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TECHNICAL REPORT ARLCD-TR-79022

KINETIC STUDIES AND
PRODUCT CHARACTERIZATION DURING
THE BASIC HYDROLYSIS OF
GLYCERLY NITRATE ESTERS

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US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND
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20. ABSTRACT cont'd

was calculated from kinetic data at 10°C, 18°C, and 25°C. The 2-MNG and 1,2-DNG in basic solutions isomerized to 1-MNG and 1,3-DNG, respectively, which subsequently hydrolysed to yield products. The main hydrolysis product in the case of 1,3-DNG was identified as glycidyl nitrate. The major products of the basic hydrolysis of TNG were calcium nitrate and calcium nitrite, accounting for about 50 percent of the degradation products. Unreacted calcium hydroxide represented another 15 percent and the minor identified products such as calcium oxalate and nitrate esters amounted to approximately 6 percent of the products. The remaining 30 percent was a mixture of calcium formate, a nitrate ester and unidentified volatiles, polymer-like substances and other organic residue.

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INTRODUCTION

In terms of modern environmental protection criteria, Army Ammunition Plants (AAP's) discharge large quantities of various pollutants into the environment in their wastewater streams. This study is concerned with the glyceryl nitrates (GN's) present in the wastewaters generated in the manufacture of glyceryl trinitrate (TNG). Typical compounds and quantities involved at Radford AAP are: glyceryl trinitrate (TNG) - 1000 parts per million (ppm); glyceryl dinitrates (DNG's) - 600 to 800 ppm; glyceryl mononitrates (MNG's) - very small (ref. 1).

Of the various alternatives that have been examined, the glyceryl nitrate (GN) desensitization process most likely to be used for the large quantities in wastewaters is basic hydrolysis with calcium hydroxide. Laboratory studies on this process are needed to simulate conditions applicable to desensitization operations at Army Ammunition Plants (AAP's). Such information is required for the design of a unit process that would ensure a decrease of GN to a level at which there would be no interference with follow-on biological treatment or to a level which would pose no environmental hazards when discharged. At such levels, GN might well be diluted to acceptable levels in receiving streams in the event of failure of the biological treatment system.

When contemplating chemical treatment, or biological degradation processes, for the abatement of pollutants, one must consider the products generated by such treatments. Accordingly, a complete study on the abatement of any pollutant must include qualitative and quantitative data on the transformation products or accompanying materials that might constitute an environmental hazard. This report describes the kinetics of the basic hydrolysis of GN's as related to the design of the proposed unit process and furnishes some vital information about the products of degradation.

EXPERIMENTAL

Description of Equipment

Kinetic Apparatus

A photograph of the apparatus used in the study of the kinetics of hydrolysis is shown in Figure 1. A typical hydrolysis experiment involved an initial reaction volume of approximately 1 liter, consisting of 500 milliliters (ml) of glyceryl nitrate solution and 500 ml of calcium hydroxide solution.

The reaction vessels A and B were jacketed for thermostatic control; and they were equipped with magnetic stirrers for efficient thermal equilibration of their contents. To remove carbon dioxide, which is

normally present in ambient air, the system was flushed with nitrogen (N_2) presaturated with water vapor. The glyceryl nitrate and calcium hydroxide ($Ca(OH)_2$) solutions were added to reaction vessels A and B, respectively, through separatory funnels equipped with gas bypass. After conditioning both solutions at a preselected temperature, the $Ca(OH)_2$ solution was siphoned into the glyceryl nitrate ester solution. This time of mixing determined the zero reaction time. The reaction mixture was kept at the preselected constant reaction temperature and was continuously deaerated by bubbling N_2 through the mixture. A Beckman pH electrode was used to monitor the OH^- concentration in the reaction mixture throughout the hydrolysis reaction.

At frequent and variable time intervals, samples of the hydrolyzing solution were withdrawn for quantitative determination of the glyceryl nitrate content by reverse phase liquid chromatography; the hydroxide ion concentration by titration; the nitrite ion concentration by a modified Griess procedure; and the nitrate ion concentration with a specific ion electrode.

High Performance Liquid Chromatographic (HPLC) Analysis

In order to monitor the disappearance of reactants and product formation for the kinetics of the basic hydrolysis of glyceryl nitrates (GN's) effectively, it was deemed necessary to use an analytical method that would be rapid, accurate, and require minimum sample preparation. A cursory examination of the literature reveals that some methods that have been used for these compounds were: titrimetry (ref. 2), spectrophotometry (ref. 3,4), thin-layer chromatography (ref. 5-10), gas chromatography (ref. 11,12), and liquid chromatography (LC) (ref. 13-15). Of these methods, LC appeared to meet the analytical requirements best, especially in terms of rapidity, accuracy and resolution of the reaction mixture.

Reverse-phase LC was used, in the present studies, for the quantitative determination of GN's in the aqueous hydrolysis solutions without involving any extractions which are usually required in normal phase LC. However, under the experimental conditions used, the pH was too high to allow direct injection of the reaction mixture onto the liquid chromatography column. This problem was avoided by adding enough strong acid, either hydrochloric acid (HCl) or nitric acid (HNO_3), to bring the pH to between 3-7. Furthermore, the experimental data indicated that lowering the pH resulted in quenching of the hydrolysis reaction.

A Perkin-Elmer 1220 liquid chromatograph with a Model LC-55 variable wavelength detector was used for separation and quantification. The separations were accomplished on either an ODS-HO Sil-X-I (Perkin-Elmer Corp) 10 microns (μ), 0.26 centimeters (cm) (i.d.) X 25 cm (length) or

a Lichrosorb RP-8 (Applied Science Labs) 5 μ , 0.42 cm (i.d.) X 25 cm column. The mobile phase consisted of 15:85 acetonitrile and water at a flow rate of 1.0 ml/minute with a column temperature of 55°C. The sample was injected with a Valco injector using a 30 microliter (μ l) loop. Aliquots of the reaction mixture taken throughout the course of the hydrolysis were acidified to pH 2-7 with 0.1M HNO₃ or 0.1M HCl and diluted with water to avoid saturating the detector and overloading the column. Quantification was accomplished by measuring peak heights. Response factors were obtained by preparing solutions from neat materials. These materials are discussed in the Reagents section. Response factors were obtained for each kinetic run and checked during the run. The accuracy of this method was estimated to be $\pm$ 5%. The ultraviolet (UV) detector was operated at 220 or 205 nanometers (nm) depending on sensitivity needed. The glyceryl nitrate contents of the hydrolyzing mixtures were monitored from an approximate initial concentration of 500 ppm to a terminal concentration of 1 ppm. A column, 0.42 cm (i.d.) X 25 cm, packed with Lichrosorb, RP-8, 5 μ was used for monitoring 2-MNG and 1-MNG; and a 0.26 cm (i.d.) X 25 cm column packed with ODS-HC Sil-X-I for 1,3-DNG, 1,2-DNG and TNG. Typical chromatograms for mixtures of these compounds with experimental conditions used are shown in Figures 2 and 3.

Reagents

Carbon Dioxide-Free Water

Distilled water was boiled for at least ten minutes. The hot water was poured into stoppered bottles and cooled in a plastic glove bag filled with nitrogen.

Glyceryl Trinitrate

This material is sparingly (approximately 1.8 grams (g) per liter (l) at 25°C (ref. 16)) and difficultly soluble in water. Accordingly, excess glyceryl trinitrate was stirred using a magnetic stirrer in carbon dioxide-free distilled water in a stoppered glass bottle for a minimum of 8 hours. The bottle was transferred to a nitrogen-filled plastic glove bag. The desired amount of solution was filtered through E&D # 515 filter paper to remove any suspended material into a separatory funnel equipped with a gas bypass. The bottle was refilled with carbon dioxide-free distilled water as long as any undissolved glyceryl trinitrate remained visible in the bottle. A small sample of the filtered solution was reserved for determination of its concentration by liquid chromatography.

Calcium Hydroxide

Solid calcium hydroxide (approximately 700 milligrams) (Fisher certified reagent grade) was weighed into a nitrogen-filled volumetric

flask. The flask was put into a nitrogen-filled plastic glove bag, filled with carbon dioxide-free distilled water and vigorously shaken. The solution was filtered through E&D # 515 filter paper into a separatory funnel with a gas bypass for the removal of any calcium carbonate contaminant. A five milliliter sample was reserved for the determination of the hydroxide ion concentration by titration.

Glycerol Dinitrates

Each isomer was available in stock solution of 50/50 hexane/ethyl acetate. An appropriate amount of dinitrate solution was pipetted into a platinum evaporating dish and exposed to air for a minimum of 16 hours to allow the solvents to evaporate. The liquid dinitrate was carefully weighed into a platinum crucible. The crucible was put into a nitrogen-filled plastic glove bag, and the contents were carefully washed into a volumetric flask with carbon dioxide-free distilled water. The flask was filled with carbon dioxide-free distilled water and carefully shaken (solubility of the DNG's is approximately 8 grams per 100 grams water). The solution was poured into a separatory funnel with a gas bypass. A small sample of the solution was reserved for determination of its concentration by liquid chromatography.

Glyceryl Mononitrates

These materials are solids which are quite soluble in water. The solid was weighed into a nitrogen-filled volumetric flask. Subsequently, the flask was put inside a plastic glove bag containing nitrogen and filled to the mark with carbon dioxide-free distilled water. The solution was poured into a separatory funnel with a gas bypass. A small sample was reserved for the determination of its concentration by liquid chromatography.

TNG Reaction Mixture For Product Identification

Excess calcium hydroxide was added to 2.5 liters of distilled water and the slurry-like mixture was filtered through a No. 41 Whatman filter paper. A two liter volumetric flask was filled to the mark with the clear filtrate (pH of 12.) and a magnetic stirring bar was added. The filled flask was placed on a stirrer and nitrogen gas introduced to avoid formation of carbonates. Several layers of asbestos board were placed between the flask and the stirrer top to minimize heat transfer from the stirrer motor to the mixture.

Three grams of TNG (MIL SPEC N-246) were slowly added to the alkaline solution and the stirring bar slowly set in motion to attain a speed sufficient to disperse the nitroglycerin globules in the saturated aqueous solution of calcium hydroxide. The reaction mixture was stirred

at ambient temperatures (ca. 24°C) for 24 hours or until unreacted TNG was no longer detected by high pressure liquid chromatography. On completion of the run, the reaction mixture (pH of 10.4) appeared straw-yellow in color and contained brown solids.

Analytical Procedures

Hydroxide Ion Titration Determination

A five ml sample of the reaction mixture was added to 10 ml of standard hydrochloric acid (approximately 0.01N) and back titrated with standard sodium hydroxide (approximately 0.01N) to a phenolphthalein end point.

Nitrite Ion Determination

Nitrite ion concentration was determined using the modification of the Griess procedure developed by Saltzman for the continuous estimation of NO_2 in air (ref. 17).

Nitrate Ion Determination

Nitrate ion concentration was determined using a nitrate specific ion electrode after destruction of nitrite ion by sulfamic acid (ref. 20).

Nuclear Magnetic Resonance (NMR) Analysis

The spectra were scanned with a Varian T-60 spectrometer at 14,092 gauss and a rotating field frequency of 60 megahertz (MHz). The samples were analyzed in conventional NMR tubes (0.5 cm o.d.) as dilute (10 percent weight/volume) solutions. The required sample volume was 0.3 to 0.6 ml. A standard development time of two hours was routinely observed. Only three solvents were used, deuterioacetone, deuterodimethylsulfoxide (DMSO), and deuterium oxide. The internal reference standards, whose resonance lines are conventionally set to zero, were tetramethylsilane for acetone and DMSO, and sodium 2,2-dimethyl-2-sila pentane-5-sulfonate for deuterium oxide.

Separation of Reaction Products

An outline of the scheme developed for the separation and isolation of the products of alkaline hydrolysis of glyceryl trinitrate is presented in figure 4. A one liter portion of the 2.5 liters of reaction mixture was filtered through a No. 41 Whatman filter paper to obtain fractions Solid I and Filtrate I. A methylene chloride extraction of Filtrate I resulted in Aqueous Phase I and Extract I. The weight of

Extract I was obtained by evaporation of the extraction solvent under a stream of dry air, followed by air drying. Flash evaporation of Aqueous Phase I, using a Precision Scientific Co., Varispeed Flash Evaporator at 10 millimeters (mm) of Hg pressure and ambient temperatures, yielded a viscous fraction and Condensate I. The viscous fraction was brought to constant weight by vacuum pumping, to give a weight for Solid II. The weighed Solid II was treated with ethanol to dissolve the soluble calcium salts. The ethanol treatment yielded an alcohol soluble fraction which, on evaporation of the ethanol, was quantitatively transferred to a micro distillation apparatus. A weight for Solid III was obtained by heating the ethanol solubles at 200°C until constant weight was obtained. Condensate II, which was obtained from the heated ethanol solubles, was reserved for further examination. Through vacuum pumping, the ethanol insolubles were brought to constant weight to yield a weight for Solid IV.

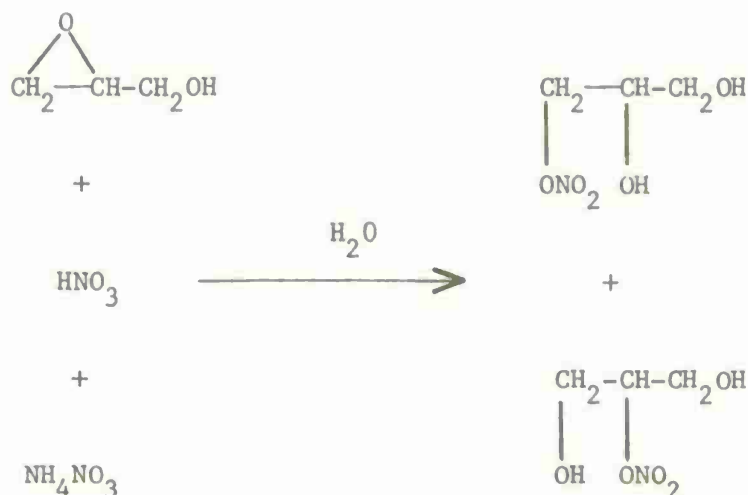
The fraction designated Solid IV was redissolved in water, adding hydrochloric acid to aid in the dissolution of the ethanol insolubles. The aqueous solution was added to a batch of cation exchange resin, Amberlite IR-120M, to exchange calcium for hydrogen. The solution was kept in contact with the resin for 10 minutes or until the oxalate test for calcium was negative. The mixture was then poured onto an ion-exchange column and washed with distilled water until neutral pH was obtained. Flash evaporation of the combined eluate and washings yielded a viscous fraction, which on drying in a vacuum desiccator, yielded a weight for Viscous Fraction (VR).

Synthesis of MNG's and DNG's

The procedures used for the synthesis of MNG's and DNG's were based on those described earlier (ref. 18,19,20), except for a minor change. In the synthesis of 1,2-DNG, the volume of the solution was reduced from 50 ml to 30 ml prior to column chromatographic purification in order to obtain a sharper separation and hence a purer product. The procedures used are reproduced in their entirety in this report for convenient referral.

MNG's

Both 1-MNG and 2-MNG were prepared simultaneously via the same reaction. The reaction scheme and details of the synthesis are given below:



One hundred grams (g) of glycidol were added, dropwise, over a period of 25 minutes, to a solution which was maintained at 60°C and contained 40 ml of H₂O, 85 ml of 70% HNO₃, and 250 g of NH₄NO₃. After an additional 15 minutes, the solution was neutralized with NaHCO₃ (powder) until the evolution of CO₂ ceased. An extra 100 ml of H₂O was added, followed by extraction with 250 ml of ethyl ether to remove DNG's. The ether solution was discarded. The aqueous solution was extracted with ethyl ether using a continuous liquid-liquid extractor for 24 hours. The ether extract contained 80-120 g (30-50% yield) of 1- and 2-mononitroglycerin in a 3:1 ratio, respectively.

The ether solution was dried over sodium sulfate and diluted to 500 ml. After removal of the sodium sulfate, 200 g of CaCl₂ solution was added slowly with vigorous stirring. After standing overnight, the solution was decanted and the precipitate was washed with three 100 ml portions of ether. The combined ether solutions contained 80-90% 2-MNG. The CaCl₂ complex contained about 90% 1-MNG.

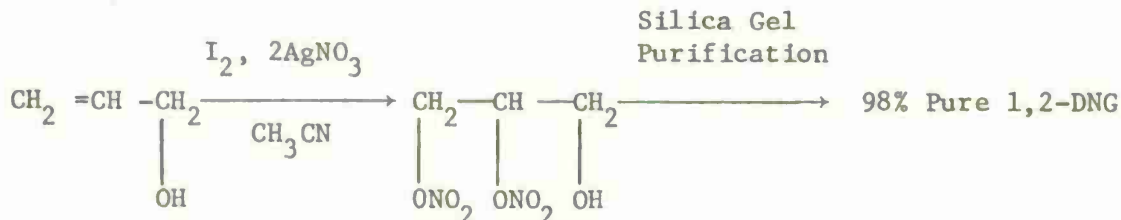
The 2-MNG was further purified by passing 50 g batches through a 2 inch x 24 inch chromatographic column packed with CaCl₂ in ether. This gave a high purity of 2-MNG. The material recrystallized from benzene/ether (1:1) to give small needles.

The 1-MNG was recovered by the addition of water to the CaCl₂ complex and continuous extraction with ethyl ether. Repeating the

complexing and recovery procedure gave material which, after two recrystallizations, was 99% 1-MNG. The material recrystallized readily from benzene/ether (1:1).

1,2-DNG

The synthesis of 1,2-DNG was carried out according to the method described previously (ref. 23). The reaction scheme together with procedure details are given below:

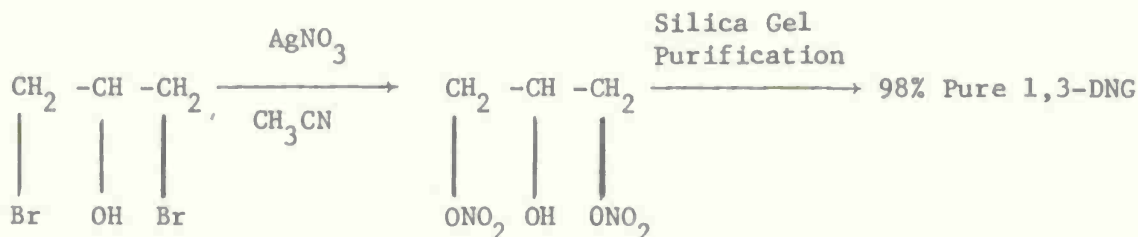


To a solution of 11.6 g (0.2 mole) of allyl alcohol and 67.9 g (0.4 mole) of silver nitrate dissolved in 300 ml acetonitrile was added 25.4 g (0.2 mole) of iodine dissolved in 500 ml of acetonitrile during a 2.5-hour period. After 2 hours, the mixture was placed in a water bath at 50°C for 24 hours. The mixture was filtered to remove the silver iodide and concentrated to between 100 and 200 ml. The filtrate was again placed in a water bath at 50°C. After 3 days, additional silver nitrate (5 g) was added. After 7 days, the reaction mixture was filtered. To remove excess silver nitrate, the filtrate was poured into 100 ml of water saturated with sodium chloride; the mixture was filtered to remove silver chloride. Acetonitrile was removed under water vacuum (about 20 mm Hg). The water solution was extracted three times with 60 ml portions of ether. The ether extracts were combined, dried over anhydrous magnesium sulfate, diluted with 75 ml hexane/ethyl acetate (2:1) and the volume reduced to about 50 ml under water vacuum. The approximate concentration of material per ml was determined by evaporating the solvent from a 1.0 ml aliquot and weighing.

Purified 1,2-DNG was obtained by column chromatography on silica gel (40:1 ratio of silica gel to material) using hexane/ethyl acetate (2:1) as eluant. The fractions (100 ml) were monitored by thin-layer chromatography (Brinkmann silica gel F-254, hexane/ethyl acetate (2:1)). Two column chromatographings were required to give pure material (>98%). Six preparations gave an average of 6.9 g (24% yield) per preparation. The purified material was stored at a 20-30% concentration in hexane/ethyl acetate (2:1), protected from light at 3-5°C.

1,3 DNG

The sample was also prepared by a method similar to that reported previously (ref. 21). The reaction scheme and experimental details are shown below:



To a solution of 34.0 g (0.2 mole) of silver nitrate in 100 ml of acetonitrile was added, dropwise, 21.8 g (0.1 mole) of 1,3-dibromo-2-propanol. After 2 days at 50°C, 5 g of silver nitrate dissolved in 50 ml of acetonitrile were added. After 7 days at 50°C the solution was filtered and the filtrate poured into 100 ml of water saturated with sodium chloride to remove excess silver nitrate. The solution was filtered to remove silver chloride followed by removal of acetonitrile under vacuum generated by a water pump. The water solution was extracted four times with 150 ml portions of ethyl ether. The combined ether solutions were dried over sodium sulfate, filtered, and concentrated to about 30 ml. This solution was divided into two equal volumes and each chromatographed on 240 g of silica gel (Brinkmann, 70-230 mesh) using hexane/ethyl acetate (2:1). After two column chromatographings per portion, 15 g (82% yield) of >98% pure material was obtained. The purified material was stored at a 20-30% concentration in hexane/ethyl acetate (2:1), protected from light at 3-5°C.

The yields and purity of the nitrate esters as determined by HPLC, infrared (IR) spectrophotometry and mass spectrometry (MS) were comparable to those reported by Midwest Research Institute (MRI).

Synthesis of Reaction Products

Glycidyl Nitrate From 1,3-DNG

Glycidyl nitrate was prepared according to the procedure described by Naoum (ref. 16). Liquid 1,3-DNG (1.34 g) was mixed with 3 g of 30% NaOH aqueous solution for four hours at room temperature. The reaction product was separated and washed with water. It was obtained in a yield of 0.56 g and a purity of >99% as indicated by IR.

Glycidol From 2-MNG

Four grams of 2-MNG were mixed with 22 ml of 30% NaOH aqueous solution for six minutes at room temperature. The reaction mixture was then diluted with water to a concentration of 15% NaOH and extracted with CH_2Cl_2 . The CH_2Cl_2 was stripped from the extract by a stream of dry air. The IR spectrum of the residue was compared to reference standard spectra (ref. 22) and identified as that of glycidol.

Qualitative and Quantitative Determination of Reactants and Reaction Products

Calcium Hydroxide

The alkaline concentrations of the prepared saturated aqueous solution of calcium hydroxide and of Filtrate I were determined by acid-base titration. A known volume of standard hydrochloric acid was added to an aliquot of each mixture and back-titrated with standard sodium hydroxide solution. The difference, in milli-equivalents, was calculated as the hydroxide concentration.

Calcium Nitrate

The nitrate content of Solid III was determined by the specific ion electrode procedure. The nitrate content was calculated as calcium nitrate.

Calcium Nitrite

The red color resulting from the reaction between the Greiss reagent and the nitrite ion was measured spectrophotometrically to obtain the nitrite content. The nitrite was calculated as the calcium nitrite content in Solid III.

Calcium

The calcium content of Solid III and other fractions was determined by Atomic Absorption Spectrophotometry.

Calcium Oxide

The unidentified third component of Solid III was considered to be calcium oxide and its weight was determined by totaling the quantities of calcium nitrate and calcium nitrite and subtracting the sum from the Solid III weight.

Calcium Oxalate, Organic Residue, Methylene Chloride Solubles

The determination of the weight of these components and fractions is described under "Separation of Reaction Products".

RESULTS

Kinetics of the Basic Hydrolysis of Glyceryl Nitrate Esters

Rates of reactant disappearance and product formation were determined by withdrawing from the reaction mixture samples which were analyzed with a liquid chromatography apparatus equipped with a UV detector. In all cases studied here, the disappearance of the glyceryl nitrate esters obeyed second order kinetics and rate constants were calculated using the expression:

$$\log \frac{(A_o - X)}{(B_o - X)} = \log \frac{(A_o)}{(B_o)} - \frac{(B_o - A_o)}{2.303} K t \quad (1)$$

where A_o , B_o denote initial concentrations in moles/liter (M) of glyceryl nitrate ester and OH^- , respectively, K is the rate constant, and t refers to the reaction time in seconds (sec). Initial concentrations were determined immediately after mixing the glyceryl nitrate ester and $Ca(OH)_2$ solutions. Reaction time started immediately after mixing and the concentration of OH^- at different reaction times was calculated from the expression $OH^- = B_o - X$ where X corresponds to the amount of glyceryl nitrate ester which has been hydrolysed during reaction time t . X was determined by liquid chromatography at preselected reaction intervals.

Hydrolysis of 1-MNG

Figure 5 shows the hydrolysis of 1-MNG, at 25°C, as a function of reaction time. The rate constant calculated from this plot was found to be equal to:

$$K = 3.135 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}$$

Hydrolysis of 2-MNG

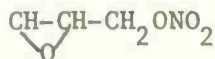
The data of 2-MNG hydrolysis, at 25°C, are shown plotted in figure 6. The kinetic data indicates that 2-MNG initially undergoes isomerization and hydrolysis to form 1-MNG and possibly other products with a rate constant $K = 1.88 \times 10^{-2} \text{ M}^{-1} \text{ sec}^{-1}$. After ~ 150 min the rate of reaction assumes a new value from which a rate constant equal to $K = 5.816 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}$ was calculated.

