constant when the concentration of hydrochloric acid is varied, while the total salt concentration is kept constant. In order to see if the values of K at different salt concentrations agree among them-

TABLE 4

Decomposition of α-nitroisobutyric acid in hydrochloric acid at 17.84°C.

(HCl)	PREPA-RATION	φ	$\alpha_\infty k^*$	α_∞	K	$-\text{LOG } K$	μ	$\dfrac{-\text{LOG } K}{+0.998\sqrt{\mu}}$	$\dfrac{1.928}{+0.873\mu}$	$\delta \times 10^3$
0.3006	1	1006	0.003165	0.0706	0.0229	1.641	0.3008	2.190	2.190	0
0.1994	1		0.00445	0.0993	0.0220	1.657	0.1997	2.103	2.102	+1
0.1001	1	999	0.00746	0.1665	0.0200	1.699	0.1006	2.016	2.016	0
0.5005†	1	1000	0.01286	0.2870	0.0202	1.696	0.1009	2.013	2.016	−3
0.05005†	2	1000	0.01272	0.2839	0.0198	1.702	0.1009	2.019	2.016	+3
0.05005	1	997	0.01196	0.2670	0.0182	1.739	0.0509	1.964	1.972	−8
0.03337	1	997	0.01560	0.3482	0.0178	1.749	0.0345	1.935	1.958	−23
0.02016‡	1	(910)								
0.01008§	1	(991)								

† Containing 0.0500 M sodium chloride.
‡ Containing 0.0800 M sodium chloride.
§ Containing 0.0900 M sodium chloride.

TABLE 5

Decomposition of α-nitroisobutyric acid in hydrochloric acid at 9.78°C.

(HCl)	PREPARA-TION	$\alpha_\infty k^*$	α_∞	K	$-\text{LOG } K$	μ	$\dfrac{-\text{LOG } K}{+0.986\sqrt{\mu}}$	$\dfrac{1.871}{+0.873\mu}$	$\delta \times 10^3$
0.3006	2	0.001052	0.0754	0.0245	1.611	0.3009	2.152	2.133	+19
0.2007	2	0.001548	0.1110	0.0251	1.601	0.2011	2.044	2.046	−2
0.2014	2	0.001538	0.1103	0.0250	1.603	0.2018	2.047	2.047	0
0.1004†	4	0.00276	0.1978	0.0248	1.606	0.2011	2.049	2.046	+3
0.1001	3	0.00257	0.1842	0.0226	1.646	0.1007	1.959	1.959	0
0.05005	3	0.00412	0.2953	0.0210	1.678	0.0512	1.902	1.916	−14

† Containing 0.100 M sodium chloride.

selves and to find the activity dissociation constant K_0 we proceed in the following way. According to the Debye-Hückel law we have

$$-\log K = -\log K_0 - A\sqrt{\mu} + B\mu \qquad (8)$$

where μ is the ionic strength and A a constant (at 18°C. 0.998, and at 10°C. 0.986), while B approaches to a constant value when $\mu \to 0$. For μ we use a mean value found by adding $\frac{1}{2}\alpha_0 c$ to the sum of the concentrations of hydrochloric acid and sodium chloride. If we plot $-\log K + A\sqrt{\mu}$

against μ for each of the two series of experiments, the points fall fairly well on straight lines. Only the points for the most dilute hydrochloric acid deviate a little, probably owing to the greater error in computing the velocity constants. The neglect of these points in extrapolating to zero salt concentration is to some extent justified by the results on nitroacetic acid in hydrochloric acid (tables 6 and 7), where we have no con-

TABLE 6

Decomposition of nitroacetic acid in hydrochloric acid at 17.84°C.

