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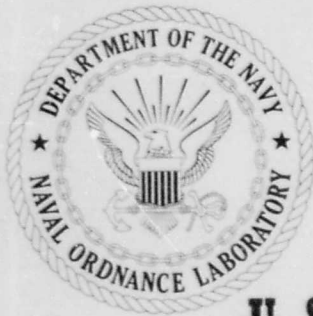
NAVORD REPORT

4027

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A KINETIC STUDY OF THE TER MEER REACTION

19 DECEMBER 1955



**U. S. NAVAL ORDNANCE LABORATORY**  
**WHITE OAK, MARYLAND**

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A KINETIC STUDY OF THE TER MEER REACTION

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ABSTRACT: The ter Meer reaction has been used to prepare 1,1-dinitroethane from 1-halonitroethanes in good yield, as described in NAVORD Report No. 3777. This reaction has now been studied kinetically in dilute solution in water and aqueous dioxane containing excess acetic acid-sodium acetate buffer.

The reaction is second order, the rate-determining step involving a nitrite ion and the aci-form of the 1-halonitroethane. Certain effects of changing buffer ratio and concentration are discussed in terms of an equilibrium between the anionic and the nitro and nitronic acid (aci-) forms of the substrate. Under the conditions described, this equilibrium is established very rapidly compared to the subsequent ter Meer reaction with nitrite.

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19 December 1955

This report describes a kinetic study of the ter Meer reaction performed under the Task NOL-B2c-19-1-55. The reliability of the work and the validity of the conclusions are the responsibility of the authors and of the Chemistry Division, Explosives Research Department, U. S. Naval Ordnance Laboratory.

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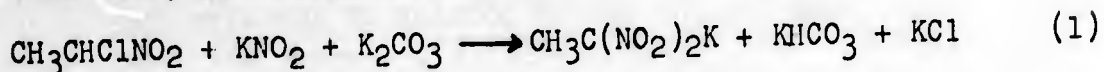
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## A KINETIC STUDY OF THE TER MEER REACTION

### INTRODUCTION

The reaction of 1-bromonitroethane with potassium nitrite and potassium hydroxide in aqueous methanol to give the salt of 1,1-dinitroethane was first reported by Ter Meer<sup>(1)</sup>. Johnson, Ferguson and Jensen<sup>(2)</sup> substituted potassium carbonate for the hydroxide and carried out the reaction with 1-chloronitroethane below room temperature, achieving yields as high as 70%. This represents the best laboratory and commercial preparation of 1,1-dinitroethane, 1,1-dinitropropane and their homologs.



The present kinetic study was initiated with the intention of determining the nature of the reacting species and if possible the details of the mechanism. While this work was being carried out an excellent report on a similar study by Dr. M. Frederick Hawthorne was released by the Rohm and Haas Company Laboratory at Huntsville, Alabama<sup>(3)</sup>. Hawthorne measured the rate of formation of dinitroethane (DNE) from 1-chloronitroethane and excess sodium nitrite in 50% ethanol. The reaction was observed to follow a very clean pseudo-first order path to over 80% completion when the nitrite ion was in large (100-fold) excess. The rate constant at 30° was calculated for a wide variety of substrate and nitrite concentrations, and generally fell into the range 0.02-0.03 l./mol.min.

In the present study most of the work was done with 1-bromonitroethane (BNE) as substrate since 1-chloronitroethane (CNE), though more readily available, cannot be purified as easily. Both of these halonitroethanes are weak pseudo-acids, but an accurate measurement of their ionization constant cannot be made since they decompose readily when titrated against base. The nature of the decomposition by base was explored as a preliminary to this work<sup>(4)</sup>.

### PRELIMINARY RESULTS IN 70% DIOXANE

Dinitroethane, the anion of which has an intense yellow color, did not appear when (a) potassium nitrite was added to a solution of BNE in excess dilute aqueous potassium hydroxide or (b) BNE was added to nitrous acid in a dioxane water solution in the absence of base. On the other hand, when BNE was dissolved in 70% aqueous dioxane containing

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only an excess of potassium nitrite, a yellow color developed immediately and 45% yield of dinitroethane (DNE) was eventually detected (Table I). When the same experiment was conducted with added sodium acetate acting as a buffer, yields of DNE reached a maximum of nearly 70% before starting to decline (Table I). These results indicated that the reaction involved only the unionized halonitroethane and nitrite ion and that the function of the added base in the optimum synthetic procedure was to convert the DNE to its less reactive and less soluble salt and to neutralize acidic by products.