Figure 7 shows that during the early stages of hydrolysis, 2-MNG isomerizes to 1-MNG which subsequently decays with a rate constant equal to $K = 4.14 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}$. The small discrepancy between this rate constant and that obtained from figure 5 is probably due to some uncertainty in determining the concentration of OH^- at approximately 100 minutes of reaction time (fig. 7). This concentration of OH^- was considered to be the new initial concentration of OH^- and was used in converting the pseudo first order rate constant of figure 7 to bimolecular units.

The 2-MNG hydrolysed in strongly basic solutions (30% NaOH) yielded IR spectroscopic evidence for the formation of glycidol (2,3-epoxy-1-propanol). It is quite possible that glycidol is also formed during the hydrolysis of 2-MNG and 1-MNG in $\text{Ca}(\text{OH})_2$ solutions. The mechanism of glycidol formation will be mentioned in the discussion.

Hydrolysis of 1,2-DNG

The data of 1,2-DNG hydrolysis with $\text{Ca}(\text{OH})_2$ were analyzed and are shown plotted in figure 8. The rate constant calculated from the linear plot of figure 8 was found to be equal to $K = 10.42 \times 10^{-2} \text{ M}^{-1} \text{ sec}^{-1}$. The LC data shown in figure 9 indicates that 1,2-DNG undergoes isomerization to 1,3-DNG which in turn hydrolyzes, as shown in figure 10, to form glycidyl nitrate



and possibly other products with a rate constant $K = 5.63 \times 10^{-2} \text{ M}^{-1} \text{ sec}^{-1}$.

Hydrolysis of 1,3-DNG

The 1,3-DNG hydrolyzes in aqueous solutions of $\text{Ca}(\text{OH})_2$ to form glycidyl nitrate and other products. Data pertaining to two independent runs of this reaction are shown plotted in figures 11 and 12. The corresponding values calculated from the slopes of the linear plots of figures 11 and 12 were found to be equal to $K = 1.26 \times 10^{-1} \text{ M}^{-1} \text{ sec}^{-1}$ and $1.058 \times 10^{-1} \text{ M}^{-1} \text{ sec}^{-1}$, respectively.

Hydrolysis of TNG

The TNG was hydrolyzed at 25°C, 18°C and 10°C in order to determine an activation energy for the hydrolysis reaction. Two independent runs were performed at each temperature. The experimental data are shown plotted in figures 13 through 18. The rate constants calculated from the linear plots of these figures are listed in table 1.

The kinetic data presented in this report indicate that 1,2-DNG and 1,3-DNG are more reactive than TNG. This is in conflict with the findings reported in an earlier communication (ref. 23). However, it should be emphasized that the bimolecular rate constants reported earlier were determined, in 90% v/v ethanol solutions containing NaOH, by monitoring the rate of disappearance of OH⁻ with titration.

The rate constants listed in table 1 were plotted according to the Arrhenius equation:

$$\log K = \log A - \frac{E_a}{2.303R} \left(\frac{1}{T} \right) \quad (2)$$

where K represents the rate constant at temperature T°K, E_a the activation energy of the hydrolysis reaction and R the gas constant which is equal to 1.9872 calories/degree/mole (cal/deg/mole).

The result is shown in figure 19, from the slope of which an activation energy of 27.53 kilocalories (Kcal)/mole was calculated. This value seems to be in fair agreement with that reported in the literature (ref. 24) for the basic hydrolysis reaction of isopropyl and t-butyl nitrate esters.

Yields and Kinetics of Nitrites and Nitrates Formed During the Alkaline Hydrolysis of Glyceryl Nitrate Esters

The concentrations of nitrites and nitrates formed during the basic hydrolysis of glyceryl nitrate esters are shown as a function of reaction time in tables 2 through 7.

The kinetics of NO₂⁻ and NO₃⁻ formation were treated by assuming the reaction scheme:

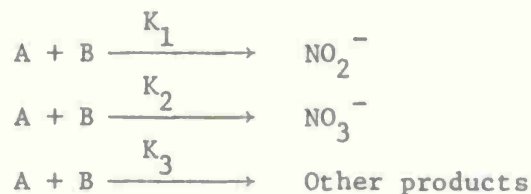


Table 1. Rate constants of TNG hydrolysis ^a

<u>Temperature of reacting solution °C</u>	<u>Rate constant K (M⁻¹sec⁻¹)</u>
25°C	2.36 x 10 ⁻²
25°C	1.94 x 10 ⁻²
18°C	8.36 x 10 ⁻³
18°C	6.07 x 10 ⁻³ ^b
10°C	2.17 x 10 ⁻³
10°C	1.46 x 10 ⁻³ ^b
10°C	1.24 x 10 ⁻³

^a See figures 13-18

^b In these runs the Ca(OH)₂ was added as solid in the TNG solution.

Table 2. Formation of NO_3^- during the basic hydrolysis of 1-MNG at 25°C

Reaction time (minutes)	Concentration of NO_3^- (moles/liter) $\times 10^{33}$
8	0.88
73	1.7
123	2.2
193	2.8
269	3.9
378	3.6
477	3.6
543	3.6
588	3.4

Initial concentration of reactants:

$$[\text{1-MNG}] = 5.20 \times 10^{-3} \text{ M} = A_0 \quad (\text{fig. 5})$$

$$[\text{OH}^-] = 3.46 \times 10^{-2} \text{ M} = B_0 \quad (\text{fig. 5})$$

$$K_{\text{HYD}} = 3.14 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}$$

Table 3. Formation of glycidyl nitrate, NO_2^- and NO_3^- during basic hydrolysis of 1,3-DNG at 25°C

Time (minutes)	Glycidyl Nitrate (moles/liter) $\times 10^3$	$[\text{NO}_2^-]$ (moles/liter) $\times 10^6$	$[\text{NO}_3^-]$ (moles/liter) $\times 10^4$
0	0	0	0
2	-	0.31	0.155
13	0.764	-	-
19	-	2.01	1.035
31	1.403	-	-
39	-	3.31	1.815
47	1.657	-	-
55	-	4.01	2.045
61	1.719	-	-
72	-	4.71	2.585
85	-	5.41	2.725
93	1.783	-	-
103	-	5.91	2.725
134	-	6.81	3.035
162	1.783	-	-
209	-	8.21	3.375
214	1.719	-	-
249	-	8.71	3.375
276	1.657	-	-
298	-	9.01	3.035
1309	-	12.21	3.935
1313	0.8286	-	-

Initial concentration of reactants

$$[1,3\text{-DNG}] = 2.508 \times 10^{-3} \text{ M} = A_0 \quad (\text{fig. 12})$$

$$[-\text{ONO}_2] = 2 \times [1,3\text{-DNG}] = 5.016 \times 10^{-3} \text{ M}$$

$$[\text{OH}^-] = 6.9 \times 10^{-3} \text{ M} = B_0 \quad (\text{fig. 12})$$

$$K_{\text{HYD}} = 1.06 \times 10^{-1} \text{ M}^{-1} \text{ sec}^{-1}$$

Table 4. Formation of NO_2^- during the basic hydrolysis of TNG at 25°C

<u>Reaction time</u> <u>(minutes)</u>	<u>Concentration of NO_2^-</u> <u>(moles/liter) $\times 10^3$</u>
1	0.64
29	2.0
55	3.2
88	3.9
113	4.4
149	4.7
193	5.5
253	6.5
307	5.8
367	5.5
430	5.8

Initial concentrations of reactants:

$$[\text{TNG}] = 2.794 \times 10^{-3} \text{ M} = A_0 \quad (\text{fig. 13})$$

$$[-\text{ONO}_2] = 3 \times [\text{TNG}] = 8.382 \times 10^{-3} \text{ M}$$

$$[\text{OH}^-] = 7.4 \times 10^{-3} \text{ M} = B_0 \quad (\text{fig. 13})$$

$$K_{\text{HYD}} = 2.36 \times 10^{-2} \text{ M}^{-1} \text{ sec}^{-1}$$

Table 5. Formation of NO_2^- during basic hydrolysis of TNG with solid Ca(OH)_2 at 18°C

Time (minutes)	$[\text{NO}_2^-]$ (moles/liter) $\times 10^3$
1	-
48	1.16
69	1.56
90	1.46
119	1.76
166	1.96
207	2.16
262	2.26
337	2.26
1276	2.56

Initial concentration of reactants:

$$[\text{TNG}] = 1.392 \times 10^{-3} \text{ M} = A_0 \quad (\text{fig. 16})$$

$$[-\text{ONO}_2] = 3 \times [\text{TNG}] = 7.176 \times 10^{-3} \text{ M}$$

$$[\text{OH}^-] = 3.02 \times 10^{-2} \text{ M} = B_0 \quad (\text{fig. 16})$$

$$K_{\text{HYD}} = 6.07 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}$$

Table 6. Formation of NO_2^- and NO_3^- during the basic hydrolysis of TNG at 10°C

<u>Time (minutes)</u>	<u>Concentration of NO_2^- (moles/liter) $\times 10^5$</u>	<u>Concentration of NO_3^- (moles/liter) $\times 10^5$</u>
12	1.8	1.4
38	7.5	2.4
66	14.9	2.4
91	18.4	5.4
119	24.0	1.4
181	33.8	7.4
257	43.4	13.4
323	49.2	17.4
393	55.6	18.4
469	60.3	22.4
544	64.2	22.4
607	66.2	24.4
691	-	22.4
736	71.1	20.4

Initial concentration of reactants:

$$[\text{TNG}] = 5.724 \times 10^{-4} \text{ M} = A_0 \quad (\text{fig. 17})$$

$$[-\text{ONO}_2] = 3 \times [\text{TNG}] = 1.717 \times 10^{-3} \text{ M}$$

$$[\text{OH}^-] = 1.95 \times 10^{-2} \text{ M} = B_0 \quad (\text{fig. 17})$$

$$K_{\text{HYD}} = 2.17 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}$$

Table 7. Formation of NO_2^- and NO_3^- during the basic hydrolysis of TNG at 10°C

<u>Reaction time</u> <u>(minutes)</u>	<u>Concentration of NO_2^-</u> <u>(moles/liter) $\times 10^3$</u>	<u>Concentration of NO_3^-</u> <u>(moles/liter) $\times 10^3$</u>
2	0	-
41	0.32	0.21
70	0.65	0.21
95	1.35	0.44
133	1.25	0.74
202	1.65	0.74
265	2.05	0.98
332	2.25	1.04
390	2.65	1.3
462	2.75	-
546	2.85	1.42

Initial concentration of reactants:

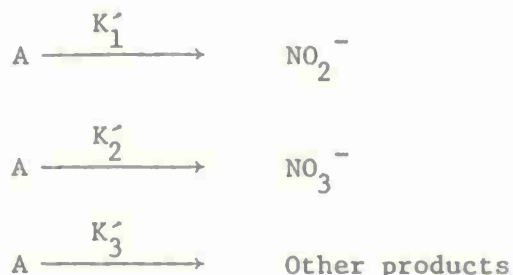
$$[\text{TNG}] = 2.783 \times 10^{-3} \text{ M}$$

$$[-\text{ONO}_2] = 3 \times [\text{TNG}] = 8.349 \times 10^{-3} \text{ M}$$

$$[\text{OH}^-] = 2.04 \times 10^{-2} \text{ M}$$

$$K_{\text{HYD}} = 1.24 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}$$

where [A] represents the concentration of glyceryl nitrate ester and [B] the concentration of OH^- . When B is present at much larger concentrations than A, the kinetic scheme shown above can be reduced to the following parallel pseudo-first order reactions:



where $K'_1 = K_1 [B]$; $K'_2 = K_2 [B]$ and $K'_3 = K_3 [B]$.

The final kinetic expressions which were utilized (ref. 25) for the analysis of the kinetic data of NO_2^- and NO_3^- are listed below.

$$[\text{NO}_2^-] = \frac{K'_1 [A_o]}{K'} [1 - \exp(-K't)] \quad (3)$$

$$[\text{NO}_3^-] = \frac{K'_2 [A_o]}{K'} [1 - \exp(-K't)] \quad (4)$$

where $[A_o]$ denotes the initial concentration of the glyceryl nitrate ester and $K' = K'_1 + K'_2 + K'_3$ is the overall pseudo-first order rate constant for the alkaline hydrolysis of the glyceryl nitrate ester.

In the various hydrolysis runs where NO_2^- and NO_3^- were quantitatively determined as a function of reaction time, the initial hydroxyl ion concentration $[\text{OH}^-]$ was at least several times larger compared to the glyceryl nitrate ester concentration, thus establishing conditions for pseudo-first order reaction. The rate constant K' , was evaluated by plotting, on a semilog paper, the concentration of glyceryl nitrate ester versus reaction time. The pseudo-first order rate constant K' , expressed in sec^{-1} , was calculated from the resulting linear plot and represents the overall rate constant for the disappearance of the glyceryl nitrate ester to form NO_2^- , NO_3^- and other products.

The concentrations of $[\text{NO}_2^-]$ and $[\text{NO}_3^-]$, listed in tables 2 through 7, were plotted versus the expression $[1 - \exp(-K't)]$. The slopes of the resulting linear plots were set equal to $K_1' [\text{A}]_0 / K'$ and $K_2' [\text{A}]_0 / K'$ for NO_2^- and NO_3^- respectively, as indicated by equations 3 and 4, and the rate constants K_1' and K_2' were calculated. For TNG, K_1' and K_2' were evaluated by substituting $3 \times [\text{TNG}]$ initial for $[\text{A}]$, since the material balance, shown in figure 20 indicates that 3.963×10^{-2} M of nitrate ester groups contained in 1.32×10^{-2} M of TNG eventually hydrolyze to yield $\sim 4.00 \times 10^{-2}$ M of total NO_2^- and NO_3^- . By analogy, for 1,3-DNG, K_1' and K_2' were evaluated by substituting $2 \times [\text{DNG}]$ initial for $[\text{A}]$. The kinetic plots employed for calculating the various K_1' and K_2' rate constants are shown in figures 21 through 30 and the calculated rate constants listed in table 8.

Identification and Quantitative Determination of Products Formed During the Basic Hydrolysis of TNG

In carrying out the TNG product identification, attempts were made to simulate, as closely as possible, a proposed plant desensitization procedure. At the plant, excess calcium hydroxide would be added to the wastewaters to hydrolyze the dissolved glyceryl trinitrate. However, it was felt that exact duplication of this proposed procedure in the laboratory would lead to the masking of solid reaction products by the excess calcium hydroxide, making separation of products difficult.

Preliminary qualitative test of the reaction mixture had indicated the presence of nitrite (ref. 26) and nitrate (ref. 26) ions and a 1,2-diol type polyhydroxy alcohol (ref. 27). However, this testing did not produce a technique satisfactory for identification of the product molecules and subsequent material balance. As a consequence, the separation scheme outlined in figure 4 was evolved and adopted. In carrying out the scheme it was recognized that removal of the aqueous phase might possibly alter the integrity of the reaction mixture. This could occur as the pH of the solution increased from 10 to 12 on evaporation of the aqueous phase effecting additional hydrolysis of any free nitrate ester in the mixture. However, there was evidence that the glyceryl trinitrate was completely hydrolyzed. In addition, a solvent extraction of the reaction mixture ("as is" and "acidified") indicated negligible amounts of free esters in the reaction mixture. It was concluded from this, that the reaction products were predominately present as calcium salts and that an increase of the calcium hydroxide concentration through evaporation would not affect seriously the integrity of the reaction mixture. Since the evaporation of the aqueous phase was carried out at ambient temperature, it was felt there would be little danger of the products undergoing changes. Any volatile components, present in the mixture would be part of the condensate. The latter

Table 8. Rate constants for the formation of NO_2^- , NO_3^- and glycidyl nitrate

Glyceryl nitrate ester	Temp °C	Rate constants					
		NO_2^-		NO_3^-		Glycidyl nitrate	
		Pseudo 1st order, sec^{-1}	bimolecular $\text{M}^{-1} \text{sec}^{-1}$	Pseudo 1st order, sec^{-1}	bimolecular $\text{M}^{-1} \text{sec}^{-1}$	Pseudo 1st order, sec^{-1}	bimolecular $\text{M}^{-1} \text{sec}^{-1}$
1-MNG	25	-	-	8.07×10^{-5}	2.33×10^{-3}	-	-
1,3-DNG	25	5.16×10^{-7}	7.48×10^{-5}	2.66×10^{-5}	3.86×10^{-3}	2.40×10^{-4}	3.47×10^{-2}
TNG	25	1.31×10^{-4}	1.77×10^{-2}	-	-	-	-
	18*	1.05×10^{-4}	3.47×10^{-3}	-	-	-	-
	10	2.17×10^{-5}	1.12×10^{-3}	6.97×10^{-6}	3.58×10^{-4}	-	-
	10	4.54×10^{-5}	2.23×10^{-3}	8.41×10^{-6}	4.12×10^{-4}	-	-

* Solid Ca(OH)_2

presented a characterization problem which was not resolved during this study. Several preliminary reaction runs were carried out for development of the separation scheme and the identification of reaction products. Each fraction, obtained through the separation scheme, is reported separately using the designated nomenclature.

Aqueous Phase I

An examination of this fraction in the ultra-violet region indicated a strong absorption band with a maximum at 203 nm and a minor band maximizing at 283 nm. The 203 nm band was assigned to the nitrate and nitrite component present. The 283 nm band was not identified.

Condensate I

This fraction represented the water and any volatile components removed by evaporation from the reaction mixture. An ultra-violet spectrophotometric examination of the colorless fraction revealed the absence of any UV absorbers, indicating the absence of nitrates. The fraction represented about seven percent of the reaction product. Characterization of this fraction was not attempted.

Extract I

The quantity of this fraction was negligible, amounting to about 0.05 percent. An infra red spectrum, (fig. 31) of the fraction shows intense absorption bands at 1640, 1276 and 860 cm^{-1} , respectively, indicating a nitrate ester. Further attempts to resolve the fraction were not made.

Solid I

This brown colored fraction was essentially calcium oxalate; the oxalate salt was identified by x-ray diffraction technique. Efforts to obtain an accurate quantitative measure of the oxalate by a permanganate titration procedure proved difficult due to a fading end point. The nature of the interfering product was not determined during the study. The fading, however, could be due to the presence of poly-hydroxy (diol type) compounds which could have been slowly oxidized by the permanganate.

Solid II

The fraction remaining after the flash evaporation of the aqueous phase appeared like a mixture made up of light yellow solids and a viscous liquid. Initially, it was thought the liquid portion might be glycerin, but this was disproved by IR spectrophotometric examination. This fraction represented 86 percent of the combined weights of the initial reactants.

Solid III

Qualitative tests of this fraction indicated a high concentration of nitrate and nitrite. The NMR Spectra of the Solid III sample, obtained during the preliminary runs, before and after being heated at 110°C, indicated the absence of hydrocarbons. The solubility of the fraction in ethanol indicated it to be essentially a mixture of calcium nitrate and calcium nitrite, however, positive identification of these salts by x-ray diffraction techniques was not possible because patterns for the mixture could not be observed. Initially, this could not be explained, since diffraction patterns of these salts have been reported in the literature. For an explanation, controls simulating a mixture of calcium nitrate, nitrite, and hydroxide were prepared. This was done by bubbling NO₂ gas into two separate portions of saturated calcium hydroxide solution, until pH's of 6 and 10, respectively, were obtained. The solutions were then subjected to flash evaporation and the solids, after drying at 110°C, were examined. Neither residue yielded a diffractogram on exposure to x-rays. With another control, to which calcium nitrate was added, similar results were obtained. An explanation of the behavior of Solid III is the extreme hygroscopicity of the calcium salts. This was observed when the controls and Solid III were dried and exposed to atmospheric conditions. The salts deliquesced immediately forming a viscous mixture, making x-ray diffraction patterns impossible.

Positive identification of the salts was made by other techniques. Examination of Solid III by ESCA showed the presence of nitrite, nitrate and calcium. It also showed the presence of some carbonate, indicating carbonate formation had occurred during separation. An IR spectrum of Solid III further supported the presence of the calcium salts, as shown in figure 32. The absorption band at 1380 cm⁻¹ was indicative of calcium nitrate. The identification of the nitrite was based on the minor bands at 850 cm⁻¹ and 2500 cm⁻¹; both specific for calcium nitrite. The band at 1440 cm⁻¹ may be due to calcium oxide or calcium carbonate. Water of hydration is indicated by the broad absorption band at 3440 cm⁻¹ and a band at around 1620 cm⁻¹. This indicated calcium nitrite and calcium nitrate were present as hydrated salts. Since both calcium salts deliquesce rapidly, extreme care was taken in obtaining the IR spectrum of Solid III. A portion of Solid III was heated to 110°C and mixed with potassium bromide, preheated at 110°C. The hot mixture was pressed in a heated die and the resulting potassium bromide disc was examined immediately. At 110°C hydrated calcium nitrite does not lose its water of hydration and hydrated calcium nitrate does not decompose. A similar technique could not be used for the x-ray diffraction measurements since it would require elaborate instrumentation, which was considered too time consuming and costly to construct for this study.

The quantitative estimation of the calcium salts also indicated the Solid III fraction to be essentially a mixture of these salts. However, the combined percentage of the calcium nitrate and calcium nitrite shown in table 9 is not necessarily equal to the actual percentage. The ethanol soluble fraction had been heated to 200°C prior to its quantitative analysis, to achieve constant weight. As a consequence, Solid III probably underwent partial change in composition. Evidence for this was found in the stoichiometrically unaccounted for calcium, probably present as the oxide, in Solid III and in the 0.247 g loss in weight for the fraction, reported as volatiles in figure 20. Additional quantitative analyses to obtain more accurate data were not possible during this characterization study.

Solid IV

As described in the Experimental section, this fraction was obtained via a flash evaporation of Filtrate I and the subsequent ethanol wash of Solid II. During the evaporation step, it was observed that as the volume of the reaction mixture decreased, yellow-orange solids appeared. These solids were a mixture of calcium hydroxide, calcium formate and organic residues somehow bound to calcium ions or to the hydroxide. The bound organic residues were not very soluble in the regenerated saturated aqueous solution of calcium hydroxide. This insolubility was further observed during the preparation of Solid IV for ion exchange. It was noted that 175 ml of water dissolved about 40 percent of Solid IV, yielding a solution, pH of 9.6, containing suspended light orange colored solids. These solids slowly dissolved as the pH of the solution was decreased to 3 by dropwise addition of concentrated hydrochloric acid, leaving a white solid amounting to about one percent of the initial reactants. The latter solid contained calcium and dissolved very slowly in concentrated hydrochloric acid. The presence of this solid indicated a slight change in the integrity of the reaction products in the Solid IV fraction.

The characteristics of Solid IV indicated the organic residue to be essentially polymeric or resinous in nature, since most known salts are soluble in dilute hydrochloric acid with little difficulty. This fraction presented a difficult characterization problem, one which was not completely resolved during this study.

Because of its insolubility in most organic solvents, including dimethyl formamide and dimethyl sulfoxide, chromatographic separation of components in Solid IV could not be carried out. As a consequence, the ion exchange technique was used to exchange calcium for hydrogen, to minimize the effect of the calcium ion on the resolvability of the organic residue. It was recognized that in using the ion-exchange technique, the protonated compounds might react with each other

altering the integrity of this fraction of the reaction mixture. It was felt, however, that this chance of reaction was minimized by the prior separation of the calcium nitrate and calcium nitrite from Solid IV. Their separation prevented the oxidation of the organic residues by generated nitric and nitrous acids.

Viscous Fraction, VR

The ion-exchange treatment of Solid IV produced a viscous, tacky, yellowish-brown residue with a slightly sweetish odor. The residue was easily soluble in water and to some extent soluble in acetone. The latter solubility made it possible to use thin-layer and gas liquid chromatography to detect the presence of about six compounds. An effort to isolate and identify these compounds was not made during the present study.

Nitrate esters and formic acid (ref. 28) were detected by chemical spot tests; the latter indicated the presence of formate in the reaction mixture. Mass spectral data for the acetone soluble portion of VR also indicated the presence of nitrate ester and a diol type polyhydroxy compound.

The nitrate ester detected in this fraction VR was probably formed from intermediates produced during the hydrolysis reaction and may be part of a polymeric molecule. To survive the mild alkaline hydrolysis, the nitrate ester group must be attached to a polymer which blocked its hydrolysis. Support for this was found in the chemical test for the nitrate ester. It was observed that when an aqueous solution of VR was tested with the Greiss reagent a negative test was obtained. However, on addition of potassium hydroxide, the usual red color appeared. This indicated that strong alkali hydrolyzed the ester while a mild alkaline solution did not.

From the data thus far accumulated, the fraction VR is considered to be a mixture of formic acid, a polymer containing nitrate ester, a polymer containing polyhydroxy groups, and other unidentified compounds. The presence of polymers is supported by the viscous tacky appearance of VR.

Table 9. Material balance for a hydrolysis reaction between glyceryl trinitrate and an aqueous solution of calcium hydroxide.

<u>Reaction products</u>	<u>Percentages of reactant</u>
calcium nitrite, calcium nitrate	56.3 ⁽¹⁾
calcium hydroxide, unreacted	14.9
calcium oxlate plus minor unidentified products	6.3
ester nitrate (methylene chloride soluble)	0.05
calcium formate ⁽²⁾ and other unidentified products, e.g., ester nitrate, polymers, etc	11.3
volatiles, unidentified (by difference)	<u>11.2</u>
Total percentage of reactants	100.05
 <u>Reactants</u>	
glyceryl trinitrate, g	3.0
calcium hydroxide, g	<u>2.68</u>
Total weight, g	5.68

(1) Assumed to contain a small percentage of calcium oxide, probably formed during heating of Solid III at 200°C.

