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**KINETICS AND MECHANISM FOR THE BASIC
HYDROLYSIS OF BIS (2,2-DINITROPROPYL)
ACETAL (BDNPA) AND BIS (2,2-DINITROPROPYL)
FORMAL (BDNPF)**

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RESEARCH AND TECHNOLOGY DEPARTMENT

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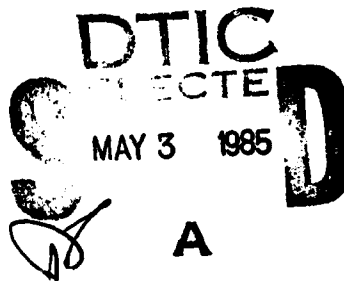
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$-d(\text{BDNPA})/dt = k_1(\text{BDNPA}) = k_2(B) (\text{BDNPA})$, where k_1 is the first order rate constant with excess base, B , BDNPA and BDNPF were found to react faster in dioxane-water than in water. The rates of disappearance of both BDNPA and BDNPF were very nearly equal to one half the combined rates for the formation of nitrite and 1,1-dinitroethane anions, and suggest concurrent competing E-2 elimination (78 ± 5%) and SN-2 nucleophilic displacement (20 ± 3%) reactions with base. On the basis of relative k_2 values, BDNPA and BDNPF were found to react forty times faster with aqueous base than triethyleneglycol dinitrate (TEGDN), but one thousand times slower than 1,3,5-triaza-1,3,5-trinitro-cyclohexane (RDX). The kinetics of the alkaline hydrolysis of BDNPA and BDNPF are discussed in terms of the products formed, and mechanisms are suggested for the formation of these products.

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EXECUTIVE SUMMARY

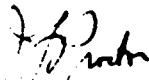
The kinetics for the alkaline homogeneous hydrolysis of bis(2,2-dinitropropyl) acetal (BDNPA) and bis (2,2-dinitropropyl) formal (BDNPF) in water and 53 percent dioxane-water with sodium hydroxide concentrations between 0.14 and 1.9 molar and temperatures between 40° and 70° have been investigated. Both BDNPA and BDNPF were found to react with slightly more than four moles of base to yield nitrite, 1,1-dinitroethane, acetate, and formate anions. Good second order rate constants were obtained for both BDNPA and BDNPF for the expression, $-d(\text{BDNPA})/dt = k_1(\text{BDNPA}) = k_2(\text{B}^-)(\text{BDNPA})$, where k is the first order rate constant with excess base, B^- . BDNPA and BDNPF were found to react faster in dioxane-water solutions than in water. The rates of disappearance of both BDNPA and BDNPF were very nearly equal to one half the combined rates for the formation of nitrite and 1,1-dinitroethane anions, and suggest concurrent competing E-2 elimination (78 ± 5 percent) and S_N -2 nucleophilic displacement (20 ± 3 percent) reactions with base. On the basis of relative k_2 values, BDNPA and BDNPF were found to react forty times faster with aqueous base than triethylene glycol dinitrate (TEGDN), but one thousand times slower than 1,3,5-triaza-1,3,5-trinitrocyclohexane (RDX). The kinetics of the alkaline hydrolyses of BDNPA and BDNPF are discussed in terms of the products formed, and mechanisms are suggested for the formation of these products.

FOREWORD

This work was supported by the Naval Sea Systems Command (SEA 62R), Washington, D.C. 20362, under the title: "Pollution Potential of Explosives in Water;" on Task No. SF 65559691 as part of the Ordnance Pollution Abatement Block Program.

Since the loading and reclamation of Navy PBX ingredients often involve large quantities of water which can become contaminated, it is essential that reliable methods be available to measure the extent of this contamination so that clean up procedures can be initiated. Adsorptive, hydrolytic, and photolytic methods are being investigated in order to assess their potential as means to remove these contaminants efficiently and with no adverse effect on the environment. This report describes the alkaline hydrolysis of bis (2,2-dinitropropyl) acetal (BDNPA) and bis (2,2-dinitropropyl) formal (BNDPF).

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INTRODUCTION

During the loading or reclamation of Naval ordnance, large volumes of water often become contaminated with in-service energetic materials. In order to assess the extent of this contamination and to monitor the efficiency of any clean-up procedure employed, it is essential that reliable methods be available for the detection and analysis of the specific materials involved. For hydrolytic^{1,2,3} photolytic^{4,5} or microbiological^{6,7} procedures which involve chemical changes, it is extremely important that the chemistry be understood as much as possible, and that the respective transformation products be identified so that reasonable procedural choices may be made. Ideally, these transformation products should not produce any adverse effects on the environment. This report describes the kinetics and mechanisms for the basic hydrolysis of bis (2,2-dinitropropyl) acetal (BDNPA) and bis (2,2-dinitropropyl) formal (BDNPF).

EXPERIMENTAL

MATERIALS

Bis (2,2-dinitropropyl) acetal (BDNPA) and bis (2,2-dinitropropyl) formal

1. Hoffsommer, J.C., Glover, D.J. and Burlinson, N.E., "Kinetics and Mechanism for the Alkaline Homogeneous Hydrolysis of 1,1,1-Trimethylolethane Trinitrate (MTN)," J. Org. Chem., Vol 48, 1983, pp. 315-321.
2. Hoffsommer, J.C., Kinetics and Mechanism for the Alkaline Homogeneous Hydrolysis of Triethyleneglycol Dinitrate (TEGDN), NSWC TR 83-110, 23 May 1983.
3. Hoffsommer, J.C., Kubose, D.A., and Glover, D.J., "Kinetic Isotope Effects and Intermediate Formation for the Aqueous Alkaline Homogeneous Hydrolysis of 1,3,5-Triaza-1,3,5-trinitrocyclohexane (RDX)," J. Phys. Chem., Vol 81, 1977, pp. 380-385.
4. Glover, D.J., Photolysis of Metriol Trinitrate II, Ultraviolet Radiation Plus Ozone, NSWC TR 82-428, 1 Aug 1982.
5. Glover, D.J. and Hoffsommer, J.C., Photolysis of RDX. Identification and Reaction of Products, NSWC TR 79-349, 1 Dec 1979.
6. Hoffsommer, J.C., Kaplan, L.A., Glover, D.J., Kubose, D.A., Dickinson, C., Goya, H., Kayser, E.G., Groves, C.L., and Sitzman, M.E., Biodegradability of TNT: A Three Year Pilot Study, NSWC TR 77-136, 13 Feb 1978.
7. McCormick, N.G., Cornell, J.H., and Kaplan, A.M., "Biodegradation of Hexahydro-1,3,5-Trinitro-1,3,5-Triazine (RDX)," Applied and Environmental Microbiology, Vol 42, No. 5, 1981, pp. 817-823.

(BDNPF) were prepared and purified from 2,2-dinitropropanol and acetaldehyde or formaldehyde in sulfuric acid according to the procedure of Shipp and Hill.⁸ 2-Nitro-1-propanol (Aldrich Chemical Company) was checked for purity by liquid chromatography (LC). Formic acid (Eastman Organic Chemicals) was determined to be 98.2% pure by acid titration. Glacial acetic acid and sodium nitrite were obtained commercially as analytical reagents, and together with formic acid were used as ion chromatographic (IC) standards. Distilled water and LC grade organic solvents were used in all experiments.