TABLE I

REACTION OF 1-BROMONITROETHANE (0.04M)  
WITH  $\text{KNO}_2$  (0.10M) IN 70% DIOXANE AT 50° WITH AND  
WITHOUT ADDED BUFFER:  $\text{BNE} + \text{NO}_2^- \longrightarrow \text{DNE} + \text{Br}^-$

Time Min.	NO BUFFER		SODIUM ACETATE (0.20M) ACETIC ACID (0.02M)	
	DNE %	Br <sup>-</sup> %	DNE %	Br <sup>-</sup> %
10	11.0	12.3	13.4	14.4
20	16.5	18.4	26.7	28.9
30	21.9	24.0	38.1	44.2
40	26.8	28.9	53.5	60.6
60	35.1	39.3	68.4	78.8
90	41.1	49.8	66.1	87.2
120	44.7	56.0	62.3	89.1

The reactions of Table I were monitored by (a) determining spectrophotometrically the DNE produced and (b) determining the amount of bromide liberated by Volhard titration. It can be seen that the initial rate of bromide ion production was substantially equal to that of DNE formation. Thus, in the reaction of BNE with nitrite there was initially no significant accumulation of intermediate products and all steps (if any) succeeding the breaking of the carbon-bromine bond were rapid ones. As the reaction proceeded, however, the amounts of bromide ion and DNE produced began to differ substantially, the DNE concentration reaching a maximum, then beginning to fall off rapidly. This difference may be attributed to side reactions which had the effect of producing more bromide ion than DNE and which became more important in the later stages of the reaction. Such side reactions may have involved decomposition of BNE catalyzed by bases or by the products of the ter Meer



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had any value. The results of a typical experiment involving equimolar concentrations of BNE and nitrite in 70% dioxane-water at 50° and in the presence of an acetic acid-sodium acetate buffer are given in Table III. It can be seen that the reaction showed moderately good second order kinetics to about 30% completion, but that beyond this point the rate constant began to fall off rapidly.

TABLE III

REACTION OF 1-BROMONITROETHANE (0.02M) WITH  
KNO<sub>2</sub> (0.02M) IN 70% DIOXANE AT 50° WITH ADDED BUFFER  
SODIUM ACETATE = ACETIC ACID = 0.10M

$$kt = (1/A_0 - x) - (1/A_0)$$

Time Min.	OD 381/ <u>a</u> mu	(DNE) M	A <sub>0</sub> -x M	kt	k 1./mol.min.
0		0	.0192		
30	.287	.0017	.0175	5.0	.167
45	.407	.0024	.0168	7.4	.164
60	.520	.0030	.0162	9.6	.160
75	.630	.0036	.0156	12.0	.160
90	.736	.0043	.0149	15.0	.167
120	.362/ <u>b</u>	.0052	.0140	19.3	.161
150	.427/ <u>b</u>	.0062	.0130	24.8	.165
240	.534/ <u>b</u>	.0077	.0115	36.9	.145

$k_{ave} = 0.163 \pm .003$  (excluding last point)  
/a Diluted 1:100                      /b Diluted 1:250

To confirm that the reaction was second order and first order in both nitrite and BNE, a series of experiments was carried out under conditions identical with those of Table III in which the BNE and nitrite concentrations were each varied over a four-fold range. As before, only the early portions of the reactions were studied and the results are given in Table IV. Within the rather broad experimental limits imposed by the competing side reactions a first order dependence on the BNE concentration and a first or slightly greater than first order dependence on the nitrite concentration was observed.

TABLE IV  
 ASSEMBLED RATES OF TER MEER REACTION  
 in 70% DIOXANE AT 50°

$$(\text{CH}_3\text{COOH}) = (\text{CH}_3\text{COO}^-) = 0.10$$

Initial Concentrations (BNE)	(NO <sub>2</sub> -)	k 1./mole min.	Completion %
0.02	0.02	0.163	36
.01	.01	.143	20
.03	.03	.154	40
.04	.04	.171	42
.02	.04	.184	42
.04	.02	.143	56

$$k_{\text{ave}} = 0.163 \pm 0.013 \text{ 1./mole min.}$$

THE TER MEER REACTION IN WATER

In the mechanism postulated by the Rohm and Haas group, the rate determining step involved the nitrite catalyzed ionization of the halonitroethane(3). If this mechanism were to apply in the present case it would require that the rate of bromination of the halonitroethane, which has been found to be substantially equal to the rate of ionization of these pseudo acidic compounds(6), also be substantially equal to the rate of the ter Meer reaction under similar conditions. Since attempts to determine bromination rates in 70% dioxane-water were frustrated by a side reaction of bromine with dioxane, further experiments on the ter Meer reaction were carried out in aqueous solution at 50°.

