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GENERAL BASIC CATALYSIS ON THE  
ISOMERISATION OF NITROMETHANE  
THE DISSOCIATION OF PSEUDO-ACIDS

BY

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KØBENHAVN

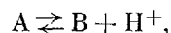
HOVEDKOMMISSIONÆR: ANDR. FRED. HØST & SØN, KGL. HOF-BOGHANDEL

BIANCO LUNOS BOGTRYKKERI A/S

1932



According to BRØNSTED's<sup>1</sup> definition of acids and bases any neutral molecule or ion which can split off a proton is called an acid, and any neutral molecule or ion which can take up a proton is called a base. When



A is an acid and B the corresponding base. The proton being unable of independent existence, an acid can only give off a proton to a base. Thus the characteristic acid and base function is the transference of protons from the acid to the base. BRØNSTED<sup>2</sup> calls this a protolytic reaction.

It has been found, especially by BRØNSTED and his coworkers, that many reactions are catalyzed by acids or bases in general, that is, all sufficiently strong acids or bases catalyze, and the effect increases with increasing acid or basic strength. BRØNSTED<sup>3</sup> has developed a theory of general acid and basic catalysis. According to this the velocity depends on the velocity of transference of protons between the substrate and the catalyst.

One of the best known forms of reversible isomerisation is that characterized by the change of position in the

<sup>1</sup> BRØNSTED, Rec. trav. chim. Pays-Bas 42 (1923) 718.

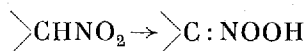
<sup>2</sup> BRØNSTED, Z. angew. Chem. 43 (1930) 229.

<sup>3</sup> BRØNSTED, "Om Syre- og Basekatalyse" Festskrift. University of Copenhagen. (1926). — Chem. Reviews 5 (1928) 231. — Trans. Faraday Soc. 24 (1928) 630.

molecule of a hydrogen atom. LOWRY<sup>1</sup> has called this form of isomerism prototropy.

From the work in this field it seems justified to conclude that the hydrogen atom cannot move spontaneously from one place in the molecule to the other. Isomerisation can only take place in the presence of an acid and a base. The prototropic molecule gives off a proton to the base and receives one in another place of the molecule from the acid. In addition, a rearrangement of valency electrons in the molecule takes place. This point of view has been discussed more thoroughly in another paper which is ready for publication. Thus the prototropic change depends on protolytic reactions. Consequently prototropic isomerisations show general acid or basic catalysis or both. This has been experimentally established in a number of cases. The mutarotation of glucose<sup>2</sup> and the enolisation of acetone<sup>3</sup> are catalyzed by both acids and bases. The enolisation of acetoacetic ester and acetoacetic acid are only catalyzed by bases.<sup>4</sup>

In this paper it is shown that the prototropic isomerisation of aliphatic nitrocompounds to the aci-form



is catalyzed by bases in general.

JUNELL<sup>5</sup> has studied the velocity of bromination and chlorination of nitromethane, mono- and di-bromo nitromethane and secondary nitropropane in 1 n. hydrogen halide.

<sup>1</sup> LOWRY, Chem. Reviews 4 (1927) 231.

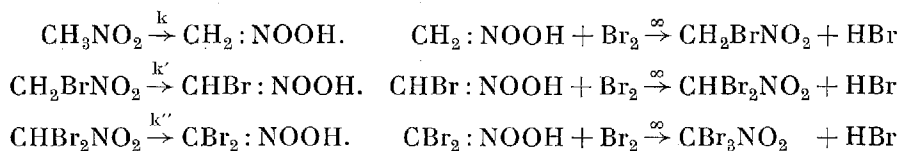
<sup>2</sup> BRØNSTED and GUGGENHEIM, J. Amer. Chem. Soc. 49 (1927) 2554.

<sup>3</sup> DAWSON, J. Chem. Soc. (1929) 1217.

<sup>4</sup> PEDERSEN, Ber. om 18. skandinaviske Naturforsker møde (1929) 451 and yet unpublished work.

<sup>5</sup> JUNELL, Z. physik. Chem. A 141 (1929) 71.