ANALYSES

Concentrations of bis (2,2-dinitropropyl) acetal (BDNPA) and bis (2,2-dinitropropyl) formal (BDNPF) were determined with a liquid chromatograph (Hewlett-Packard, Model 1084A), equipped with a variable wavelength detector (HP Model 1030) and a variable injector using a 10 micrometer RP-8 column, 25 cm X 4.6 mm ID at 40°C; eluent, 53% methanol/water (v/v); flow, 2.5 ml/min.; detector wavelength, 220 nm; attenuation, 0.0064 AU/cm. Under these conditions, a 100 microliter injection of 8.60×10^{-5} M BDNPF gave a peak height of 107.8 mm with a retention time of 4.0 minutes, while a 100 microliter injection of 8.32×10^{-5} M BDNPA gave a peak height of 83.1 mm with a retention time of 5.1 minutes.

In some cases, due to the low solubility of BDNPA and BDNPF in water (approximately 4.7×10^{-5} M at room temperature), analyses were conducted by gas chromatography (GC) employing the nickel-63 electron capture (ec) detector.⁹ A research gas chromatograph, HP model 5754, equipped with a Model 5763A nickel-63 electron capture (ec) detector and a Model 7128A Mosely dual channel recorder was used for the analyses of BDNPA in water under the following conditions: 4 ft X 1/4 in. glass column, packed with 3.52% Dexsil 300 GC on 80/100 high performance chromosorb W (Varian Associates); column, 175°C; injector, 185°C; 209 ml/min, argon/methane, 95/5 (v/v); Ni-63 ec

8. Shipp, K.G., and Hill, M.E., "Acetal Preparation in Sulfuric Acid," J. Org. Chem., Vol 31, 1956, p. 835.

9. Hoffsommer, J.C., Kubose, D.A., and Glover, D.J., Microanalysis of Selected Energetic Nitro Compounds by Gas/Liquid Chromatography (GC/LC), NSWC TR 80-535, 14 Jan 1981.

detector, 285°C; attenuation, 10 X 80. Under these conditions a 1.0 microliter injection of 6.37×10^{-6} M BDNPA and 1.69×10^{-6} M TNT (as internal standard) in pesticide grade benzene (Fisher Scientific Company) gave the following peak heights and retention times: 145.5 mm, 1.57 min. (TNT); and, 126 mm, 4.64 min. (BDNPA).

Peak heights at the respective retention times for both the LC and GC analysis of BDNPA and BDNPF were used to calculate unknown concentrations by comparison to standards of BDNPA and BDNPF of known concentrations. Precision of repeated injections was usually better than $\pm 3\%$.

Nitrite ion concentrations were measured with an ion chromatograph (Dionex Model 10) using a 3 mm by 500 mm anion separator column with a 3 mm by 150 mm pre-column, and a 6 mm by 250 mm anion suppressor column; eluent, 0.003 M sodium bicarbonate and 0.0024 M sodium carbonate in distilled water; flow rate, 2.3 ml/min.; sensitivity, 3 micromhos, full scale. Typically, under these conditions, a 100 microliter injector of a 4.33×10^{-4} M aqueous nitrite ion solution gave a peak height of 175 mm with a retention time of 5.4 minutes.

Formate and acetate ion concentrations were ascertained by using a 0.005 M borax solution in water as eluent under the conditions outlined for the nitrite ion analysis. Typically, a 100 microliter injection of a mixture of 3.49×10^{-4} M acetate ion and 5.3×10^{-4} M formate ion gave the following peak heights and retention times: 54.0 mm, 4.5 min. (acetate ion); and, 115.2 mm, 6.5 min. (formate ion).

For quantitative measurements the peak heights of nitrite, formate and acetate ions were compared to those of standard solutions. Precision of repeated injections was usually better than $\pm 3\%$.

Concentrations of 1,1-dinitroethane anion were monitored spectrometrically¹⁰ at 380 nm where the 1,1-dinitroethane anion is reported to have a molar absorbancy of 16,880.

10. Glover, D.J., "Spectrophotometric Method for the Quantitative Analysis of Trinitromethyl Compounds," Tetrahedron, Vol 19, Suppl. 1, 1963, pp. 219-233.

KINETICS

Stock aqueous or dioxane/water [53/47 (v/v)] solutions of BDNPA or BDNPF and sodium hydroxide were thermostated separately in 10 ml volumetric flasks in a constant temperature bath held to $\pm 0.05^\circ\text{C}$ at least one-half hour before a run. Concentrations of stock solutions were chosen so that on mixing the final base concentration was at least fifty times the BDNPA or BDNPF concentration. Appropriate aliquots were taken periodically by means of a micropipet and added to a known volume of distilled water, resulting in concentrations of BDNPA or BDNPF between 10^{-4} and 10^{-5} M. Base concentrations were determined at the conclusion of a run by standard acid titration of an aliquot of the reaction solution. Ion chromatographic (IC) analyses for nitrite, acetate and formate anions were carried out directly on the diluted aqueous samples as were the spectrophotometric determinations of 1,1-dinitroethane anion. Liquid chromatographic (LC) analyses were conducted on a one to two millimeter portion of the diluted sample after adjusting the pH to 7-8 by the addition of small portions of solid potassium dihydrogen phosphate. Whenever gas chromatography (GC) was used to analyze BDNPA, appropriate aliquots of the reaction mixture at various times were added to 4.0 millimeters of 0.1 M aqueous potassium dihydrogen phosphate, followed by extraction with 4.0, 3.0, or 2.0 milliliters of benzene (depending on the extent of the reaction) containing TNT as an internal standard.

RESULTS AND DISCUSSION

The alkaline hydrolyses of both BDNPA and BDNPF were found to be complex and involved a number of bond-scissions. The products formed (Table 1) were nitrite, 1,1-dinitroethane, acetate and formate anions; while, in addition, a trace of 2-nitro-1-propanol was detected among the BDNPF hydrolysis products. The formation of these products involved cleavage of carbon-nitrogen, as well as carbon-oxygen bonds. The formation of nitrite anion accounted for about 50% of the available nitrogen present for both BDNPA and BDNPF (Tables 2 and 3) while, 1,1-dinitroethane anion represented only about 25% of the available nitrogen. Together, these two products comprised about 75% of the available nitrogen and left 25% among the hydrolysis products.

The formation of acetate and formate anions (Table 1) for both BDNPA and BDNPF showed disruption of the acetal and formal carbon-oxygen bonds.

Regression of BDNPA or BDNPF formation,^{8,11} would be expected to produce two moles of 1,1-dinitroethane anion, two moles of formaldehyde, and one mole of acetaldehyde from BDNPA, but two moles of 1,1-dinitroethane anion, and three moles of formaldehyde from BDNPF. That this was not the case is seen in Table 1, where only 19.5% of the theoretical 1,1-dinitroethane anion was formed from BDNPA hydrolysis ($19.5\% = (12.7)/(2)(32.6) \times 100$), and 25% of the theoretical 1,1-dinitroethane anion was formed from BDNPF ($25.0\% = (18.4)/(2)(36.7) \times 100$). In addition, no formaldehyde was detected among the hydrolysis products of either BDNPA or BDNPF by the chromatropic acid test.¹² Furthermore, the absence of methanol among the reaction products, as shown by gas chromatographic analysis, precludes a Cannizzaro-type reaction with formaldehyde and base.¹³

Although both acetate (CH_3COO^-) and formate (HCOO^-) ions might be expected to result from BDNPA hydrolysis, it is somewhat surprising that the acetate ion concentration (Table 1) was almost twice the formate ion concentration. These results indicate carbon-carbon bond cleavage in the 2,2-dinitropropyl group. Support for this theory is the formation of acetate ion in the hydrolysis of BDNPF although in a smaller yield than observed for BDNPA. The total carbon found among the products identified was 32.4% from BDNPA hydrolysis and 37.6% from BDNPF hydrolysis.