Under these new conditions values of the DNE concentration appeared to fall off far more rapidly with time than had been the case in 70% dioxane and it is believed that in water the dimerization reaction assumed major proportions. While this precluded the possibility of monitoring the reaction by following the appearance of DNE spectrophotometrically, it was possible to follow the appearance of bromide by Volhard titration and the disappearance of nitrite as determined by diazotization of sulfanilic acid and subsequent coupling with  $\alpha$ -naphthylamine(7). Agreement between nitrite and bromide rates was usually only fair and often poor since neither

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method gave high precision at low concentrations, and the rate constants tabulated below should be taken only as approximations.

The measurements in water, the results of which are given in Table V, were all with  $(\text{BNE}) = (\text{NO}_2^-) = 0.01 \text{ M}$ . Under these conditions, and in the presence of 0.1 M acetic acid and sodium acetate, the rate was about six times the average rate at the same buffer concentration in 70% dioxane. If the buffer ratio was kept constant, the values of the experimental second order rate constants (Columns 5 and 6) were relatively independent of the total buffer concentration over a ten-fold range (runs 1-6). Variations were in the same direction and of the same order of magnitude as those caused by changing the ionic strength to the same extent by the addition of sodium perchlorate (runs 11-13). As discussed below, this indicated the absence of general acid or base catalysis in the rate determining step.

A more marked effect on the experimental second order rate constants was observed when the buffer ratio was changed. Comparison of runs 2, 8 & 10, runs 3, 4, 9 & 15, and runs 5, 6, 12, 13 & 14 shows a definite trend with changing pH. Decreasing the acetic acid/acetate ratio resulted in a slight but unmistakable decrease in the reaction rate. When the acetic acid was withdrawn entirely the decrease was substantial.

Coupled with our previous findings that the ter Meer reaction proceeded to a negligible extent in either very acidic or very basic media, these results give a fair qualitative picture of the effect of pH on the reaction. To discuss this effect it is necessary to anticipate our consideration of the detailed reaction mechanism and to accept the fact that in the presence of a buffer system the rate determining step involves the reaction of an unionized form of BNE with nitrite anion.

Figure 1 shows the effect of pH on the experimental rate. According to this scheme the failure to react at very low pHs is due to removal of the nitrite anion as nitrous acid ( $pK = 3.4$ ). Failure to react at high pHs is due to removal of BNE as its conjugate base. Only at intermediate acidities, where substantial amounts of the two reactive species are simultaneously present is there any reaction. The rate is greatest at that pH where the product of the concentrations of BNE and nitrite is at its maximum, pH 4.5 to 5.5 in Figure 1.

TABLE V  
ASSEMBLED RATES OF THE TER MEER REACTION  
IN WATER AT 50°

(BNE) = (NO<sub>2</sub><sup>-</sup>) = 0.01M

Run	NaOAc	HOAc	NaClO <sub>4</sub>	$\frac{k_{exptl.}, 1./mole \text{ min.}}{\text{as calculated from (Br)}} (NO_2^-)$	% ionized	$\frac{k_{corr.}, 1./mole \text{ min.}}{\text{as calculated from (Br)}} (NO_2^-)$
1	0.20	0.20	---	0.70	5	0.73
2	.10	.10	---	.87	"	.91
3	.05	.05	---	.92	"	.97
4	.05	.05	---	.85	"	.89
5	.02	.02	---	---	"	---
6	.02	.02	---	.80	"	.84
7	0.20	0.05	---	0.77	17	0.93
8	.10	.02	---	.44	20	.55
9	.05	.20	---	1.08	1	1.09
10	.10	---	---	.17	50	.34
11	0.05	0.05	0.05	0.70	5	0.74
12	.02	.02	.08	.58	"	.61
13	.02	.02	.18	.54	"	.57
14	.02	---	.08	.49	27	.67
15	.05	---	.05	.28	39	.46

