and analyzed using a F & M Model 720 gas chromatograph with an 8-ft., 20% SE-52 column. No methylphenylcarbinol could be detected. It was possible using this instrument and column to separate methylphenylcarbinol from any other components if it had been present. The material from the rearrangement was then chromatographed over 40 g. of alumina. Petroleum ether and 10% ether–90% petroleum ether eluted 0.757 g. (51%) of recovered ether while 30% ether–70% petroleum ether and 40% ether–60% petroleum ether eluted 0.579 g. (39%) of 2,3-diphenyl-2-butanol. The first cut of the above alcohol solidified and was recrystallized once from petroleum ether to give material, m.p. 72.0–75.5° (lit.[35] for the higher melting isomer, m.p. 83.5–84.5°).

A sample of this recrystallized material was purified by preparative v.p.c. Its n.m.r. spectrum (CCl_4) was in complete accord with the structure for the expected rearrangement product: multiplet at 7.22 (aromatic protons, area 10), quartet at 3.04 ($J = 7.0$ c.p.s., benzylic proton, area 1), singlet at 1.48 (hydroxyl proton, area 1), singlet at 1.27 (methyl protons, area 3), and doublet at 1.06 p.p.m. ($J = 7.0$ c.p.s., methyl protons split by the benzylic proton, area 3).

Rearrangement of Benzyl α-Methylbenzyl Ether. In the usual manner 2.29 g. (0.01 mole) of benzyl α-methylbenzyl ether[21] dissolved in 40 ml. of THF was treated with 31 ml. of 1.6 N methyllithium in ether (0.05 mole). After 1 hr. the reaction was quenched by addition of 2 g. of deuterium oxide. The reaction was extracted with ether and washed with water. The residue left after evaporation of the solvent, which had been dried over sodium sulfate, was chromatographed over 43 g. of alumina. Petroleum ether and 10% ether–90% petroleum ether eluted 1.46 g. (64%) of the starting ether while 30% ether–70% petroleum ether and 40% ether–60% petroleum ether eluted 0.55 g. (24%) of the isomeric alcohols from rearrangement.

Of the alcohols isolated 0.55 g. (19%) was 1,2-diphenyl-2-propanol[36] while the remaining 81% was essentially a 50:50 mixture of *erythro-* and *threo-*1,2-diphenyl-1-propanol. These components were verified by having infrared spectra and v.p.c. behavior identical with those of authentic samples. The amounts of the various isomers were determined by comparison with known mixtures of the authentic samples. This indicates a 4:1 preference for metalation at the unsubstituted benzylic position.

If metalation is relatively fast compared to rearrangement one would expect to have metalated ether present in the reaction mixture when it was quenched with deuterium oxide. This would lead to incorporation of deuterium into the benzylic position of the recovered ether. Thus the recovered ether was subjected to n.m.r. analysis. Within the limits of error, integration of the signal from the benzylic protons (compared to the aromatic protons as an internal standard) indicated *no* deuterium in the benzylic position of the recovered ether.

Acknowledgments. We are grateful to the U. S. Army Research Office (Durham) for generous support of these investigations. We also appreciate a gift of 1-adamantanol from Professor Paul von R. Schleyer.

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(35) W. R. Brasen, S. W. Kantor, P. S. Skell, and C. R. Hauser, *J. Am. Chem. Soc.*, 79, 397 (1957).

(36) F. A. Elhafez and D. J. Cram, *ibid.*, 75, 339 (1953).

The Michael Reaction in Nonalkaline Media. IV. Kinetics and Mechanisms of the Reactions in the Nitroform–Methyl Acrylate System

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Contribution from The Organic Chemistry Division, U. S. Naval Ordnance Laboratory, Silver Spring, Maryland 20910. *Received August 16, 1965*

Abstract: The kinetics of the addition of nitroform to methyl acrylate to form methyl 4,4,4-trinitrobutyrate and methyl 4,4-dinitro-2-hydroxybutyrate in 50% dioxane have been studied in the presence of perchloric acid and in acetic acid–acetate buffers. The reaction forming methyl 4,4,4-trinitrobutyrate was found to be subject to general acid catalysis. In acetic acid–acetate buffers the mechanism involves a rapid and reversible addition of trinitromethide ion to the double bond of methyl acrylate followed by a rate-determining protonation of the resulting carbanion intermediate to form methyl 4,4,4-trinitrobutyrate. In perchloric acid solutions, the rate of protonation gradually increases as the acidity of the medium increases until the formation of the intermediate carbanion becomes rate determining. The reaction forming methyl 4,4-dinitro-2-hydroxybutyrate was found to compete for the intermediate carbanion with the protonation of this intermediate to methyl 4,4,4-trinitrobutyrate. The rate of formation of the α-hydroxy ester is kinetically first order in the intermediate carbanion and inversely proportional to the acidity. From the kinetic data and the results of synthetic scale experiments in dioxane–H_2O^{18}, a mechanism for the formation of this product from the intermediate carbanion is suggested.

Previous communications in this series[1,2] have shown that the addition of nitroform to methyl acrylate produced a number of products in addition to the expected Michael adduct, methyl 4,4,4-trinitrobutyrate (MeTNB). The yields of the various products appeared to be dependent upon the acidity and solvent composition of the reaction medium. In a recent report,[3] the reaction sequence for this complex system was elucidated. In an aqueous dioxane–acetic acid–acetate buffer, the reaction proceeded as in Scheme I. The primary products of this reaction are methyl 4,4,4-trinitrobutyrate, (MeTNB) and a nitrite elimination product, methyl 4,4-dinitro-2-hydroxybutyrate (DNS). Depending upon the specific reaction conditions, each of these primary reaction products can undergo further reaction. Methyl 4,4,4-trinitrobutyrate loses the elements of nitrous acid to form methyl 4,4-dinitro-2-butenoate (DNU), and DNS acts as the addend in a Michael addition to a second mole of

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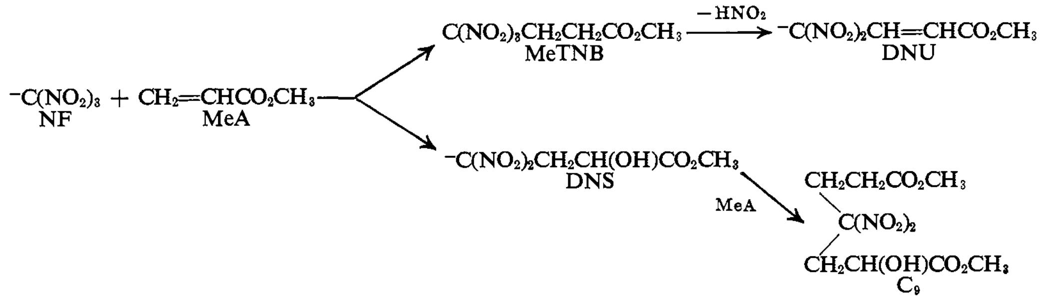
(1) L. A. Kaplan and M. J. Kamlet, *J. Org. Chem.*, 27, 780 (1962).

(2) M. J. Kamlet and L. A. Kaplan, *ibid.*, 28, 2128 (1963).

(3) L. A. Kaplan, *ibid.*, 29, 2256 (1964).

Scheme I



methyl acrylate to form dimethyl 4,4-dinitro-2-hydroxypimelate (C_9).

Studies of the kinetics of the Michael reaction[4,5] have shown that a mechanism change occurs on changing the addend from barbituric acid (pK_a = 4.05) to nitroform (p$K_a \approx 0$) in the addition to β-nitrostyrene.

$$Y^- + C_6H_5CH{=}CHNO_2 \rightleftharpoons C_6H_5CHY{-}\bar{C}HNO_2 \qquad (1)$$

$$C_6H_5CHY{-}\bar{C}HNO_2 + HA \rightleftharpoons C_6H_5CHYCH_2NO_2 + A^- \qquad (2)$$

$Y^- = C_4H_3N_2O_3^-$ or $C(NO_2)_3^-$; HA and A^- are the buffer acid and its conjugate base.

The reactions were found to be reversible with either barbituric acid or nitroform as the addend. With barbituric acid as the addend, the formation of the intermediate carbanion was rate determining,[4] whereas with nitroform as the addend, the reaction was found to be subject to general acid catalysis[5]; reaction 2 was rate determining.[6] Because of the complexity of the nitroform–methyl acrylate system as compared to the above systems, a kinetic study of the nitroform–methyl acrylate system was initiated.

Results and Discussion

The Over-All Reaction. The reactions observed previously[1-3] in the nitroform–methyl acrylate system are depicted by the following equations

$$NF + MeA \rightleftharpoons An^- \qquad (3)$$

$$An^- + HA \rightleftharpoons MeTNB + A^- \qquad (4)$$

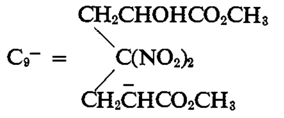
$$An^- \longrightarrow DNS + NO_2^- \qquad (5)$$

$$DNS + MeA \rightleftharpoons C_9^- \qquad (6)$$

$$C_9^- + HA \rightleftharpoons C_9 + A^- \qquad (7)$$

$$MeTNB + OH^- \longrightarrow DNU + NO_2^- \qquad (8)$$

where $An^- = C(NO_2)_3CH_2\bar{C}HCO_2CH_3$;



$$C_9^- = \begin{matrix} CH_2CHOHCO_2CH_3 \\ \diagdown \\ C(NO_2)_2 \\ \diagup \\ CH_2\bar{C}HCO_2CH_3 \end{matrix}$$

HA and A^- are the buffer acid and its conjugate base.

Since the polynitro carbanions NF, DNS, and DNU have characteristic absorption maxima in the ultraviolet,[2,3,5] most of the reactions could be followed by spectrophotometric measurements. However, the large number of reactions occurring in this system complicates the study of the reaction kinetics. The approach selected was to determine whether any of the above reactions could be disregarded because they made an insignificant contribution to the system when the reaction was carried out under a set of standard conditions.

As the primary interest at this time was in the addition of nitroform to methyl acrylate to form MeTNB and DNS and not the decomposition of MeTNB to DNU,[7] the conditions selected were at least as acidic as acetic acid–acetate buffers in 50% dioxane with the buffer ratio AcOH/OAc⁻ equal to or greater than unity. Spectrophotometric and synthetic studies[3] have shown that the rate of addition of nitroform to methyl acrylate in a 1:1 acetic acid–acetate buffer is more than 100 times faster than the decomposition of MeTNB (reaction 8) under these conditions. Therefore, reaction 8 will not make any significant contribution to the polynitro carbanion or nitrite ion concentrations during a 5-hr. period.[8] Initial concentrations of nitroform and methyl acrylate were adjusted so that the disappearance of nitroform could be followed throughout one to three half-lives during this time interval.