Both BDNPA and BDNPF consumed approximately four moles of base for each mole hydrolyzed, Table 1. The fact that each mole of BDNPA and BDNPF contains four nitro groups, and that nearly four moles of base were consumed for each mole reacted may be somewhat fortuitous since only about 75% of the theoretical nitro groups were accounted for among the products listed in Tables 1, 2, and 3. However, the molar yields of NO_2^- and $\text{CH}_3\text{C}(\text{NO}_2)_2^-$,

8. Shipp, K.G. and Hill, M.E., "Acetal Preparation in Sulfuric Acid," J. Org. Chem., Vol 31, 1956, p.835.

11. Hall, T.N., "Reactions of Nitro Alcohols II. The Kinetics of Dissociation of 2,2-Dinitropropanol in Aqueous Buffers," J. Org. Chem., Vol 30, 1965, p. 3157.

12. Eegriwe, E., Z. Anal. Chem., Vol 110, 1937, p. 22 (with modifications by Cares, J.W., Amer. Ind. Hyg. Assoc. Vol 29, 1968, p. 405).

13. Beringer, F. M., Ed. Formaldehyde (New York: Reinhold, 1964), p. 214 (reporting work of Fry, H. S., Uber, J. J., and Price, J. W., Recl. Trav. Chim Pays-Bas., Vol. 50 1931, pp 1060-1065).

(Tables 2 and 3) were found to be fairly independent of solvent and base strength, and indicate similar concurrent competing reactions.

Rate constants for the alkaline hydrolysis of BDNPA or BDNPF are given in Table 4. Where the NaOH concentration was at least fifty times the BDNPA or BDNPF concentration, pseudo first order rate constants, k_1 , were calculated from the expression, $k_1 = t^{-1} \ln(C_0/C_t)$, where t is the time in seconds, and C_0 and C_t represent the initial concentrations of BDNPA or BDNPF and the concentrations at the time, t . Values of k_1 were obtained from the slopes of $\ln C_t$ versus time plots. Linear regression equations for the specific data points were generated by a least squares method which gave the error in k_1 and the correlation coefficient to a straight line fit. At the 95% confidence level, the correlation coefficients were better than 0.99 for the number of data points listed. A typical plot is shown in Figure 1. Second order rate constants, k_2 , listed in Table 4, were calculated from k_1 by the expression, $k_2 = k_1/(\text{NaOH})$. Since the NaOH concentrations were determined by acid titration and are more accurate than the k_1 values, the errors listed for the k_2 values reflect errors in k_1 . The relationships of k_1 and k_2 to the rate expressions for the disappearance of BDNPA or BDNPF are shown in equations (1) through (4) and illustrated for BDNPA.

- (1) $-d(\text{BDNPA})/dt = k_2(\text{NaOH})^x(\text{BDNPA})^y$ (rate expression for disappearance of BDNPA)
- (2) $(\text{NaOH}) \gg (\text{BDNPA})$ (concentration of NaOH much greater than concentration of BDNPA)
- (3) $k_1 = k_2(\text{NaOH})^x = t^{-1} \ln(\text{BDNPA})_0/(\text{BDNPA})_t = t^{-1} \ln(\text{BDNPA})_0/(\text{BDNPA})_t$ (pseudo first order rate expression for disappearance of BDNPA)
- (4) $k_2 = k_1/(\text{NaOH})^x$ (relationship between first and second order rate constants)

According to equation (4), if $x = 1$, then k_1 should vary linearly with sodium hydroxide concentration, since k_2 is constant. In this case, the order with respect to the sodium hydroxide concentrations would be one. That this was the case is shown for runs 4 and 5 for BDNPA, as well as for runs 12, 13, and 14 for BDNPF (Table 4).

At a given temperature, both BDNPA and BDNPF were found to hydrolyze much faster in dioxane-water than in water alone. For example, at 70°C (runs 5 and

6, Table 4) BDNPF was found to hydrolyze 9.1 times faster ($62.1/6.8 = 9.1$) in dioxane-water than in water alone. The same was true for BDNPF at 70°C (comparing runs 12, 13, and 14 with runs 15, and 16, Table 4), but in this case BDNPF was found to hydrolyze only 3.1 times faster ($31/10 = 3.1$) in dioxane-water than in water alone.

A reasonable explanation for the hydrolysis rate differences between BDNPA and PDNPF in dioxane-water can be made based on the activation parameters for BDNPA and BDNPF in water (Table 7). The heats of activation, $\Delta H^\ddagger$ are different for BDNPA (23.9 kcal/mole) and BDNPF (27.3 kcal/mole), while the free energy of activation, $\Delta F^\ddagger$ (25.1 kcal/mole) for both BDNPA and BDNPF are practically the same.

Since $\Delta F^\ddagger$ is directly proportional to the rate of reaction by the expression, $\Delta F^\ddagger = -RT \ln (k_2 h) / (kT)$, where h is Planck's constant, and k is Boltzmann's constant; the changes in $\Delta F^\ddagger$ are directly proportional only to the changes in the entropy of activation, $\Delta S^\ddagger$, where $\delta \Delta F^\ddagger$ is zero. Under these conditions, an isokinetic (where rates of reaction are equal) relationship exists and may be expressed in equation (5).¹⁴

$$(5) \quad \delta \Delta H^\ddagger = \beta \delta \Delta S^\ddagger$$

From the data in Table 7, the isokinetic temperature, β , for BDNPA and BDNPF in water was calculated to be 324°K (or 51°C) which is close to 55°C where the hydrolysis rates of BDNPA and BDNPF were observed to be practically the same (Table 4, runs 3 and 8). However, at temperatures higher than the isokinetic temperature, e.g., at 70°C, BDNPF was found to react about 1.5 times faster ($10/6.8 = 1.5$) than BDNPA. Conversely, at temperatures lower than the isokinetic temperature, BDNPF would be expected to hydrolyze slower than BDNPA.