He finds that the reaction is always of the first order with respect to the nitrocompound. The velocities of bromination and chlorination are the same, and the concentration of the halogen is without influence. Consequently, it must be assumed that the velocity is determined by the unimolecular rearrangement of the nitrocompound to the aci-form, which takes up halogen instantaneously. According to JUNELL the rate of bromination of nitromethane is determined by three consecutive unimolecular reactions. The ratio of their constants  $k$ ,  $k'$  and  $k''$  is approximately 1:270:13000. The mechanism is assumed to be



JUNELL found for the first step at  $69.85^\circ$   $k = 36 \cdot 10^{-5}$ , at  $59.93^\circ$   $k = 14 \cdot 10^{-5}$  and at  $49.91^\circ$   $k = 4.9 \cdot 10^{-5}$  ( $\text{min}^{-1}$ ). From this we find by extrapolation, if we assume that the heat of activation is independent of the temperature, at  $20^\circ$   $k = 1.4 \cdot 10^{-6}$  or  $k^* = 0.6 \cdot 10^{-6}$ . By an asterisk we denote that the constant has been calculated by means of decadic logarithms. Thus  $k^* = 0.4343 k$ .

In the present paper are described some very rough determinations of the velocity of bromination of nitromethane in solutions of acetic acid + sodium acetate, glycolic acid + sodium glycolate and chloroacetic acid + sodium chloroacetate. The experiments were carried out at room temperature in wide cylindrical weighing glasses with ground glass stoppers. The nitromethane was purified by distillation (b.p.  $100.7^\circ$ - $100.9^\circ$ ). Nitromethane solution and buffer solution were mixed. The reaction was started by adding a certain

volume of bromine water of known strength. The time  $t$  in minutes from the start to the disappearance of the brown colour was determined. The volume during the reaction was always 50 cc. The results are given in the Tables 1–5.  $c$  is the initial concentration of nitromethane, and  $x$  that of bromine in equivalents per l.

Table 1.  
Bromination of nitromethane. Temp. 22° (in No. 1 about 20°).

Nr.	(CH <sub>3</sub> COOH)	(CH <sub>3</sub> CO <sub>2</sub> Na)	$c$	$x \cdot 10^3$	$t$	$k_B^* \cdot 10^8$
1	0.00	0.00	0.105	7.4	4560	..
2	0.20	0.20	0.105	7.4	17	1.5
3	0.10	0.10	0.105	7.4	36	1.4
4	0.20	0.20	0.105	7.4	17.5	1.5
5	0.20	0.20	0.070	7.4	28.5	1.4
6	0.60	0.20	0.070	7.4	28.5	1.4
7	0.20	0.20	0.105	7.4	17.5	1.5
8	0.20	0.20	0.070	5.0	17.5	1.5

In Exp. 1 (Table 1) nitromethane was brominated at about 20° in water without addition of a catalyst. The reaction is extremely slow. It is possible to calculate a very rough value of the constant  $k$ , when we use the result found by JUNELL that  $k'' > k' \gg k$ , that is, the rearrangement of the nitromethane is instantaneously followed by a disappearance of 6 atoms of bromine per mole nitromethane. From Exp. 1 we thus find

$$k^* = \frac{1}{4560} \log \frac{0.1050}{0.1050 - \frac{1}{6} 0.0074} = 10^{-6}.$$

From JUNELL's determination in 1 n. HBr was calculated  $k^* = 0.6 \cdot 10^{-6}$  at 20°. A better agreement could not be expected.

In Exps. 2—8 the rate of bromination was determined in different acetic acid-sodium acetate solutions. In Exps. 2 and 3 the initial concentrations of nitromethane and bromine were the same as in Exp. 1. The velocity is several hundred times as great. The experiments show that the velocity at constant hydrogen ion concentration is proportional to the acetate concentration.

Exps. 4 and 5 show that the velocity in a given acetate buffer is proportional to the nitromethane concentration.

Exps. 5 and 6 show that the concentration of acetic acid at constant acetate concentration is without influence. Consequently, the hydrogen and hydroxyl ion concentration of the buffer are without influence as long as the acetate concentration is kept constant.

Exps. 7 and 8 show, that the bromine which is decolourized in a certain time in a given acetate buffer is proportional to the nitromethane concentration. From this result and the fact that the reaction is of first order with respect to nitromethane it follows that the concentration of bromine is without influence on the velocity of bromination in the buffer solution.