(2) As formic acid in the organic fraction, VR.

Condensate II

This fraction represented ethanol and other volatile components from Solid III. Characterization of Condensate II was not carried out during this study. It probably contained the decomposition products of the calcium nitrate and nitrite salts generated in Solid III by heating at 200°C.

Material Balance

Since the present study has resulted in only a partial characterization of the reaction products, a balanced chemical equation for the hydrolysis reaction could not be evolved for a material balance. In lieu of the equation, however, the scheme outlined in figure 4, based on the Separation of Reaction Products procedures (see Experimental), was used for the material balance. Essentially, the scheme uses the weight of the separated fractions, reactant weights and percentages of the identified products. Table 9 shows a material balance for the hydrolysis reaction. Since volatile fractions were obtained by difference, the reaction products should total to 100 percent of the reactants.

The unreacted calcium hydroxide, its weight determined from Filtrate I, was carried through to Solid IV during separation. Therefore, when its weight was added to the organic residue weight (fig. 20) the sum totaled more than the weight for Solid IV, indicating a material imbalance for the fraction. Theoretically, the calcium due to the unreacted calcium hydroxide when subtracted from the calcium stripped from the ion exchanger, should give the weight of calcium bound to the organics. An explanation of this imbalance can be found in poor calcium values obtained for the stripped calcium. Consistent calcium values were not obtainable. It is felt that more work should be done in this area to obtain a meaningful material balance for Solid IV.

Glycidyl Nitrate

One of the unknown products of hydrolysis was detected by HPLC. This unknown was a major product in the kinetic studies of hydrolysis of both DNG isomers but not of TNG. Although this product was observed to disappear with time, its half-life in dilute aqueous calcium hydroxide was long enough to make possible its isolation for identification. The isolation was carried out after HPLC had shown that all of the DNG had disappeared. Examination of the IR and NMR spectra of the unknown product, (fig. 33 and 34) indicated that the unknown was a low molecular weight alkyl nitrate. The IR and NMR spectra of several available nitrate esters within this category, e.g., allyl nitrate, butyl nitrate, diethylene glycol dinitrate, and triethylene glycol dinitrate, did not match the spectra of the unknown.

A review of the chemistry of the basic hydrolysis of glyceryl nitrate esters suggested that the unknown might be glycidyl nitrate, i.e., the nitrate ester of 2,3-epoxy-1-propanol. Glycidyl nitrate, is reported (ref. 16) to be formed readily from either of the DNG isomers by the action of concentrated potassium or sodium hydroxide, as discussed later on.

To test this hypothesis, 1,3-DNG was treated with 30% aqueous NaOH according to the procedure described previously (ref. 16). The IR and NMR spectra of the synthesized product matched the spectra of the unknown product of hydrolysis of DNG's.

DISCUSSION

Hydrolysis Reactions

Earlier studies (ref. 29) on the basic hydrolysis of alkyl nitrate esters have lead to the conclusion that the reaction schemes primarily responsible for product formation are the following:

1. Nucleophilic substitution



2. Elimination of beta-hydrogen



3. Elimination of alpha-hydrogen



Reactions of this type can occur in neutral hydrolysis, with water acting as the nucleophilic agent, and can be pure second order or pseudo-first order, depending on the concentration of the reactants. The substitution reaction, giving alcohol and nitrate ion, predominates in both alkaline and neutral hydrolysis of primary and secondary nitrate esters, although some products of both elimination processes are obtained from alkaline hydrolysis.

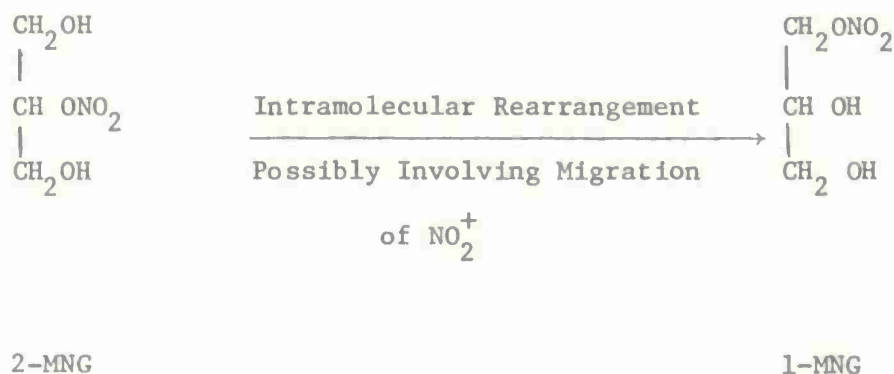
These reactions are expected to be operative during the basic hydrolysis of glyceryl nitrate esters since both NO_2^- and NO_3^- are formed from these esters as presented earlier in this report. The formation of glycidol by the reaction of 2-MNG with NaOH described in the Synthesis of Reaction Products section, provides some support for the probable occurrence of reaction 1. However, the nature of the

products detected in the present work suggests that, in addition to processes 1,2 and 3, other processes, such as isomerization reactions and C-C scission are operative in the basic hydrolysis of glyceryl nitrate esters.

One of the most significant and surprising features of glyceryl nitrate ester hydrolysis by calcium hydroxide is the fact that there seems to be no evidence of stepwise hydrolysis from TNG to simpler homologs (DNG's and MNG's). This is especially surprising in view of the metabolism of TNG and DNG's and MNG's reported by three different groups (ref. 30, 31).

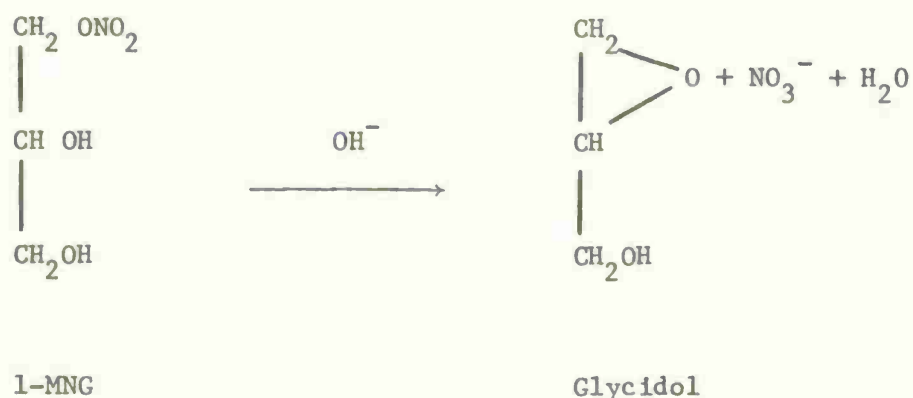
Isomerization Reactions

The 2-MNG isomerized to 1-MNG which probably hydrolyzed to form glycidol. The kinetic data clearly show the formation of 1-MNG during the early stages of 2-MNG hydrolysis. Mechanistic details of the isomerization reaction can only be of a speculative nature, since this type of reaction has not been observed by previous investigators.



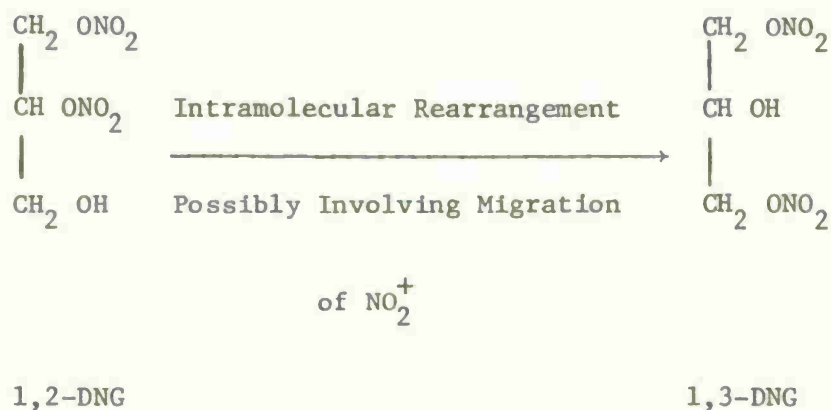
The only reason that can be offered, at present, for this migration is the apparently higher stability of the ONO_2 group in the 1-carbon position as compared to the carbon-2 position. This is consistent with the isomerization of 1,2-DNG to 1,3-DNG which will be discussed later on.

It was mentioned earlier in the Synthesis of Reaction Products Section that 2-MNG hydrolyzes in 30% NaOH solution to form glycidol. Logically, then, 1-MNG would also be expected to hydrolyze in alkali to form glycidol, as shown below:

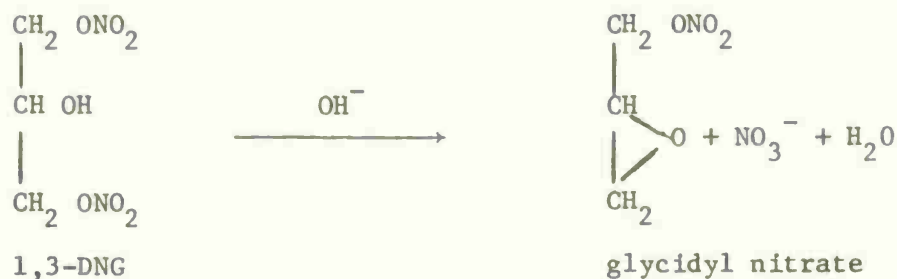


However, this could not be verified, since the experimental conditions employed for the LC determinations were not appropriate for the detection of glycidol.

Similarly, the isomerization of 1,2-DNG could proceed as follows:



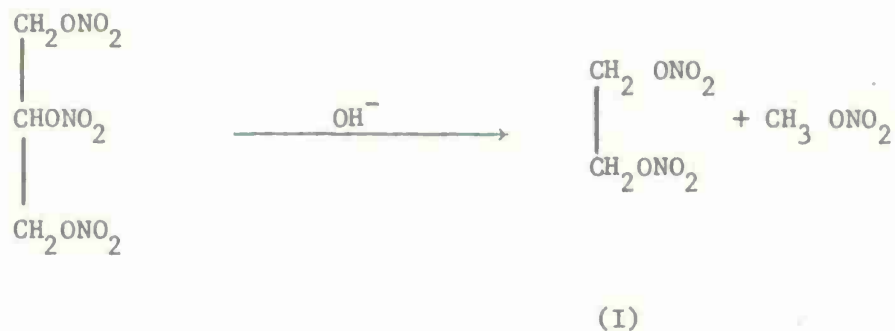
Subsequently, 1,3-DNG would hydrolyze to form glycidyl nitrate.



Glycidyl nitrate would be expected to hydrolyze with a very slow rate to yield products, most likely glycidol.

C-C Scission

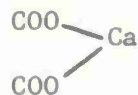
This process is evidenced by the appreciable amount of calcium oxalate formed during the basic hydrolysis of TNG. According to table 9, approximately 7% of the TNG is converted to calcium oxalate. A possible mechanism for the formation of the oxalate could be the following:



Hydrolysis of product (I) leads to :



which could be oxidized in the presence of Ca^{++} to form eventually:



The experimental data indicating that during the basic hydrolysis of TNG there is no formation of DNG's and MNG's and similarly that there is no formation of MNG's in the basic hydrolysis of DNG's was, initially, interpreted by assuming the following stoichiometries:



Integration of the corresponding rate expression, within the appropriate concentration and time limits led to the following equations:

$$\frac{1}{(B_o - 3A_o)^2} \ln \frac{(A_o - X)B_o}{(B_o - 3X)A_o} + \frac{1}{2(B_o - 3X)^2} + \frac{1}{(B_o - 3A_o)(B_o - 3X)} = \frac{1}{2B_o} + \frac{1}{B_o(B_o - 3A_o)} - (B_o - 3A_o) k t \quad (5)$$

$$\ln \frac{(A_o - X)}{(B_o - 2X)} - \frac{2X(2A_o - B_o)}{B_o(B_o - 2X)} = \ln \frac{A_o}{B_o} - (2A_o - B_o)^2 k t \quad (6)$$

However, treating the data according to equations 5 and 6 indicated that these stoichiometries can not be operative during the basic hydrolysis of TNG and DNG's.

The remaining possible alternative is that the hydrolysis of the functional group $-\text{CH}_2\text{ONO}_2$ leads to an aldehyde or unsaturated group with the simultaneous formation of NO_3^- and NO_2^- , respectively (reaction schemes 2 and 3, presented earlier).

Calculation of Destruction Rate for TNG in a Planned Treatment Facility¹

1. The following data are required [K calculated from equation (3)]:

$T^{\circ}\text{C}$	$K_{\text{calc}} \text{ (M}^{-1} \text{ sec}^{-1}\text{)}$	$[\text{OH}^{-}]^2 \text{ (M)}$	$K_{\text{obs}} = K_{\text{calc}} \times [\text{OH}^{-}] \text{ (sec}^{-1}\text{)}$
10	1.79×10^{-3}	0.0460	8.23×10^{-5}
18	7.05×10^{-3}	0.0441	3.109×10^{-4}
25	2.15×10^{-2}	0.0420	9.03×10^{-4}
30	4.71×10^{-2}	0.0404	1.90×10^{-3}
35	1.00×10^{-1}	0.0388 (est)	3.88×10^{-3}
40	2.046×10^{-1}	0.0372 (est)	7.61×10^{-3}
45	4.11×10^{-1}	0.0356 (est)	1.46×10^{-2}
50	9.81×10^{-1}	0.0340 (est)	3.34×10^{-2}

¹ This facility is planned for installation at Radford Army Ammunition Plant, where aqueous TNG wastes will be "desensitized" with calcium hydroxide prior to biological treatment. Although the desensitizers could be operated as stirred-flow reactors, they will actually be used in the batch mode (ref. 1).

² Calculated from saturation concentration of $\text{Ca}(\text{OH})_2$, (ref. 32).

2. Calculations based on planned batchwise operations³

Two 5000-gallon tanks will be filled alternately (filling time 1/2 hour) with wastewater containing about 1000 ppm of TNG and more than sufficient lime to give a saturated solution. The lime-wastewater slurry will be stirred one hour and discharged over a period of 1 1/2 hours. It will go through a flocculator (1/2 hour) and be held at least two hours in a clarifier, after which the solution will be acidified. Thus, the TNG will be exposed to high pH for a period of about 3 1/2 hours. This time sequence permits treatment of up to 80,000 gallons of waste per day.

The usual first-order kinetic rate laws apply. Let C_1 be the concentration of TNG in the raw wastewater, C_0 the concentration of TNG after one hour of mixing and C_0^1 the concentration of TNG following clarifier treatment. Let $t = 1$ hour = 3600 sec and $t^1 = 3 \frac{1}{2}$ hrs = 12,600 sec.

$$C_0 = C_1 e^{-Kt} = C_1 e^{-3,600 K}$$

$$C_0^1 = C_1 e^{-Kt^1} = C_1 e^{-12,600 K}$$

Using values of K_{obs} presented above, one obtains the following results (assuming $C_1 = 1000$ ppm):

<u>T°C</u>	<u>C_0 (ppm)</u>	<u>C_0^1 (ppm)</u>
18	326	19.9
25	38.7	0.011
40	1.26×10^{-9}	2.28×10^{-39}

³ Mr. Leonard Smith, Radford Army Ammunition Plant, provided a description of the operation (ref. 1).

3. Calculations assuming reaction only in a stirred-flow reactor ⁴

Assume an average flow, V, of 35,000 gallons per day, and the use of two 5,000-gallon reactors (Q = 10,000 gal.) in which glyceryl trinitrate is denitrated with calcium hydroxide at saturation. In stirred-flow reactors, with TNG input concentration C_i and output concentration C_o (which is also the actual concentration in the reactor):

$$VC_o = VC_i - \text{loss rate}$$

Since the loss rate is $Q(dC/dt) = QK_{obs}C_o$, it follows that

$$VC_o = VC_i - QK_{obs}C_o$$

Hence

$$C_i = [1 + (Q/V)K_{obs}]C_o$$

Whence

$$C_o = C_i \div [1 + (Q/V)K_{obs}]$$

In the present instance,

$Q/V = 10,000 \div 35,000 = 0.2857 \text{ day} = 24,686 \text{ sec}$ (the residence time).

Using the values of K_{obs} presented above, one obtains the following results (assuming $C_i = 1000 \text{ ppm}$):

<u>T°C</u>	<u>C_o (ppm)</u>
18	115
25	42.9
40	5.3

⁴ Flow rate and reactor sizes are taken from reference 33.

4. Calculations assuming reaction in a stirred-flow reactor (as above) followed by 2 1/2 hours at high pH for flocculation and clarification before neutralization.

Here C_o^1 is the final TNG concentration, where $C_i = 1000$ ppm:

<u>T°C</u>	<u>C_o^1 (ppm)</u>
18	7.01
25	0.012
40	9.54×10^{-30}

5. At this time there is no clear data to support the assumption that biological treatment would lead to significant degradation of TNG beyond that achieved in the desensitization process. In the judgement of the authors, a TNG discharge level in the ppm range will probably not be acceptable. Hence, according to the results shown in paragraphs 2 and 3 (above) the desensitization process should be conducted well above 18°C. The reactor design allows for heating to about 40°C, and this would probably permit adequate destruction of TNG within the reactors (batch mode) in the winter season, when the temperatures in the flocculation and clarification steps might be considerably lower than 40°C or even 25°C.

6. In summary, correct operation of the desensitization process, with particular attention to temperature, will be important to assure adequate destruction of TNG. The limited data on hydrolysis of MNG and DNG isomers do not permit prediction of destruction rates at other than 25°C, at which temperature the rates are slightly greater than for TNG. Nor can any conclusions be drawn concerning the persistence of glycidol or glycidyl nitrate, which are formed from the MNG and DNG isomers during hydrolysis. (It would appear, at all events, that the wastewaters contain very little MNG from which to form glycidol, so that the latter compound would originate, if at all, only from glycidyl nitrate.)

Hydrolysis of DNG's

1. The isomerization of 1,2-DNG to 1,3-DNG is obviously very rapid. From figure 10, it appears to be about 50% complete in 43 seconds, for an estimated first-order rate constant of $1.6 \times 10^{-2} \text{ sec}^{-1}$. From the same graph, the first-order rate constant for disappearance of 1,3-DNG is estimated at $5.1 \times 10^{-4} \text{ sec}^{-1}$. If both reactions show a first-order dependency on $[\text{OH}^-]$, then the 1,2-DNG isomerization rate constant is about 30 times as great as the 1,3-DNG hydrolysis rate constant.

2. When 1,3-DNG was treated with $\text{Ca}(\text{OH})_2$, the main product initially formed was glycidyl nitrate (GN). The highest analyzed concentration was $1.783 \times 10^{-3} \text{ M}$, found at 93 and 162 minutes. Because the rise in concentration was faster than the decline, the maximum concentration should have occurred between these two times, but closer to the first (less than 127.5 min). Curve-fitting was best achieved by a third-order plot of concentration against $\log t$, to give an equation whereby it was possible to show $[\text{GN}]_{\text{max}} = 1.796 \times 10^{-3} \text{ M}$ and $t_{\text{max}} = 116.2 \text{ min}$.

Since the initial concentration of 1,3-DNG was $2.508 \times 10^{-3} \text{ M}$, at least 71.6% of the reaction went by way of glycidyl nitrate. A better comparison of the rate constant for formation of GN versus that for disappearance of 1,3-DNG might be obtained by comparing the concentration of GN at 13 min ($7.64 \times 10^{-4} \text{ M}$) with the concentration of 1,3-DNG lost at 13 min. ($8.9 \times 10^{-3} \text{ M}$, according to the graph, (fig. 11)). This comes to 85.8%, and does not depend on any knowledge of $[\text{OH}^-]$ during the reaction. The formation constant, k_f , for glycidyl nitrate, should be 85.8% of the hydrolysis rate constant for 1,3-DNG. (A linear plot of $[\text{GN}]$ extended back to zero time gives 75%.) If an average value for the hydrolysis rate constant for 1,3-DNG of $1.159 \times 10^{-1} \text{ M}^{-1} \text{ sec}^{-1}$ is assumed, and $[1,3\text{-DNG}]$ (read from the graph, fig. 11, at 116.2 min.) is $3.7 \times 10^{-5} \text{ M}$ at the maximum, then the second-order rate constant for disappearance of GN should be

$$\begin{aligned} k_{\text{GN}} &= k_f \times 3.7 \times 10^{-5} \div 1.7962 \times 10^{-3} \\ &= 0.858 \times 1.159 \times 10^{-1} \times 3.7 \times 10^{-5} \div 1.7962 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1} \\ &= 2.05 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1} \end{aligned}$$

Thus the ratio of the disappearance rate constant for 1,3-DNG to the disappearance rate constant for GN is about 57:1.

Another estimate of k_{GN} , which posits a value for $[\text{OH}^-]$ of $6.9 \times 10^{-3} \text{ M}$ is obtained from GN concentrations ($1.657 \times 10^{-3} \text{ M}$ and $0.8286 \times 10^{-3} \text{ M}$) at 276 and 1313 minutes in table 3, assuming first-order kinetics:

$\ln (1.657/0.8286) \div [(1313-276) \times 6.9 \times 10^{-3} \times 60] = 1.61 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}$. This is fortuitously close to the previously calculated value of $2.05 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}$, considering the assumptions made with regard to $[\text{OH}^-]$ and the kinetic order, and the fact that so much weight had to be attached to individual data points.

3. Even without consideration of kinetics, it is apparent that a holding time of 3 1/2 hours (210 minutes) at 25°C with initially saturated $\text{Ca}(\text{OH})_2$ would result in a concentration of GN about $1.719/2.508 \approx 2/3$ of the initial DNG concentration.

4. Assume that $[\text{OH}^-] \gg 1,3\text{-DNG}$, and that the appropriate kinetic equations for the 1,3-DNG/GN system are:

$$-d[1,3\text{-DNG}] = k[\text{OH}^-] [1,3\text{-DNG}] dt$$

$$+ d[\text{GN}] = k_f [\text{OH}^-] [1,3\text{-DNG}] dt$$

$$- d[\text{GN}] = k_d [\text{OH}^-] [\text{GN}] dt$$

at constant (OH^-) , let

$$k[\text{OH}^-] = c$$

$$k_f[\text{OH}^-] = c_f$$

$$k_d [\text{OH}^-] = c_d.$$

The kinetic model can then be derived in a manner similar to system 15 in Capellos and Bielski (ref. 25) yielding the following equation:

$$[\text{GN}] = [1,3\text{-DNG}]_0 \frac{c_f}{(c_d - c)} [e^{-ct} - e^{\frac{c_d}{c}t}]$$

Biological Concerns

The formation of the persistent epoxy-compounds glycidyl nitrate and glycidol, must be a source of some concern, since epoxides are automatically suspect as potential carcinogens. Glycidol is already being considered by the National Cancer Institute for testing. (NCI No. C55549 , a "chemical tentatively selected for testing" as of 5 January 1979). The recent discovery that TNG is a carcinogen in rats (ref. 34) occasions speculation that metabolic pathways involving glycidyl nitrate or glycidol should be sought, and that a comparison might be made between the organ specificities of these compounds and TNG.

CONCLUSIONS

1. The present findings serve to aid in establishing operating conditions for the desensitization of TNG wastes. In view of the uncertainty as to the efficiency of biological degradation as a means of destroying TNG, and of the known carcinogenicity of TNG, the conditions should be chosen so as to achieve virtually complete destruction of this compound, i.e., perhaps to the level of 10^{-5} ppm or less. The proper conditions can easily be prescribed using the data given in this report.
2. The toxicological significance of the probable formation of glycidyl nitrate and glycidol in TNG wastewaters on treatment with calcium hydroxide should be carefully assessed by competent authority.
3. The chemistry of glyceryl nitrate ester reactions with calcium hydroxide shows a number of unusual features, including isomerizations, epoxide formation and failure to form expected denitration products. Additional research is needed to characterize the products, especially those from glyceryl trinitrate.
4. The activation energies of some of the reactions studied were not obtained. In view of the possible toxicological implications, they should be determined.