A further simplification of the above system can be made by eliminating the reversal of reaction 4 from the kinetic equations. This is justified because the predominant path for the decomposition of MeTNB is reaction 8.[3] Since this path makes a negligible contribution to the nitroform–methyl acrylate system at these acidities, reaction 4 can be considered irreversible under these conditions.

Addition of Nitroform to Methyl Acrylate in Perchloric Acid Solutions. From the previous considerations, the reactions taking place in perchloric acid solutions are as follows.[9]

$$NF + MeA \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} An^- \qquad (9)$$

$$An^- + H_3O^+ \xrightarrow[k_{H^+}]{} MeTNB + H_2O \qquad (10)$$

$$An^- + H_2O \xrightarrow[k_{H_2O}]{} MeTNB + OH^- \qquad (11)$$

$$An^- \xrightarrow[k_2]{} DNS + NO_2^- \qquad (12)$$

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(4) M. J. Kamlet and D. J. Glover, *J. Am. Chem. Soc.*, **78**, 4556 (1956).

(5) J. Hine and L. A. Kaplan, *ibid.*, **82**, 2915 (1960).

(6) The rate-determining step for the reversal of the adduct 2-phenyl-1,1,1,3-tetranitropropane, $Y = C(NO_2)_3$, to nitroform and β-nitrostyrene in strong acid solution is the decomposition of the intermediate carbanion, reaction 1. Therefore, the formation of the carbanion would be rate determining when the addition reaction is carried out under these conditions: J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, p. 73.

(7) This decomposition currently is being investigated more thoroughly in these laboratories.

(8) In more strongly acidic media, reaction 8 would make an even smaller contribution since its rate is proportional to the hydroxide ion concentration.[7]

(9) The formation of DNS from An^- has been treated as a first-order reaction, $d[DNS]/dt = k_2[An^-]$. The justification for this assumption will be found in the agreement of the observed rate constants with those calculated from the rate expression based on this assumption. It is possible that k_2 contains a water concentration term, $k_2 = k_2'[H_2O]$, but the kinetic data to be presented cannot distinguish between the two possibilities.

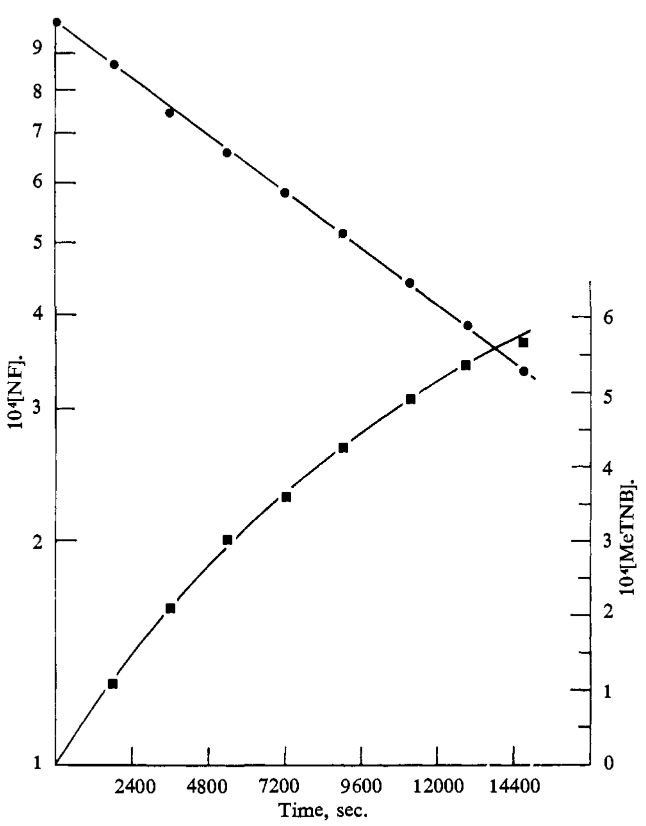

Figure 1. Log [NF] (●) and [MeTNB] (■) *vs.* time. $10^4[NF]_0 = 9.90$, $[MeA]_0 = 0.0500$, $[HClO_4] = 0.0497$ at 45°.

Protonation of the intermediate carbanion An^- by undissociated nitroform was considered to be negligible under these conditions. From the results obtained in the nitroform-β-nitrostyrene system,[5] it can be estimated that at the formal nitroform concentration used in the kinetic run in 50% dioxane and 0.15 *M* perchloric acid (Table I), less than 10% of the protonation of An^- attributed to water, about 0.1% of the total protonation reaction, would be due to undissociated nitroform. At lower acidities, the fraction of An^- protonated by water is somewhat larger, but the fraction of nitroform undissociated is correspondingly smaller so that the amount of An^- protonated by undissociated nitroform in any of the kinetic runs in this study would never be greater than 1% of the total protonation reaction. Additionally, reactions 6 and 7 leading to the formation of C_9 can be ignored in strongly acidic media since the concentration of the dinitro carbanion DNS is essentially zero under these conditions.[10]

Kinetic runs were carried out at various perchloric acid concentrations under pseudo-first-order conditions in the presence of at least a tenfold excess of methyl acrylate. The disappearance of trinitromethide ion and the appearance of DNS were conveniently followed by spectrophotometric measurements at 350 and 380 mμ, the respective absorption maxima of NF and DNS.[11] Satisfactory values of the pseudo-first-order rate constants for the disappearance of trinitromethide ion were obtained by either numerical or graphical methods (Figure 1). These constants were converted to the second-order rate constant k_T by dividing by the formal concentration of methyl acrylate.[12] At higher perchloric acid concentrations, the values of k_T were corrected for the fraction of undissociated nitroform present in the reaction mixture. The corrected values are summarized in Table I.

Additionally, the reaction mixture was analyzed for MeTNB for the same time interval as each NF-DNS assay by the hydrogen peroxide procedure described by Glover.[13] From these measurements, the observed second-order rate constant for the formation of MeTNB, k_M, was calculated from the following equation.

$$k_M = \frac{\left(\frac{d[MeTNB]}{dt}\right)_t}{[NF]_t[MeA]_0} \tag{13}$$

Values of d[MeTNB]/d*t* at appropriate times were obtained by measuring the slopes at these times of plots of the concentration of MeTNB *vs.* time (Figure 1) with a tangent meter consisting of a partially transmitting mirror mounted normal to a straight edge.[14] At least two determinations were made for each point and these generally agreed to within 3%. The mean values of k_M for each run, corrected for the fraction of undissociated nitroform where necessary, are summarized in Table I.

From the values of k_M in Table I, it is apparent that k_M does not vary linearly with the concentration of hydrogen ion,[15] although a dependence upon the hydrogen ion concentration is observed. Utilizing eq. 9-12, we may make the steady-state approximation for the concentration of the carbanion intermediate An^-.

$$[An^-] = \frac{k_1[NF][MeA]}{k_{-1} + k_2 + k_{H^+}[H^+] + k_{H_2O}[H_2O]} \tag{14}$$

The rate of formation of MeTNB is then given by

$$\frac{d[MeTNB]}{dt} = \frac{k_1[NF][MeA](k_{H^+}[H^+] + k_{H_2O}[H_2O])}{k_{-1} + k_2 + k_{H^+}[H^+] + k_{H_2O}[H_2O]} \tag{15}$$

Equating eq. 13 and 15 and rearranging terms, k_M, the observed second-order rate constant for the formation of MeTNB, is expressed by

$$k_M = \frac{k_1([H^+] + r_2)}{r_1 + r_2 + [H^+]} \tag{16}$$

where $r_1 = (k_{-1} + k_2)/k_{H^+}$ and $r_2 = k_{H_2O}[H_2O]/k_{H^+}$.

Utilizing the least-squares procedure with the data in Table I and eq. 16 gives values of k_1, r_1, and r_2 equal to 19.5×10^{-4} l. mole⁻¹ sec.⁻¹, 2.14×10^{-2}

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[10] The conjugate acid of the dinitro carbanion DNS has a pK_a of 4.2 in 50% dioxane ($\mu = 0.1$). It therefore would be about 1% dissociated in 0.005 *M* perchloric acid in 50% dioxane.

[11] To obtain values of the concentration of DNS at time *t*, aliquots of the reaction mixture were quenched in excess sodium acetate solution to buffer out the perchloric acid prior to measuring the optical density of the solution.

[12] It will be shown that methyl acrylate is essentially unprotonated at these acidities in 50% dioxane; see discussion of the mechanism of the reactions.

[13] D. J. Glover, *Tetrahedron Suppl.*, 1, 219 (1963).

[14] R. Livingston in "Technique of Organic Chemistry," Vol. VIII, A. Weissberger, Ed., 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1961, p. 211.

[15] The concentration of hydrogen ion can be taken as equal to the formal concentration of perchloric acid in 50% dioxane. Estimates of the pK_a of perchloric acid in this solvent system from the value in water (R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, p. 93) and the values of the pK_a of hydrochloric acid in water and 45 w./w. % dioxane (H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd Ed., Reinhold Publishing Corp., 1958, p. 453) give a value of about −3.

Table I. Reaction of Trinitromethide Ion (NF) with Methyl Acrylate (MeA) and Perchloric Acid in 50% Dioxane (μ = 0.1[a])

10^4[NF]	10^2[HClO$_4$]	10^4k_T	10^4k_M	[DNS]/[MeTNB]	10^4k_D
45°, 10^2 [MeA] = 5.000					
4.89	0.497	10.4	4.37 ± 0.20	1.43 ± 0.02	6.25
9.90	1.243	12.2	7.80 ± 0.07	0.624 ± 0.008	4.87
9.90	2.485	13.5	10.6 ± 0.2	0.349 ± 0.009	3.70
9.90	4.970	14.7	13.4 ± 0.3	0.198 ± 0.006	2.65
10.22	9.940	16.2	16.0 ± 0.2	0.123 ± 0.060	1.97
10.05	14.91[b]	18.7	17.2 ± 0.3	0.113 ± 0.004	1.94
35°, 10^2 [MeA] = 10.00					
4.98	0.482	5.35	2.48 ± 0.13	1.33 ± 0.01	3.30
9.92	1.243	6.18	4.11 ± 0.05	0.550 ± 0.005	2.26
9.89	2.485	7.15	5.70 ± 0.10	0.301 ± 0.011	1.72
9.97	4.816	7.93	7.00 ± 0.09	0.194 ± 0.011	1.36
10.33	9.783	8.54	7.86 ± 0.18	0.112 ± 0.011	0.88
10.00	10.02	8.68	8.27 ± 0.05	0.127 ± 0.007	1.12

[a] Rate constants in units of l. mole^{-1} sec.$^{-1}$, concentrations in mole l.$^{-1}$. [b] μ = 0.15.

mole l.$^{-1}$, and 1.29 × 10^{-3} mole l.$^{-1}$ at 45° and 9.50 × 10^{-4} l. mole^{-1} sec.$^{-1}$, 1.78 × 10^{-2} mole l.$^{-1}$, and 1.44 × 10^{-3} mole l.$^{-1}$ at 35°. These values of k_1, r_1, and r_2 reproduce the values of k_M in Table I with an average deviation of 1.8% at 45° and 1.2% at 35°. Dividing r_2 by 28.3 mole l.$^{-1}$, the concentration of water in 50 v./v. % dioxane, gives 4.56 × 10^{-5} (5.09 × 10^{-5} at 35°) for the ratio k_{H_2O}/k_{H^+} at 45°.