In Exps. 1—8 it is established that acetate ions have a very marked catalytic effect on the rearrangement of the nitromethane, while acids do not catalyze. In the last column of Table 1 the catalytic constant  $k_B^* = k^*/(\text{CH}_3\text{CO}_2^-)$  has been calculated from the experiments. The constancy of  $k_B^*$  shows that the experiments agree among themselves.  $k^*$  has been calculated by means of the equation

$$k^* = \frac{1}{t} \log \frac{c}{c - \frac{x}{6}} \quad (1)$$

that is, we have assumed that here, as in 1 n. HBr, the rearrangement of mono- and di-bromo nitromethane are practically instantaneous compared with that of nitromethane.

Table 2.

Bromination of nitromethane in  
0.30 m  $\text{CH}_3\text{COOH} + 0.30$  m  $\text{CH}_3\text{CO}_2\text{Na}$  at  $22^\circ$ .  $c = 0.0210$ .

$x \cdot 10^3$	t	$\log \frac{c}{c - \frac{x}{6}}$	$k \cdot 10^5$
1.48	11	0.0052	47
4.44	36	0.0156	43
8.88	76	0.0317	42
13.22	121	0.0485	40

Mean value  $k^* = 43 \cdot 10^{-5}$ .  $k_B^* = 1.4 \cdot 10^{-3}$  ( $22^\circ$ ).

In Table 2  $k_B^*$  for the acetate ion has been calculated from 4 experiments in 0.30 m  $\text{CH}_3\text{COOH} + 0.30$  m  $\text{CH}_3\text{CO}_2\text{Na}$  at  $22^\circ$ . The value agrees well with that found in Table 1.

Table 3.

Bromination of nitromethane in  
0.60 m  $\text{CH}_3\text{COOH} + 0.60$  m  $\text{CH}_3\text{CO}_2\text{Na}$  at  $20^\circ$ .  $c = 0.0192$ .

$x \cdot 10^3$	t	$\log \frac{c}{c - \frac{x}{6}}$	$k \cdot 10^5$	$10^5 \frac{1}{t} \log \frac{c}{c - \frac{x}{2}}$	$10^5 \frac{1}{t} \log \frac{c}{c - \frac{x}{4}}$
8.87	50	0.0348	70	229	107
17.7	104	0.0727	70	258	109
26.6	161	0.1139	71	318	115
35.5	237 <sup>1</sup>	0.1598	(67)	474	114
44.3	319 <sup>1</sup>	0.2111	(66)	$(c < \frac{x}{2})$	117

Mean value  $k^* = 70 \cdot 10^{-5}$ .  $k_B^* = 1.17 \cdot 10^{-3}$  ( $20^\circ$ ).

<sup>1</sup> The solution was opaque at the end of the experiment.



Table 3 contains the results of 5 experiments in 0.60 m  $\text{CH}_3\text{COOH} + 0.60 \text{ m } \text{CH}_3\text{CO}_2\text{Na}$  at  $20^\circ$ . The constancy of  $k$  calculated by means of equation (1) is good. In the two last experiments, where rather much bromine was taken up, the solutions were opaque at the end of the experiments. From the value of  $k^*$  we calculate  $k_B^* = 1.17 \cdot 10^{-3}$  at  $20^\circ$ . In order to compare this result with that at  $22^\circ$  we assume that the temperature coefficient of the acetate catalysis is the same as that found in 1 n.  $\text{HBr}$  by JUNELL. From the experiments in Table 3 we then find  $k_B^* = 1.5 \cdot 10^{-3}$  at  $22^\circ$  in good agreement with the values found in the other acetate solutions. It has thus been shown that  $k_B^*$  is constant even when the acetate concentration varies from 0.1 to 0.6 m.

In addition to using equation (1)  $k^*$  in Table 3 has been calculated according to the assumption that the nitromethane is brominated to mono- or di-bromo nitromethane instead of tri-bromo nitromethane. The results are given in the two last columns of the table. The first assumption is disproved,  $\frac{1}{t} \log \frac{c}{c - \frac{x}{2}}$  being not constant. Furthermore,

in the last experiment more bromine than corresponds to monobromo nitromethane has been used. The experiments are not accurate enough to disprove the second possibility. However, it seems most probable that also in acetate solutions the rearrangement of mono- and di-bromo nitromethane are so much quicker than that of nitromethane, that only the latter determines the rate of disappearance of 6 atoms of bromine per mole of nitromethane.