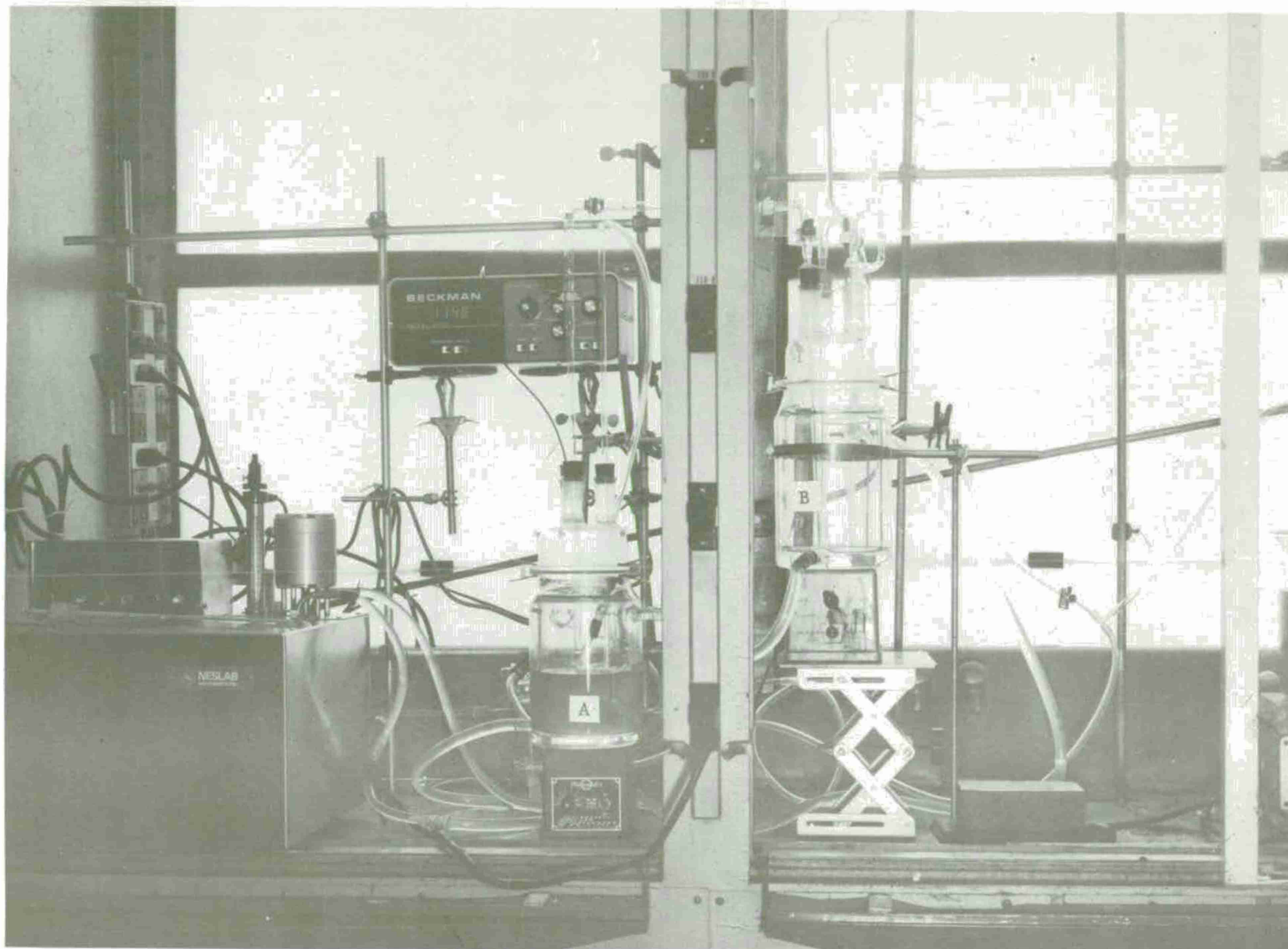


Figure 1. Apparatus used for the study of the kinetics of glyceryl nitrate ester hydrolysis

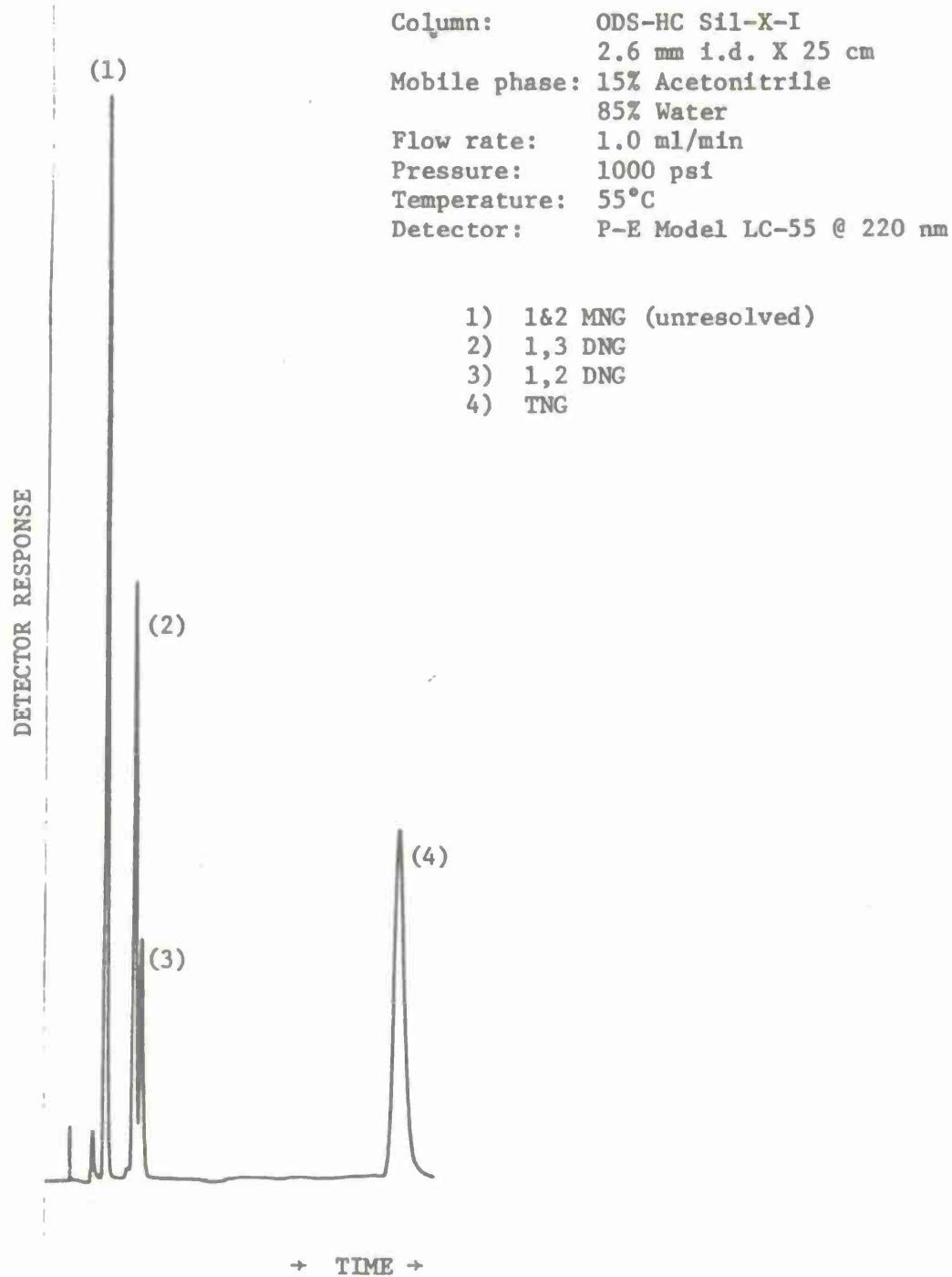


Figure 2. High performance liquid chromatogram of glyceryl nitrates.

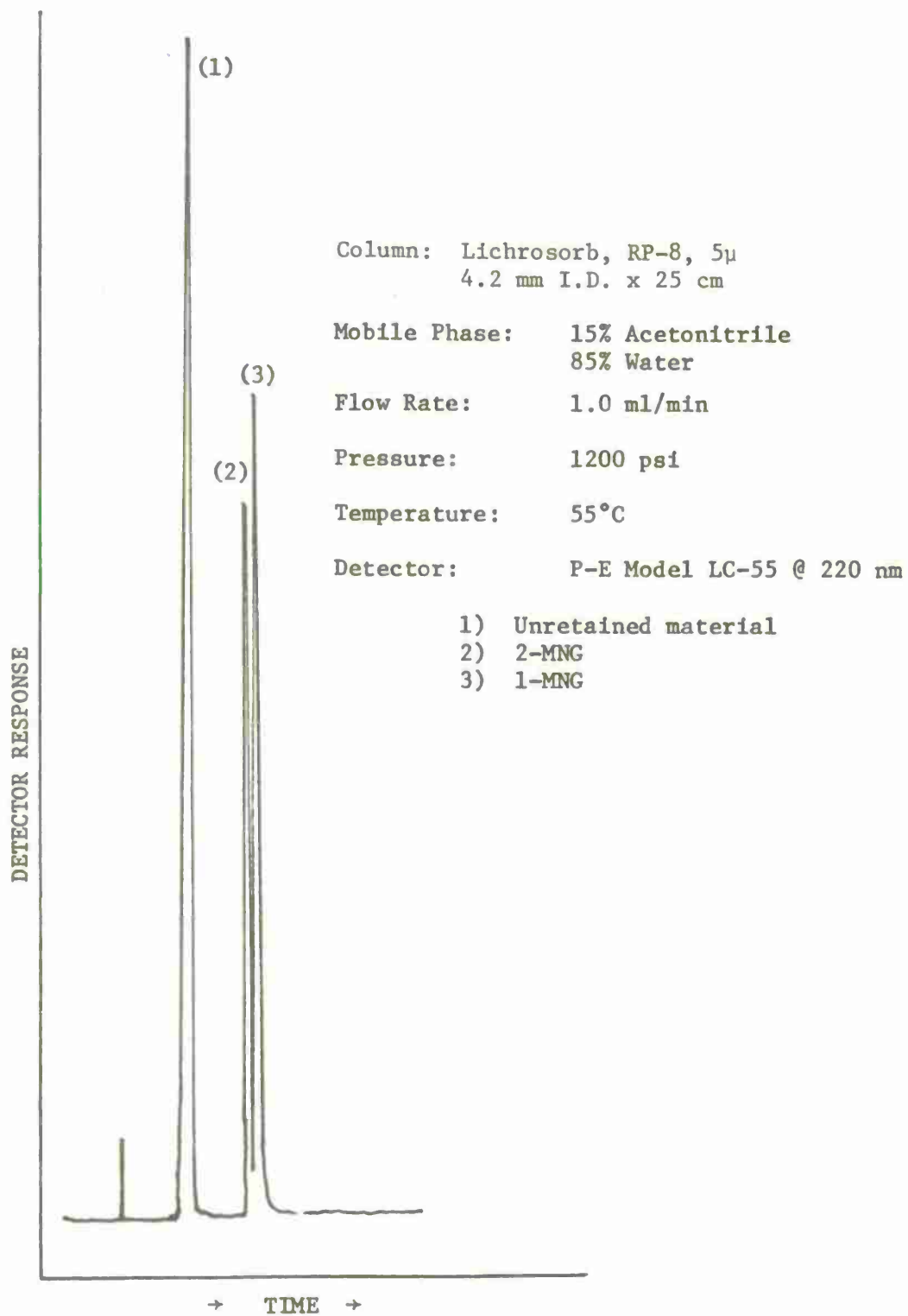
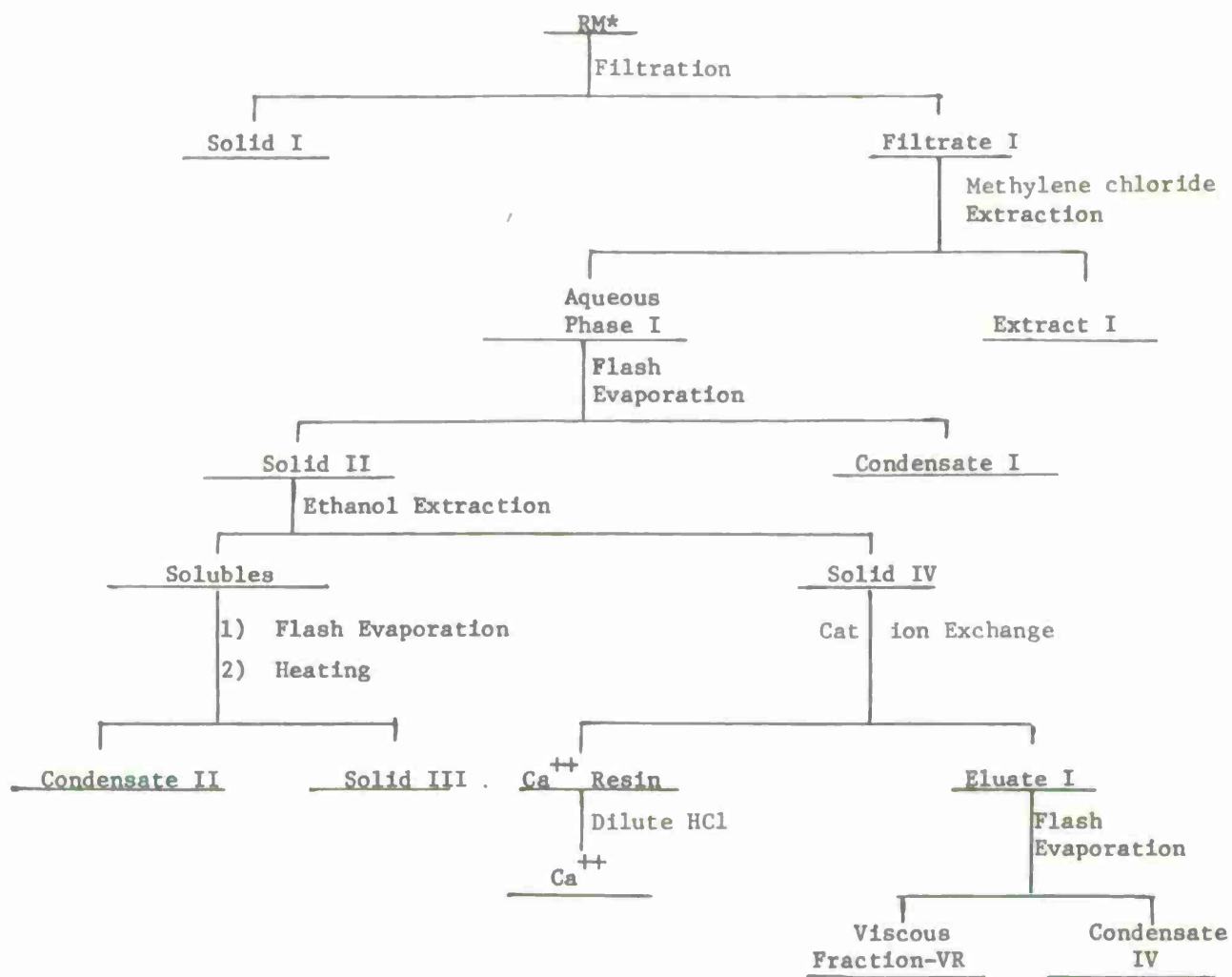


Figure 3. High performance liquid chromatogram of glyceryl mononitrates.



* Reaction mixture: TNG + sat'd aqueous $\text{Ca}(\text{OH})_2$ solution.

Figure 4. Separation scheme for reaction products.

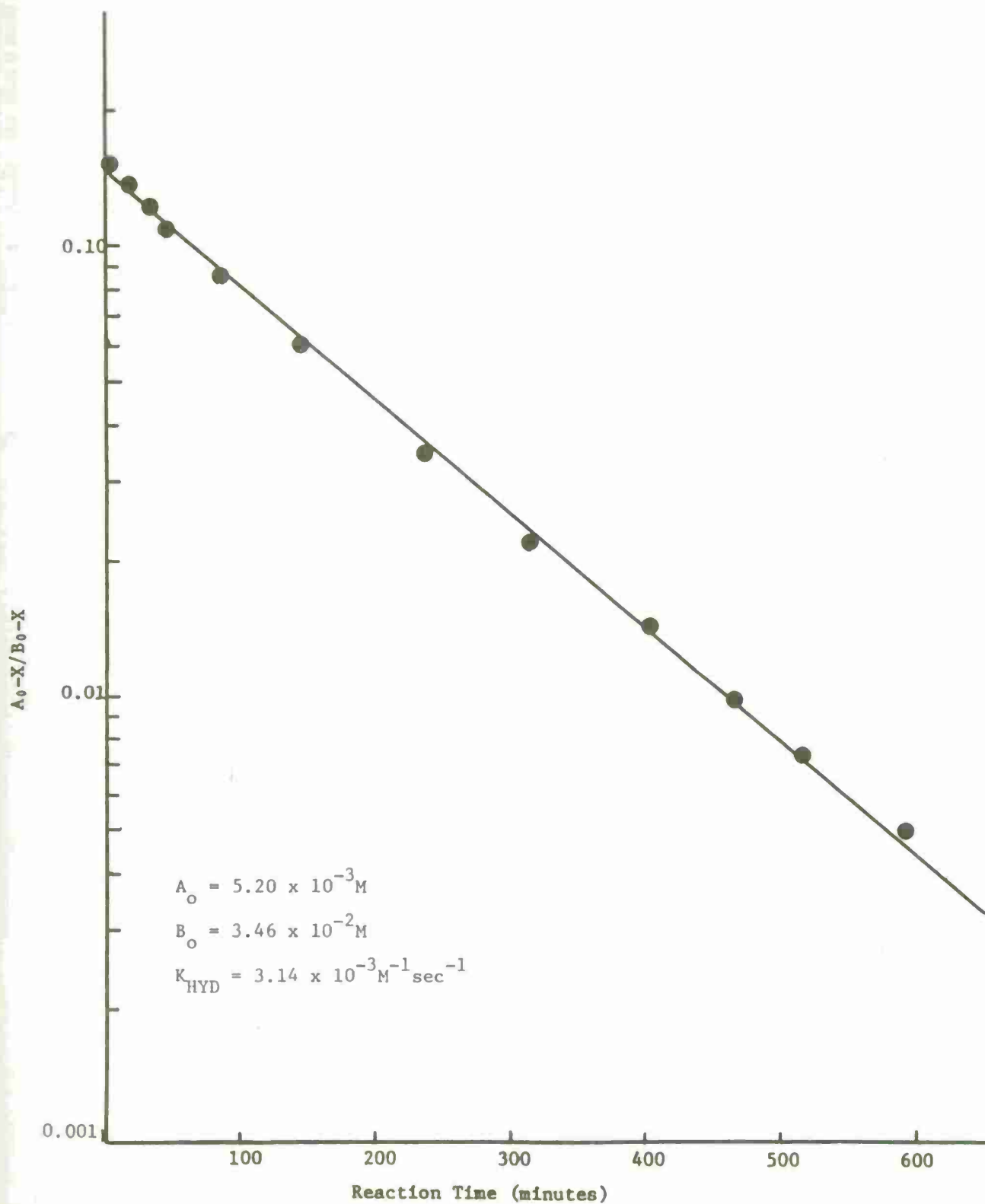


Figure 5. Hydrolysis of 1-MNG in aqueous $Ca(OH)_2$ solution at 25°C.

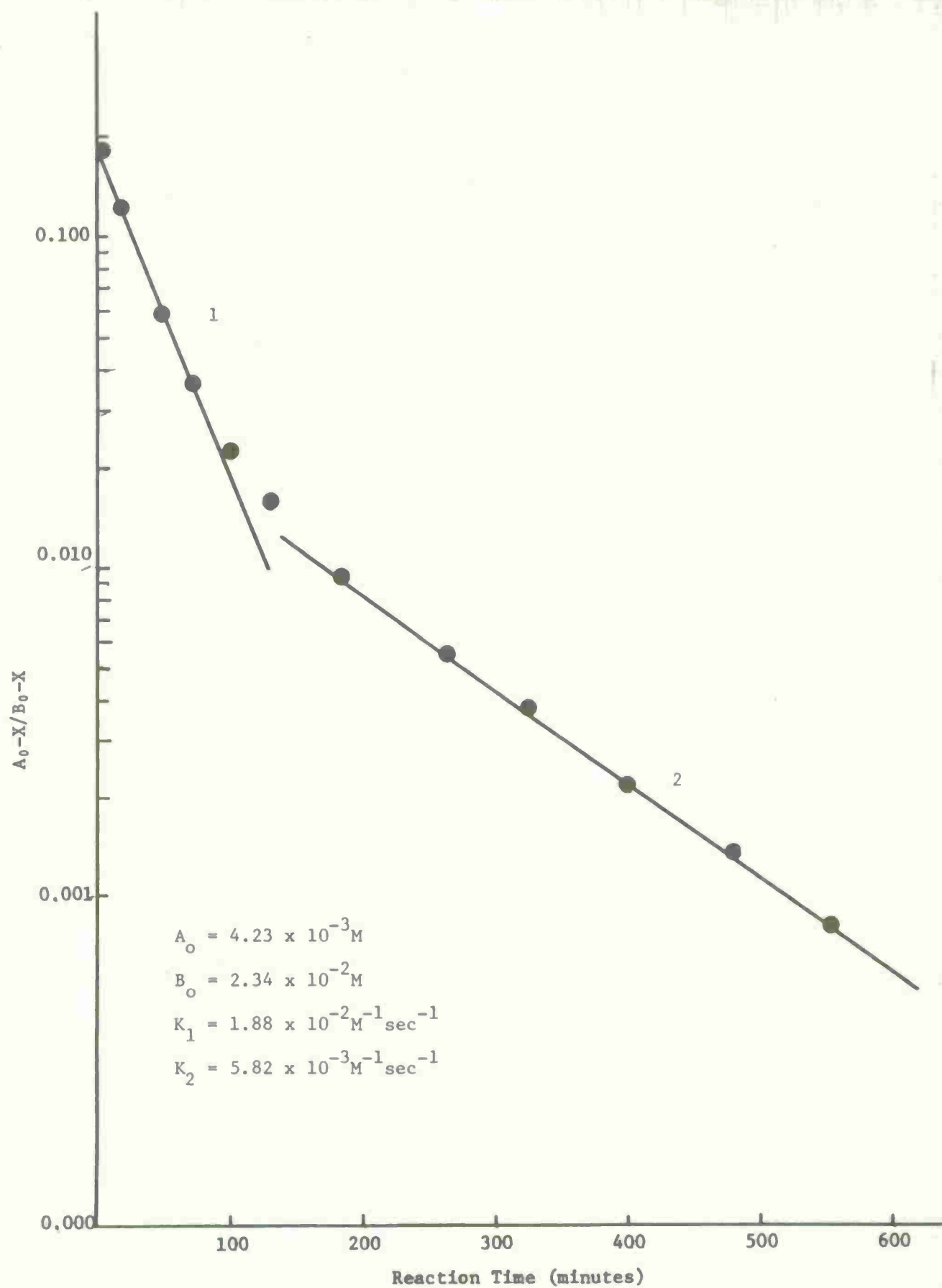


Figure 6. Hydrolysis of 2-MNG in aqueous $\text{Ca}(\text{OH})_2$ solution at 25°C .

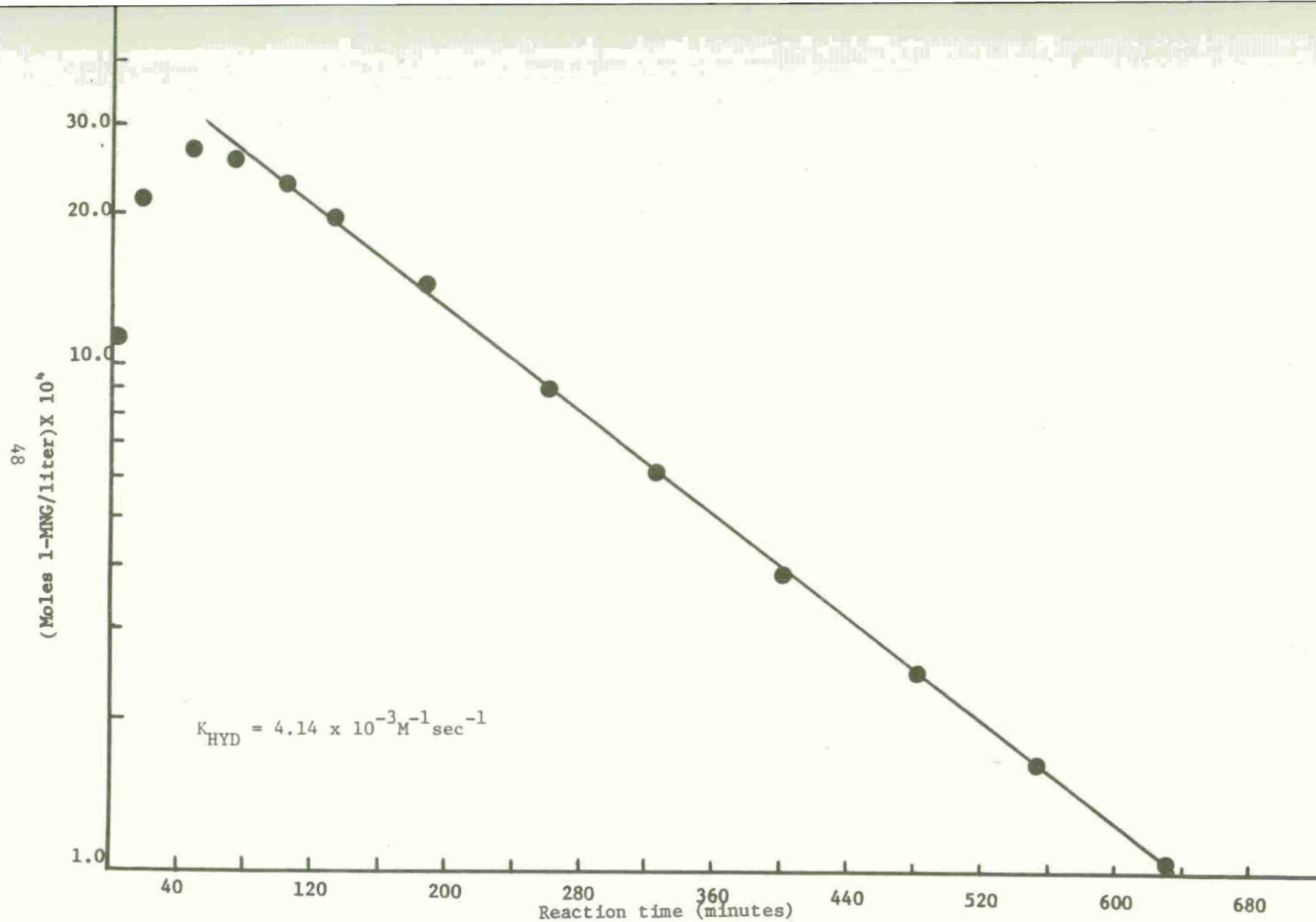


Figure 7. Formation and subsequent hydrolysis of 1-MNG during hydrolysis of 2-MNG in aqueous $\text{Ca}(\text{OH})_2$ solution at 25°C .