(HCl)	$\alpha_\infty k^*$	α_∞	K	$-\mathrm{LOG}\ K$	μ	$\dfrac{-\mathrm{LOG}\ K}{+0.998\sqrt{\mu}}$	$\dfrac{1.682}{+0.927\mu}$	$\delta \times 10^3$
0.3006	0.002816	0.1145	0.0389	1.410	0.3011	1.959	1.960	−1
0.2007	0.00388	0.1577	0.0376	1.425	0.2015	1.874	1.869	+5
0.1000	0.00632	0.2569	0.0346	1.461	0.1014	1.779	1.775	+4
0.05010	0.00952	0.3870	0.0316	1.501	0.0519	1.728	1.730	−2
0.05010	0.00950	0.3862	0.0315	1.502	0.0519	1.729	1.730	−1
0.02014	0.01432	0.5821	0.0280	1.552	0.0228	1.703	1.703	0
0.01009	0.01777	0.7224	0.0262	1.581	0.0131	1.695	1.694	+1

TABLE 7

Decomposition of nitroacetic acid in hydrochloric acid at 9.78°C.

(HCl)	$\alpha_\infty k^*$	α_∞	K	$-\mathrm{LOG}\ K$	μ	$\dfrac{-\mathrm{LOG}\ K}{+0.986\sqrt{\mu}}$	$\dfrac{1.661}{+0.927\mu}$	$\delta \times 10^3$
0.2007	0.001280	0.1654	0.0398	1.400	0.2016	1.844	1.848	−4
0.1000	0.002067	0.2671	0.0364	1.438	0.1015	1.757	1.755	+2
0.0501	0.003065	0.3960	0.0328	1.484	0.0523	1.710	1.709	+1

TABLE 8

K_0 and k^* for nitroisobutyric acid nitroacetic acids

ACID	K_0		k^*		Q
	At 17.84°C.	At 9.78°C.	At 17.84°C.	At 9.78°C.	
					kg.-cal.
Nitroisobutyric acid............	0.0118	0.0135	0.0448	0.01395	32.7
Nitroacetic acid................	0.0208	0.0218	0.0246	0.00774	23.5

secutive reaction. Here there is a linear relation between $-\log K + A\sqrt{\mu}$ and μ down to the greatest dilution ($0.3 - 0.01\ M$). The last column in tables 4 to 7 shows the agreement of the experimental results for nitroisobutyric and nitroacetic acids with expression 8, using the values of K_0 and B computed in this way. δ is the difference $(-\log K + A\sqrt{\mu}) - (-\log K_0 + B\mu)$.

Table 8 gives the dissociation constants K_0 and the velocity constants

k^* for the two acids. In the last column is given the heat of activation (Q kg-cal.) calculated from k^* in the usual way.

THE VELOCITY OF BROMINATION OF NITROISOBUTYRIC ACID

In the explanation given in the schemes 1 and 2 it is assumed that the decomposition leads directly to the aci-form of the nitro-hydrocarbon. In order to test this some experiments on the bromination of nitroisobutyric acid were carried out.

The aci-forms of aliphatic nitro compounds are brominated practically instantaneously, while the nitro compounds themselves are not brominated directly. From the work of Junell (4) we know that secondary nitropropane is brominated extremely slowly at 18°C. in a strong acid, the velocity being probably determined by the slow isomerization to the aci-form (see also Pedersen (10)).

TABLE 9

Bromination of nitroisobutyric acid at 17.84°C.

| IN 0.0998 M HCl				IN 0.0101 M HCl + 0.0900 M NaCl			
t	$c \times 10^3$	$x \times 10^3$	αk^*	t	$c \times 10^3$	$x \times 10^3$	αk^*
10.7	7.340	1.18	0.00711	2.8	7.181	1.186	0.0280
19.8	8.002	2.212	0.00710	8.8	5.808	2.49	0.0276
35.6	7.271	3.260	0.00726	17.1	5.324	3.49	0.0270
46.5	8.110	4.375	0.00724				
56	7.293	4.451	0.00730	Mean value...............			0.028
82	7.425	5.495	0.00714	(Indirectly from decompo-			
105.5	7.967	6.557	0.00713	sition experiments........			0.028)
Mean value...............			0.0072				
(From decomposition ex-							
periments...............			0.0074)				

If the explanation expressed in the schemes 1 and 2 is true, the secondary nitropropane should be brominated as soon as it is formed. Thus it should be possible to determine the velocity of decomposition of the nitroisobutyric acid by measuring the velocity of disappearance of the bromine, when the acid is dissolved in bromine water.