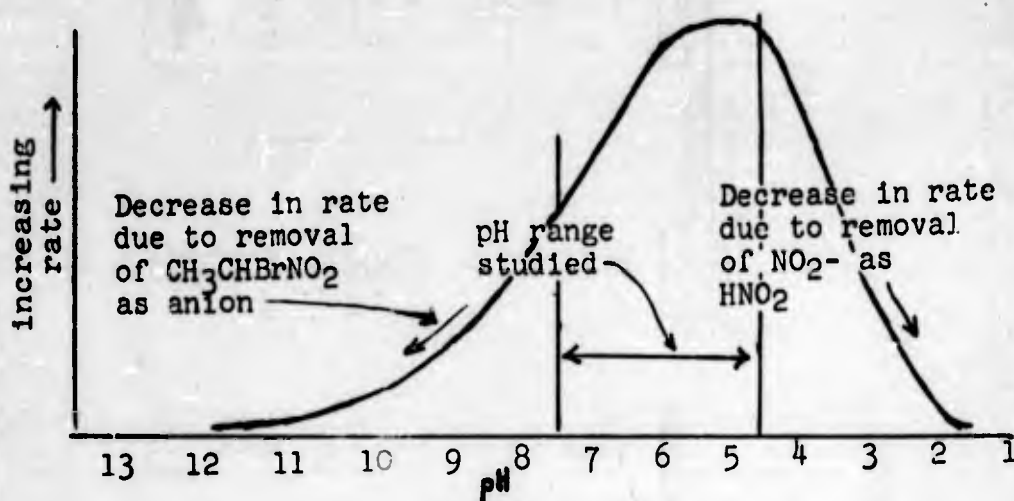


FIGURE 1  
 Effect of pH on Rate of ter Meer Reaction

The data of Table V is consistent with such a picture if the nitrite was substantially completely ionized over the entire pH range studied while the BNE was completely unionized only at the higher acetic acid concentrations and only partially in its unionized form at lower acetic acid concentrations or in the absence of acetic acid. It can be shown that under such conditions the proper experimental rate constant would be given by the expression,

$$k_{\text{corrected}} = \frac{k_{\text{experimental}}}{\text{proportion BNE unionized.}}$$

An accurate determination of this proportion would require a good value for the ionization constant of BNE. While such a value is unfortunately unavailable due to the decomposition of this pseudo acid when titrated against base, Pearson and Dillon<sup>(6)</sup> have estimated the ionization constant of the chloronitro compound to be somewhat lower than  $10^{-6}$ .

Rather to illustrate the type of treatment which might illuminate the effect of acidity on the rate in this pH range than to give accurate corrected rate constants, the value of  $8.1 \times 10^{-7}$  was chosen as the ionization constant of bromonitroethane in water at  $50^{\circ}$ . This was chosen a) because it seems of the right order of magnitude, b) because it is exactly 1/20th the ionization constant of acetic acid, thus facilitating calculations and c) because it makes the data fit.

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Using this figure it was possible to calculate the proportion of BNE ionized and, hence, not available for reaction at any concentration of acetic acid and sodium acetate. (The proportion BNE ionized is independent of the total BNE concentration providing the buffer is present in sufficient excess). These values are given in Column 7 of Table V. From these values the "corrected" rate constants were calculated and are presented in Columns 8 and 9.

It can be seen that this type of treatment more or less eliminated the variation in rate constants with buffer ratio, again within the rather broad limits of experimental error. The validity of the treatment depends on how closely the figure chosen as the ionization constant of BNE approaches the true value. To the extent that this treatment was valid it can be said that the rate constant, but not the rate, is independent of pH.

A number of experiments with chloronitroethane (CNE) as the substrate were also carried out under similar conditions and monitored only by following the disappearance of nitrite ion. The results of these runs are given in Table VI. The rates were about the same as with BNE and the effects of varying buffer concentration, buffer ratio and ionic strength were also similar.