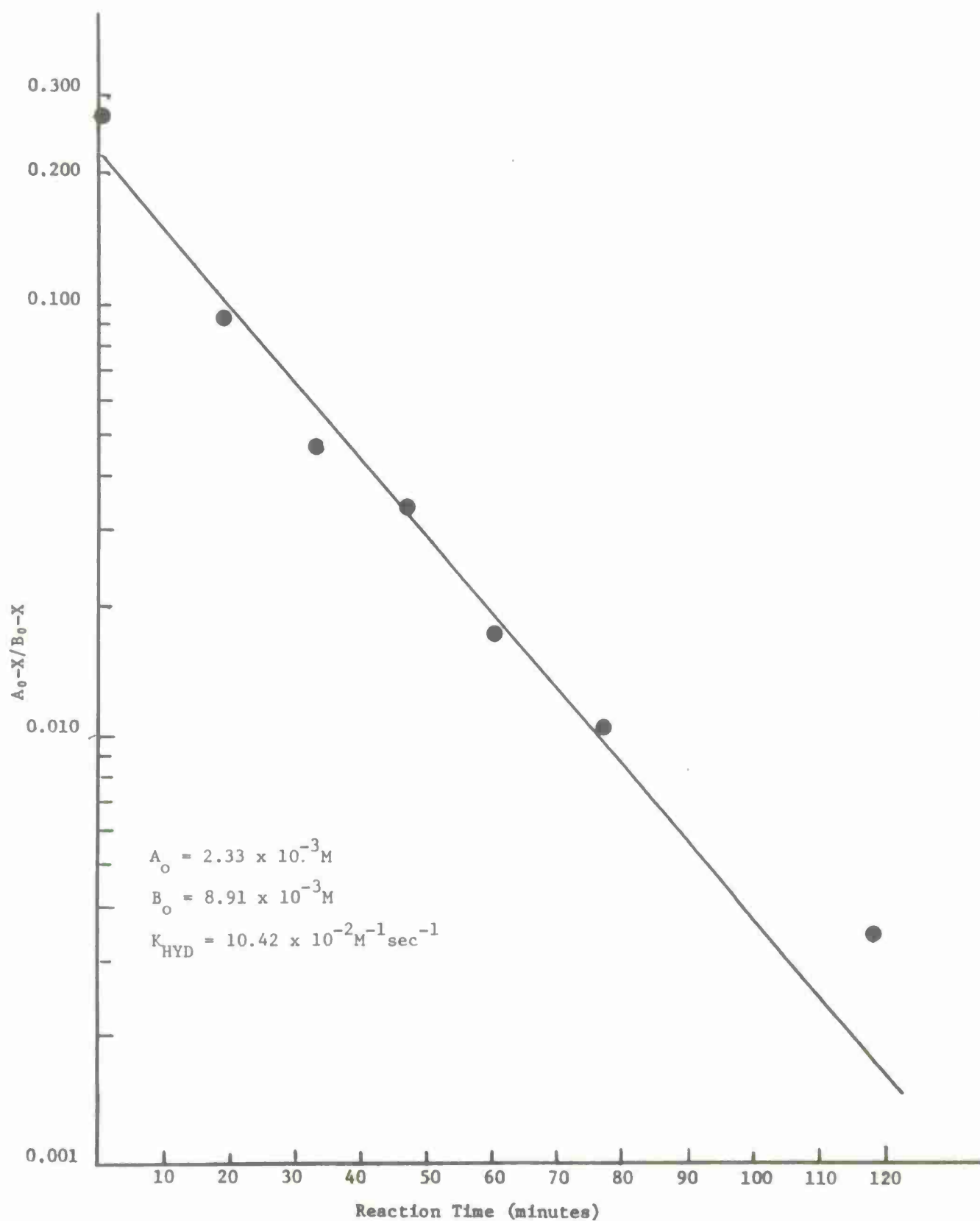


Figure 8. Hydrolysis of 1,2-DNG in aqueous $Ca(OH)_2$ solution at $25^\circ C$

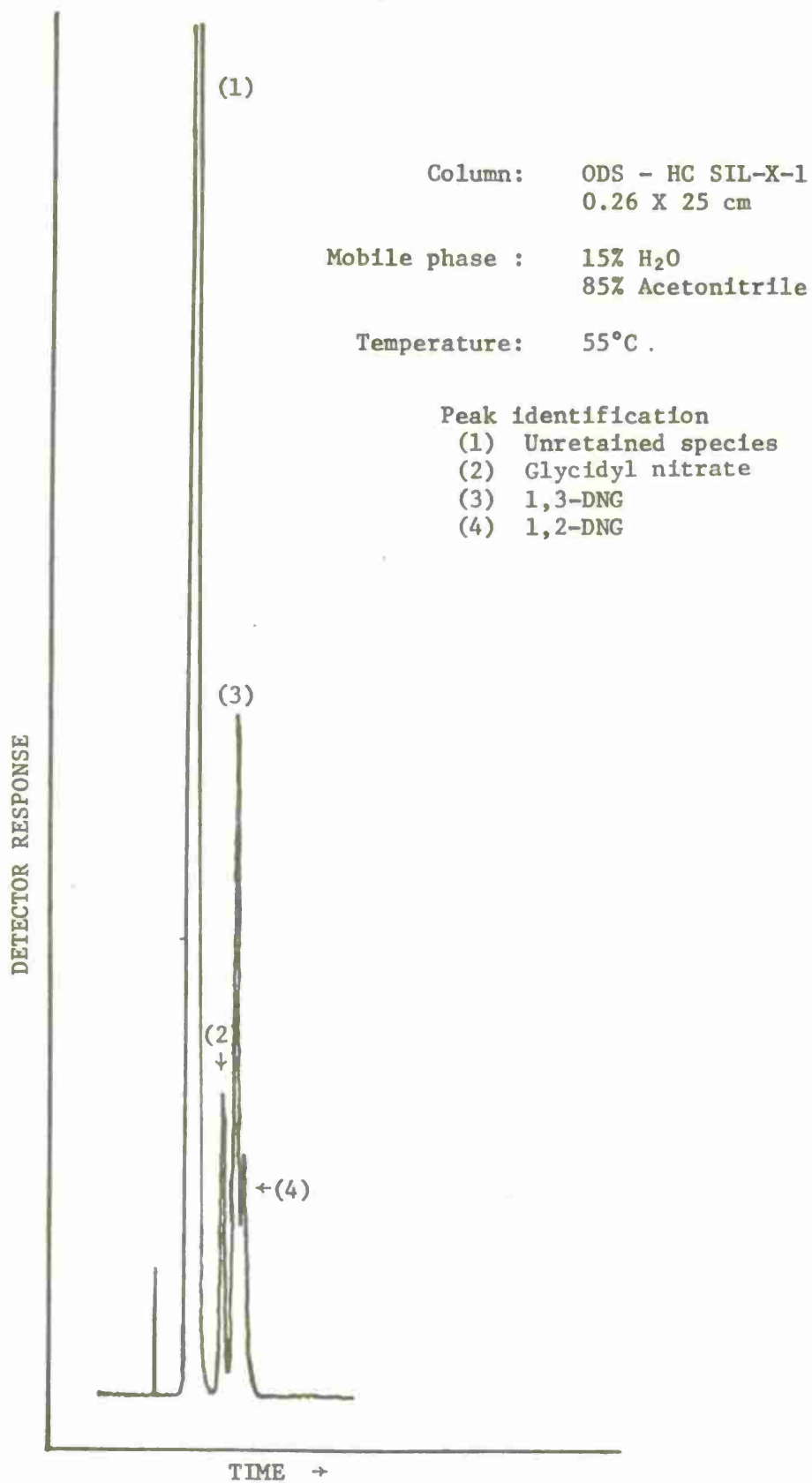


Figure 9. High performance liquid chromatogram of 1,2 DNG hydrolysis in aqueous Ca(OH)₂ solution at 25°C.

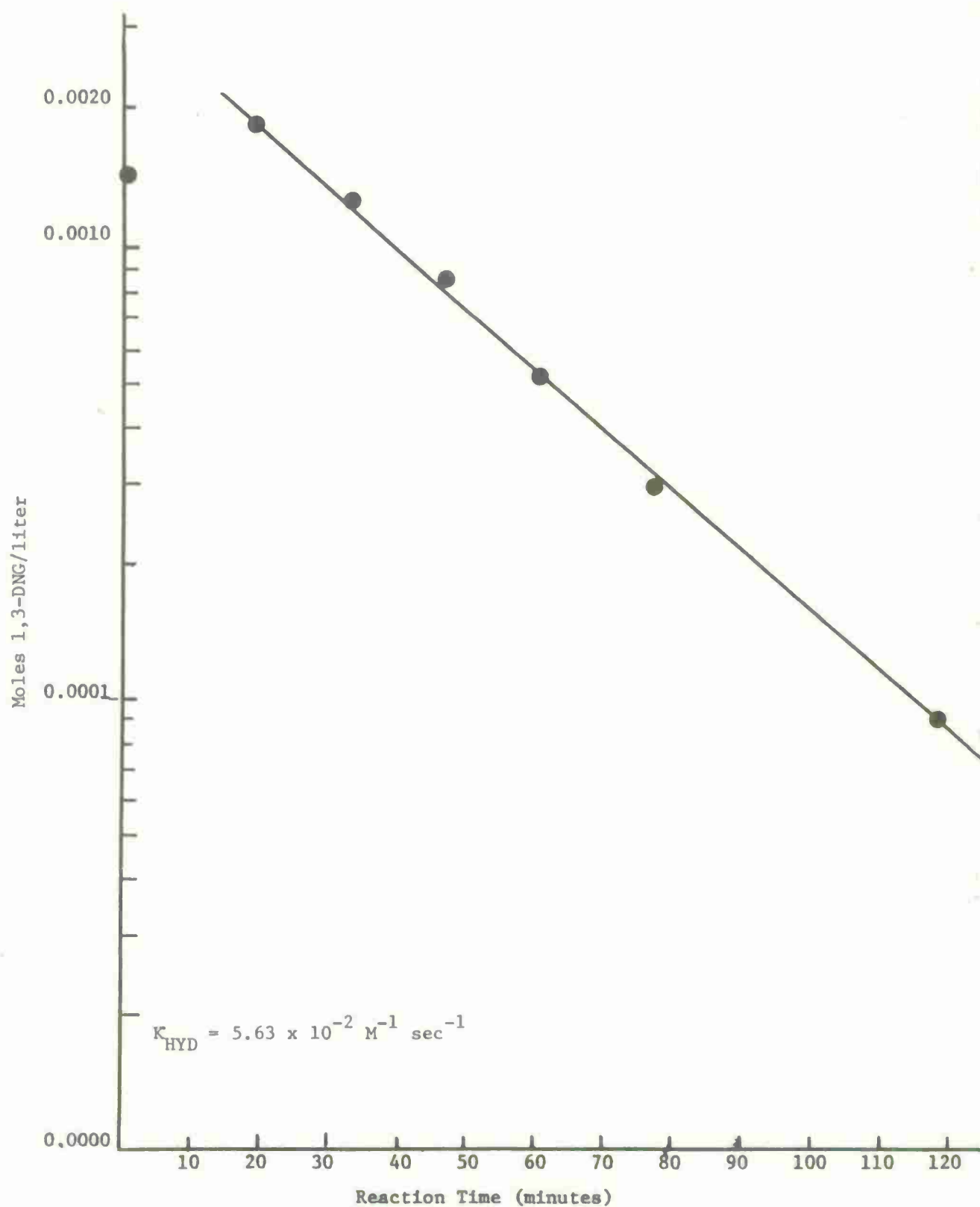


Figure 10. Formation and subsequent hydrolysis of 1,3-DNG during hydrolysis of 1,2-DNG in aqueous $\text{Ca}(\text{OH})_2$ solution at 25°C.

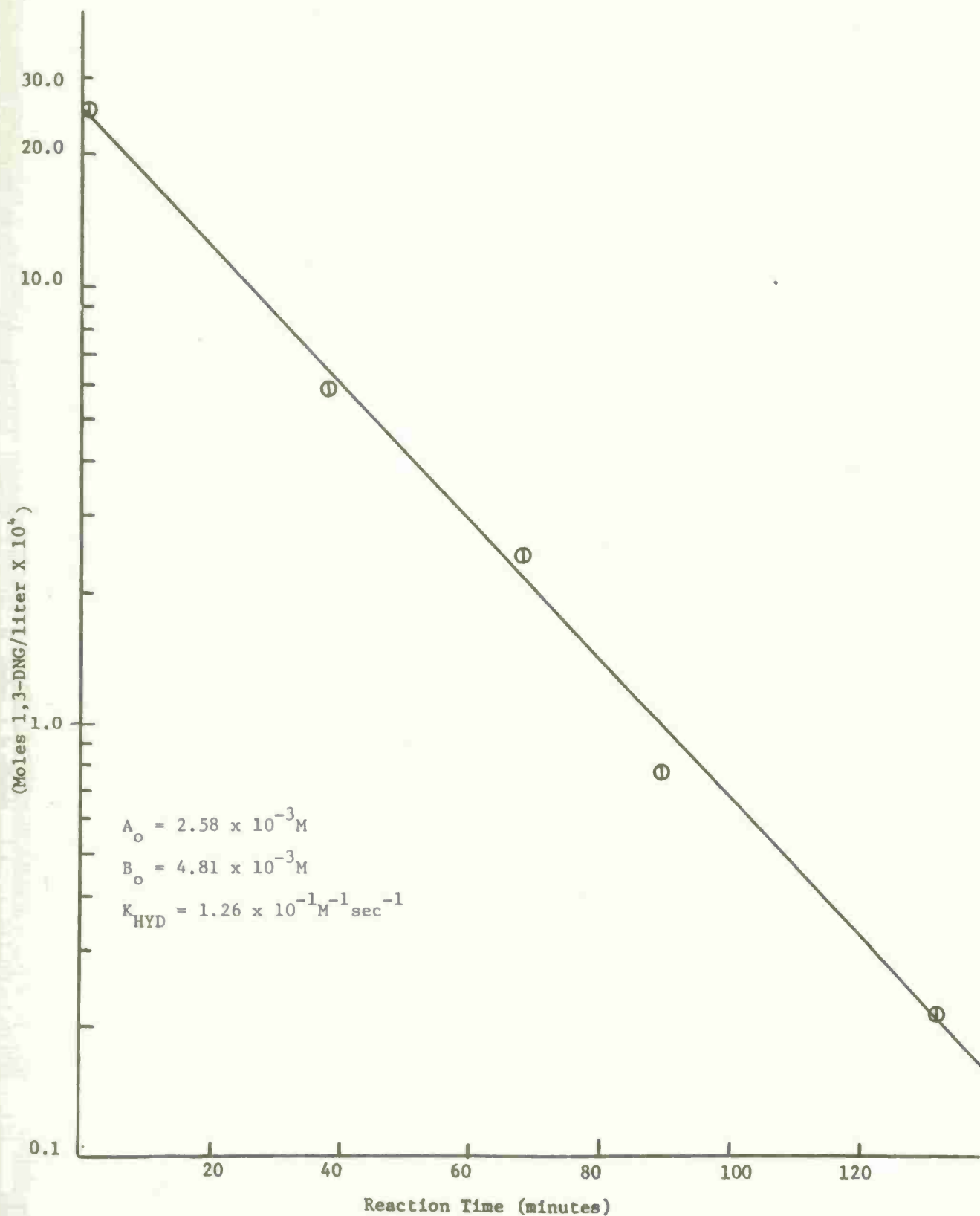


Figure 11. Hydrolysis of 1,3-DNG in aqueous $Ca(OH)_2$ solution at $25^\circ C$.

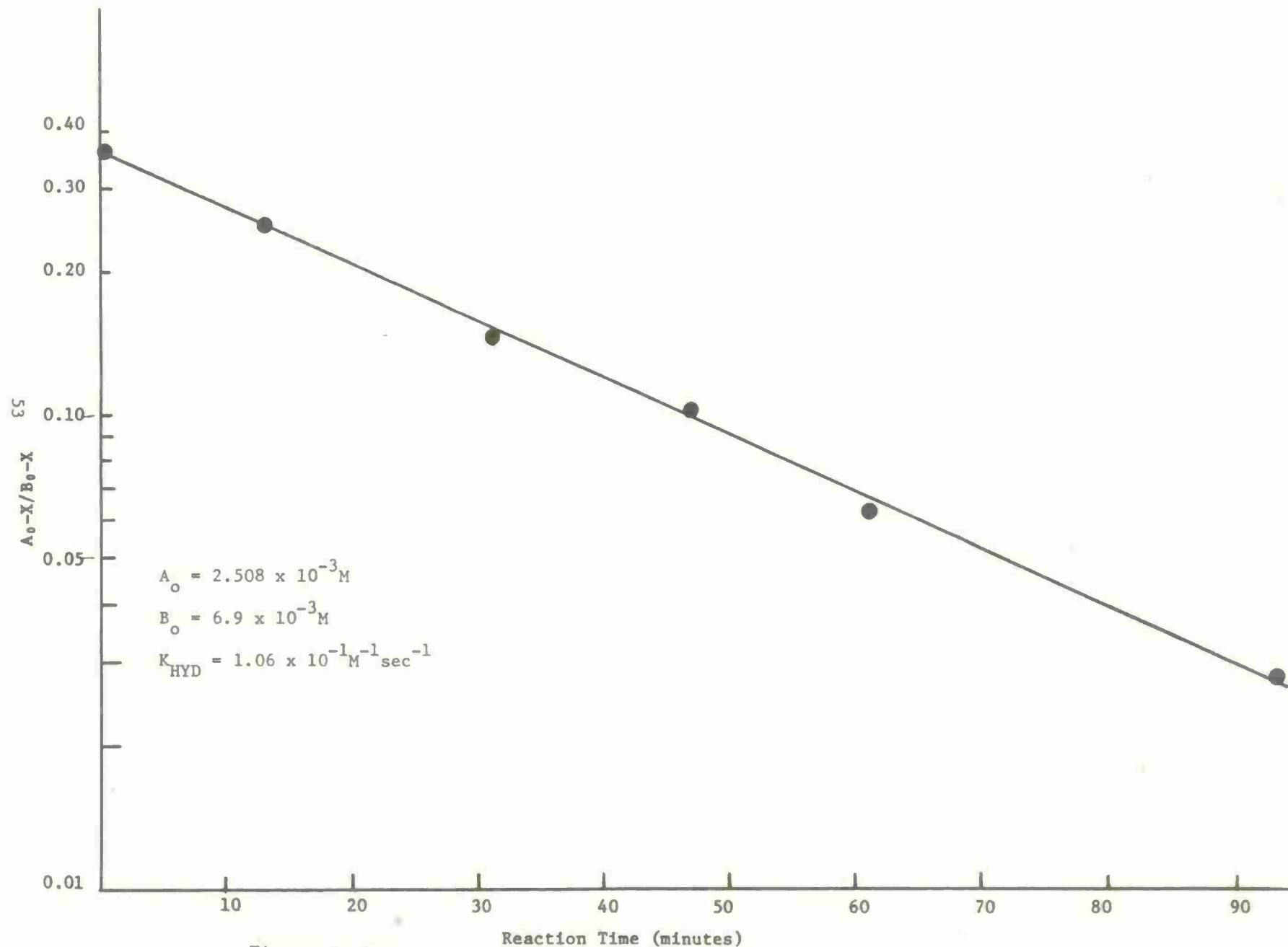


Figure 12. Hydrolysis of 1,3-DNG in aqueous $Ca(OH)_2$ solution at $25^\circ C$

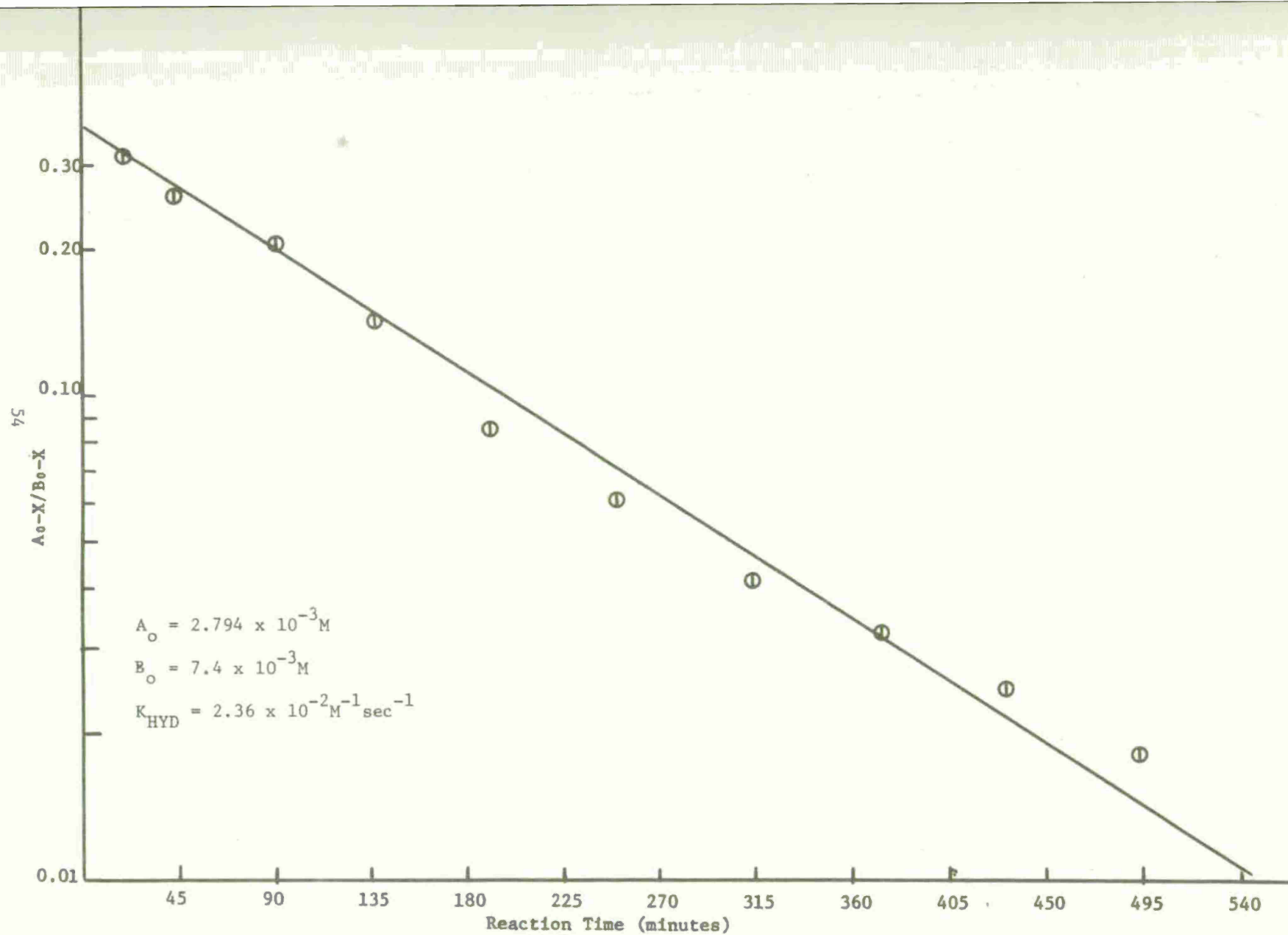


Figure 13. Hydrolysis of TNG in aqueous $\text{Ca}(\text{OH})_2$ solution at 25°C