To 0.0998 M hydrochloric acid containing bromine at 17.84°C. in a flask with glass stopper was added a known excess of nitroisobutyric acid. The time t which elapsed between the addition of the substance and the disappearance of the brown color was determined. In different experiments with the same concentration of hydrochloric acid and nearly the same initial concentration, c, of nitroisobutyric acid the time of reaction was varied by varying the concentration of bromine. The decrease in the molar concentration of bromine during the time t serves as a measure of the

decrease x in concentration of nitroisobutyric acid. In table 9 the unimolecular velocity constant $ak^* = \frac{1}{t} \log \frac{c}{c-x}$ has been calculated. The mean value $ak^* = 0.0072$ is in agreement with the constant $ak^* = 0.0074$ found by measuring the gas pressure for the same concentration of hydrochloric acid.

In the bromination experiments we avoid the troublesome secondary reaction. It is of interest to do experiments in a solution where the secondary reaction made it impossible to determine directly the velocity constant of the carbon dioxide cleavage. In 0.0101 M HCl + 0.0900 M NaCl the velocity constant of the bromination $ak^* = 0.028$ was found (table 9). In order to compare this result with those for the gas evolution experiments we make the following calculation. From experiments in more acid solution we know that $K = 0.0200$, when $\mu = 0.1$. The hydrogen-ion concentration is $(H^+)_\infty = 0.0101$, when $t = \infty$, and $(H^+)_0 = 0.010 + 0.004 = 0.014$, when $t = 0$, or in average $(H^+) = 0.012$. Hence we find $\alpha = 0.0200/0.032 = 0.62$ and $ak^* = 0.62 \times 0.0448 = 0.028$, in good agreement with the bromination experiments. This shows that the impossibility of determining the constant directly by the pressure method in the most dilute solutions of hydrochloric acid actually is due to a secondary reaction.
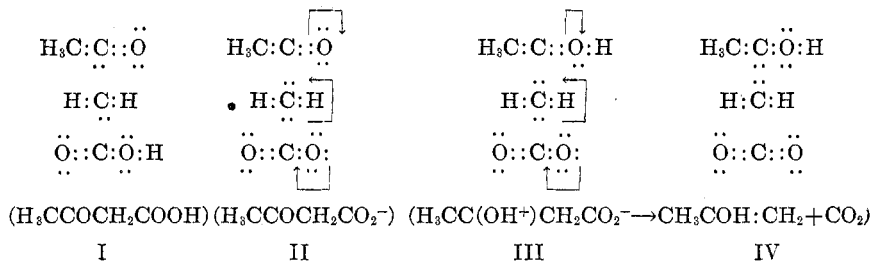
We have now seen that the carbon dioxide cleavages of nitroacetic and α-nitroisobutyric acids follow the same laws. In both cases the undissociated acid is stable, while the univalent ion is decomposed. The velocities are of the same order of magnitude and the heats of activation are the same. From this we may conclude that the unstable form of α-nitrocarboxylic acids in general is not the aci-form of the nitro compound, but the ordinary ion $>CNO_2CO_2^-$. The decomposition leads directly to the aci-form of the corresponding nitrohydrocarbon. From these facts we may try to form a picture of the details of the decomposition. The reaction may be expressed as follows by means of electron valency formulas. It is suggested that the decomposition is caused by a displacement of valency electrons in the direction shown by the arrows.


$$(O_2NCH_2COOH) \qquad (O_2NCH_2CO_2^- \qquad \rightarrow \qquad {}^-O_2N{:}CH_2 + CO_2)$$
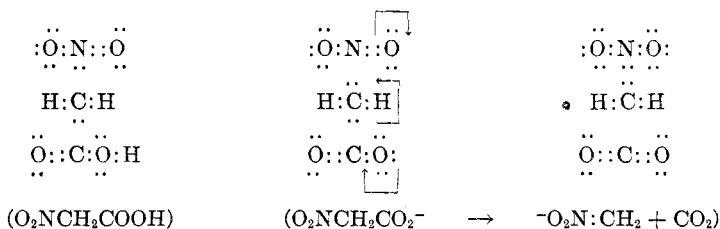
THE DECOMPOSITION OF β-KETOCARBOXYLIC ACIDS