From the value of r_2 at 45°, it can be calculated that for the runs in Table I, with the exception of the one in 0.005 *M* perchloric acid, between 90.6 and 99.1% of the protonation of the intermediate carbanion An$^-$ is accomplished by hydrogen ion. Since the protonation of An$^-$ by water is relatively unimportant in most of these runs, the least-squares value of the term r_2 may not be very reliable. In fact, if this term is neglected in the numerator and denominator of eq. 16, the least-squares values of k_1 and r_1 (18.8 × 10^{-4} l. mole^{-1} sec.$^{-1}$ and 1.76 × 10^{-2} mole l.$^{-1}$ at 45°) so obtained will reproduce the values of k_M in Table I with an average deviation of only 2.4%.

Equation 16 demonstrates that the rate-determining step for the formation of MeTNB undergoes a change as the acidity of the medium changes. As the hydrogen ion concentration becomes much larger than the sum ($r_1 + r_2$), the denominator is essentially equal to [H$^+$] and the equation reduces to[16]

$$k_M = k_1 \tag{17}$$

In this acidity region the rate-determining step is the formation of the intermediate carbanion An$^-$.[8] Although it was not practical to carry out kinetic runs at these high perchloric acid concentrations, the observed values of k_M in 0.1 and 0.15 *M* perchloric acid (Table I) are approaching the limiting value of k_1 obtained by the least-squares procedure.

When the concentration of hydrogen ion is less than about 5 × 10^{-4} *M*, then the [H$^+$] may be disregarded in the denominator but not in the numerator of eq. 16. The expression for k_M then becomes

$$k_M = \frac{k_1([H^+] + r_2)}{r_1 + r_2} \tag{18}$$

In this acidity region, k_M will vary linearly with the concentration of hydrogen ion, and the protonation of the intermediate carbanion An$^-$ is rate determining. Due to analytical difficulties, it was not possible to carry out kinetic runs at these low hydrogen ion concentrations. However, values of k_M were calculated for several perchloric acid concentrations in this acidity region using eq. 16 and the least-squares values of k_1, r_1, and r_2. As expected, these values of k_M, when plotted against the concentration of perchloric acid, gave a straight line (Figure 2). The deviation of the calculated points from the straight line at higher acidities is due to the rate of protonation of the intermediate carbanion An$^-$ having increased to the point where it is now comparable with the rate of addition of NF to MeA. The kinetics are therefore complex and k_M would not be expected to be directly proportional to the concentration of hydrogen ion in this acidity region (see Figure 3).

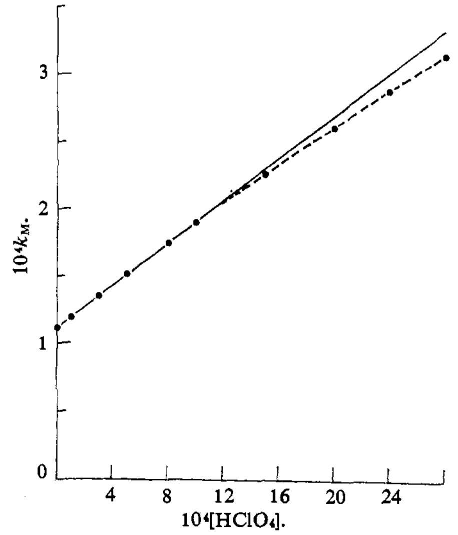

Figure 2. Calculated values of k_M (eq. 16) at 45° *vs.* [HClO$_4$].

Finally, when [H$^+$] is much less than r_2, eq. 16 reduces to

$$k_M = \frac{k_1 r_2}{r_1 + r_2} \tag{19}$$

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[16] The water catalysis term, $k_1r_2/(r_1 + r_2 + [H^+])$, in eq. 16 can be neglected under these conditions of high acidity since its calculated contribution to the value of k_M is less than 1.3% in 0.1 *M* perchloric acid.

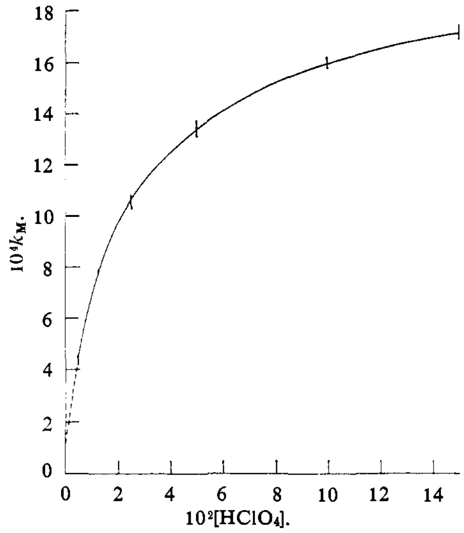

Figure 3. Observed values of k_M at 45° *vs.* [HClO$_4$].

and k_M is equal to 1.11×10^{-4} l. mole^{-1} sec.$^{-1}$ at 45° (0.71×10^{-4} l. mole^{-1} sec.$^{-1}$ at 35°). This is the lower limiting value of k_M in this solvent system. Under these conditions, the protonation of the intermediate carbanion An$^-$ is accomplished solely by water. It should be noted that the intercept of the experimental pH profile (Figure 3) agrees quite well with this calculated value.

In the region of acidities in which the experimental data were gathered, the rate of formation of the intermediate carbanion An$^-$ is about equal to or somewhat larger than its rate of protonation, and mixed kinetics are obtained. The experimentally obtained pH profile is presented in Figure 3.

The experimental data also permitted the evaluation of k_D, the observed second-order rate constant for the formation of DNS. This constant is defined by

$$k_D = \frac{\left(\frac{d[DNS]}{dt}\right)_t}{[NF]_t[MeA]_0} \tag{20}$$

under the pseudo-first-order reaction conditions. Evaluation of k_D from the above equation by the slope–time procedure used to evaluate k_M was considered. For most of the runs in Table I, DNS was a secondary reaction product accounting for only 10 to 30% of the total nitroform consumed at any time. Therefore, the optical density contribution of DNS to the total optical density of the reaction mixture at any time would be small and an accurate measurement of the concentration of DNS, especially early in the reaction, would be somewhat difficult. Since the slope–time procedure requires a good quality concentration–time plot, this method of evaluating k_D was not deemed practical.

The evaluation of k_D from the experimental data was accomplished by taking advantage of the fact that since the conjugate acid of DNS is essentially undissociated in this acidity region,[10] reaction of the dinitro carbanion DNS with methyl acrylate to form C$_9$ *via* reactions 6 and 7 would be completely suppressed.[17] If this assumption is valid, then the ratio $[DNS]_t/[MeTNB]_t$ should be constant throughout a given kinetic run. The data in Table I confirm this. With a knowledge of this ratio and k_M for a given run, k_D can be obtained from the expression

$$k_D = \frac{k_M[DNS]_t}{[MeTNB]_t} \tag{21}$$

The values of k_D summarized in Table I were obtained in this manner.[18]

A knowledge of k_D at various acidities allows us to obtain the ratio k_2/k_{H^+}. From the steady-state approximation for the concentration of the intermediate carbanion An$^-$ (eq. 14) the expression

$$\frac{d[DNS]}{dt} = \frac{k_1k_2[NF][MeA]}{k_{-1} + k_2 + k_{H^+}[H^+] + k_{H_2O}[H_2O]} \tag{22}$$

is obtained for the rate of formation of DNS. Equating 20 and 22 and rearranging terms, k_D, the observed second-order rate constant for the formation of DNS, is given by

$$k_D = \frac{k_1r_3}{r_1 + r_2 + [H^+]} \tag{23}$$

where $r_3 = k_2/k_{H^+}$.

The values of k_D in Table I, together with the previously determined least-squares values of k_1, r_1, and r_2, could be used to evaluate r_3. Because of the inherent errors in the experimentally obtained values of k_D in the perchloric acid runs, r_3 was evaluated from the values of k_D obtained from the results of kinetic runs in acetic acid–acetate buffers. Under these weakly acidic conditions, the reaction path governed by k_D accounts for 67 to 83% of the total nitroform consumption. Therefore, values of k_D obtained in this buffer system should be considerably more reliable than those obtained from the kinetic runs in perchloric acid solutions.

Addition of Nitroform to Methyl Acrylate in Acetic Acid–Acetate Buffers. In acetic acid buffers, an additional reaction path must be added to those considered in perchloric acid solutions. In this buffer system, protonation of the intermediate carbanion An$^-$ can be accomplished by

$$\text{An}^- + \text{HOAc} \xrightarrow{k_{HOAc}} \text{MeTNB} + \text{OAc}^- \tag{24}$$

Direct measurement of d[MeTNB]/dt in this buffer system is difficult as only 17 to 33% of the total nitroform reacting per unit time is converted to MeTNB. Since the analytical method for determining MeTNB involves its conversion to methyl 4,4-dinitrobutyrate, λ_{max} 380 mμ,[13] and then subtraction of the optical density contributions of DNS, λ_{max} 380 mμ,[3] and NF,

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(17) The reported hydrolysis of dinitro carbanions to carboxylic acids (M. J. Kamlet, L. A. Kaplan, and J. C. Dacons, *J. Org. Chem.*, **26**, 4371 (1961)) did not occur at these acidities as evidenced by the observation that DNS in 0.1 *M* hydrochloric acid, 50% dioxane, and 45° showed no change in its specific extinction at 380 mμ or in the shape of the envelope of its complete spectrum after 24 hr.