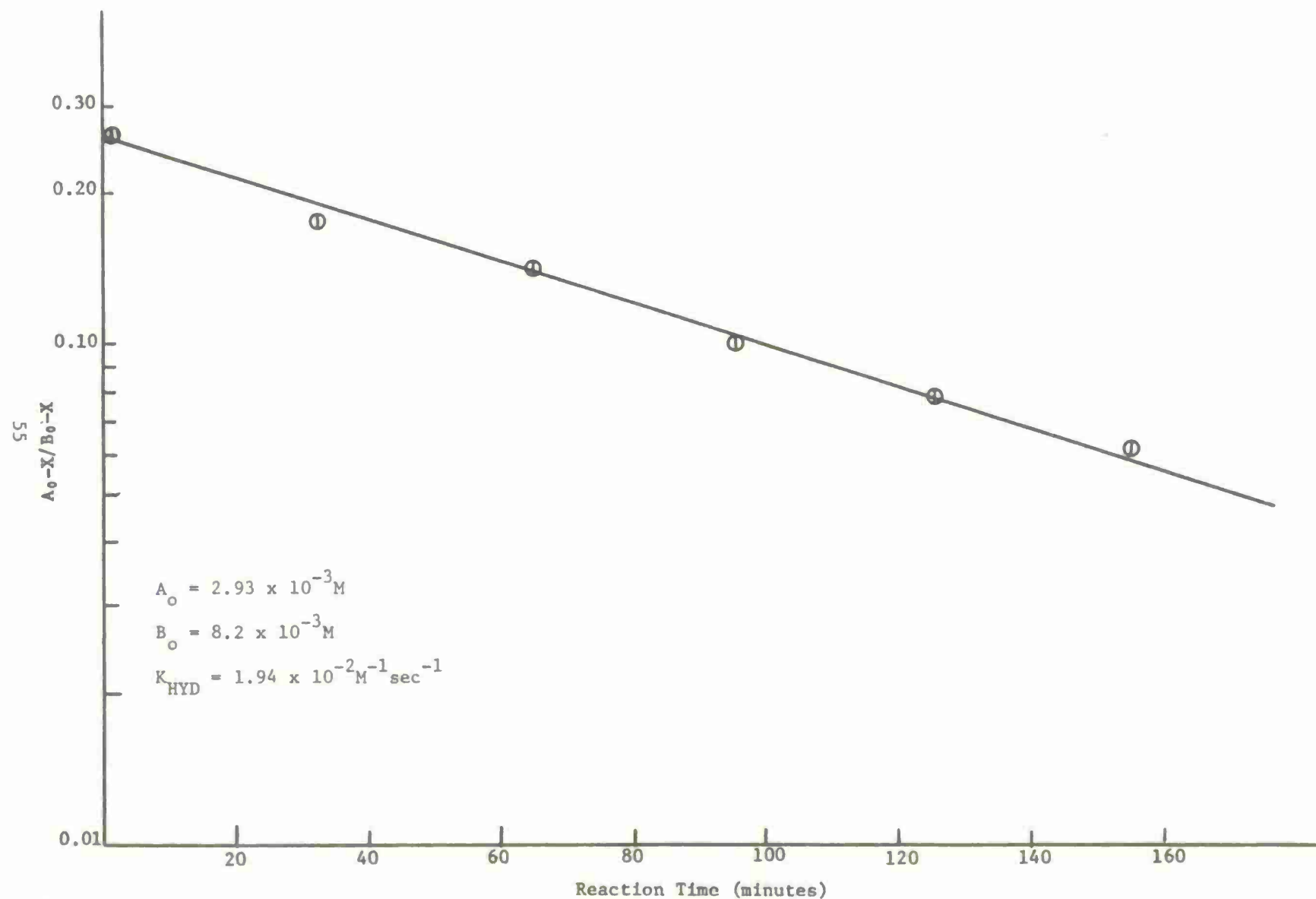


Figure 14. Hydrolysis of TNG in aqueous $Ca(OH)_2$ solution at $25^\circ C$

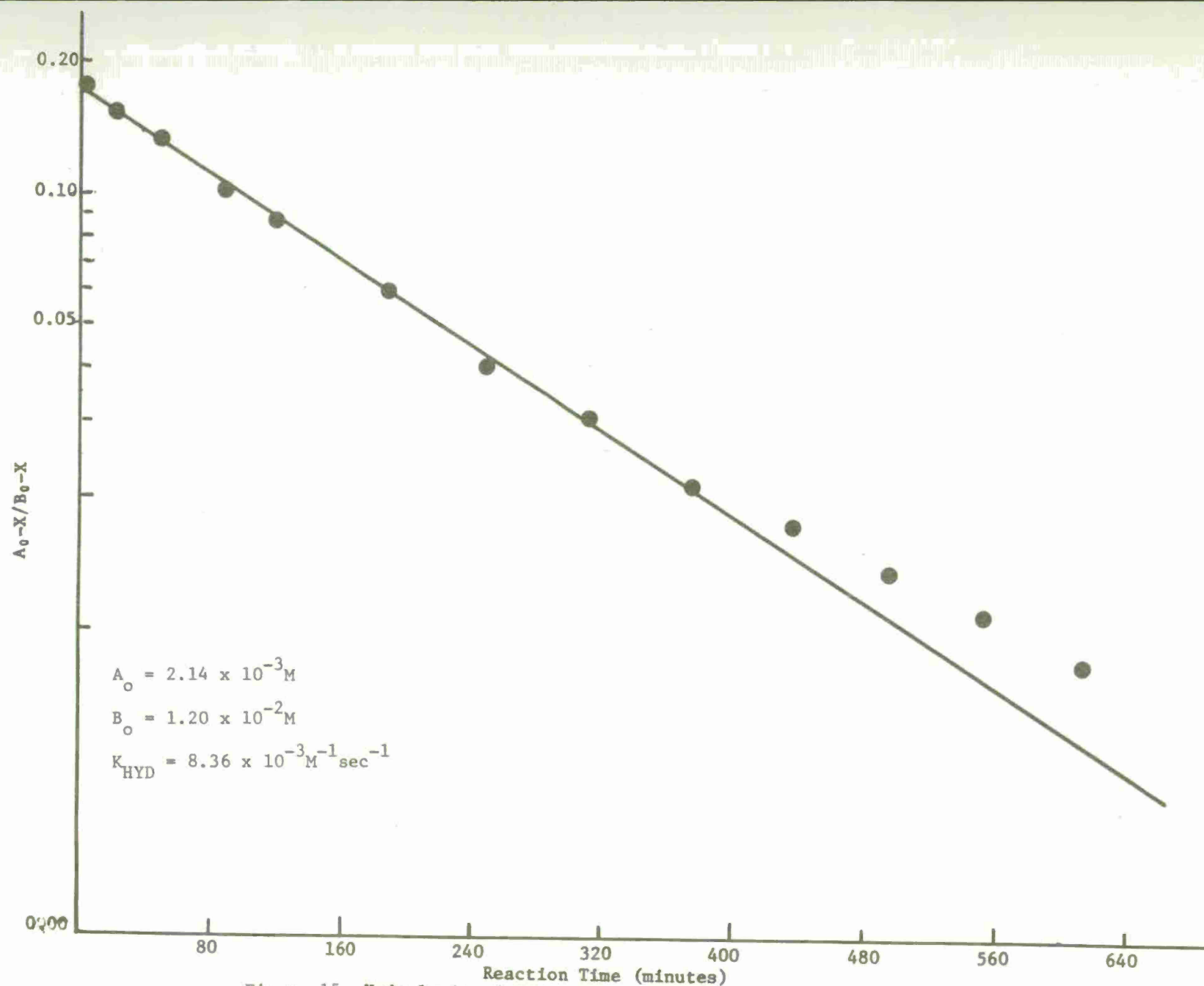


Figure 15. Hydrolysis of TNG in aqueous $Ca(OH)_2$ solution at $18^\circ C$

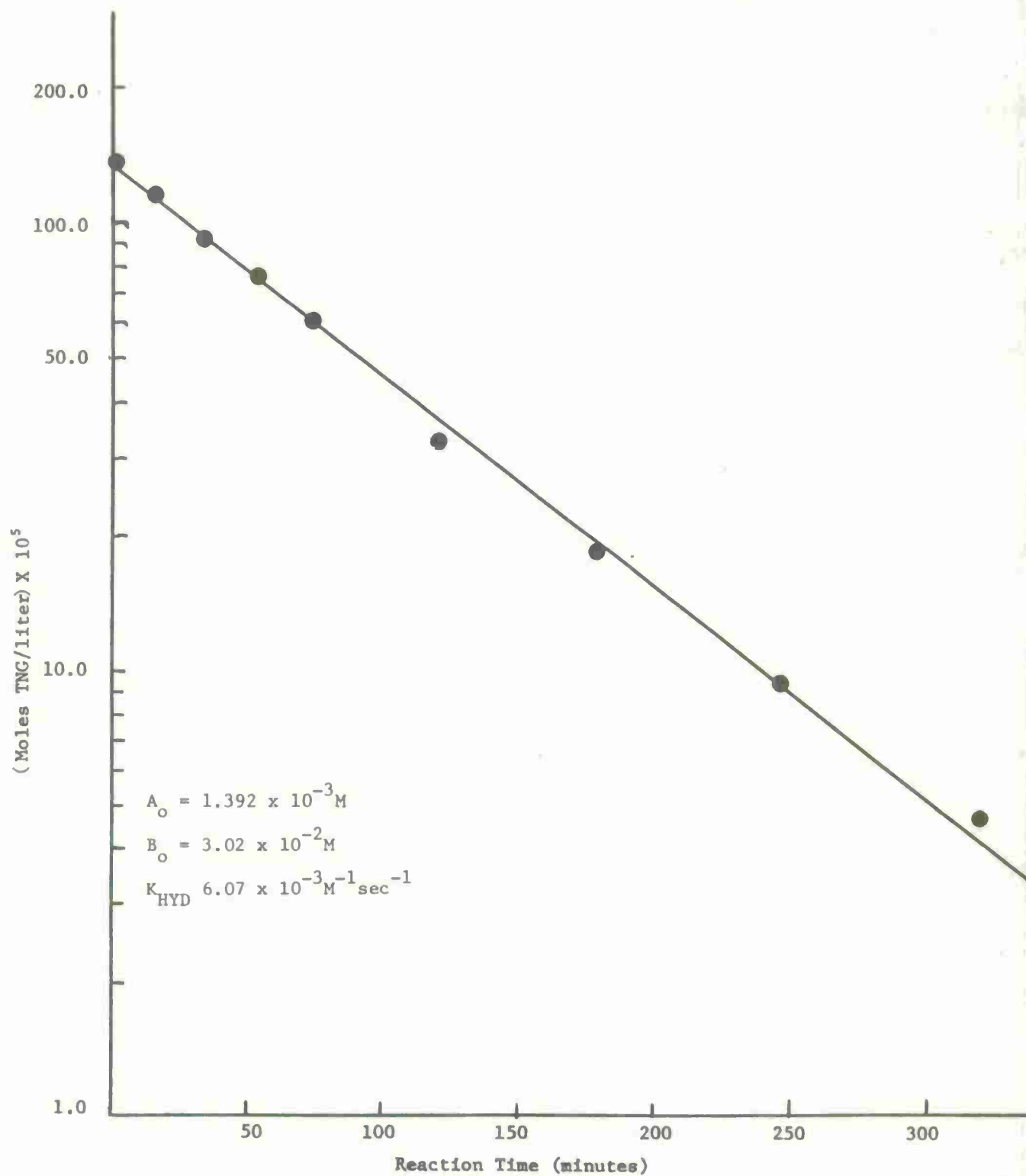


Figure 16. Hydrolysis of TNG with solid $Ca(OH)_2$ at $18^\circ C$

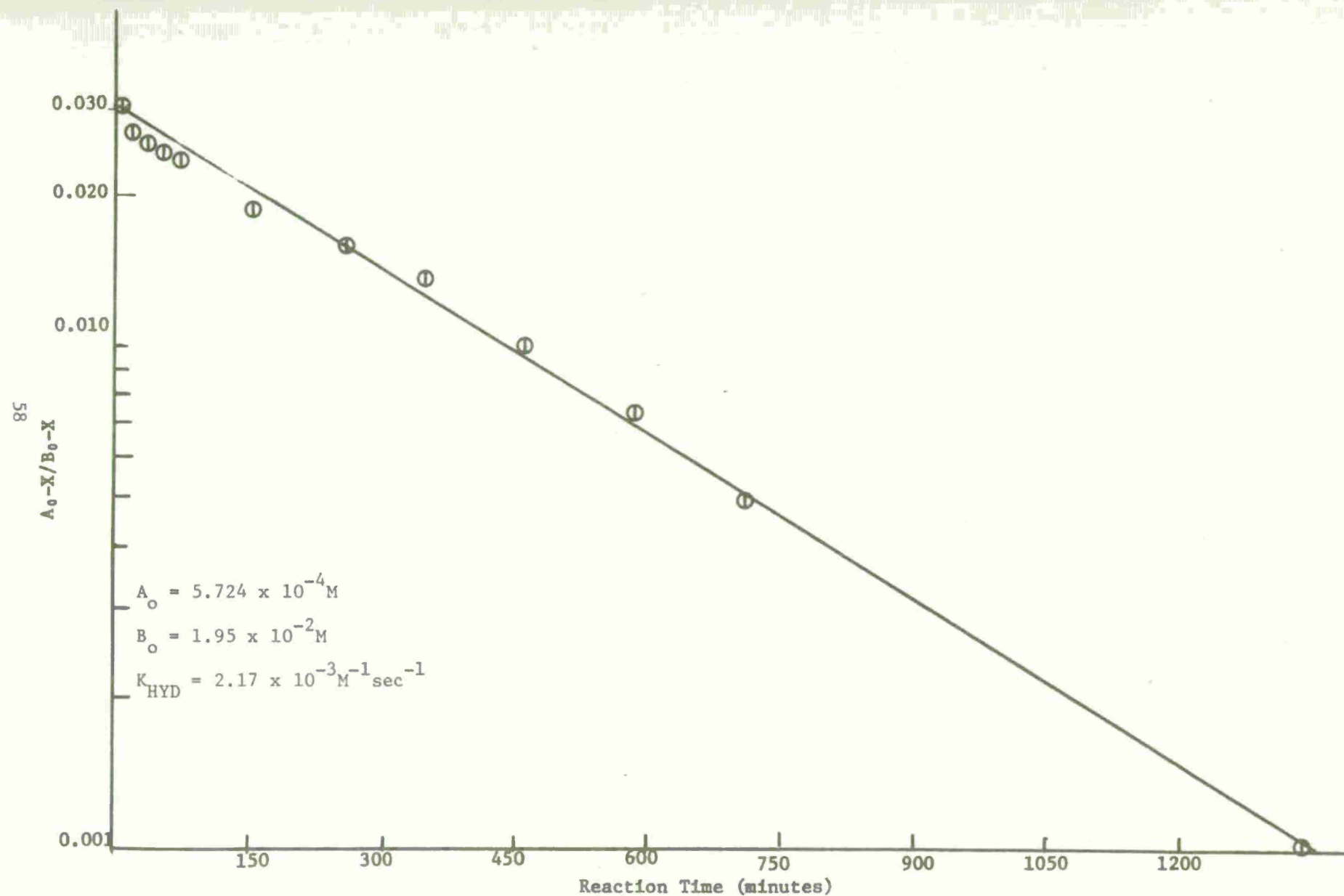


Figure 17. Hydrolysis of TNG in aqueous $Ca(OH)_2$ solution at $10^\circ C$

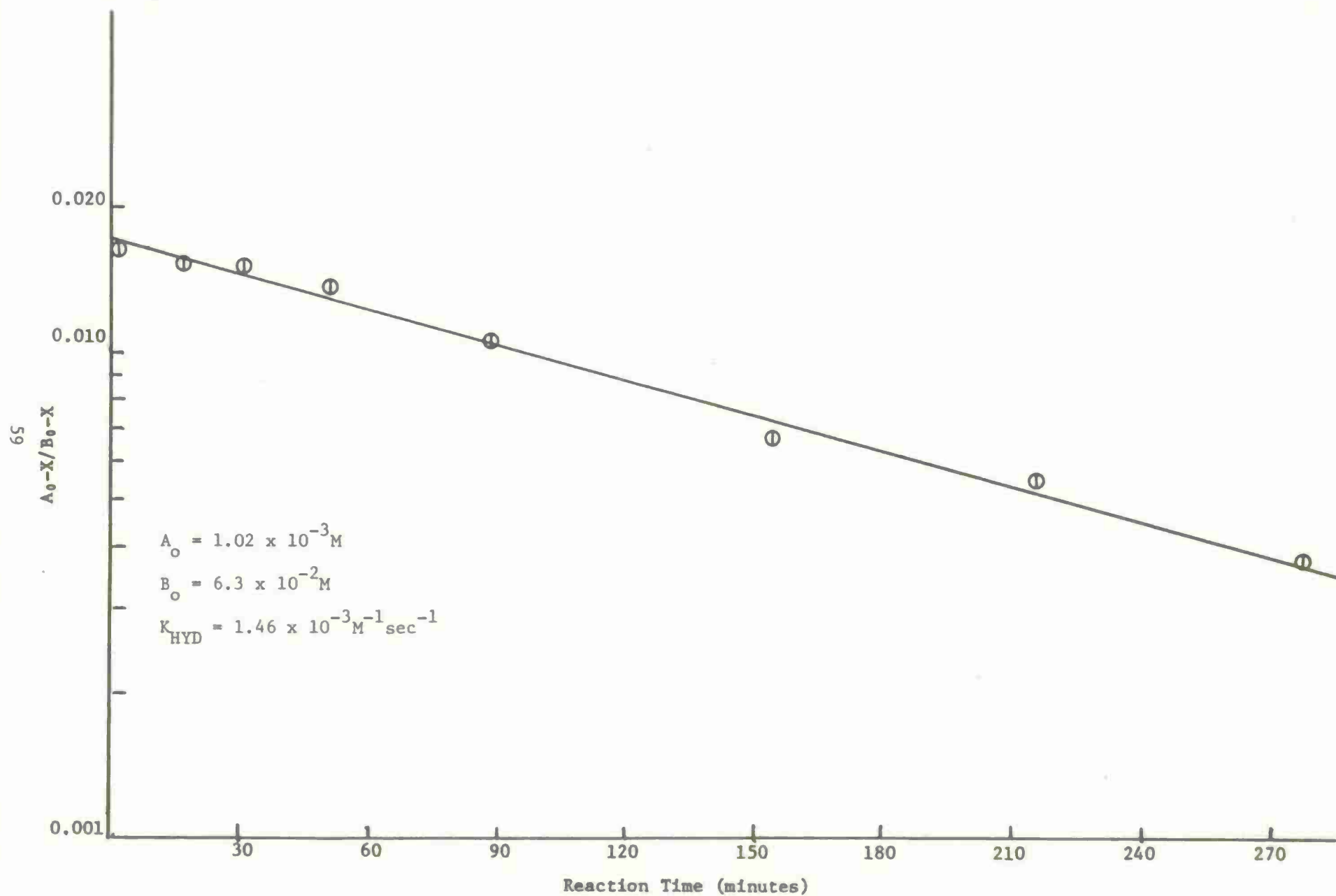


Figure 18. Hydrolysis of TNG with solid $Ca(OH)_2$ at $10^\circ C$

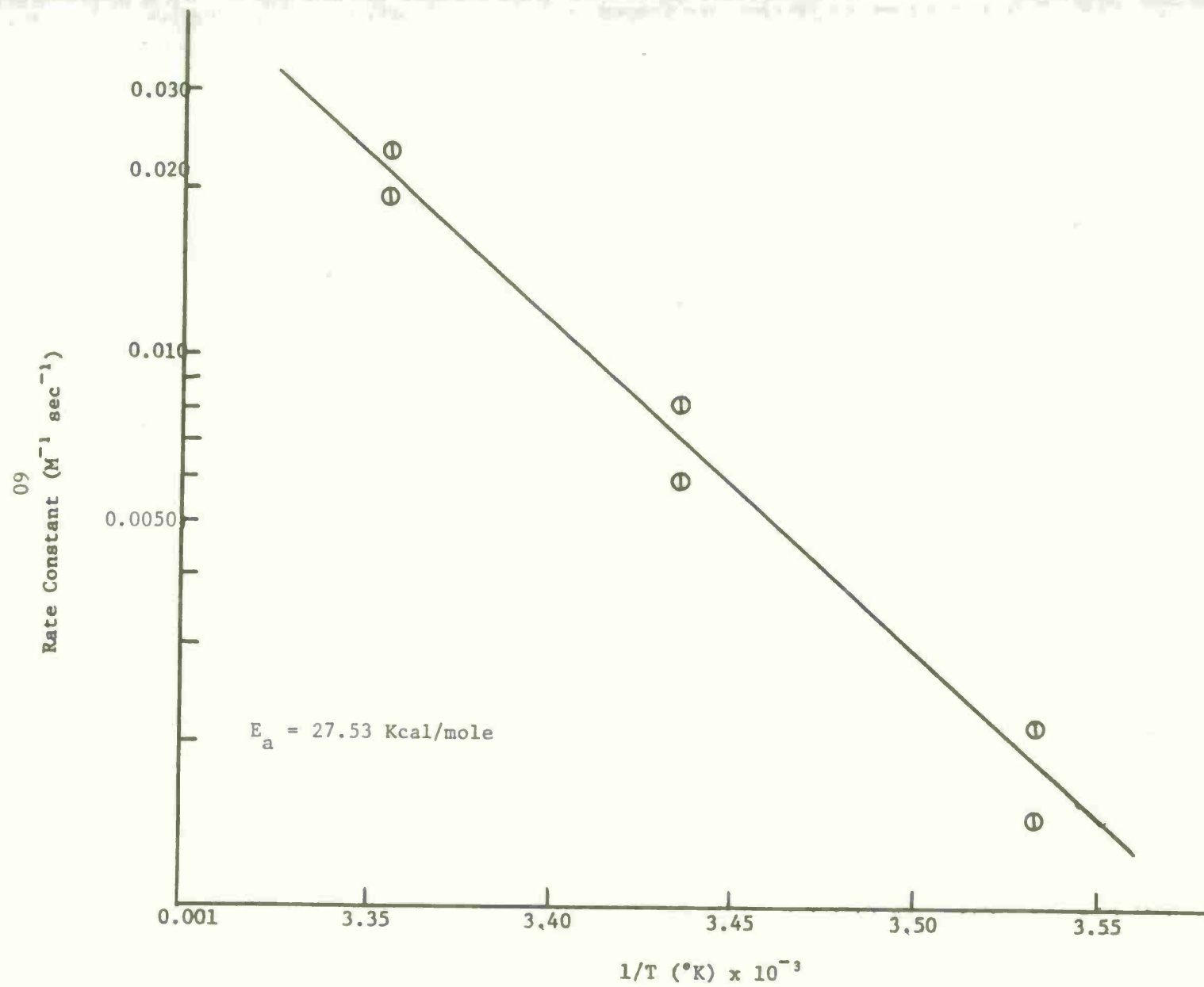


Figure 19. Activation Energy (E_a) of the basic hydrolysis of TNG

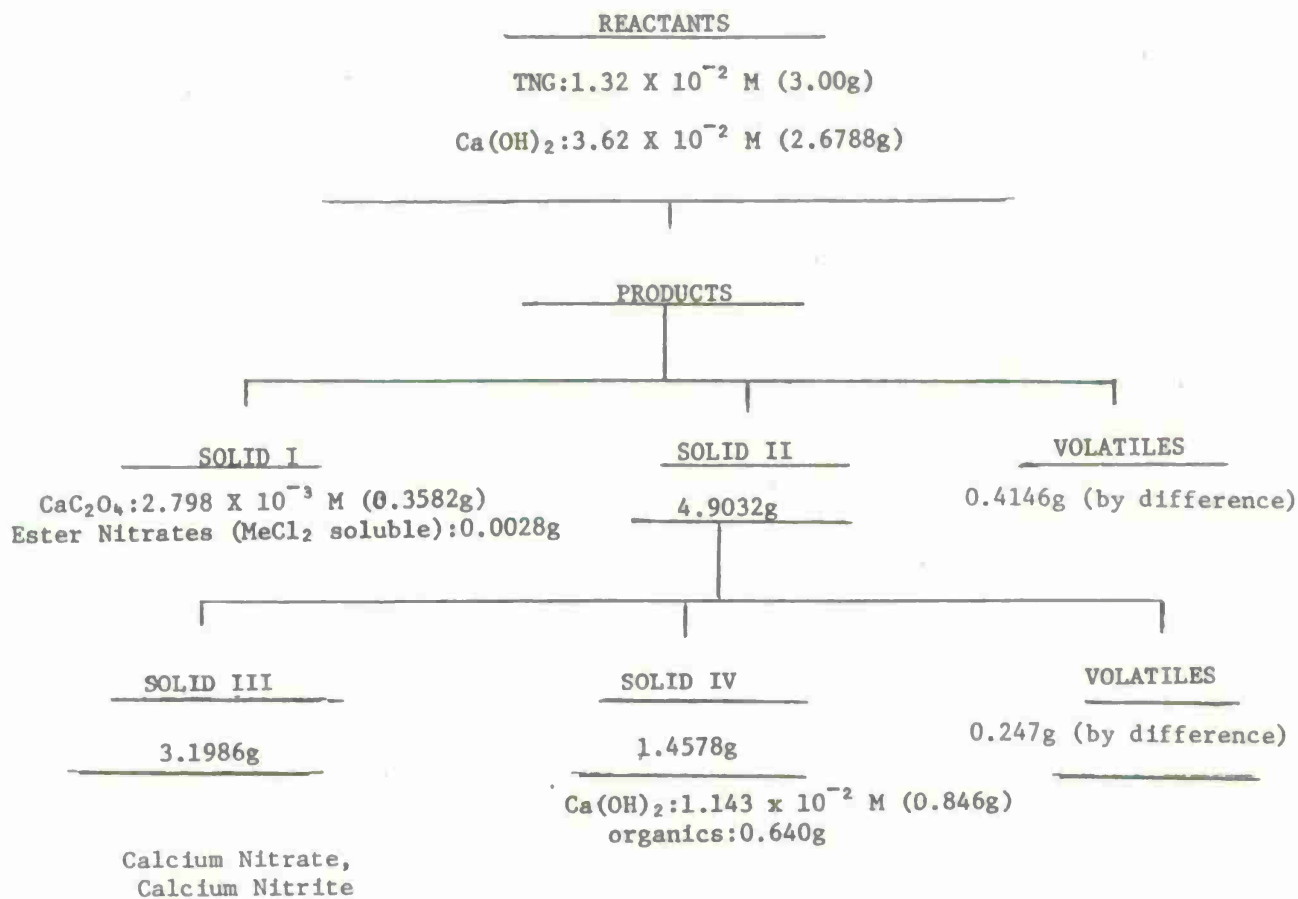


Figure 20. Material balance of the basic hydrolysis of TNG at 25°C.