It is interesting to compare the α-nitrocarboxylic acids with another group of unstable acids, the β-ketocarboxylic acids. The simplest acid of this type, acetoacetic acid, has mainly been examined by Widmark (12, 13) and Ljunggren (5). Here the undissociated acid decomposes with considerable velocity ($CH_3COCH_2COOH \rightarrow CH_3COCH_3 + CO_2$), while the ion decomposes very slowly. The reaction is catalyzed by primary amines. Secondary amines have a small and tertiary amines hardly any effect. From the work on acetoacetic acid it was impossible to decide whether the keto or enol form is active. By studying α,α-dimethylaceto-acetic acid, which can not be rearranged into an enol form, Pedersen (8) found that the keto form is unstable. To this can now be added the following result. By making kinetic experiments on the bromination of α,α-dimethylacetoacetic acid in the same way as described above for nitro-isobutyric acid and comparing them with earlier experiments on the rate of evolution of carbon dioxide, it was found that bromine is taken up with the same velocity as the keto acid is decomposed (one mole of bromine per mole of keto acid). From these experiments we may conclude that the decomposition of β-ketocarboxylic acids leads directly to the enol form of the reaction product. Thus, there seems to be a close analogy between the mechanism of decomposition of α-nitrocarboxylic acids and β-keto-carboxylic acids.

For β-ketocarboxylic acids we may tentatively suggest the following mechanism. The ordinary form of the undissociated acid (I) is stable. The acetoacetate ion (II) decomposes very slowly. Owing to the weak basic properties of the keto group it will to a small extent take up hydrogen ions. The concentration of the ampho ion (III) thus formed is proportional to the concentration of the ordinary undissociated acid. Consequently it is impossible to decide from the kinetic experiments which of them is unstable. Owing to the attraction of the positive charge it is reasonable to assume that the ampho ion decomposes much more quickly than the ion (II). By the decomposition we get the enol form of the reaction product (IV).

$$(H_3CCOCH_2COOH)\quad(H_3CCOCH_2CO_2^-)\quad(H_3CC(OH^+)CH_2CO_2^- \rightarrow CH_3COH:CH_2 + CO_2)$$

| I | II | III | IV |

In order to explain the amine catalysis we assume that an equilibrium of the type

$$> CO + H_2NR \rightleftharpoons > CNR + H_2O \tag{9}$$
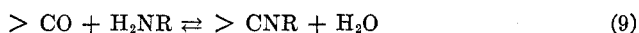
is quickly established. The group CNR has much stronger basic properties than the keto group. Although the substance >CNR may only be formed in very small concentration by equilibrium 9, we may get a greater concentration of ampho ion than before, and a quicker decomposition.

SUMMARY

This paper contains a kinetic study of the decomposition of α-nitroisobutyric and nitroacetic acids at 17.84°C. and 9.78°C. in acetate buffer solutions and in hydrochloric acid of different concentrations.

From the results it is concluded that the carbon dioxide cleavage of the α-nitrocarboxylic acids consists of a decomposition of the ion with a negative charge at the carboxyl group and leads directly to the aci-form of the corresponding nitro hydrocarbon

$$> C(NO_2)CO_2^- \rightarrow > CNO_2^- + CO_2$$
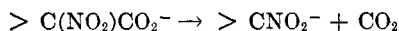
The dissociation constants of the two acids have been calculated from the kinetic experiments.

The analogy between the carbon dioxide cleavage of the α-nitrocarboxylic acids and the β-ketocarboxylic acids has been pointed out. An attempt has been made to suggest a mechanism which explains the decomposition of both groups of acids and the amine catalysis of the cleavage of the keto acids.

My thanks are due to Professor Niels Bjerrum for his kind interest in my work.

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