(18) The constant k_D may also be calculated from the expression $k_D = k_T - k_M$. Values of k_D obtained in this manner would suffer from the magnification of the experimental errors in both k_T and k_M. Since the reaction path governed by k_D accounts for only about 10 to 30% of the total nitroform consumption in most of the runs in Table I, this method of calculating k_D will not yield as reliable values as eq. 21 and will fail most severely at higher acidities where the fraction of nitroform converted to DNS is at a minimum. It should also be noted that as the acidity of the reaction medium increases and the fraction of nitroform converted to DNS decreases, the error in measuring $[DNS]_t$ will increase. Thus, the values of k_D (Table I) calculated from eq. 21 will not be as reliable at the higher perchloric acid concentrations.

λ_{max} 350 mμ,[5] present from the total optical density of the resulting solution, the determination of small quantities of MeTNB in the presence of large quantities of DNS and NF will obviously not be precise. However, it should be possible to measure d[DNS]/dt quite precisely in this buffer system and thereby obtain reliable values of k_D by the slope–time procedure used to evaluate k_M in the runs in perchloric acid solutions.

The above procedure would be suitable for obtaining values of k_D were it not for the fact that DNS reacts further with methyl acrylate at an appreciable rate in this buffer system as its conjugate acid is completely dissociated at these acidities. However, from the stoichiometry of the DNS-forming reaction, 1 mole of nitrite ion is produced per mole of DNS. Therefore, the relation

$$\frac{d[NO_2^-]}{dt} = \frac{d[DNS]}{dt} = k_D[NF][MeA]_0 \qquad (25)$$

can be used to obtain values of k_D by the slope–time procedure from plots of the concentration of nitrite ion *vs.* time.[19] Figure 4 displays the data from a typical reaction in this buffer system. It should be noted that very early in the reaction the concentrations of DNS and nitrite ion are essentially equal. As the reaction proceeds, the rate of formation of DNS is decreasing more rapidly with time than the rate of formation of nitrite ion. This apparent change in the rate of formation of DNS is caused by the subsequent reaction of DNS with methyl acrylate to yield C_9 *via* reactions 6 and 7.

In addition to measuring the concentration of nitrite ion at time t, the reaction mixture was assayed for NF and DNS for the same time interval. From these data, the rate of the over-all reaction was obtained. Figure 4 presents a plot of the log [NF] *vs.* time for a typical run. Since all of the reactions were carried out under pseudo-first-order conditions in the presence of at least a tenfold excess of methyl acrylate, linear plots of the log [NF] *vs.* time were obtained. The pseudo-first-order rate constants and k_T, the second-order rate constant for the over-all reaction, were evaluated by the same procedures used for the data obtained from the kinetic runs carried out in perchloric acid solutions. The results are summarized in Table II.

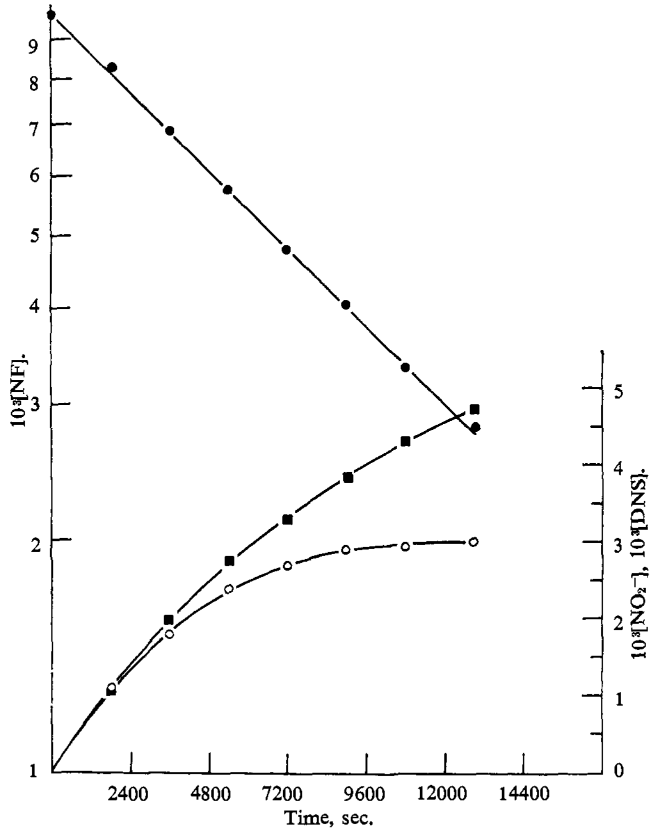

Figure 4. Log [NF] (●), [NO_2^-] (■), and [DNS] (○) *vs.* time. $10^3[NF]_0 = 9.68$, $[MeA]_0 = 0.100$, [HOAc] = 0.3099, [OAc^-] = 0.1000 at 45°.

Table II. Reaction of Trinitromethide Ion (NF) with Methyl Acrylate (MeA) and Acetic Acid–Acetate Buffers in 50% Dioxane (μ = 0.1)[a]

10^3[NF]	[AcOH]	[OAc^-]	10^4k_T	10^4k_M	10^4k_D
		45°, 10^2 [MeA] = 10.00			
9.68	0.3099	0.1000	9.87	3.29	6.58 ± 0.28
10.10	0.2066	0.1000	9.42	2.32	7.10 ± 0.08
5.05	0.2066	0.0666	9.82	2.85	6.97 ± 0.08
4.96	0.2066	0.0666	9.63	2.41	7.22 ± 0.10
9.92	0.1033	0.1000	8.84	1.27	7.57 ± 0.20
2.45	0.1033	0.0333	9.20	1.62	7.58 ± 0.20
		35°, 10^2[MeA] = 20.00			
10.70	0.3045	0.1000	5.08	2.15	2.93 ± 0.03
10.33	0.2030	0.1000	4.80	1.55	3.25 ± 0.10
10.35	0.2030	0.1000	4.77	1.55	3.22 ± 0.05
10.46[b]	0.1015	0.1000	4.42	0.83	3.58 ± 0.06
10.56	0.1015	0.1000	4.37	0.90	3.47 ± 0.15

[a] Rate constants in units of l. mole^{-1} sec.$^{-1}$, concentrations in mole l.$^{-1}$. [b] 10^2[MeA] = 14.00.

Inspection of the values of k_D in Table II shows that this rate constant varies inversely with the concentration of acetic acid, but exhibits no definite trend on changing the buffer ratio at a fixed concentration of acetic acid. From the expression for the steady-state approximation for the concentration of the intermediate carbanion An^- in the acetic acid–acetate buffer system, the rate equation for the formation of DNS is given by

$$\frac{d[DNS]}{dt} = \frac{k_1k_2[NF][MeA]}{k_{-1} + k_2 + k_{H^+}[H^+] + k_{H_2O}[H_2O] + k_{HOAc}[HOAc]} \qquad (26)$$

Equating eq. 25 and 26 and rearranging terms, the second-order rate constant k_D has the form

$$k_D = \frac{k_1r_3}{r_1 + r_2 + [H^+] + r_4[HOAc]} \qquad (27)$$

where $r_3 = k_2/k_{H^+}$, $r_4 = k_{HOAc}/k_{H^+}$, and r_1 and r_2 have been defined previously. Since $K_{HOAc} \approx 5 \times 10^{-7}$ mole l.$^{-1}$ in 50% dioxane,[20] the term [H^+] is never greater than 2×10^{-6} M in any of the kinetic runs in

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(19) Control experiments with fixed nitrite ion concentrations in acetic acid–acetate buffers, HOAc/OAc^- = 3, [HOAc] = 0.3 M, in 50% dioxane, at 45°, showed that there was only a 1% decrease in the nitrite ion concentration after 4 hr. This is within the experimental error of the determination. At higher acidities, phthalic acid buffers, the decrease in the nitrite ion concentration was too rapid to permit kinetic measurements to be made.

(20) In 45 w./w. % dioxane at 45°, $K_{HOAc} = 4.6 \times 10^{-7}$ mole l.$^{-1}$: H. S. Harned and G. L. Kazanjian, *J. Am. Chem. Soc.*, **58**, 1912 (1936).

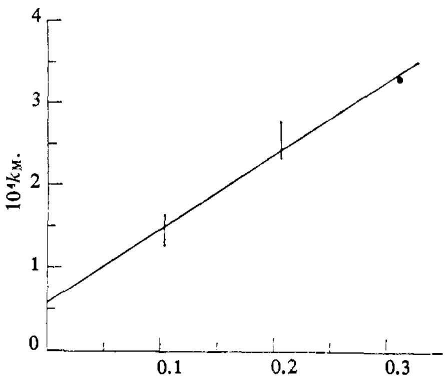

Figure 5. Observed values of k_M at 45° *vs.* [HOAc].

Table II. As this is negligible when compared to the sum ($r_1 + r_2$), the term [H$^+$] may be omitted from the denominator of eq. 27 to give the working equation

$$k_D = \frac{k_1 r_3}{r_1 + r_2 + r_4[\text{HOAc}]} \tag{28}$$

which was used to evaluate r_3 and r_4 in this buffer system.

It is now apparent that k_D should vary inversely with the concentration of acetic acid but not with the concentration of hydrogen ion in this buffer system. For buffers generating hydrogen ion concentrations of about 10^{-3} *M* or larger, a dependence of k_D upon the buffer ratio at fixed buffer acid concentrations will be observed.[21]

Utilizing the least-squares procedure with the data in Table II, the previously determined values of k_1, r_1, and r_2, and eq. 28 gives values of r_3 and r_4 equal to 9.54×10^{-3} mole l.$^{-1}$ and 1.70×10^{-2} at 45° and 7.91 $\times 10^{-3}$ mole l.$^{-1}$ and 2.03×10^{-2} at 35°. These values of r_3 and r_4, together with the least-squares values of k_1, r_1, and r_2 obtained from the kinetic data in perchloric acid solutions, reproduced the observed values of k_D (Table II) with an average deviation of 0.8% at 45° and 0.9% at 35°.

To test the least-squares value of r_3 obtained in the acetic acid–acetate buffer system, it was substituted into eq. 23 together with the least-squares values of k_1, r_1, and r_2 obtained from the kinetic data in perchloric acid solutions and values of k_D were calculated for the kinetic runs in perchloric acid solution. These constants reproduced the experimentally obtained values of k_D with an average deviation of 6.5% at 45° and 7.5% at 35°.[22]

In addition to k_D, it was possible to obtain values of k_M from the data in this buffer system with the expression $k_M = k_T - k_D$. The data in Table II were obtained in this manner. Although this expression undoubtedly gives values of k_M that are not too reliable,[18] it is not possible to evaluate the ratio $[\text{NO}_2^-]_t/[\text{MeTNB}]_t$ precisely in these kinetic runs since the accurate determination of small concentrations of MeTNB in the presence of large quantities of DNS is not possible (*vide supra*). This fact negated the possibility of treating the kinetic data to obtain k_M in a manner similar to that used to obtain k_D in perchloric acid.