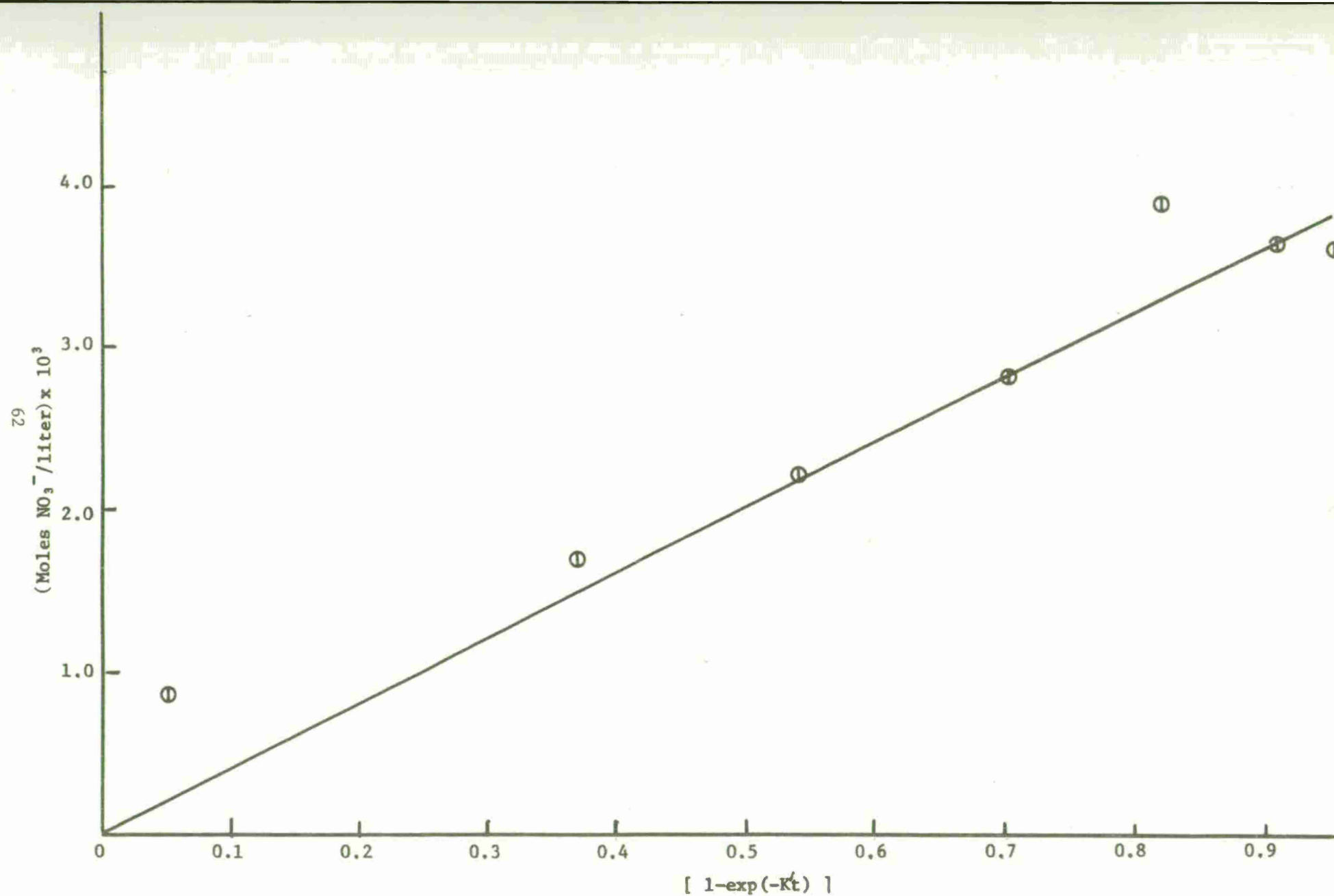


Figure 21. Formation of NO_3^- during hydrolysis of 1-MNG in aqueous $\text{Ca}(\text{OH})_2$ solution at 25°C
(See Tables 2 and 8)

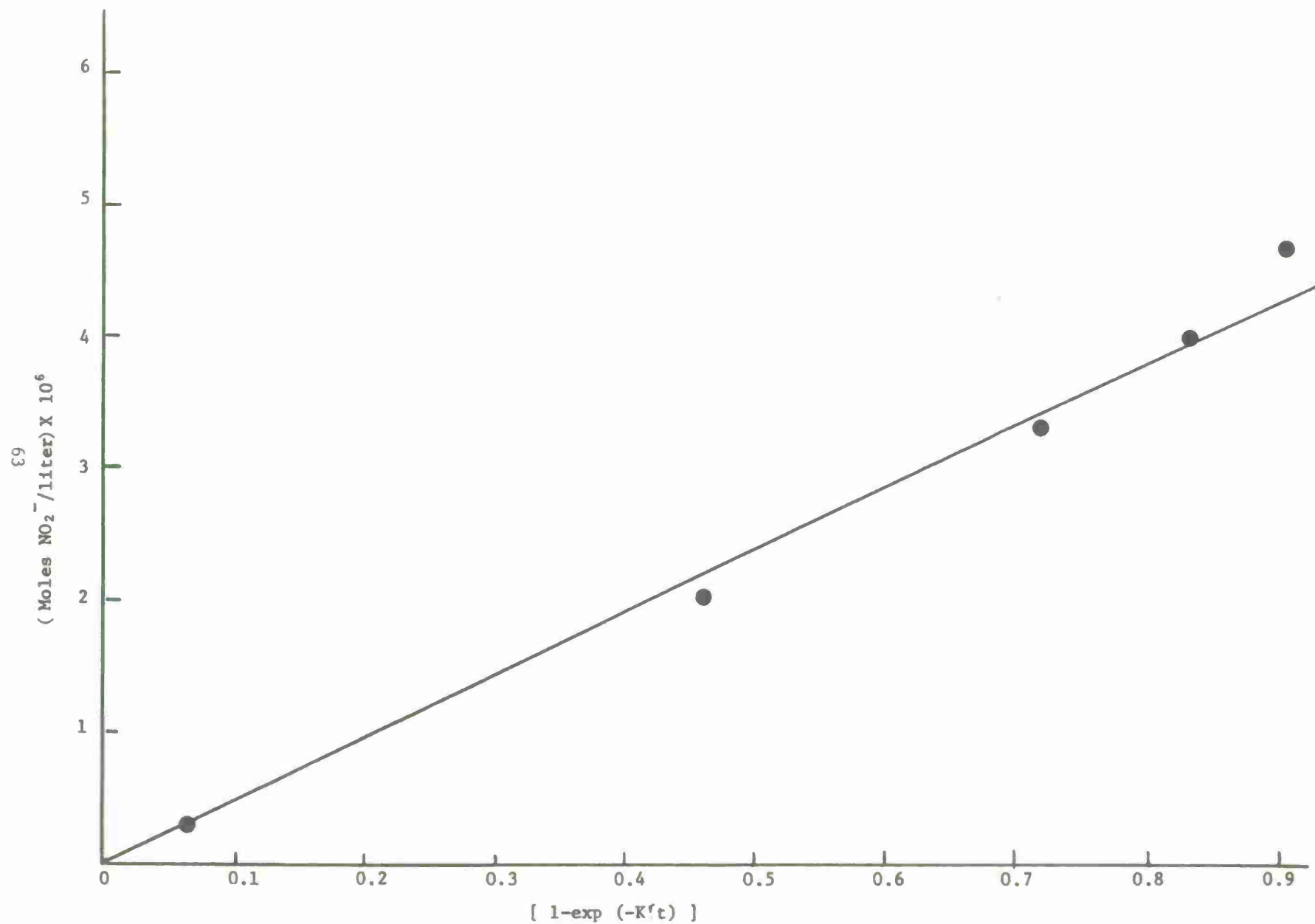


Figure 22. Formation of NO_2^- during hydrolysis of 1,3-DNG in aqueous $\text{Ca}(\text{OH})_2$ solution at 25°C .
(See Tables 3 and 8)

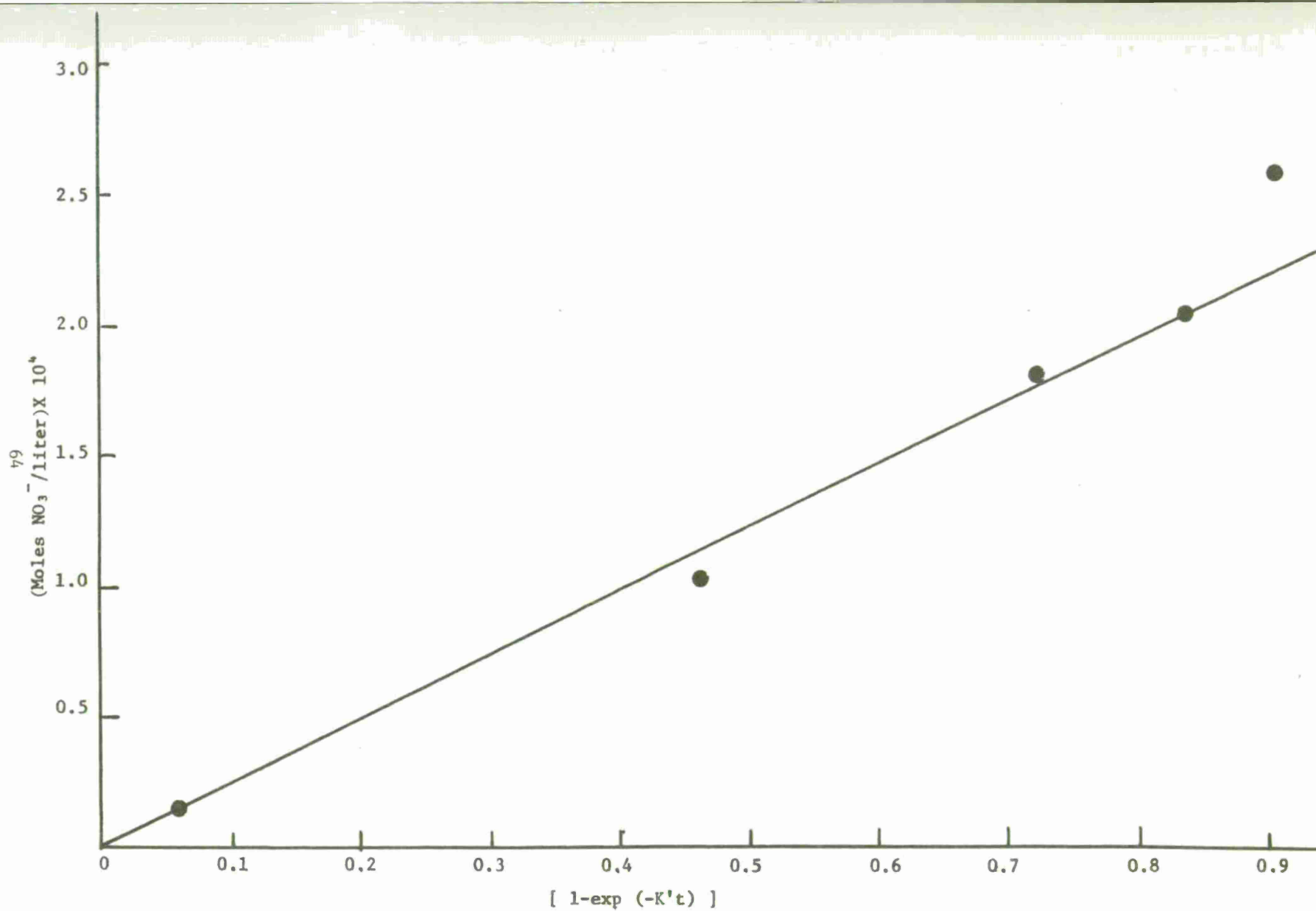


Figure 23. Formation of NO_3^- during hydrolysis of 1,3-DNG in aqueous $\text{Ca}(\text{OH})_2$ solution at 25°C .
(See Tables 3 and 8.)

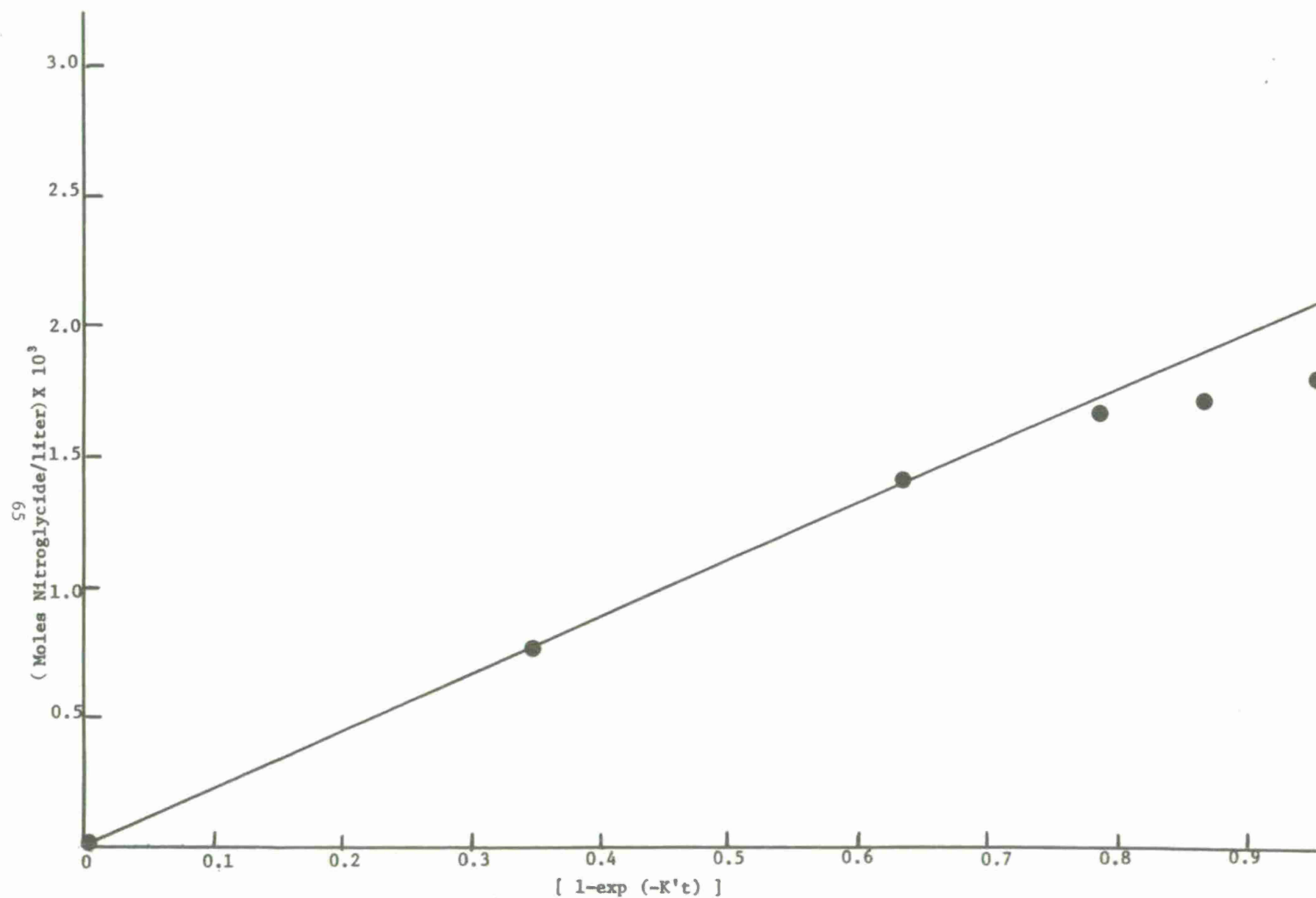


Figure 24. Glycidyl nitrate product formation during hydrolysis of 1,3-DNG in aqueous $\text{Ca}(\text{OH})_2$ solution at 25°C.

(See Tables 3 and 8.)

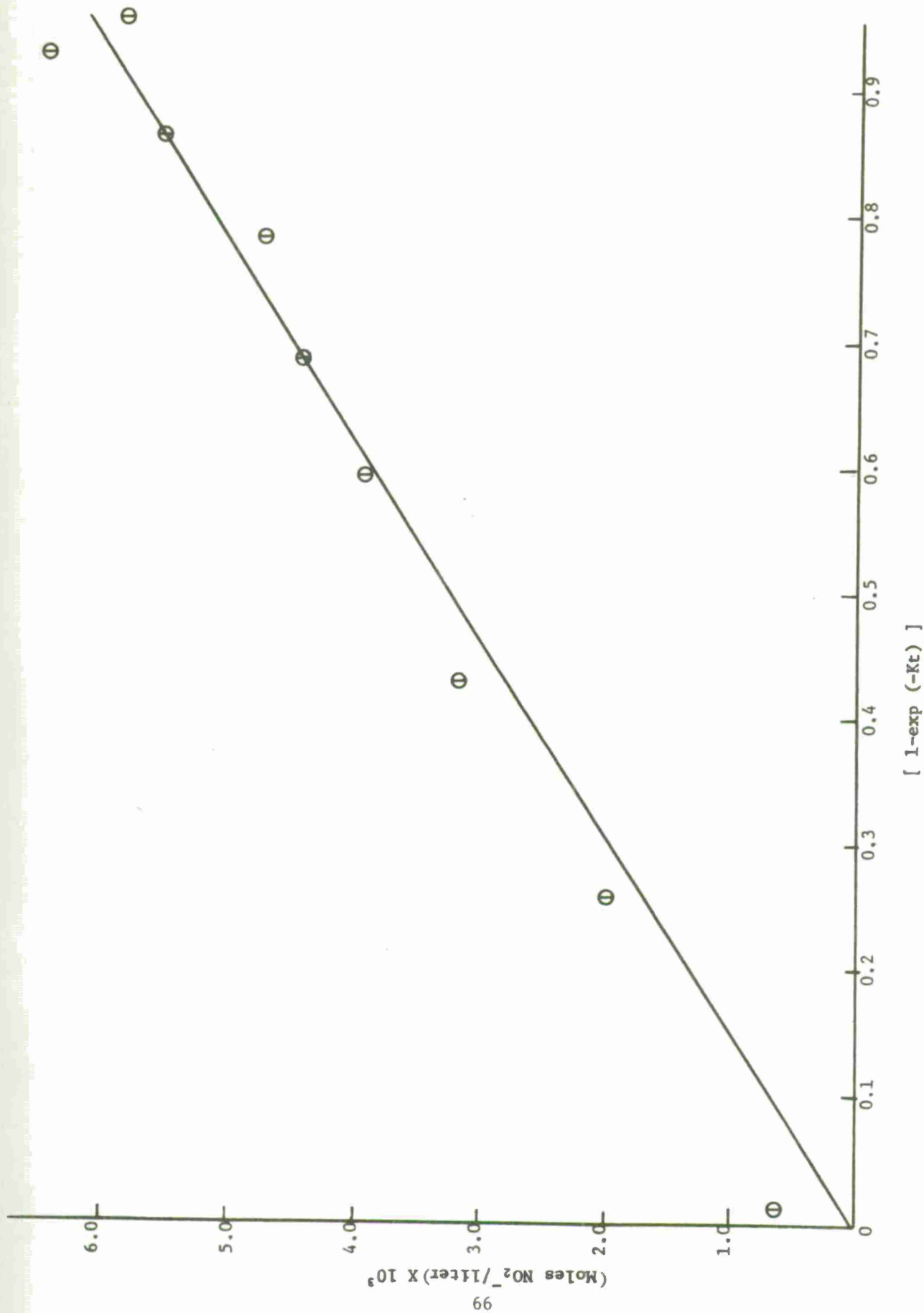


Figure 25. Formation of NO_2^- during hydrolysis of TNG in aqueous $\text{Ca}(\text{OH})_2$ solution at 25°C
(See Tables 4 and 8.)

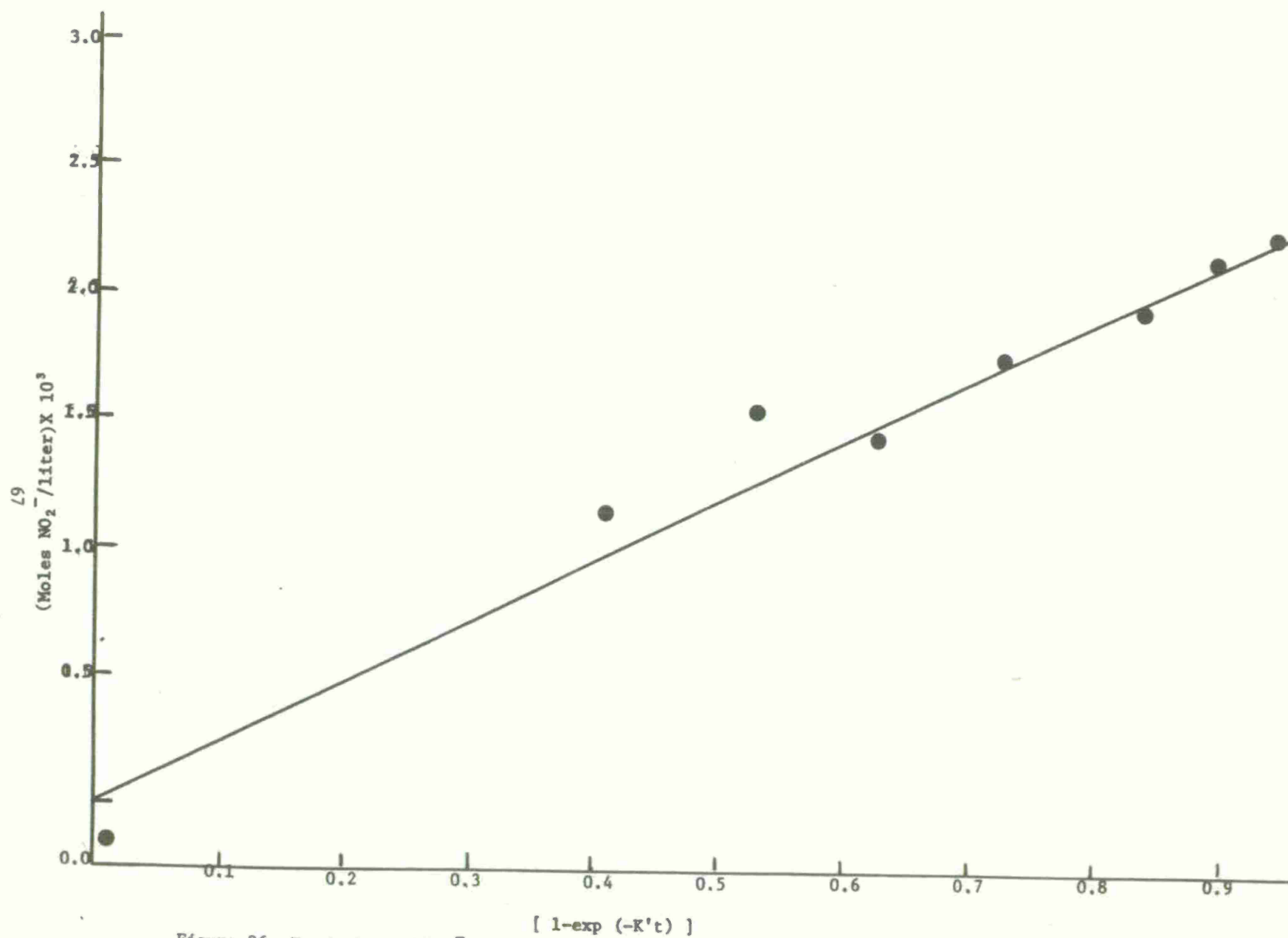


Figure 26. Formation of NO_2^- during hydrolysis of TNG with solid $\text{Ca}(\text{OH})_2$ at 18°C .

(See Tables 5 and 8.)

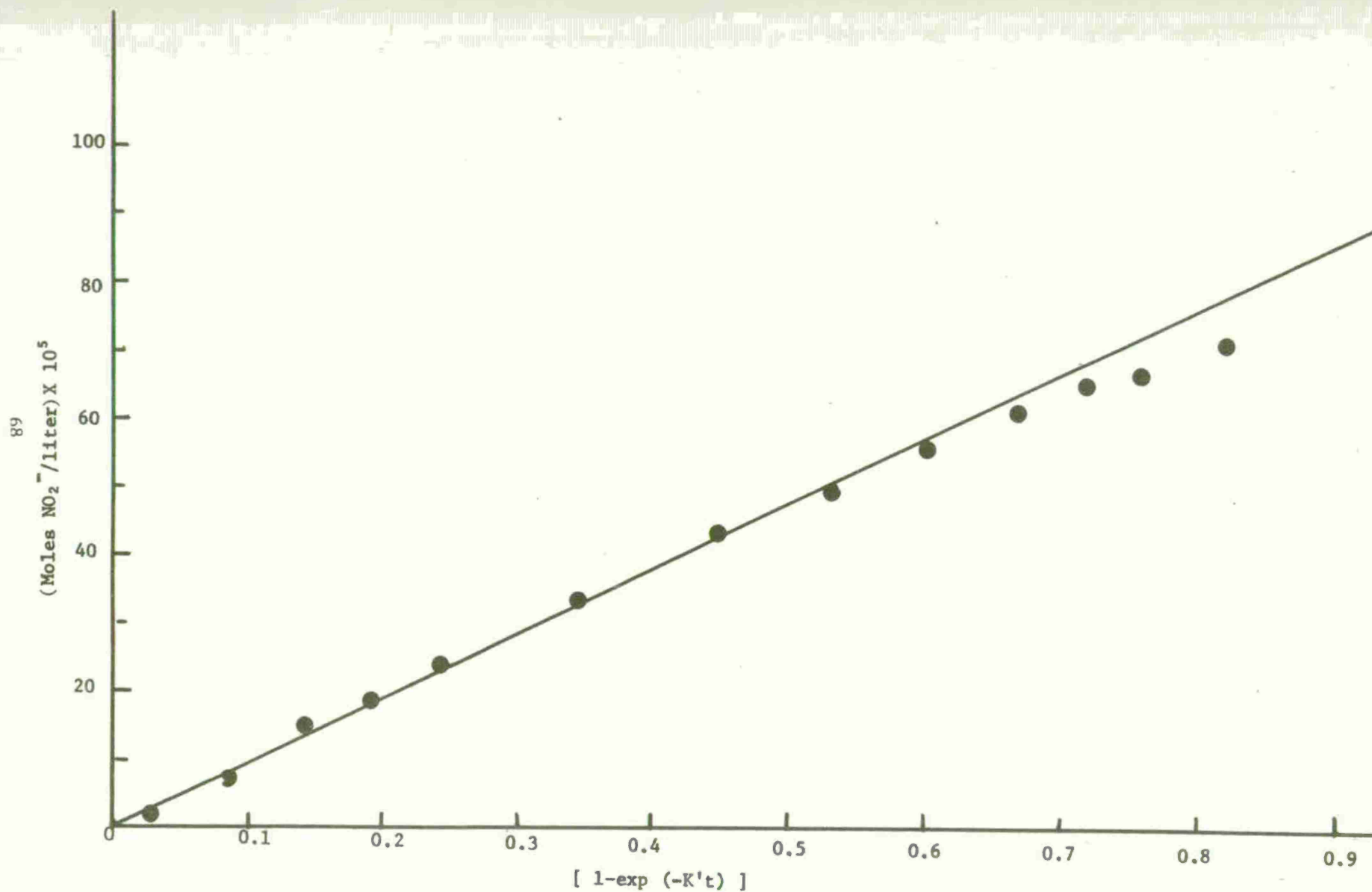


Figure 27. Formation of NO_2^- during hydrolysis of TNG in aqueous $\text{Ca}(\text{OH})_2$ solution at 10°C .