TABLE VI  
THE TER MEER REACTION OF CHLORONITROETHANE  
IN WATER AT 50°

<u>(CH<sub>3</sub>COO<sup>-</sup>)</u>	<u>(CH<sub>3</sub>COOH)</u>	<u>(NaClO<sub>4</sub>)</u>	<u>k<sub>exptl.</sub></u> <u>1./mole min.</u>
0.10	0.10	----	0.96
.05	.05	0.05	.84
.02	.02	.08	.75
.10	.02	----	.54
.02	.10	----	.77

BROMINATION OF THE HALONITROETHANES

Brominations were carried out under conditions substantially identical with those of Tables IV and V. Instead of nitrite an excess of saturated bromine water was added to the aqueous buffered solutions of BNE. The

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reactions were monitored by quenching in dilute nitric acid, blowing out the excess bromine with air, and analyzing for bromide by the Volhard method. Again the analytical method was not too sensitive and duplicate runs agreed with each other only moderately well.

TABLE VII  
ASSEMBLED RATES OF BROMINATION OF BROMONITROETHANE  
IN WATER AT 50°

Run	(NaOAc)	(HOAc)	(BNE) = 0.01 M	
			k, min <sup>-1</sup>	k/(AcO <sup>-</sup> ) = k <sub>spec</sub> l/mole min.
1a	0.15	0.15	0.191	
1b	"	"	.173	
1c	"	"	.208	
1d	"	"	.156	
		Average	.182	1.21
2a	0.10	0.10	0.109	
2b	"	"	.110	
2c	"	"	.103	
2d	"	"	.099	
		Average	.105	1.05
3a	0.05	0.05	0.056	
3b	"	"	.056	
		Average	.056	1.12
4	0.02	0.02	0.0213	1.06
5a	0.10	0.01	0.099	
5b	"	"	.131	
5c	"	"	.116	
5d	"	"	.118	
5e	"	"	.098	
		Average	.112	1.12
6	0.023	0.10	0.239	1.04

Comparison of Series 2 and 5 and of Runs 4 and 6, Table VII shows the experimental rate constant to be independent of the buffer ratio at a constant buffer base concentration. The constancy, under these conditions, of  $k_{\text{exptl}}/(\text{OAc}^-)$  at all buffer ratios and buffer concentrations shows the bromination to conform with the general picture

of general base catalysis where most of the catalysis is by the buffer base.

The bromination of chloronitroethane conforms with the same general picture (Table VIII). The rate is about 15% lower.

TABLE VIII  
 BROMINATION OF CHLORONITROETHANE IN WATER AT 50°  
 (CNE) = 0.01 M

Run	(NaOAc)	(HOAc)	$k, \text{min.}^{-1}$	$k/(\text{AcO}^-) = k_{\text{spec.}}$ l./mole min.
1a	0.10	0.10	0.084	
1b	"	"	.084	
1c	"	"	.097	
		Average	.088	0.88
2a	0.10	0.01	0.106	
2b	"	"	.109	
2c	"	"	.073	
		Average	.096	0.96

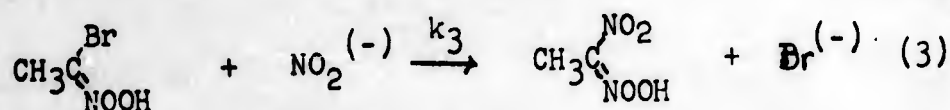
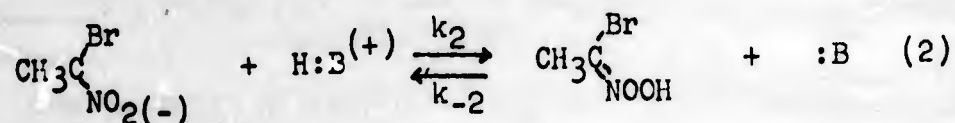
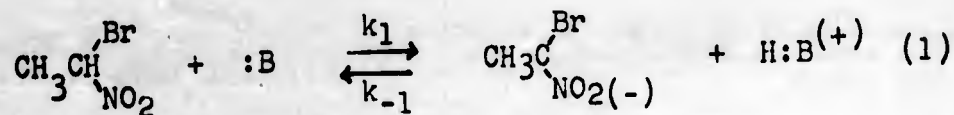
MECHANISM

If the molecular form of the halonitroalkane were the reactive species in the ter Meer reaction, the secondary nitrohalides might be expected to undergo the same type of reaction at a somewhat more rapid rate if the  $S_N1$  mechanism applied or a somewhat (but not very much) slower rate if the  $S_N2$  mechanism applied. When an attempt was made to detect a reaction between nitrite ion and 2-nitropropane or 1,1-dichloro-1-nitro-ethane, neither gave a measureable amount of chloride ion after three days in 70% dioxane under conditions comparable to those of Tables I and III.