Inspection of the data in Table II shows a definite dependence of k_M upon the concentration of acetic acid, but no apparent dependence upon the concentration of hydrogen ion in this buffer system. From the expression for the steady-state approximation for the concentration of the intermediate carbanion An$^-$ in this buffer system, the following equation for k_M is obtained.

$$k_M = \frac{k_1([\text{H}^+] + r_4[\text{HOAc}] + r_2)}{r_1 + r_2 + [\text{H}^+] + r_4[\text{HOAc}]} \tag{29}$$

Since the concentration of hydrogen ion is never greater than 2×10^{-6} *M* in any of the kinetic runs in Table II,[20] the terms $k_1[\text{H}^+]$ in the numerator and [H$^+$] in the denominator of eq. 29 are negligible and may be disregarded to give the working equation

$$k_M = \frac{k_1 r_4[\text{HOAc}] + k_1 r_2}{r_1 + r_2 + r_4[\text{HOAc}]} \tag{30}$$

As all of the constants in eq. 30 have been evaluated, k_M can now be calculated for the kinetic runs in Table II. It was found that the values of k_M obtained from eq. 30 were all larger than the observed values in Table II. However, a reasonably good plot of the observed values of k_M *vs.* the concentration of acetic acid was obtained (Figure 5), indicating that the reaction was subject to general acid catalysis. The rather poor agreement between the observed and calculated values of k_M is undoubtedly due to the magnitude of the water catalysis term $k_1 r_2$ in the numerator of eq. 30. It was previously shown that the value of this term may not be very reliable since it was obtained from the runs in perchloric acid solutions in which less than 10% of the protonation of the intermediate carbanion An$^-$ is accomplished by water. An indication of the magnitude of this error can be obtained by comparing the intercept of Figure 5 (0.57×10^{-4} l. mole^{-1} sec.$^{-1}$) with the value of k_M for the water-catalyzed protonation in perchloric acid solutions as calculated from eq. 19 (1.11×10^{-4} l. mole^{-1} sec.$^{-1}$ at 45°). Since the observed values of k_M vary between 1.62 and 3.49 $\times$ 10^{-4} l. mole^{-1} sec.$^{-1}$, an error of 0.54×10^{-4} l. mole^{-1} sec.$^{-1}$ in the uncatalyzed reaction would introduce a sizeable error into the calculated values of k_M for this buffer system. If the water catalysis terms $k_1 r_2$ in the numerator and r_2 in the denominator of eq. 30 are disregarded, the calculated and observed values of k_M are in reasonably good agreement.

The Mechanism of the Reaction. From the foregoing discussion, the formation of MeTNB is best described by the sequence (9–11) in perchloric acid solutions and (9), (11), and (24) in acetic acid–acetate buffers. At moderate acidities, the reaction exhibits general acid catalysis and the protonation of the intermediate carbanion An$^-$ is rate determining. In the acidity region studied in perchloric acid solutions, neither the formation of An$^-$ nor the protonation of An$^-$ is solely rate determining. At still higher acidities, the addition of trinitromethide ion to methyl acrylate to form An$^-$ becomes rate determining.[23]

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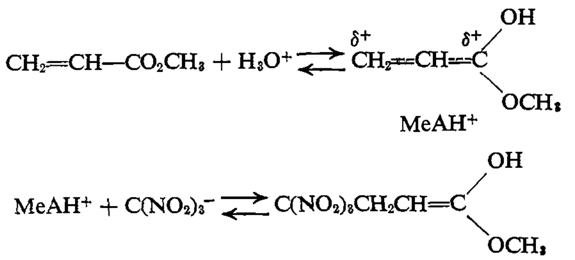
[21] Inspection of the data in Table I shows that k_D does indeed vary inversely with the hydrogen ion concentration.

[22] These deviations do not include those for the values of k_D calculated for the kinetic runs in 0.1 and 0.15 *M* perchloric acid. For these runs, in which the reaction path governed by k_D accounts for 10% or less of the total nitroform reacting, the error was 23 and 65% at 45° and 27 and 40% at 35°.

[23] The effect of the basicity of the intermediate carbanion upon the rate-determining step will be considered in the next paper in this series.

It may be argued that in perchloric acid solutions the formation of MeTNB occurs by the following mechanism



$$CH_2{=}CH{-}CO_2CH_3 + H_3O^+ \rightleftharpoons \overset{\delta+}{C}H_2{=}CH{=}\overset{\delta+}{C}(OH)(OCH_3) \quad \text{MeAH}^+$$

$$\text{MeAH}^+ + C(NO_2)_3^- \rightleftharpoons C(NO_2)_3CH_2CH{=}C(OH)(OCH_3)$$

I

which involves a rapid and reversible prior protonation of methyl acrylate followed by the slow addition of trinitromethide ion to this species. A proton transfer converts the enol I to MeTNB. This mechanism would exhibit hydronium ion catalysis.

However, the above mechanism may be discarded on the following grounds. The pK of the conjugate acid of dioxane is -3.22.[24] Although specific data for the pK of the conjugate acid of methyl acrylate could not be found in the literature, the pK of the conjugate acid of ethylene diacetate is reported to be greater than -4.5[25] and the results of studies of the solubility of hydrogen chloride in esters and ethers indicate that alkyl acetates and benzoates are considerably weaker bases than dioxane.[26] Therefore, in 50% dioxane with 0.005 M perchloric acid, methyl acrylate would certainly not be protonated. As the acidity of the medium increases, the above mechanism predicts that k_M, the observed rate constant for the formation of MeTNB, should increase until the methyl acrylate is completely protonated. It can be calculated from eq. 16 that k_M will be constant at hydrogen ion concentrations of 1 M and larger in this solvent system. Thus, the above mechanism requires that methyl acrylate be completely protonated at a minimum hydrogen ion concentration of 1 M.[27] Since the pK data indicate that methyl acrylate is too weak a base to be completely protonated in 50% dioxane at a hydrogen ion concentration of 1 M, the above mechanism may be discarded.

As a further check on the mechanism proposed for the methyl 4,4,4-trinitrobutyrate forming reactions, it is instructive to compare k_1, the specific rate constant for the addition of trinitromethide ion to methyl acrylate, with the specific rate constant for the addition of trinitromethide ion to β-nitrostyrene in methanol at 40°.[5] Using the values of k_1 at 35 and 45° and the expression for the rate constant derived from transition state theory,[28] we have calculated $\Delta H^* = 13.4$ kcal. mole^{-1} and $\Delta S^* = -28.9$ cal. deg.$^{-1}$ for the addition of trinitromethide ion to methyl acrylate to form the intermediate carbanion An$^-$ (reaction 9). From these activation parameters, $k_1^{40°} = 13.9 \times 10^{-4}$ l. mole^{-1} sec.$^{-1}$. For the addition of trinitromethide ion to β-nitrostyrene, Hine and Kaplan[5] find this rate constant, k_{-3} in their notation, to be 32.3×10^{-4} l. mole^{-1} sec.$^{-1}$ at 40°.

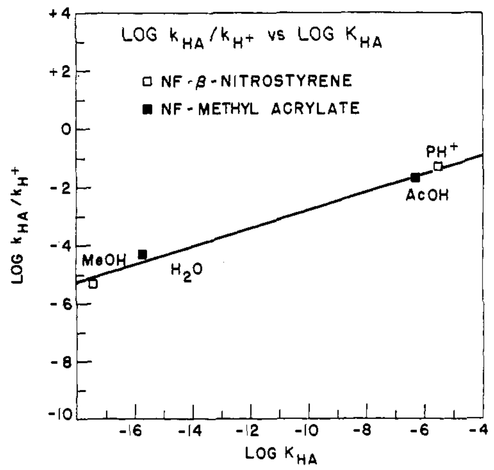


Figure 6. Log k_{HA}/k_{H^+} vs. log K_{HA} for the reaction of trinitromethide ion with methyl acrylate (■) and with β-nitrostyrene (□).

We also find that the rate constant ratios for the protonation of the intermediate carbanion An$^-$ in the nitroform–methyl acrylate system are comparable with those obtained in the nitroform–β-nitrostyrene system.[5] These data are summarized in Table III.

Table III. Rate Constants for the Addition of Trinitromethide Ion to β-Nitrostyrene and Methyl Acrylate

β-Nitrostyrene[a]	Methyl Acrylate[b]
$[k_3/k_{-2}]_{40°} = 10^{-1}$ mole l.$^{-1}$ [c]	$[k_{-1}/k_{H^+}] = 1.1 \times 10^{-2}$ mole l.$^{-1}$ [d]
$[k_{PH^+}/k_{MeOH_2^+}]_{40°} = 5.2 \times 10^{-2}$	$[k_{HOAc}/k_{H^+}] = 2.2 \times 10^{-2}$
$[k_{MeOH}/k_{MeOH_2^+}]_{40°} = 4.6 \times 10^{-6}$	$[k_{H_2O}/k_{H^+}] = 4.8 \times 10^{-5}$
$K_{MeOH} \approx 4 \times 10^{-18}$ mole l.$^{-1}$	$K_{H_2O} \approx 2 \times 10^{-16}$ mole l.$^{-1}$ [e]
$K_{PH^+} \approx 3 \times 10^{-6}$ mole l.$^{-1}$ [f]	$K_{HOAc} \approx 5 \times 10^{-7}$ mole l.$^{-1}$

[a] See ref. 5. [b] Average values of rate constant ratios at 35 and 45°. [c] k_{-1}/k_{H^+} in the Hine–Kaplan notation. [d] $k_{-1}/k_{H^+} = r_1 - r_3$. [e] In 45 w./w. % dioxane at 40°: H. S. Harned and L. D. Fallon, *J. Am. Chem. Soc.*, **61**, 2374 (1939), corrected to $\mu = 0.1$. [f] PH$^+$ = pyridinium ion.

Using these data, we have constructed a modified Brønsted plot by graphing the rate constant ratio k_{HA}/k_{H^+} against K_{HA}. Figure 6 presents the data for both the methyl acrylate and β-nitrostyrene systems. The single straight line fit of all the data points indicates that the degree of bonding of the proton to the carbanion intermediate in the transition state, as measured by the Brønsted parameter α, is about the same for both of these systems.[29] From the slope of the straight line (Figure 6) $\alpha = 0.31$.