A similar situation must exist for the activation parameters for BDNPA and BDNPF in dioxane-water. Although those for BDNPA were not measured in dioxane-water, a reasonable estimate of $\Delta H^\ddagger$ for BDNPA may be made by comparison with the changes in $\Delta H^\ddagger$ for BDNPF from the solvent water to dioxane-water. Assuming that a 4.5 kcal/mole decrease in $\Delta H^\ddagger$ is the same for BDNPA as for BDNPF in changing from water to dioxane-water (i.e., $\Delta H^\ddagger$ for BDNPA is 19.5

14. Leffler, J. E., J. Org. Chem., Vol. 20, 1955, p 1202

(Kcal/mole), and using the second order rate constant, k_2 , for the hydrolysis of BDNPA in dioxane-water at 70°C (Table 4, run 6), a value of -12 cal/deg for the entropy of activation for BDNPA in dioxane-water may be calculated from the expression in equation (6). The $\Delta S^\ddagger$ estimated for BDNPA in dioxane-water

$$(6) \quad \Delta F^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger = -RT \ln(k_2 h / kT)$$

is as expected on comparison with the $\Delta S^\ddagger$ of BDNPF which becomes 10.9 cal/deg more negative in dioxane-water than in water. In general, decreases in entropies of activation, $\Delta S^\ddagger$, can be expected for reactions in less polar solvents (dioxane-water) relative to the entropies found for the same reaction in polar solvents (water).¹⁵

On the basis of the similar product mole ratios of NO_2^- and $\text{CH}_3(\text{NO}_2)_2^-$ for BDNPA and BDNPF (Tables 2 and 3), there is no reason to suspect a change in mechanism from BDNPA to BDNPF even though in water there is a 3.4 kcal/mole difference in the activation energy, $\Delta H^\ddagger$, Table 7. Indeed, as has been pointed out,¹⁶ reactions having the same mechanism can often differ by activation energies of 5 kcal/mole or more. Plots of $\ln k_2$ versus $1/T$ for BDNPF in water and dioxane-water are shown in Figure 4. Slopes of these lines were used to calculate $\Delta H^\ddagger$ from the expression, $\Delta H^\ddagger = (\text{slope})(R) - RT$. Correlation coefficients were better than 0.99 for the linear regression equation fit by a least squares method.

Tables 5 and 6 show the kinetic data obtained for the disappearance of BDNPA and BDNPF, respectively, together with the formation of nitrite and 1,1-dinitroethane anions. Initial rates of disappearance of BDNPA, $[-d(\text{BDNPA})/dt]$, and the rates of formation of nitrite ion, $[+d(\text{NO}_2^-)/dt]$, and 1,1-dinitroethane ion, $[+d(\text{CH}_3\text{C}(\text{NO}_2)_2^-)/dt]$, calculated for the first 5 minutes were found to be 0.192×10^{-3} M/min., 0.32×10^{-3} M/min. and 0.068×10^{-3} M/min. respectively. Since BDNPA contains two dinitropropyl groups, a statistical correction of 1/2 needs to be applied to the rates of formation of nitrite and 1,1-dinitroethane anions. These results are shown in equation 7.

15. Gould, E. S., Mechanism and Structure in Organic Chemistry, (New York: Holt, Rinehart and Winston), 1959, p. 182.

16. Leffler, J. E., and Grunwald, E., Rates and Equilibrium of Organic Reactions, (New York: John Wiley and Sons), 1963, p. 326.

$$(7) \quad \frac{-d(\text{BDNPA})}{dt} = \frac{1}{2} \left(\frac{+d(\text{NO}_2^-)}{dt} + \frac{+d(\text{CH}_3\text{C}(\text{NO}_2)_2)}{dt} \right)$$

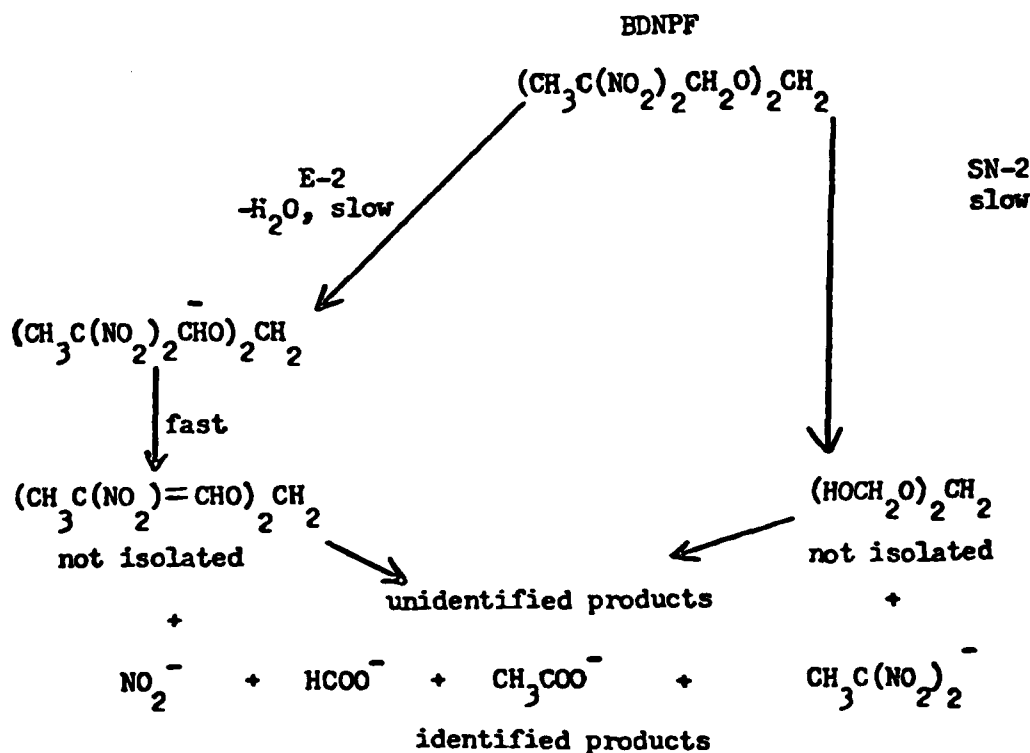
0.192 0.32 0.068 rates $\text{M} \times 10^{-3}/\text{min.}$

In a similar manner, the initial rates for the disappearance of BDNPF, calculated for the first 5 minutes were found to be approximately equal to 1/2 the combined rates for the formation of nitrite and 1,1-dinitroethane anions. These results are shown in equation 8.

$$(8) \quad \frac{-d(\text{BDNPF})}{dt} = \frac{1}{2} \left(\frac{+d(\text{NO}_2^-)}{dt} + \frac{+d(\text{CH}_2\text{C}(\text{NO}_2)_2)}{dt} \right)$$

0.194 0.282 0.090 rates, $\text{M} \times 10^{-3}/\text{min}$

The most probable mechanism for the base hydrolysis of both BDNPA and BDNPF involves two concurrent competing reactions, namely: (1) a concerted E-2 type elimination to form NO_2^- ion, involving a slow proton abstraction from the methylene carbon between the gem-dinitro group and the formal (BDNPF) or acetal (BDNPA) oxygen, followed by a rapid elimination of NO_2^- ion, and, (2) a slow SN-2 nucleophilic displacement on the same methylene carbon to form the 1,1-dinitroethane anion. A schematic for these reactions is shown for BDNPF, $(\text{CH}_3\text{C}(\text{NO}_2)_2\text{CH}_2\text{O})_2\text{CH}_2$, although the same would hold true for BDNPA, $(\text{CH}_3\text{C}(\text{NO}_2)_2\text{CH}_2\text{O})_2\text{CHCH}_3$.