In the Tables 4 and 5 are given the results of similar experiments in glycolate and chloroacetate buffers. Also there  $k^*$  was found to be proportional to the basic component

Table 4.

Bromination of nitromethane in glycollic acid - sodium glycolate solutions at 20°.  $c = 0.0516$ .

$(\text{CH}_2\text{OHCOOH})$	$(\text{CH}_2\text{OHCO}_2\text{Na})$	$\times 10^3$	t	$k^* 10^5$	$k_B^* 10^4$
0.109	0.145	2.40	71	4.8	3.3
0.109	0.145	7.57	250	4.3	3.0
0.109	0.145	12.70	450	4.2	2.9
0.075	0.087	7.57	390	2.8	3.2

Mean value  $k_B^* = 3.1 \cdot 10^{-4}$ .

Table 5.

Bromination of nitromethane in chloroacetic acid - sodium chloroacetate solutions at 20°.  $c = 0.1032$ .

$(\text{CH}_2\text{ClCOOH})$	$(\text{CH}_2\text{ClCO}_2\text{Na})$	$\times 10^3$	t	$k^* 10^5$	$k_B^* 10^5$
0.52	0.47	2.46	61	2.8	6.0
0.52	0.47	7.62	173	3.1	6.6
0.52	0.47	12.78	283	3.2	6.8
0.31	0.28	7.68	298	1.8	6.4

Mean value  $k_B^* = 6.5 \cdot 10^{-5}$ .

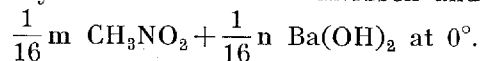
of the solution. It is seen that the catalytic effect decreases rapidly with decreasing basic strength of the catalyst (Table 7).

In the theory of general basic catalysis, the reaction in water without added catalyst is ascribed to the basic catalysis of the water. If we assume that the concentration of the water is 55.5, the catalytic constant of water is roughly  $k_{\text{H}_2\text{O}}^* = 10^{-6}/55.5$ .

The simplest explanation of the general basic catalysis on the isomerisation of nitromethane is that the reaction measured is the transference of protons from the nitromethane to the basic catalyst, that is, its velocity of dissociation in

Table 6.

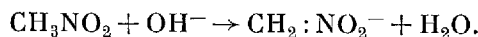
The reaction between nitromethane and hydroxyl ions. From conductivity measurements of HANTZSCH and VEIT in



t	0	1	2	3	4	15	20
$\mu$ .....	(122)	54.1	50.9	48.9	47.8	45.7	45.7
$\text{ak}_{\text{OH}^-}$ .....	..	8.1	6.8	7.6	8.8	..	..

Mean value  $\text{ak}_{\text{OH}^-} = 8$ .

the presence of the base. The neutralization of nitromethane with hydroxyl ions is a reaction of the same type, but is much quicker owing to the great basic strength of the hydroxyl ion. HANTZSCH and VEIT<sup>1</sup> have found that the velocity of neutralization of nitromethane is not immeasurably great. They have followed the decrease with the time of the conductivity of  $\frac{1}{16} \text{ m CH}_3\text{NO}_2 + \frac{1}{16} \text{ n Ba(OH)}_2$  at  $0^\circ$ . From their values of the equivalent conductivity  $\mu$ , which are given in Table 6, it is possible to get a rough estimation of the velocity constant of the reaction



The value of  $\mu$  at  $t = 0$  is the equivalent conductivity of  $\frac{1}{16} \text{ n Ba(OH)}_2$  at  $0^\circ$ . This value has been found by extrapolation to  $0^\circ$  of the values given in "International Critical Tables" VI (1929) 246. If we call the initial concentration of undissociated nitromethane  $c$ , and the concentration at the time  $t$   $x$ , the following equation holds

$$\text{k}_{\text{OH}^-} = \frac{1}{t} \frac{1}{a} \frac{x}{a-x}.$$

<sup>1</sup> HANTZSCH and VEIT, Ber. Deutschen Chem. Ges. 32 (1899) 615.