The fit of the data to a single Brønsted plot suggests that the specific rate constant, k_{H^+}, for the protonation of the intermediate carbanions by hydronium or methyloxonium ions is about the same for both of these systems. This allows us to compare the equilibrium

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(24) E. M. Arnett and C. Y. Wu, *J. Am. Chem. Soc.*, **84**, 1684 (1962).

(25) H. Lemaire and H. J. Lucas, *ibid.*, **73**, 5198 (1951). Acids stronger than those having p$K = -4.5$ cannot be measured by this procedure. These authors report pK $= -4$ for the conjugate acid of dioxane.

(26) W. Gerrard and E. D. Macklen, *J. Appl. Chem.* (London), **6**, 241 (1956); **9**, 85, 89 (1959).

(27) Spectrophotometric measurements were made of methyl acrylate in 50% dioxane with added perchloric acid. Little change in the spectrum was observed between 0.0 and 0.5 M perchloric acid, and only a slight change in the spectrum occurred on increasing the hydrogen ion concentration to 1 M.

(28) S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 195 ff.

(29) J. F. Bunnett in ref. 14, p. 239.

constants for reaction 9 and its counterpart in the β-nitrostyrene system which lead to the formation and dissociation of these carbanion intermediates. We can define a constant

$$K' = \frac{K_{\mathrm{MeA}}k_{\mathrm{H^+}}}{K_{\mathrm{NS}}k_{\mathrm{H^+}}} \tag{31}$$

where $K_{\mathrm{MeA}}k_{\mathrm{H^+}}$ and $K_{\mathrm{NS}}k_{\mathrm{H^+}}$ are equal to the ratio of k_1 to $k_{-1}/k_{\mathrm{H^+}}$ for the methyl acrylate and β-nitrostyrene systems, respectively. Using the values of $k_{-1}/k_{\mathrm{H^+}}$ in Table III and the previously stated values of $k_1^{40°}$, the equilibrium constant ratio K' is found to be 3.9.

We believe this result, $K' > 1$, is of the magnitude to be expected. Neglecting entropy changes, which would be difficult to assess even qualitatively,[30] the equilibrium position for the β-nitrostyrene system should be shifted further toward the reactants than the methyl acrylate system. A more positive enthalpy term for the equilibrium in the β-nitrostyrene system would arise from the larger gain in resonance energy on forming β-nitrostyrene when this carbanion intermediate *dissociates* as compared to the formation of methyl acrylate from the dissociation of the carbanion intermediate in the nitroform–methyl acrylate system.[31]

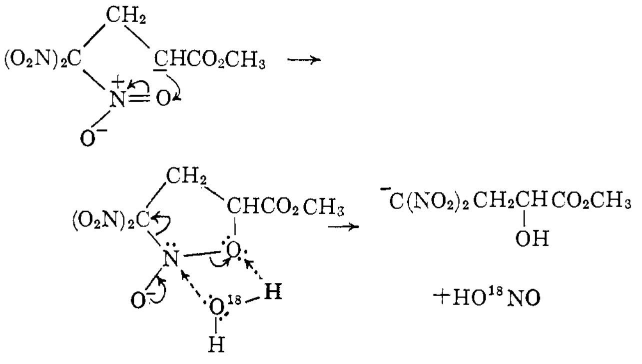
We next turned our attention to the mechanism for the formation of the α-hydroxy ester DNS. The fit of the observed rate constant k_D to eq. 23 in perchloric acid solutions and eq. 28 in acetic acid buffers ruled out catalysis by acids or bases in the rate-determining or prior steps. The kinetic results suggested either a unimolecular or a bimolecular process involving the solvent water[9] for the conversion of the intermediate carbanion An$^-$ to DNS.

To distinguish between these two possibilities, we treated trinitromethide ion with methyl acrylate in the presence of excess potassium acetate in 50% dioxane containing O^{18}-enriched water. These conditions favor the formation of DNS by reducing the rate of protonation of the carbanion An$^-$ to MeTNB. Rather than isolate the potassium salt of DNS which would be difficult to assay for O^{18} content because of its tendency to detonate on heating, we chose to isolate its Michael adduct with methyl acrylate: dimethyl 4,4-dinitro-2-hydroxyheptanedioate (C$_9$). This compound is low melting and only decomposes slowly at temperatures above its melting point.

When the product of this reaction was analyzed by mass spectrometry, the results clearly showed it to be isotopically enriched. Unfortunately, it was not possible to obtain the mass peak for the parent ion, and this made a precise determination of the O^{18} content impossible. However, from the ratio of the intensities of the peaks for mass 46 and 48 in the spectra of enriched and unenriched samples of C$_9$, we estimated that the O^{18} uptake in the reaction was no more than one-fifth of that expected. Control experiments, the synthesis of C$_9$ from DNS and methyl acrylate, and the equilibration of potassium trinitromethide, both in 50% dioxane containing O^{18}-enriched water, did not yield isotopically enriched products.[32]

When analyzed for its exact O^{18} content,[33] the enriched sample of C$_9$ was found to contain only 0.026 ± 0.003 atom % excess of O^{18}. Since the aqueous portion of the reaction solvent contained 5 atom % excess O^{18} and we expect only the hydroxyl group oxygen to pick up the oxygen isotope if the solvent is reacting with the carbanion An$^-$ at the α-carbon atom, the maximum possible enrichment would be 0.556 atom % excess O^{18}. The observed enrichment, about 6% of that expected, indicated that the solvent was not directly involved in the formation of the transition state. However, it did suggest that a secondary reaction path was available for the collapse of the transition state to the product DNS.

The kinetic and synthetic evidence suggested a cyclic transition state such as II for the conversion of the carbanion intermediate An$^-$ to DNS. Collapse of this transition state to products would occur by attack of a water molecule at the nitrogen atom to give the α-hydroxy ester DNS and nitrite or nitrous acid. A secondary path for the collapse of the transition state II would involve the attack of a water molecule at the α-carbon atom. The α-hydroxy ester produced would contain the oxygen isotope from the solvent.



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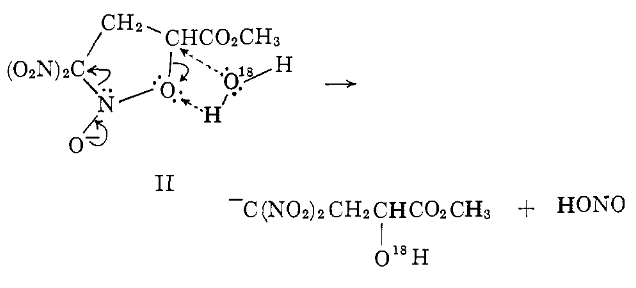

The low O^{18} enrichment found in C$_9$ when the reaction is carried out in an O^{18}-enriched solvent indicates that the path involving solvent attack at the α-carbon atom is a minor one. This result is somewhat anal-

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[30] The difficulty in estimating the effect of the ΔS term on the individual equilibria is due to our inability to appraise the ΔS of solvation for each system. Assuming this contribution to the total entropy change to be either negligible or about the same for both systems, we would expect, from the examination of molecular models, a greater decrease of steric interactions, a more favorable ΔS, for the *dissociation* of the carbanion intermediate derived from β-nitrostyrene than for the one from methyl acrylate.

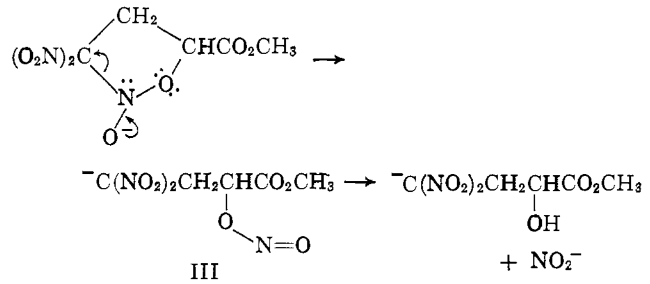
[31] A referee has suggested that the effect of the gain in resonance energy on K_{NS} as compared to K_{MeA} when the intermediate carbanion dissociates would make K' much larger than 3.9 if it was not largely compensated for by a loss in resonance energy due to the greater resonance stabilization of the intermediate carbanion by the nitro group as compared to the carbomethoxy group. (The enhanced stabilization of carbanions by nitro groups has been pointed out previously: R. G. Pearson and R. L. Dillon, *J. Am. Chem. Soc.*, 75, 2439 (1953).) Though we agree with this comment, we hesitate to attach too much significance to the absolute value of K' because of the assumptions involved in obtaining it. We do feel it is significant that K' is greater than unity.

[32] We are indebted to Dr. Fred Saalfeld of the U. S. Naval Research Laboratory for these analyses and the interpretation of the results.

[33] Analytica Corp., New York 16, N. Y.

ogous to those obtained from studies of the mechanism of hydrolysis of nitrite esters.[34,35] Alkyl and diphenylmethyl nitrites hydrolyze in acidic or alkaline media by a mechanism involving exclusive O–N bond fission. However, triphenylmethyl nitrite yields products which indicate that about 1% of the reaction proceeds by alkyl–oxygen bond fission.[35] We believe that the transition state II would collapse by both paths with solvent attack at nitrogen predominating because of the highly electronegative nature of the substituted dinitromethyl group to which it is bonded.[36]

An alternative route to the α-hydroxy ester DNS involves collapse of the transition state II to the nitrite ester III. This intermediate would hydrolyze to DNS and nitrite.[37] This mechanism is not inconsistent


III

with the results obtained from the O^{18} experiments if one assumes that hydrolysis of the nitrite ester III involves some alkyl–oxygen bond fission[35] together with the predominant path proceeding by O–N bond fission.

The formation of α-hydroxy derivatives analogous to the α-hydroxy ester DNS in the reaction of acrylamide[2] and methyl vinyl ketone[3] with trinitromethide ion undoubtedly occurs by the same mechanism as the formation of DNS.

Experimental Section

Caution! The compounds described in this work are explosives and may detonate on grinding or impact. Appropriate shielding should be used.

Preparation and Purification of Reagents. Potassium trinitromethide was prepared by reducing tetranitromethane with hydrogen peroxide and alkali. This procedure is based upon the analytical procedure described by Glover.[13] The conjugate acid, nitroform, was liberated from its salt as described previously.[5] Stock solutions of nitroform were prepared by weighing out the desired quantity of crystalline nitroform and diluting to volume with distilled water. The concentration was checked by a spectrophotometric assay. Since aqueous nitroform solutions at about pH 2 slowly decompose on standing with the formation of nitrite,[38] the nitroform stock solution was prepared just prior to each kinetic run. Nitrite ion could not be detected in freshly prepared nitroform stock solutions by the analytical procedure used in this work.