Schematic for the Alkaline Hydrolysis of BDNPF

Since $[d(\text{NO}_2^-)/dt]/[d(\text{CH}_3\text{C}(\text{NO}_2)_2/dt] = (\text{NO}_2^-)/(\text{CH}_3\text{C}(\text{NO}_2)_2)$, the ratios of nitrite anion to 1,1-dinitroethane anion listed in Tables 5 and 6 should be proportional to the ratios of the initial rates found in equations 7 and 8. The ratio found for BDNPA, equation 7, was 4.7 (equal to $0.32/0.068$) while the ratio found for BDNPF, equation 8, was 3.1 (equal to $0.282/0.090$). These values are close to the individual mole ratios, $\text{NO}_2^-/\text{CH}_3\text{C}(\text{NO}_2)_2$, for both BDNPA (Table 5) and BDNPF (Table 6). From these data, it can be seen that the E-2 elimination reaction for both BDNPA and BDNPF is about four times more rapid than the SN-2 nucleophilic reaction. The somewhat lower yield of 1,1-dinitroethane anion for BDNPA (19%) than for BDNPF (25%) indicates that the SN-2 reaction is slightly less important in the case of BDNPA.

Finally, it is of some interest to compare the second order rate constants, k_2 , obtained for the alkaline hydrolyses of several classes of nitro compounds listed in Table 8. From these rates the following order of decreasing stability towards base can be established:

TEGDN (most stable) > MTN >> BDNPA $\cong$ BDNPF >>> RDX (least stable).

The rate data given in Table 4 together with the activation parameters listed in Table 7 are useful in making predictions of the half-lives of BDNPA and BDNPF in water for any base strength desired. At 25°C , the second order rate constants, k_2 , for BDNPA and BDNPF were calculated to be $3.31 \times 10^{-6} \text{ Lmole}^{-1}\text{sec}^{-1}$ and $2.04 \times 10^{-6} \text{ Lmole}^{-1}\text{sec}^{-1}$, respectively. From these values and using equations 3 and 4 at pH 7, the half-lives of BDNPA and BDNPF would be expected to be 6.6×10^4 years and 10.7×10^4 years, respectively. In 0.1 molar sodium hydroxide at 25°C , the half-lives would be expected to be 23.9 days (BDNPA) and 38.7 days (BDNPF).

TABLE 1. ALKALINE HYDROLYSIS OF BDNPA/BDNPF: PRODUCT FORMATION
 $M \times 10^{-3}$

BDNPA ₀ ^a	BDNPF ₀ ^b	NaOH ₀ ^c	NaOH _f ^d	NO ₂ ⁻	CH ₃ C(NO ₂) ₂ ⁻	CH ₃ COO ⁻	HCOO ⁻
32.6 ^e	-	222.6	89.3	66.0	12.7	23.0	13.0
-	36.7 ^f	212.8	57.1	72.8	18.4	14.0	31.8

(a) Dioxane-water: 53/47 (v/v); 70°C; 100% hydrolysis.

(b) Dioxane-water: 53/47 (v/v); 63°C; 100% hydrolysis.

(c) Initial concentration.

(d) Final concentration.

(e) Moles NaOH reacted/Moles BMDPA reacted = 4.09.

(f) Moles NaOH reacted/Moles BDNPF reacted = 4.24.

TABLE 2. ALKALINE HYDROLYSIS OF BDNPA: FORMATION OF NITRITE AND 1,1-DINITROETHANE ANIONS AS A FUNCTION OF BASE STRENGTH AND SOLVENT

Solvent	°C	NaOH ^a	Product Mole Ratio ^b		% Hydrolysis	%Theoretical ^c Nitrogen
			NO ₂	CH ₃ C(NO ₂ ⁻) ₂		
Water ^d	70	0.2076	1.49	0.93	80.6	84
Dioxane- Water ^e	70	0.2226	2.02	0.39	100	70
Ethanol ^f	40	0.1492	2.30	0.35	98.6	75
Ethanol	55	0.1380	2.16	0.39	100	74
Ethanol	55	1.65	1.42	0.71	100	71

(a) Molarity, NaOH >> BDNPA.

(b) (Moles NO₂⁻ or CH₃C(NO₂⁻)₂ formed)/(moles BDNPA reacted).

(c) (2 X Product Mole Ratio CH₃C(NO₂⁻)₂ + Product Mole Ratio NO₂⁻)/4 X 100.

(d) See Table 4, run 4.

(e) Dioxane-water: 53/47 (v/v).

(f) See Table 4, run 1.

TABLE 3. ALKALINE HYDROLYSIS OF BDNPF: FORMATION OF NITRITE AND 1,1-DINITROETHANE ANIONS AS A FUNCTION OF BASE STRENGTH AND SOLVENT

Solvent	°C	NaOH ^a	Product Mole Ratio ^b		% Hydrolysis	%Theoretical ^c Nitrogen
			NO ₂ ⁻	CH ₃ C(NO ₂) ₂ ⁻		
Water ^d	70	0.2180	1.29	0.86	87.0	75
Water ^e	70	0.2128	1.57	0.95	67.8	87
Dioxane- Water ^f	70	0.2257	2.02	0.59	94.0	80
Dioxane- Water	55	0.2101	2.24	0.37	92.3	75

(a) Molarity, NaOH >> BDNPF.

(b) (Moles of NO₂⁻ or CH₃C(NO₂)₂⁻ formed)/(moles BDNPF reacted).(c) (2 X Product Mole Ratio CH₃C(NO₂)₂⁻ + Product Mole Ratio NO₂⁻)/4 X 100.

(d) See Table 4, run 13.

(e) See Table 4, run 12.

(f) See Table 4, run 14.

TABLE 4. KINETIC DATA: RATE CONSTANTS FOR THE ALKALINE HYDROLYSIS OF BDNPA AND BDNPF

Run	Compound	Solvent	°C	NaOH ^a	Data Points	$\times 10^{-4}$	k_2^e
						k_1^b	
1	BDNPA	Ethanol	40	0.1492	7	12.4 ± 1.1	83 ± 7
2	BDNPA	Water	55	0.9393	7	1.13 ± 0.13	1.2 ± 0.1
3	BDNPA	Water	55	1.884	7 ^d	2.9 ± 0.2	1.5 ± 0.1
4	BDNPA	Water	70	0.2076	7	1.4 ± 0.2	6.9 ± 1.1
5	BDNPA	Water	70	0.9767	8	6.6 ± 1.0	6.8 ± 1.0
6	BDNPA	Dioxane-Water ^e	70	0.2014	10 ^f	12.5 ± 0.5	62.1 ± 2.7
7	BDNPF	Dioxane-Water ^e	45	0.1977	5	$0.43 \pm .03$	2.1 ± 0.1
8	BDNPF	Water	55	0.2111	6 ^d	$0.33 \pm .02$	1.5 ± 0.1
9	BDNPF	Dioxane-Water ^e	55	0.1946	7	1.3 ± 0.1	6.5 ± 0.8
10	BDNPF	Dioxane-Water ^e	55	0.1967	6	1.1 ± 0.1	5.7 ± 0.8
11	BDNPF	Water	63	0.2111	6	0.83 ± 0.03	3.9 ± 0.1
12	BDNPF	Water	70	0.1189	7	1.3 ± 0.2	11.0 ± 1.9
13	BDNPF	Water	70	0.2128	10	1.8 ± 0.1	8.5 ± 0.3
14	BDNPF	Water	70	0.2180	7	2.3 ± 0.3	10.6 ± 1.3
15	BDNPF	Dioxane-Water ^e	70	0.2257	9	7.0 ± 0.5	31.1 ± 2.2
16	BDNPF	Dioxane-Water ^e	70	0.1961	10 ^g	6.2 ± 0.4	31.5 ± 1.9

(a) Molarity, NaOH >> BDNPA or BDNPF.