If we denote by  $\mu_t$  the equivalent conductivity at the time  $t$ , we have

$$\frac{\mu_0 - \mu_t}{\mu_t - \mu_\infty} = \frac{x}{a - x}.$$

Consequently,

$$ak_{\text{OH}^-} = \frac{1}{t} \frac{\mu_0 - \mu_t}{\mu_t - \mu_\infty}.$$

In the third line of Table 6  $ak_{\text{OH}^-}$  has been calculated from this equation.  $ak_{\text{OH}^-}$  is approximately constant. The mean value is 8. We thus find at  $0^\circ$   $k_{\text{OH}^-}^* = 0.4343 \cdot 16 \cdot 8 = 56$ . In order to compare it with the catalytic constants found in this paper we must know its value at  $20^\circ$ . If we assume that the temperature coefficient is the same here as for the water reaction in 1 n. HBr, we find at  $20^\circ$   $k_{\text{OH}^-}^* \sim 500$ .

In a number of reactions with general basic catalysis it has been shown that the dependence of the catalytic constant  $k_B$  upon the basic strength  $K_B^\circ$  of the catalyst is given approximately by the equation

$$\frac{1}{q} k_B = G \left( \frac{p}{q} K_B^\circ \right)^\beta, \quad (2)$$

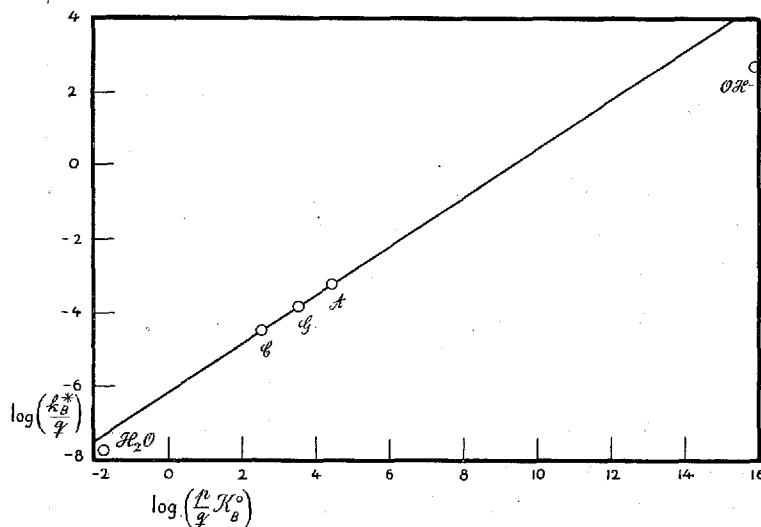
Table 7.

The dependence of catalytic constant upon basic strength.

Catalyst	$k_B^*$	$K_A$	p	q	$\log \left( \frac{1}{q} k_B^* \right)$	$\log \left( \frac{p}{q} K_B^\circ \right)$	$G \cdot 10^7$ ( $\beta = 0.67$ )
H <sub>2</sub> O	$10^{-6}/55.5$	55.5	1	1	0.26—8	—1.74	2.6
CH <sub>2</sub> ClCO <sub>2</sub> <sup>-</sup>	$6.5 \cdot 10^{-5}$	$1.41 \cdot 10^{-3}$	1	2	0.51—5	2.55	6.3
CH <sub>2</sub> OHCO <sub>2</sub> <sup>-</sup>	$3.1 \cdot 10^{-4}$	$1.48 \cdot 10^{-4}$	1	2	0.19—4	3.53	6.7
CH <sub>3</sub> CO <sub>2</sub> <sup>-</sup>	$1.17 \cdot 10^{-3}$	$1.79 \cdot 10^{-5}$	1	2	0.77—4	4.44	6.3
OH <sup>-</sup>	500	$10^{-14.15}/55.5$	1	1	2.7	15.9	0.12

where  $G$  and  $\beta$  are constants and  $p$  and  $q$  are statistical factors.<sup>1</sup>  $K_B^\circ$  is the reciprocal of the acid strength (dissociation constant)  $K_A^\circ$  of the corresponding acid.

In Table 7 the catalytic constants for nitromethane at  $20^\circ$  are compiled together with  $K_A^\circ$ . In order to test equation (2)  $\log\left(\frac{1}{q}k_B^*\right)$  is plotted against  $\log\left(\frac{q}{p}K_B^\circ\right)$ . As seen from



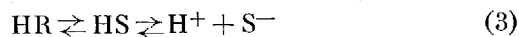
Basic catalysis on the isomerisation of nitromethane. The dependence of catalytic constant  $k_B^*$  upon basic strength  $K_B^\circ$ . A, Acetate ion. G, Glycolate ion. C, Chloroacetate ion.

the Figure the points for the three bases of the same type, acetate, glycolate and chloroacetate ions, fall on a straight line with the slope  $\beta = 0.67$ . The point for water does not fall much below the line. The point for hydroxyl ions falls a good deal too low. However, when we take into account the very great difference in basic strength, the agreement is sufficient.