Stabilized methyl acrylate was fractionated to separate it from the stabilizer and its purity checked by vapor phase chromatography. The distilled material was kept in a freezer. Stock solutions were prepared by weighing the desired quantity of methyl acrylate into a low actinic flask and diluting to volume with purified dioxane. These solutions were kept under refrigeration when not being used and were discarded after a maximum time of 2 weeks for a fresh solution.

J. T. Baker reagent grade dioxane was refluxed over sodium for at least 96 hr. and then distilled.[39] The fraction boiling at 100–101.5° was used in this work. Stocks of purified dioxane were not kept longer than 2 weeks to minimize peroxide buildup. Dioxane (50 vol. %) was prepared by pipetting equal volumes of dioxane and distilled water into a suitable receiver.

Standard perchloric and acetic acid solutions were prepared from the reagent grade chemicals in the appropriate solvent and standardized by titrating aliquots with sodium hydroxide to a phenolphthalein end point. Sodium perchlorate and sodium acetate stock solutions were prepared from the reagent grade salts without further purification.

Analytical Procedures. The determination of the concentration of the various polynitro carbanions present during a kinetic run was performed with a Beckman Model DU spectrophotometer. Table IV gives the values of the molar extinction coefficients of the various species as determined with the spectrophotometer used in this work.

Table IV. Molar Extinction Coefficients[a]

Species	ϵ_{350}	ϵ_{380}
$^-C(NO_2)_2CH_2CHOHCO_2CH_3$ (DNS)	7,370	16,870
$^-C(NO_2)_2CH_2CH_2CO_2CH_3$ (MeDNB)	7,465	17,020
$^-C(NO_2)_3$ (NF)	14,420	4,540

[a] Spectra measured in dilute aqueous sodium acetate or alkali.

For the kinetic runs in perchloric acid solutions, two identical aliquots of the reaction mixture were simultaneously quenched; one was diluted to 50 ml. with water and the other was diluted to 50 ml. with water after quenching in 25 ml. of 25% methanol containing 5 ml. of 30% hydrogen peroxide. A suitable aliquot of the aqueous quench was diluted to 50 ml. with water after adding 5 ml. of 20% sodium acetate solution to buffer out the perchloric acid. Under these conditions, the conjugate acids of the polynitro carbanions present were found to be completely dissociated. The optical density of this solution was measured at 350 and 380 mμ. Duplicate measurements were made which generally agreed to within 1%. From these data and the molar extinction coefficients of NF and DNS, it was possible to calculate the concentrations of NF and DNS present in the reaction mixture.

The concentration of MeTNB was determined by taking a suitable aliquot of the peroxide-quenched reaction mixture, *vide supra*, adding it to 8 ml. of 0.1 *M* sodium hydroxide in a 50-ml. volumetric flask, and diluting it to volume with distilled water. Under these conditions, MeTNB is quantitatively reduced to MeDNB[13] and NF and DNS were found to be unaffected. The optical density of this solution was then measured at 380 mμ using an identical dilution of the aqueous quench into water containing 5 ml. of 20% sodium acetate as the reference solution. The concentration of MeTNB was calculated by dividing the differential optical density reading by the molar extinction coefficient of MeDNB at 380 mμ.

This procedure was calibrated by analyzing several synthetic mixtures of NF, DNS, and MeTNB. For a composition equivalent to a kinetic run at about 10% reacted, the calculated and observed concentrations of NF agreed to within 1%. Those of the minor components, MeTNB and DNS, agreed to within 4 and 7%, respectively. For a composition corresponding to a kinetic run at about 50% reacted, the calculated and observed values of the concentrations of all the polynitro carbanions present agreed to within 3%. There was no evidence of a consistent error in these measurements. The sign of the deviation of the observed from the calculated values of the concentrations was random.

For the kinetic runs in acetic acid buffers, the concentrations of NF and DNS were determined by the same procedure used for determining the concentrations of these species in the perchloric acid runs. Nitrite concentrations were determined by the Griess procedure[40] with the following modifications:

To 1 ml. of sulfanilic acid reagent[40] in a 50-ml. volumetric flask was added an aliquot of standard nitrite solution containing between 2.5 and 5.5 × 10^{-7} mole of nitrite ion. The solutions were rapidly mixed by swirling and the stoppered flask was kept in the dark for exactly 5 min. from the start of addition of the nitrite solution. Then 1 ml. of 1-naphthylamine hydrochloride reagent[40] and 1 ml. of 20%

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[34] A. D. Allen, *J. Chem. Soc.*, 1968 (1954).

[35] M. Anbar, I. Dostrovsky, D. Samuel, and A. D. Yoffe, *ibid.*, 3603 (1954).

[36] J. Hine and W. C. Bailey, *J. Org. Chem.*, **26**, 2098 (1961).

[37] The nitrite ester III was suggested as an intermediate by Dr. M. J. Kamlet of these laboratories.

[38] Unpublished results from these laboratories.

[39] H. Kwart and L. A. Kaplan, *J. Am. Chem. Soc.*, 75, 3356 (1953).

[40] F. D. Snell and C. T. Snell, "Colorimetric Methods of Analysis," Vol. II, 3rd Ed., D. Van Nostrand Co., Inc., New York, N. Y., 1948, p. 804.

sodium acetate were added as rapidly as possible and the resulting magenta solution was diluted to volume with distilled water. After standing at ambient temperature for exactly 10 min., the optical density of the solution was measured at 520 mμ (1-cm. cell) at 10.0, 10.5, and 11.0 min. after the addition of the 1-naphthylamine hydrochloride reagent. The three optical density values were averaged and ϵ_{520} was calculated from the mean value of the measurements by dividing by the concentration of nitrite. For 14 determinations, ϵ_{520} was found to be $3.93 \pm 0.08 \times 10^4$ l. mole^{-1}. The above procedure must be strictly adhered to since the concentration of the azo dye formed depends upon the times allotted for the diazotization and coupling reactions. Changes in the above procedure will alter the value of ϵ_{520} obtained for a given nitrite concentration.

Nitrite determinations during a kinetic run were carried out using a suitable aliquot of the same aqueous quench that was used for determining the concentrations of NF and DNS. Since the observed optical density at 520 mμ is not a linear function of the nitrite concentration over a wide concentration range, the size of the aliquot selected was such that the optical density readings were between 0.200 and 0.400. The optical density is a linear function of the concentration of nitrite in this region. The presence of the reactants and other products formed in the kinetic run did not interfere with this analytical procedure.

Kinetic Studies in Perchloric Acid Solutions. In a typical run, 10 ml. of 0.4970 *M* perchloric acid in water, 5 ml. of 1.000 *M* methyl acrylate in dioxane, 5 ml. of 1.000 *M* sodium perchlorate in water, 20 ml. of dioxane, and about 40 ml. of 50 v./v. % dioxane were placed in a 100-ml., low-actinic volumetric flask and the solution thermostated at 45 ± 0.05° for at least 30 min. Ten milliliters of 9.90×10^{-3} *M* nitroform in water was added to the thermostated solution and it was diluted to volume with thermostated 50 v./v. % dioxane. The solution was mixed by shaking and returned to the thermostat. At various times, two identical aliquots were withdrawn and simultaneously quenched as described above. The concentrations of NF, DNS, and MeTNB were determined as described in the analytical procedures section and from these data the rate constants were evaluated as described in the discussion portion of this paper. The data from this kinetic run are given in Figure 1.

Since nitroform is not completely dissociated in 50% dioxane at perchloric acid concentrations greater than 0.025 *M*, the fraction ionized was determined for each perchloric acid concentration at which a kinetic run was carried out. In a typical determination, 5 ml. of 3.07×10^{-4} *M* nitroform in water, 5 ml. of 0.4970 *M* perchloric acid in water, 2.50 ml. of 1.000 *M* sodium perchlorate in water, and 12.50 ml. of dioxane were placed in a 50-ml. volumetric flask and thermostated at 45° for 30 min. This solution was diluted to volume with thermostated 50 v./v. % dioxane. The optical density of this solution at 350 mμ is 0.428. The optical density of 3.07×10^{-5} *M* nitroform in 0.002 *M* sodium hydroxide, 50 v./v. % dioxane, at 350 mμ is 0.442. Therefore, the fraction ionized at this acidity is 0.97. At other acidities, the following data were obtained.

[HClO$_4$]	% ionized
0.1491	86
0.0994	95
0.0497	97
0.02485	≈100

There was no significant difference between the values of the per cent ionized at 35 and 45°.

Kinetic Studies in Acetic Acid Buffers. In a typical run, 30 ml. of 1.033 *M* acetic acid in dioxane, 10 ml. of 1.000 *M* sodium acetate in water, 10 ml. of 1.000 *M* methyl acrylate in dioxane, 20 ml. of water, and about 15 ml. of 50 v./v. % dioxane were thermostated in a 100-ml., low-actinic volumetric flask at 45 ± 0.05° for at least 30 min. Ten milliliters of 0.0968 *M* nitroform in water was added to the thermostated solution and it was diluted to volume with thermostated 50 v./v. % dioxane, mixed by shaking, and returned to the thermostat. At suitable time intervals, 5-ml. aliquots were withdrawn and quenched by diluting to 100 ml. with distilled water. A 4-ml. aliquot of the aqueous quench was diluted to 50 ml. with water and 5 ml. of 20% sodium acetate and then assayed for NF and DNS as described in the analytical procedures section. The concentration of nitrite present was determined by assaying a suitable aliquot of the aqueous quench as described above. Rate constants were evaluated from these data as described in the Discussion portion of this paper. The data obtained from this kinetic run are presented in Figure 4.

Stability of Methyl 4,4-Dinitro-2-hydroxybutyrate, DNS, in Acidified 50% Dioxane. Ten milliliters of 0.100 *M* DNS in water, 20 ml. of dioxane, and about 50 ml. of 50 v./v. % dioxane were thermostated at 45 ± 0.05° for 30 min. in a 100-ml., low-actinic volumetric flask. To this solution was added 10 ml. of 0.9748 *M* hydrochloric acid. It was diluted to volume with thermostated 50 v./v. % dioxane, mixed by shaking, and returned to the thermostat. After 1 hr., a 5-ml. aliquot was diluted to 50 ml. with water and then 4 ml. of this solution was diluted to 100 ml. with water and 5 ml. of 20% sodium acetate to buffer out the hydrochloric acid. The optical density of this final dilution at 380 mμ was 0.680. For 0.100 *M* DNS similarly diluted, the calculated O.D.$_{380}$ = 0.675.