(b) First order rate constant, $k_1 = t^{-1} \ln (C_0/C_t)$, sec⁻¹. Linear regression equations for the data were calculated by a least squares method which gave the error in the rate constant and the correlation coefficient. At the 95% confidence level (Student's t test), correlation coefficients were better than 0.99. Errors in k_1 reflect the standard error/squared deviants value and the t value for the data points used.(c) Second order rate constant, $k_2 = k_1/\text{NaOH}$, Lmole⁻¹sec⁻¹. Errors in k_2 parallel errors in k_1 .

(d) See Figure 1.

(e) Dioxane-water: 53/47 (v/v).

(f) See Table 5 and Figure 2.

(g) See Table 6 and Figure 3.

TABLE 5. KINETIC DATA: ALKALINE HYDROLYSIS OF BDNPA^a

Time, min ^b	BDNPA ^c	M X 10 ⁻³		% Hydrolysis	Mole Ratio NO ₂ ⁻ /CH ₃ C(NO ₂) ₂ ⁻
		NO ₂ ⁻ ^d	CH ₃ C(NO ₂) ₂ ⁻ ^e		
0	3.55	0	0	0	-
0.67	3.38	0.278	0.029	4.79	9.5
2.45	3.03	0.988	0.166	14.6	5.9
4.06	2.71	1.45	0.269	23.7	5.4
5.75	2.45	1.93	0.382	31.0	5.1
7.97	2.02	2.55	0.508	43.1	5.0
10.37	1.64	3.20	0.634	53.8	5.0
12.78	1.39	3.58	0.725	60.8	4.9
19.88	0.95	4.43	0.886	73.2	5.0
47.44	0.098	5.98	1.180	97.2	5.1
67.87	0	6.40	1.223	100	5.2

(a) Solvent: dioxane-water: 53/47 (v/v); NaOH = 0.2014 M; 70°C; See Table 4, run 6.

(b) Obtained with an automatic timer, Precision Scientific Co., Chicago, IL.

(c) Determined by liquid chromatography (LC).

(d) Determined by ion chromatography (IC).

(e) Determined spectrophotometrically with a Cary 16 spectrometer.

TABLE 6. KINETIC DATA: ALKALINE HYDROLYSIS OF BDNPF^a

Time, min ^b	M X 10 ⁻³		Mole Ratio		
	BDNPF ^c	NO ₂ ^{-d}	CH ₃ C(NO ₂) ₂ ^e	% Hydrolysis	NO ₂ ⁻ /CH ₃ C(NO ₂) ₂ ⁻
0	3.67	0	0	0	-
0.56	3.57	0.189	0.005	2.72	-
2.90	3.08	0.890	0.277	16.1	3.2
5.01	2.70	1.41	0.452	26.4	3.1
6.50	2.57	1.64	0.566	30.0	2.9
8.03	2.38	1.75	0.659	35.1	2.7
9.87	2.22	2.01	0.763	39.5	2.6
11.52	2.12	2.20	0.863	42.2	2.5
19.48	1.61	2.88	1.205	56.1	2.4
30.77	1.13	3.56	1.565	69.2	2.3
51.97	0.48	4.60	1.870	86.9	2.5

(a) Solvent: Dioxane-water: 53/47 (v/v); NaOH = 0.1961 M; 70°C; see Table 4, run 16.

(b) Obtained with an automatic timer, Precision Scientific Co. Chicago, ILL.

(c) Determined by liquid chromatography (LC).

(d) Determined by ion chromatography (IC).

(e) Determined spectrophotometrically with a Cary 16 spectrometer.

TABLE 7. ALKALINE HYDROLYSIS OF BDNPA/BDNPF: ACTIVATION PARAMETERS^a

Compound	Solvent	$\Delta H^\ddagger$ ^b	$\Delta F^\ddagger$ ^{b,g}	$\Delta S^\ddagger$ ^{c,h}
BDNPA	Water	23.9 ^d	25.1	-3.5
BDNPF	Water	27.3 ^e	25.0	+7.0
BDNPF	Dioxane-water	22.8 ^f	24.1	-3.9

(a) Calculated from data given in Table 4.

(b) Kcal/mole, at 55°C.

(c) Cal/deg at 55°C.

(d) Calculated from slope of $\ln k_2$ versus $1/T$ for values of k_2 at 55 and 70°C. from the expression, $\Delta H^\ddagger = (\text{slope} \times R) - RT$

(e) Correlation coefficient was 0.998 for the linear regression equation of a plot of $\ln k_2$ versus $1/T$, with an error of $\pm 4.9\%$, Figure 4.

(f) Correlation coefficient was 0.999 for the linear regression equation of a plot of $\ln k_2$ versus $1/T$, with an error of $\pm 2.1\%$, Figure 4.

(g) Calculated from the expression, $\Delta F^\ddagger = -RT \ln (k_2 h/kT)$, where k_2 is the second order rate constant; h is Planck's constant; k is Boltzmann's constant and T is the absolute temperature.

(h) Calculated from the expression, $\Delta S^\ddagger = (\Delta H^\ddagger - \Delta F^\ddagger)/T$.

TABLE 8. RELATIVE RATES OF ALKALINE HYDROLYSIS OF SEVERAL CLASSES OF ENERGETIC COMPOUNDS IN WATER AT 55°C

Class	Compound	$k_2^a \times 10^{-4}$	Relative Rate
Nitrate ester	TEGDN	0.036 ^b	1.0
Nitrate ester	MTN	0.13 ^c	3.6
Geminal dinitro acetal	BDNPA	1.4 ^d	39
Geminal dinitro formal	BDNPF	1.5 ^d	41
Nitramine	RDX ^e	1500	42,000

(a) Second order rate constant in water at 55°C, $\text{Lmole}^{-1}\text{sec}^{-1}$.

(b) Reference 2.

(c) Reference 1.

(d) This study.

(e) Reference 3.