<sup>1</sup> BRØNSTED, "Om Syre- og Basekatalyse" p. 110. Chem. Reviews 5 (1928) 325.

In conclusion, the importance of modern ideas of prototropic mobility for the theory of pseudo-acids will be discussed.

According to HANTZSCH<sup>1</sup>, a pseudo-acid is a hydrogen compound which only after a rearrangement is able to split off hydrogen ions. This idea of the mechanism of the dissociation is expressed in the scheme



HR is a pseudo-acid. The genuine acid HS is called the aci-form. In pseudo-acids the undissociated acid and the ion have different constitution. HANTZSCH gives many examples of pseudo-acids, e.g. the aliphatic nitrocompounds CR'R''HNO<sub>2</sub>. Thus the mechanism of the dissociation of nitromethane is assumed to be

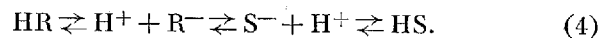


As one of the most important characteristics of pseudo-acids he mentions the following. An acid which does not react instantaneously with hydroxyl ions is a pseudo-acid. From the fact that the neutralization of the ordinary acids is practically instantaneous he concludes, that a slow neutralization shows that the substance only after an isomerisation is able to give off hydrogen ions. According to HANTZSCH the measured velocity of neutralization is the velocity of the reaction  $\text{HR} \rightarrow \text{HS}$ .

It is still the most general opinion, that the scheme (3) expresses the mechanism of the dissociation of these substances. However, the points of view given in this paper do not support this opinion. The prototropic change  $\text{HR} \rightarrow \text{HS}$  cannot take place spontaneously, but demands a basic or acid catalyst. If we add sodium hydroxide to a solution

<sup>1</sup> HANTZSCH, Ber. Deutschen Chem. Ges. 32 (1899) 575.

of HR, the mechanism will be a transference of protons from HR to  $\text{OH}^-$ . This is an ordinary dissociation of the ordinary acid HR. The reaction is slow if the acid HR is sufficiently weak. The ion  $\text{R}^-$  will probably instantaneously isomerize to the ion  $\text{S}^-$ . Thus the reaction which determines the velocity is the slow dissociation of HR and not the rearrangement  $\text{HR} \rightarrow \text{HS}$ . Instead of scheme (3) the following scheme expresses the mechanism



HR and HS are in thermodynamic equilibrium, but not in direct kinetic equilibrium.

For theoretical reasons we assume that the velocity of transference of protons from an acid to the hydroxyl ion decreases with decreasing acid strength. All ordinary acids which are strong enough for the detection of their acidity in aqueous solution in the ordinary way react as far as we know exceedingly rapidly with hydroxyl ions. The only exceptions are the pseudo-acids. Consequently, these must be extremely weak acids. The reason why they are usually considered as relatively strong acids is that the equilibrium  $\text{R}^- \rightleftharpoons \text{S}^-$  is strongly displaced in favour of  $\text{S}^-$ .

The pseudo-acids are not false acids, but acids with false strength. There is no principal difference between the acid character of the pseudo- and the aci-form. They are both genuine acids, but the pseudo-form is a much weaker acid than the aci-form. In a wider sense all prototropic systems are pseudo-acids. Their dissociation may be expressed by scheme (4). The ordinary apparent dissociation constant is

$$K = (\text{H}^+) \frac{(\text{R}^-) + (\text{S}^-)}{(\text{HR}) + (\text{HS})}.$$

The real acid strengths of the two acids HR and HS are

$$K_{HR} = (H^+) \frac{(R^-)}{(HR)} \quad \text{and} \quad K_{HS} = (H^+) \frac{(S^-)}{(HS)}.$$

The value of K is between the values of  $K_{HR}$  and  $K_{HS}$ .

The aliphatic nitrocompounds afford a good opportunity of examining the effect of different substituents on the basic catalysis and thus increasing our understanding of this important problem. In another paper it is hoped to give more accurate measurements of catalysis on a series of aliphatic nitrocompounds.

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March 1932.