Aliquots of the reaction mixture were taken and similarly diluted after 5 and 23 hr. The values of O.D.$_{380}$ for these samples were 0.677 and 0.664. From these results, DNS was considered to be stable for at least 5 hr. under typical kinetic conditions in acidic media.

In an identical run which was 0.0400 *M* in methyl acrylate, less than 3% of the DNS had been lost after 6.7 hr.

Stability of Nitrite in Acetic Acid Buffers. Thirty milliliters of 1.033 *M* acetic acid in dioxane, 10 ml. of 1.000 *M* sodium acetate in water, 20 ml. of water, and 0.340 g. of sodium nitrite were added to a 100-ml., low-actinic volumetric flask together with about 35 ml. of 50 v./v. % dioxane. After thermostating at 35 ± 0.05° for 30 min., the solution was made up to volume with thermostated 50 v./v. % dioxane, mixed by shaking, and returned to the thermostat. A 3-ml. aliquot of the solution was taken immediately and analyzed for nitrite as described above. This procedure was repeated for aliquots taken after 100 and 200 min. The data obtained are as follows: $10^3[\text{NO}_2^-]$ at 0 min., 5.24; at 100 min., 5.20; and at 200 min., 5.17.

It can be seen that about 1.3% of the total nitrite has been lost in 3.3 hr. This is about the precision of the analytical procedure. Since this buffer ratio and concentration corresponds to the most acidic buffer used in the kinetic runs, nitrite can be considered to be stable in all of the acetic acid buffers used in these kinetic studies.

Preparation of Dimethyl 4,4-Dinitro-2-hydroxyheptanedioate, C$_9$. One-hundredth of a mole (1.89 g.) of potassium trinitromethide, 0.02 mole (1.96 g.) of potassium acetate, and 0.05 mole (4.30 g.) of methyl acrylate were refluxed in 20 ml. of 50% dioxane for 150 min. The reaction was monitored by measuring the changes in its ultraviolet spectrum with time. These spectra showed that at the end of 150 min. the concentration of DNS in the reaction mixture was at a minimum; maximum yield of C$_9$.

The two-phase mixture was cooled to ambient temperature and extracted with four 25-ml. portions of ether. The combined ether extracts were washed with water, dried over Drierite, and decolorized with Darco brand charcoal. The resulting ether solution was concentrated to about 20 ml. and *n*-pentane was added to the cloud point while boiling on the steam bath. A crystalline solid separated on cooling yielding 1.30 g., m.p. 74–75° (lit.[1] m.p. 74.6–76.3°). No attempt was made to isolate additional crops from the mother liquors.

The preparation involving the use of O^{18}-enriched water was carried out by substituting 10 ml. of 5 atom % O^{18}-enriched water for the natural water in the reaction solvent.[41]

For the synthesis of C$_9$ from DNS, 0.01 mole (2.46 g.) of DNS,[3] 0.02 mole (1.72 g.) of methyl acrylate, and 0.01 mole (0.98 g.) of potassium acetate were refluxed in 14 ml. of 50% dioxane–H$_2$O^{18} for 150 min. The product was isolated as described in the previous preparation. The product (0.89 g.) melted at 73.8–74.7°.

Equilibration of Potassium Trinitromethide with 50% Dioxane–H$_2$O^{18}. To a solution of 0.01 mole (0.98 g.) of potassium acetate in 5 ml. of dioxane and 5 ml. of water, 5 atom % excess of O^{18}, was added 0.01 mole (1.89 g.) of potassium trinitromethide. The mixture was heated on the steam bath for about 150 min. and cooled in ice. The potassium trinitromethide that crystallized out was collected on a Büchner funnel, washed with methanol and ether, and air dried.

The yellow salt was immediately suspended in 30 ml. of *n*-pentane, and dry hydrogen chloride was passed through the suspension until the yellow color was discharged. The mixture was filtered to remove suspended potassium chloride and, on cooling the filtrate in a freezer, nitroform crystallized from the solution. The product was rapidly separated by filtration and stored in the freezer.

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(41) Volk Radiochemical Co., Chicago, Ill. The hydrogen/deuterium ratio of the isotopically enriched water was normalized to that of natural water.

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Appendix

After this manuscript was written, a communication appeared,[42] describing preliminary kinetic results of a study of the addition of trinitromethane to methyl acrylate in water at 20°. Reaction rates were measured under pseudo-first-order conditions. However, it is not clear whether the rate constants were calculated from raw optical density data at 350 mμ or from true trinitromethide ion concentrations at various times. At various acidities, 0.4 *M* hydrochloric acid, pH 2 (acetate ion and hydrochloric acid) and pH 7 (phosphate buffer), the second-order rate constant for the reaction was *constant;* $k_N^{20°} = 3.20 \pm 0.03 \times 10^{-4}$ l. mole^{-1} sec.$^{-1}$. It was concluded that the reactions forming MeTNB are *not* subject to acid catalysis; *the formation and not the protonation of the intermediate carbanion An$^-$ is rate determining.*

Though aware of our earlier work[3] which qualitatively describes the duality of reaction paths available for the intermediate carbanion An$^-$, they do not, in their kinetic treatment, take into account the possibility of compensating reaction rates for these paths, k_M and k_D in our notation, giving the over-all reaction rate, k_T in our notation, the appearance of an uncatalyzed reaction over a wide acidity range. Such a situation could arise as follows. Let

$$k_T = \frac{k_1(k_{HA}[HA] + k_2)}{k_{-1} + k_{HA}[HA] + k_2}$$

$$k_M = \frac{k_1 k_{HA}[HA]}{k_{-1} + k_{HA}[HA] + k_2}$$

$$k_D = \frac{k_1 k_2}{k_{-1} + k_{HA}[HA] + k_2}$$

where k_T (equivalent to Novikov's k_N), k_M, and k_D are the previously defined experimental rate constants at a given acidity, $k_{HA}[HA]$ is the specific rate of protonation of the intermediate carbanion An$^-$ by any acid including the solvent, and the other rate constants have been defined previously. For our data in 50% dioxane, the above equations completely describe the observed kinetics. We find that k_T increases by about a factor of 2 on passing from acetic acid buffers to 0.15 *M* perchloric acid (Tables I and II) whereas Novikov's k_N values are *constant* over a somewhat wider acidity range. We also find the rate of formation of MeTNB to be subject to general acid catalysis. For our system $k_{-1} \approx k_{HA}[HA] \approx k_2$.[43]

To reconcile this discrepancy between the two studies, let us consider what will be the effect on the observed kinetics of an increase in both $k_{HA}[HA]$ and k_2 to the point where $k_{HA}[HA] >> k_{-1} << k_2$ and $k_{HA}[HA] \approx k_2$ over the acidity range studied.[44] Since K_{HA} for water and carboxylic acids generally increases by about two powers of ten on going from 50% dioxane to water, k_{HA} might be expected to increase as the rate of protonation is a function of the strength of the acid.[45]

For this condition, the rate of the over-all reaction, k_N in Novikov's notation, has the form $k_T = k_1$, and is equal to the rate of formation of the intermediate carbanion An$^-$. However, the partial rates k_M and k_D have the form

$$k_M = \frac{k_1 k_{HA}[HA]}{k_2 + k_{HA}[HA]}$$

$$k_D = \frac{k_1 k_2}{k_2 + k_{HA}[HA]}$$

Therefore, the rate of disappearance of trinitromethide ion would not be subject to acid catalysis but the rate of formation of MeTNB would still be an acid-catalyzed reaction. The rate of formation of the α-hydroxy ester DNS would be inversely proportional to the acidity, except at extremely low acidities where k_2 may become much greater than $k_{HA}[HA]$ and $k_D = k_1$.

To test this hypothesis, we carried out two kinetic runs in water at 20°. The first run, 0.01243 *M* perchloric acid, was monitored similarly to those in 50% dioxane. The second run, in an acetic acid–acetate buffer, was monitored like those runs in 50% dioxane. For this run, we also followed the rate of appearance of MeTNB.[46] The data from these runs are presented in Table V.

Table V[a]. Reaction of Trinitromethide Ion with Methyl Acrylate in Water at 20° ($\mu = 0.1$)

Buffer	$10^4 k_T$	$10^4 k_M$	$10^4 k_D$
$HClO_4$, 0.01243 *M*[b]	3.75	2.78 ± 0.06	0.97
HOAc–OAc$^-$, 0.1 *M*, HA/A$^-$ = 1[c]	3.68	1.76 ± 0.07	2.07 ± 0.06

[a] Rate constants in units of l. mole^{-1} sec.$^{-1}$. [b] $10^4[NF]_0 = 9.80$, $[MeA]_0 = 0.1000$. [c] $10^4[NF]_0 = 9.93$, $[MeA]_0 = 0.1400$.

Inspection of the data in Table V shows that although the values of k_T are essentially constant, k_M increases by a factor of 1.6 on going from the acetic acid buffer to perchloric acid; *the formation of MeTNB is subject to acid catalysis.* As observed in 50% dioxane, k_D decreases with increasing acidity. Based on these preliminary results, we believe that a thorough study of this reaction in the aqueous system would yield results that are compatible with our data in 50% dioxane.

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(42) S. S. Novikov, L. A. Nikonova, and V. I. Slovetskii, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 395 (1965).

(43) For the kinetic runs at high perchloric acid concentrations, we are approaching the acidity region where $k_{-1} \approx k_2 << k_{HA}[HA]$. Under these conditions, $k_T = k_1$ and $k_M = k_1$; the rate of formation of the intermediate carbanion An$^-$ and not its protonation is rate determining for the reactions leading to the formation of MeTNB.

(44) Part of this change could be effected by a decrease in k_{-1}. Several other possibilities are available; $k_{HA}[HA] >> k_{-1} \approx k_2$, etc. As these do not fit our observed data in water, *vide infra*, they will not be considered.

(45) A referee has suggested that a decrease in the rate constants for the protonation of the carbanion would be expected because of the increased ion solvating power of the medium on going from 50% dioxane to water. However, the decrease in these rate constants due to the increased solvating power of the medium should be more than offset by the increase in catalytic efficiency of the acid.

(46) For this run, values of k_D and k_M were calculated from the slopes of plots of $[NO_2^-]$ and [MeTNB] *vs.* time (Table V) as well as from the equations $k_T = k_M + k_D$ and $[NO_2^-]/[MeTNB] = k_D/k_M = 1.12 \pm 0.03$. The values of the rate constants obtained from the ratio method, $10^4 k_D = 1.95$, $10^4 k_M = 1.73$ l. mole^{-1} sec.$^{-1}$, agreed quite well with those calculated by the slope–time procedure.