The failure of these compounds to react serves as strong presumptive evidence that an alpha hydrogen is necessary for the ter Meer reaction and that the halonitroalkane must, prior to reaction, be converted to the anion or to the nitronic acid (the aci-form). In as much as the ter Meer does not occur in very alkaline media, the anion is unreactive. It necessarily follows that the aci-form is the active substrate.

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The preferred reaction path involves the following sequence,



If step (2) were rate determining, the reaction velocity would be independent of the nitrite concentration. The first order dependence on nitrite requires either that step (3) be rate determining or that step (1) be rate determining and that nitrite be the catalytic species in this slow ionization (i.e., :B in equation 1).

Hawthorne<sup>(3)</sup> has interpreted the fact that the reaction when carried out in 50% ethanol, in the presence of large excesses of nitrite and in the absence of a buffer goes at about 1/3 the rate when chlorodeuteronitroethane is substituted for the normal compound as evidence that the C-H or C-D bond is broken in the rate determining step. Thus, under his conditions, step (1), the ionization, was rate determining.

For the same situation to prevail in the presence of the acetate buffer would require that acetate be relatively inactive as compared with nitrite in catalyzing the ionization. This would show up if the rate of the ionization (as measured by the bromination) in the presence of acetate and in the absence of nitrite were relatively slow as compared with the rate of the ter Meer reaction in the presence of both acetate and nitrite. This is not the case as evidenced by the fact that with the same buffer concentration that gave 80% ionization in 15 minutes a typical ter Meer reaction had progressed only 27% in two hours. The results of Table VII show that the ionization of BNE is general base catalyzed. The direct dependence on the nitrite concentration coupled with the independence of the experimental rate constants in Table V on the acetate concentration show that under similar conditions the ter Meer

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is not general base catalyzed. These results can only be rationalized by assuming that under our conditions step (3) is rate determining.

It would seem then that in the presence of the buffer there is a mechanism shift. That the shift is not complete is evidenced by (a) the slightly greater than first order dependence on nitrite concentration shown in the results of Table IV and Hawthorne's Table II, (b) the failure of deuterium substitution to lower the rate by more than 1/3. The C-D bond has been found to break 1/6 as fast as the C-H by other workers(8).

It may be fairly stated, therefore, that neither of these kinetic investigations of the ~~ter~~ Meer reaction has succeeded in documenting a unique mechanism, but together they offer an unusually broad survey of the reaction system. These results, taken in conjunction, illustrate that conclusions on mechanism are necessarily applicable only to the conditions from which they were derived.

It is evident that the experimental k values of Tables III, IV, V, and VI are not specific rate constants. According to the mechanism favored here the true rate expression is,

$$\frac{d(\text{DNE})}{dt} = k_3(\text{NO}_2^-)(\text{CH}_3\overset{\text{Br}}{\underset{\text{NOOH}}{\text{C}}}). \quad (4)$$

The concentration of the aci-BNE is related to that of the anion by the rapid equilibrium expressed in equation (2) and the concentration of the anion is related to that of molecular BNE by the equilibrium in equation (1). Thus

$$(\text{CH}_3\overset{\text{Br}}{\underset{\text{NOOH}}{\text{C}}}) = \frac{k_2(\text{anion})(\text{H}:\text{B}^+)}{k_{-2}(\text{:B})} \quad (5)$$

$$(\text{anion}) = \frac{k_1(\text{molecular BNE})(\text{:B})}{k_{-1}(\text{H}:\text{B}^+)} \quad (6)$$

$$\frac{d(\text{DNE})}{dt} = \frac{k_1 k_2}{k_{-1} k_{-2}} k_3 (\text{molecular BNE})(\text{NO}_2^-) \quad (7)$$

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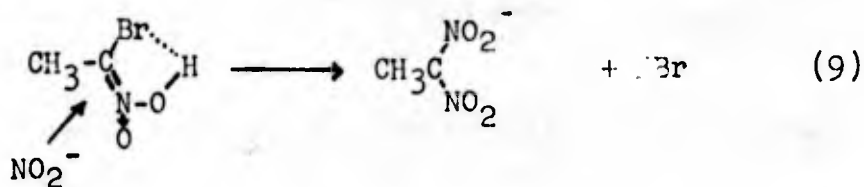
$$k_{\text{exptl}} = \frac{k_1 k_2}{k_{-1} k_{-2}} k_3 \quad (8)$$

Of these rate constants, only  $k_1$ , the specific constant for the ionization, may be evaluated.