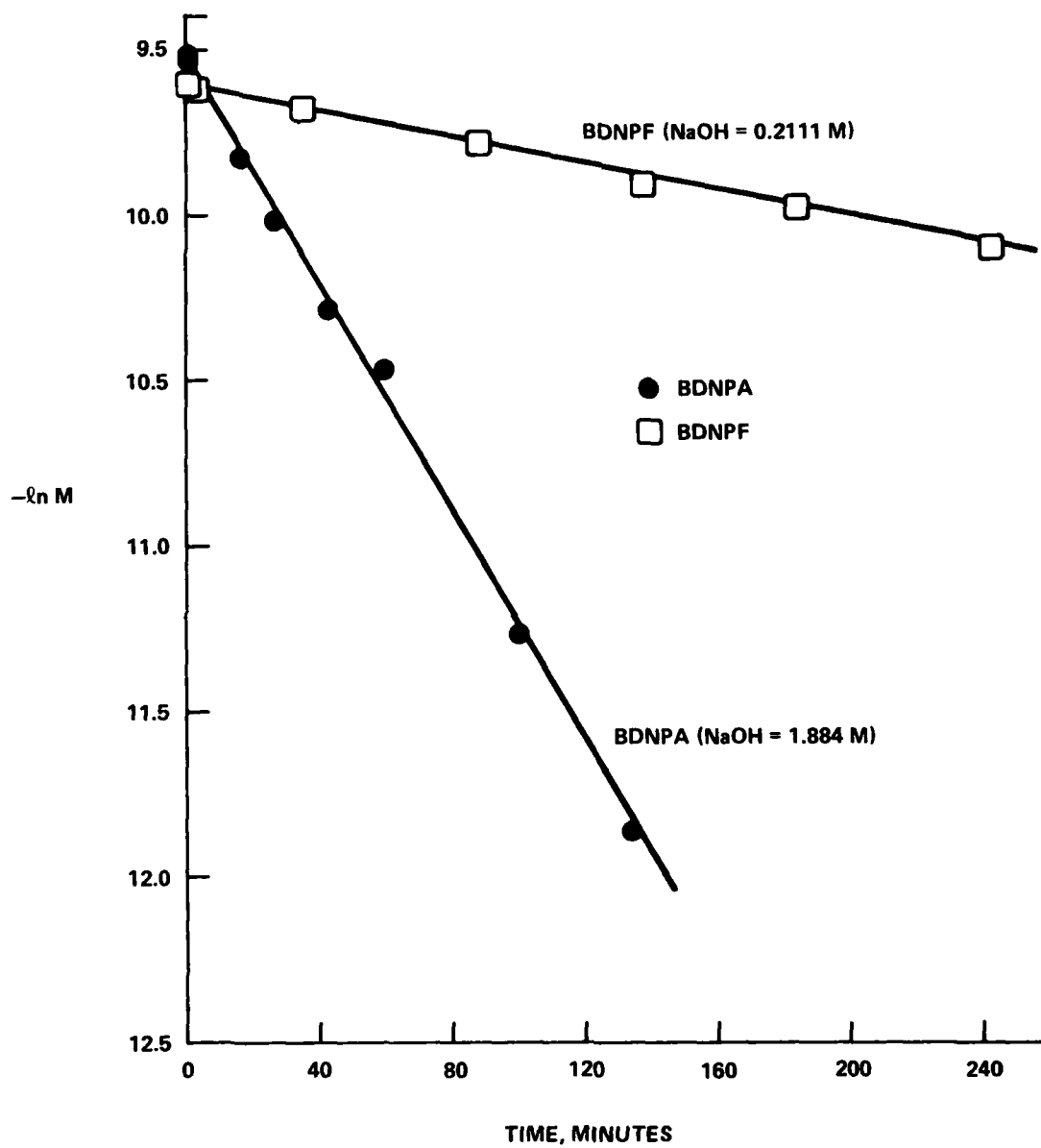


FIGURE 1. ALKALINE HYDROLYSIS OF BDNPA/BDNPF IN WATER AT 55° C
($-\ln$ CONCENTRATION VERSUS TIME)

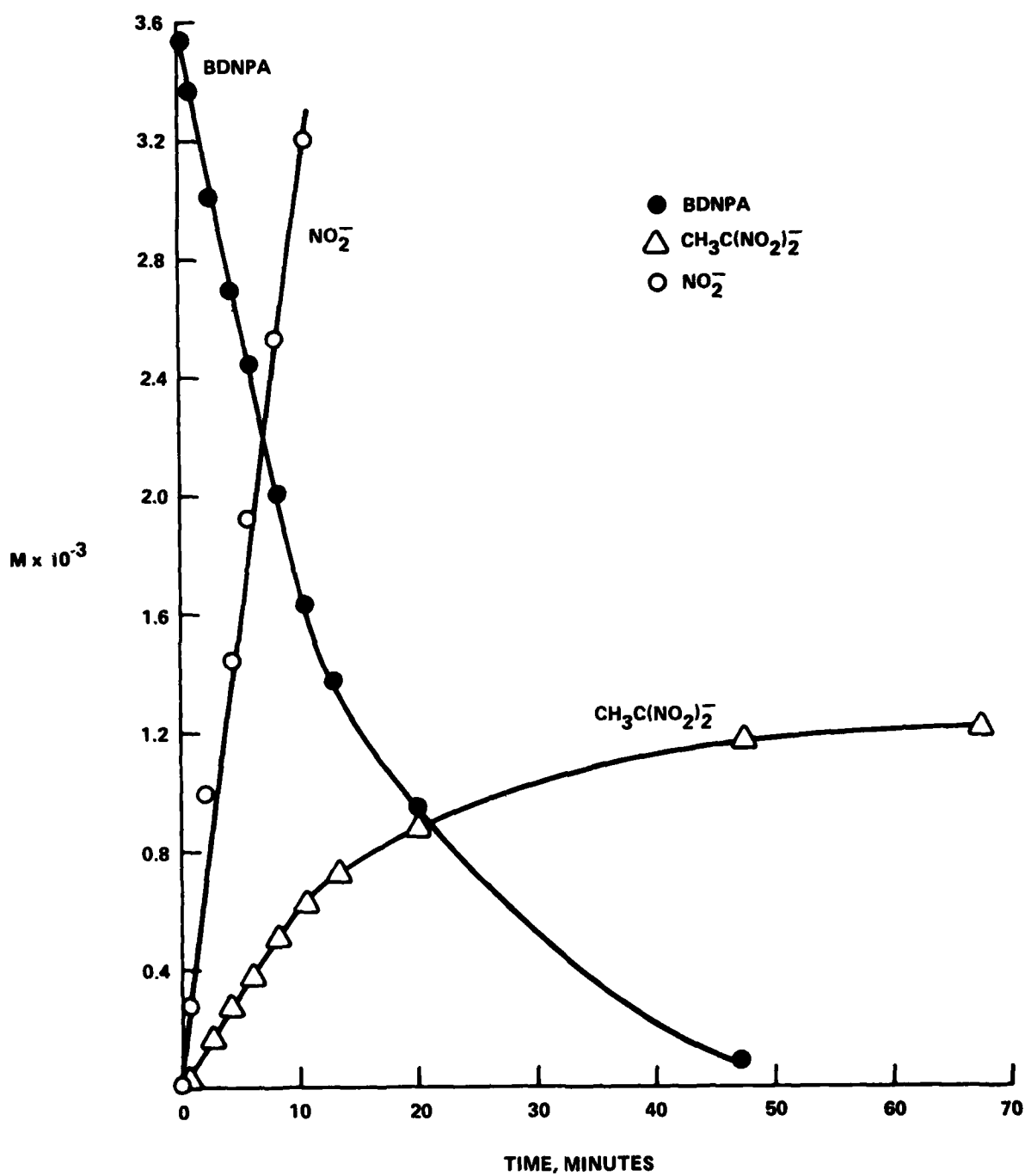


FIGURE 2. ALKALINE HYDROLYSIS OF BDNPA: FORMATION OF NITRITE AND 1,1-DINITROETHANE ANIONS (CONCENTRATION VERSUS TIME)