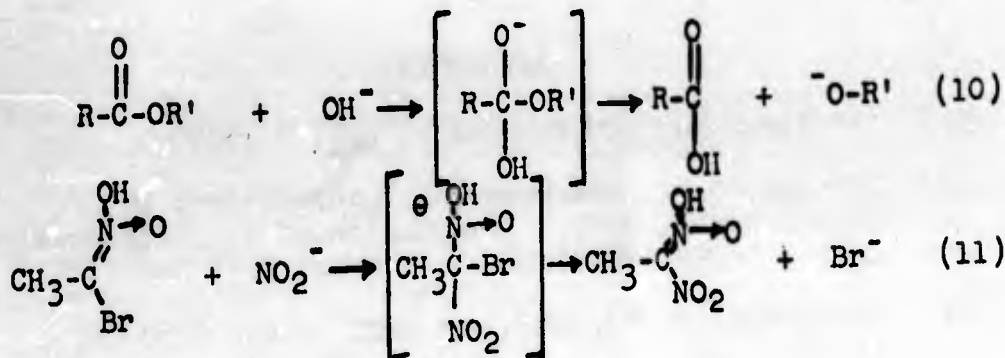
It is not essential to the preferred mechanism that a measureable amount of aci-BNE should ever be present in the reaction mixture. The pH independent equilibrium between the molecular and the aci forms, the constant for which is given by the ratio  $k_1 k_2 / k_{-1} k_{-2}$ , probably lies overwhelmingly toward the molecular form.

It had been an initial objective of this research to determine activation energies for the reaction and to elucidate the effect of solvent composition on the rate. Since both  $k_3$  and the ratio  $k_1 k_2 / k_{-1} k_{-2}$  are subject to change independently with temperature and solvent composition, however, it was impossible to isolate the effects of these changing parameters on the specific rate constant and this line of investigation was abandoned.

As to the detailed mechanism of the reaction of nitrite with aci-BNE in the rate determining step, experimental evidence gives no clues. Possible routes involve (a) displacement of the halide from BNE simultaneously with attack by nitrite or (b) an addition-elimination reaction with removal of the halide subsequent to the formation of an addition complex. For the former to apply, some special structural feature of the aci form must be essential, since a mechanism that would be equally applicable to the secondary halonitroalkanes is not admissible. For example, an internal hydrogen bonded structure might contribute to route (a), (equation 9).



The preferred alternate route (b) may be likened to Ingold's  $B_{AC}2$  mechanism for the saponification of esters (9) (equation 10) and involves addition across the double bond with subsequent elimination of halide ion (equation 11).



EXPERIMENTAL

The materials and the analytical techniques used were described in the previous report<sup>(4)</sup>.

Procedure -- In a typical experiment (Table III) 0.67 g (0.005 mole) of sodium acetate trihydrate, 0.30 g (0.005 mole) of acetic acid, 148 mg (0.00096 mole) of BNE 35.0 cc of dioxane and about 12 cc of water were added to a 50 ml volumetric flask. After an hour at 50.0°, a 2 ml aliquot of aqueous potassium nitrite (0.50 M) was added, the mixture shaken, diluted to exactly 50 ml with water, and returned to the bath. At the times indicated 1 ml aliquots were removed, diluted, and made basic with potassium hydroxide for measurement of the DNE anion at 381 mu. When the procedure was varied by adding BNE dropwise to 50 ml of nitrite containing solvent at t = 0, the identical rate constants were obtained. These reactions were also followed by determination of bromide formed and nitrite lost, and good general agreement was observed for all methods. In water, however, the rates were measured almost exclusively by nitrite determinations. Again in this solvent it was immaterial for what period the substrate was exposed to the buffered medium before mixing with nitrite. Rate constants in water (Table V) were calculated by the formula:

$$kt = \frac{1}{(\text{NO}_2^-)} - \frac{1}{(\text{NO}_2^-)_0} .$$

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