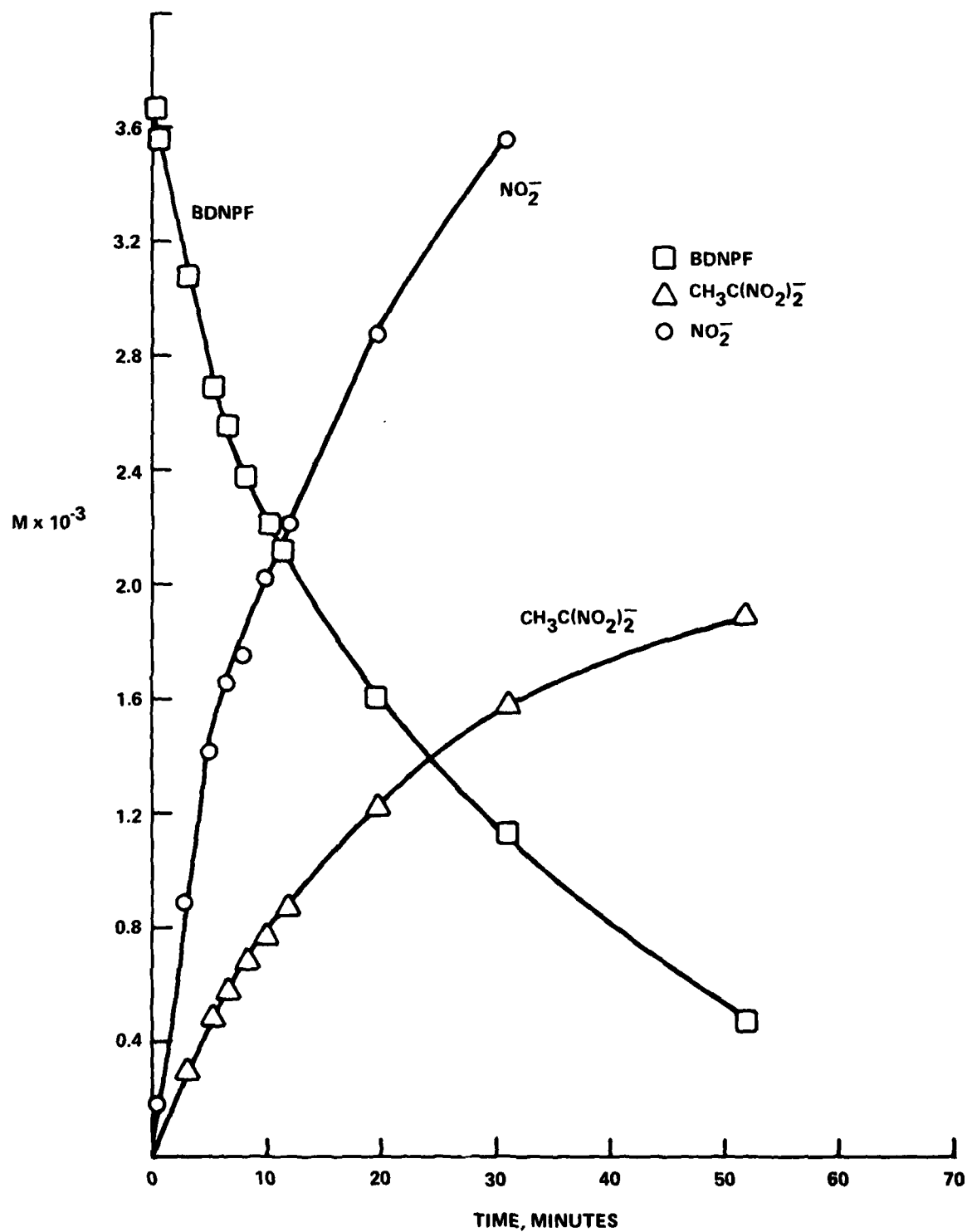


FIGURE 3. ALKALINE HYDROLYSIS OF BDNPF: FORMATION OF NITRITE AND 1,1-DINITROETHANE ANIONS (CONCENTRATION VERSUS TIME)

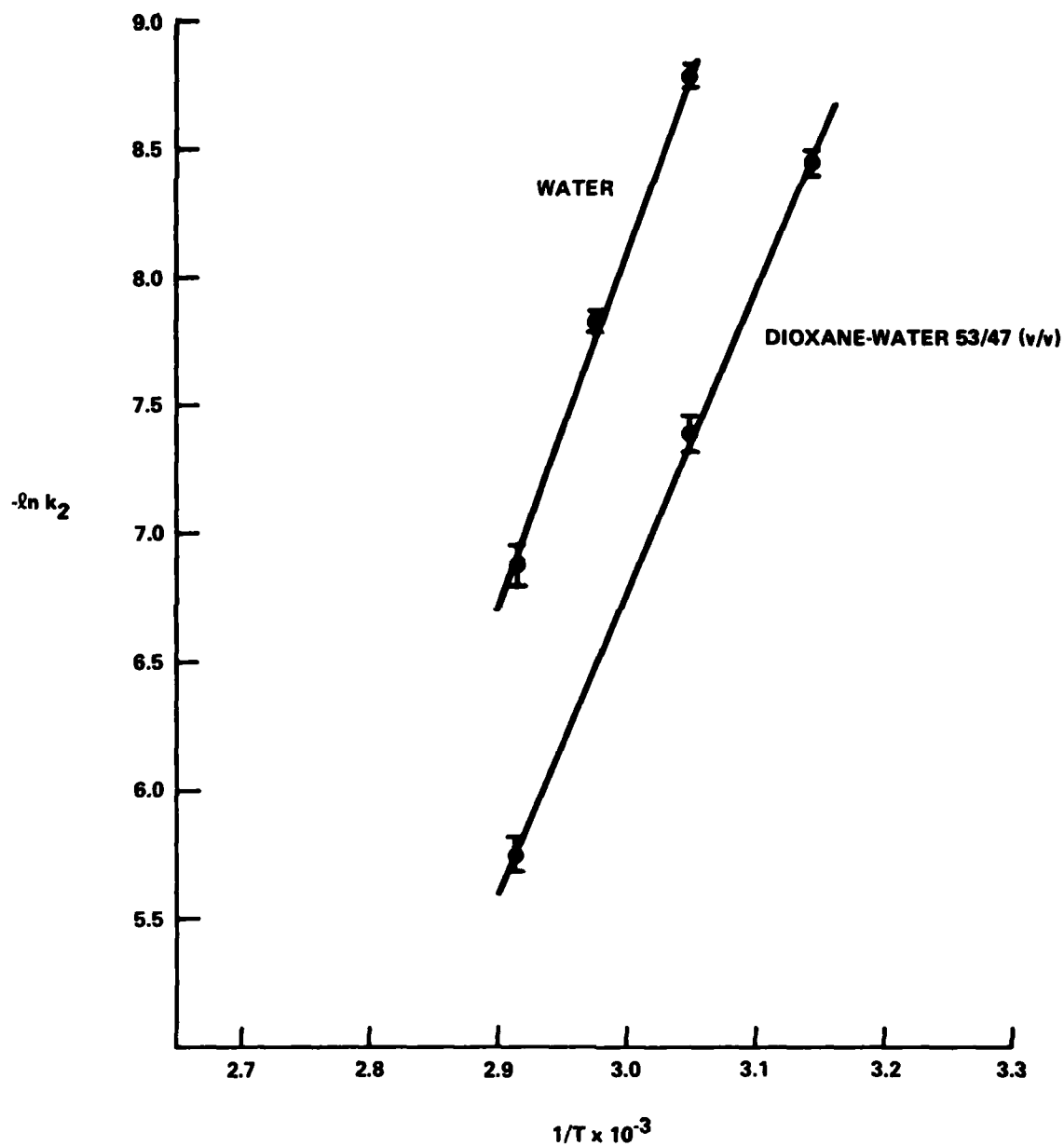


FIGURE 4. ALKALINE HYDROLYSIS OF BDNPF IN WATER AND DIOXANE-WATER
($-\ln k_2$ VERSUS $1/T$)

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