(See Tables 6 and 8.)

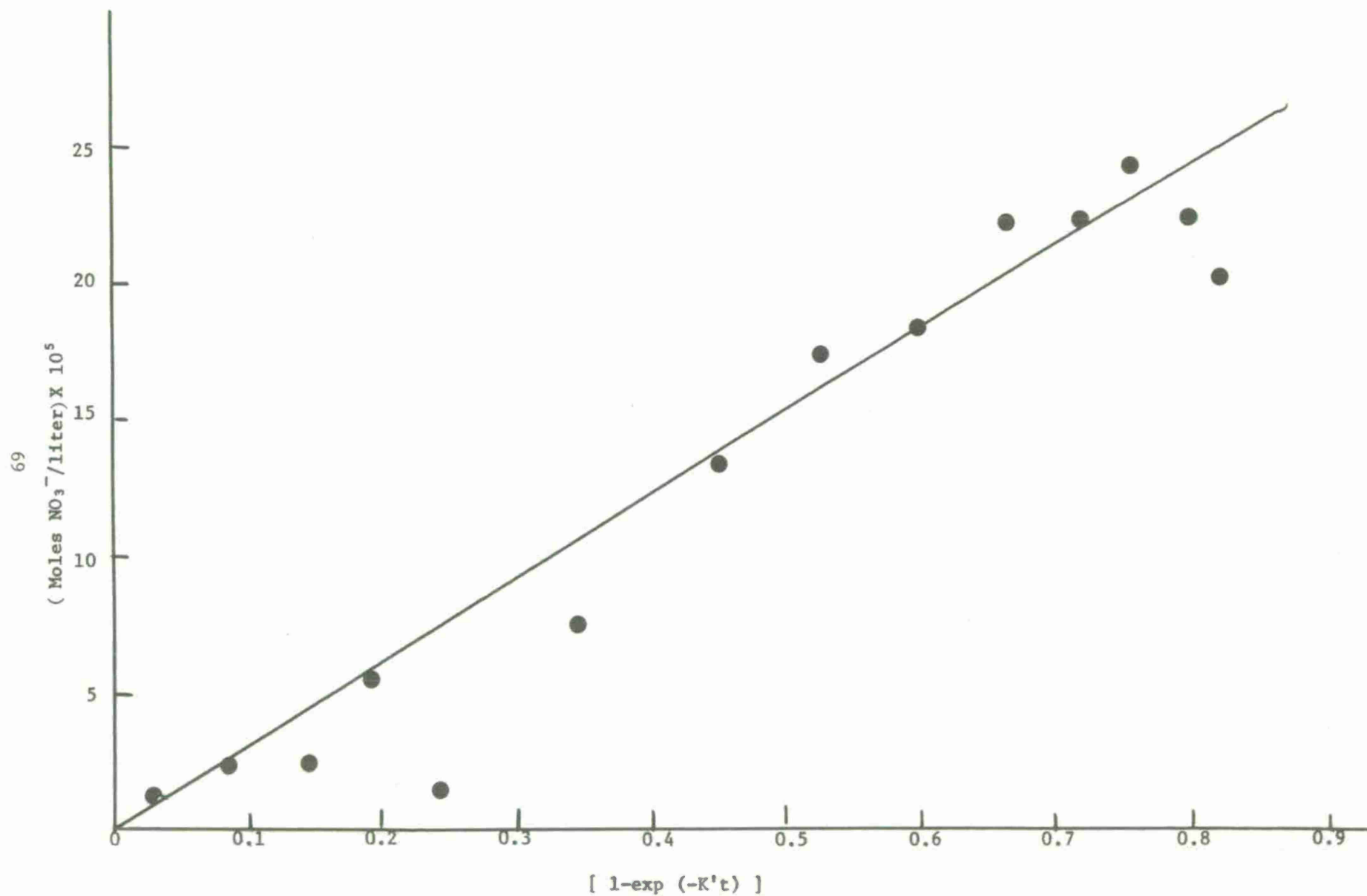


Figure 28. Formation of NO_3^- during hydrolysis of TNG in aqueous $\text{Ca}(\text{OH})_2$ solution at 10°C .

(See Tables 6 and 8.)

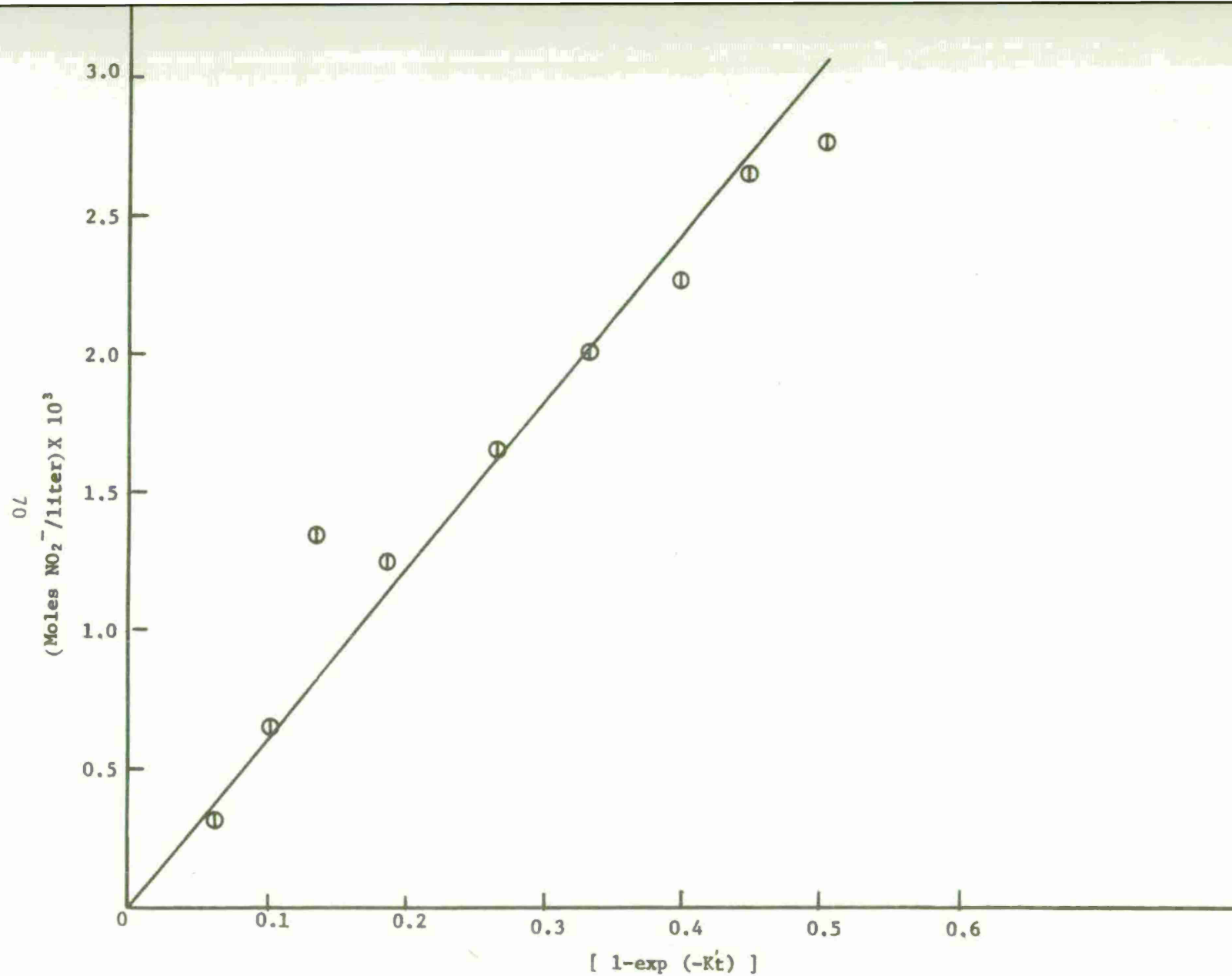


Figure 29. Formation of NO_2^- during hydrolysis of TNG in aqueous $\text{Ca}(\text{OH})_2$ solution at 10°C
(See Tables 7 and 8.)

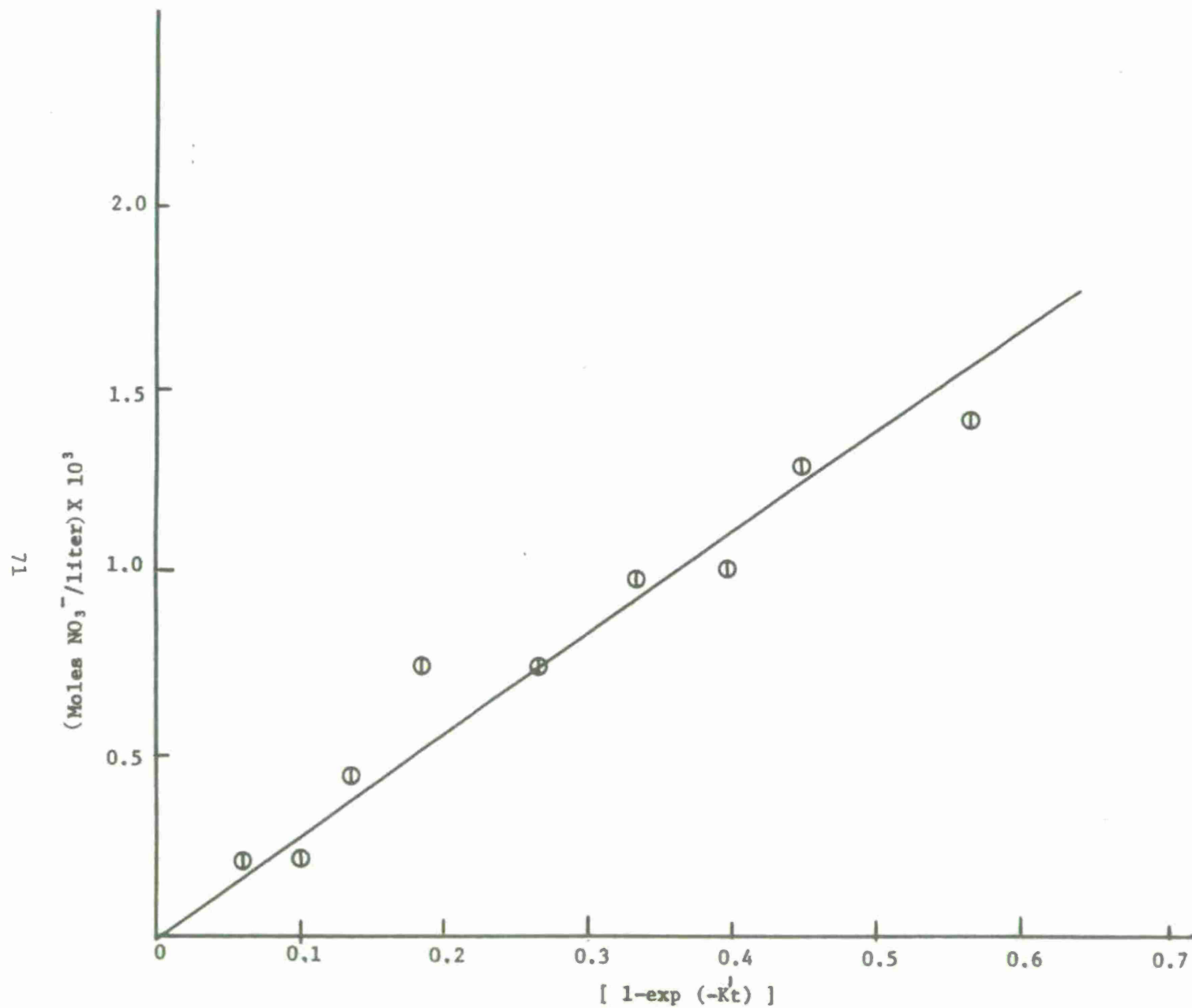


Figure 30. Formation of NO_3^- during hydrolysis of TNG in aqueous $\text{Ca}(\text{OH})_2$ solution at 10°C
(See Tables 7 and 8.)

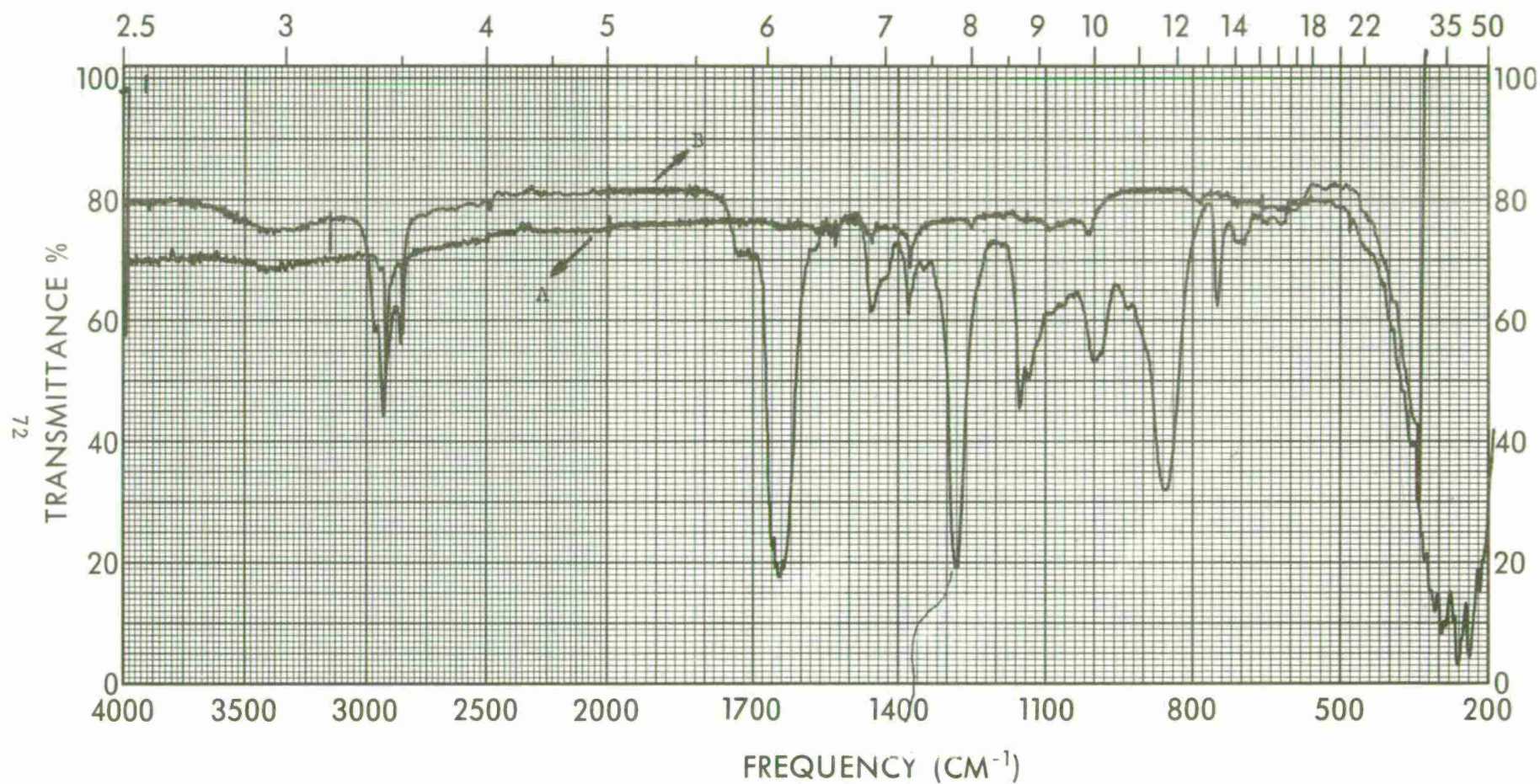


Figure 31. Infrared spectrum of methylene chloride solubles (Extract I)- Curve B.
Curve A = Blank KBr.

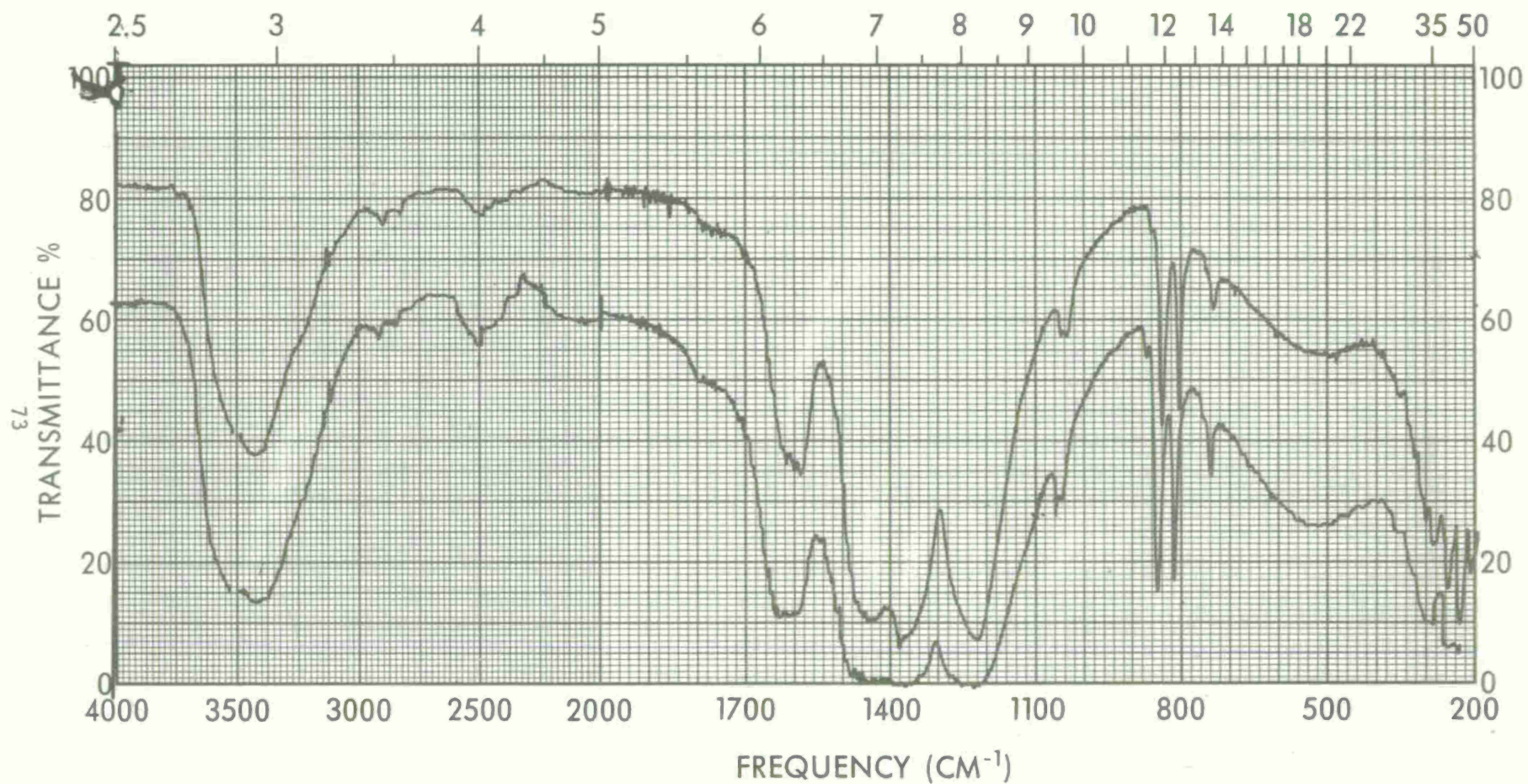


Figure 32. Infrared spectrum of Solid III, at two concentrations.

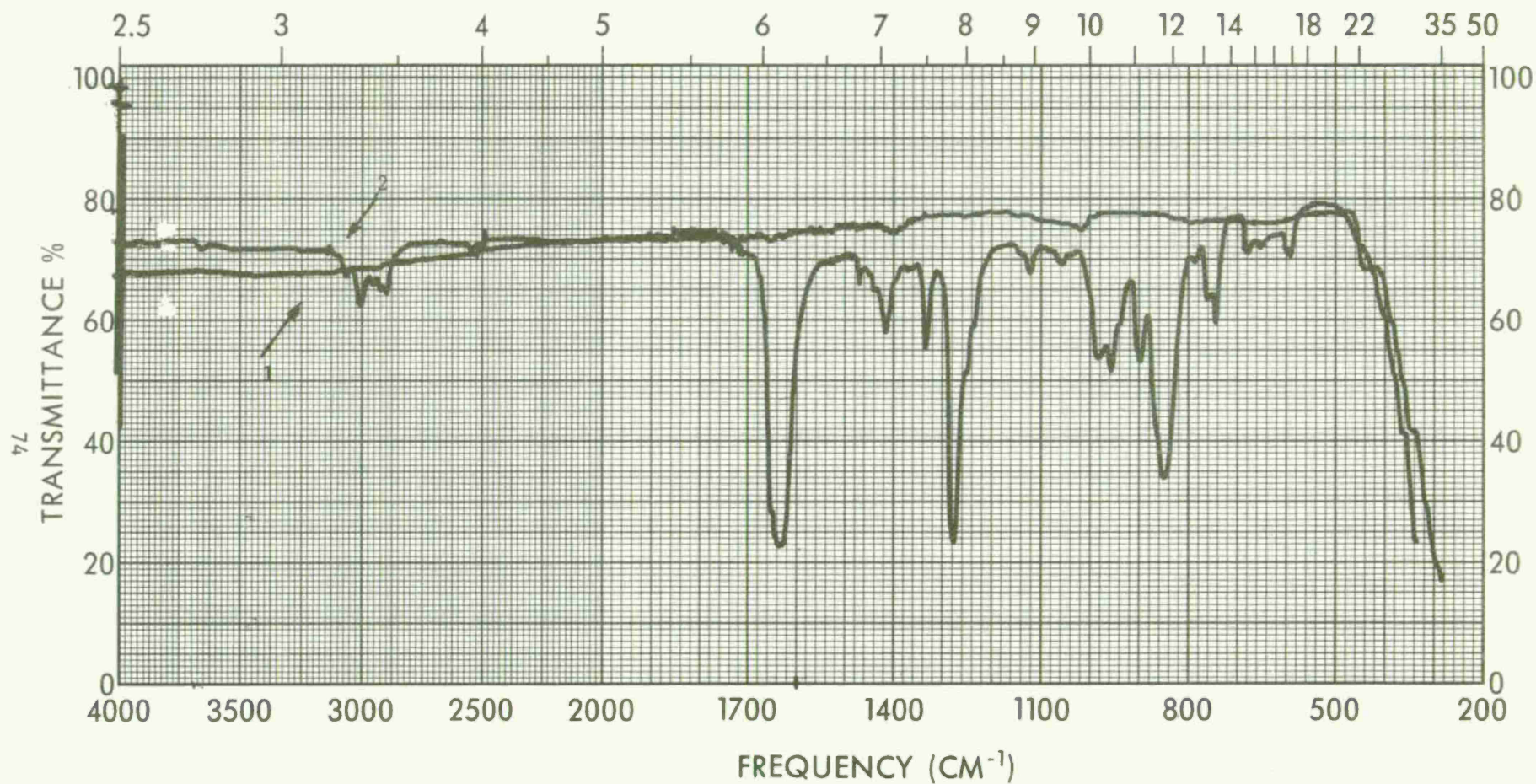


Figure 33. Infrared spectrum of methylene chloride extract of 1,3-DNG + $\text{Ca}(\text{OH})_2$ reaction mixture - Curve 2.
Curve 1 = Blank KBr.

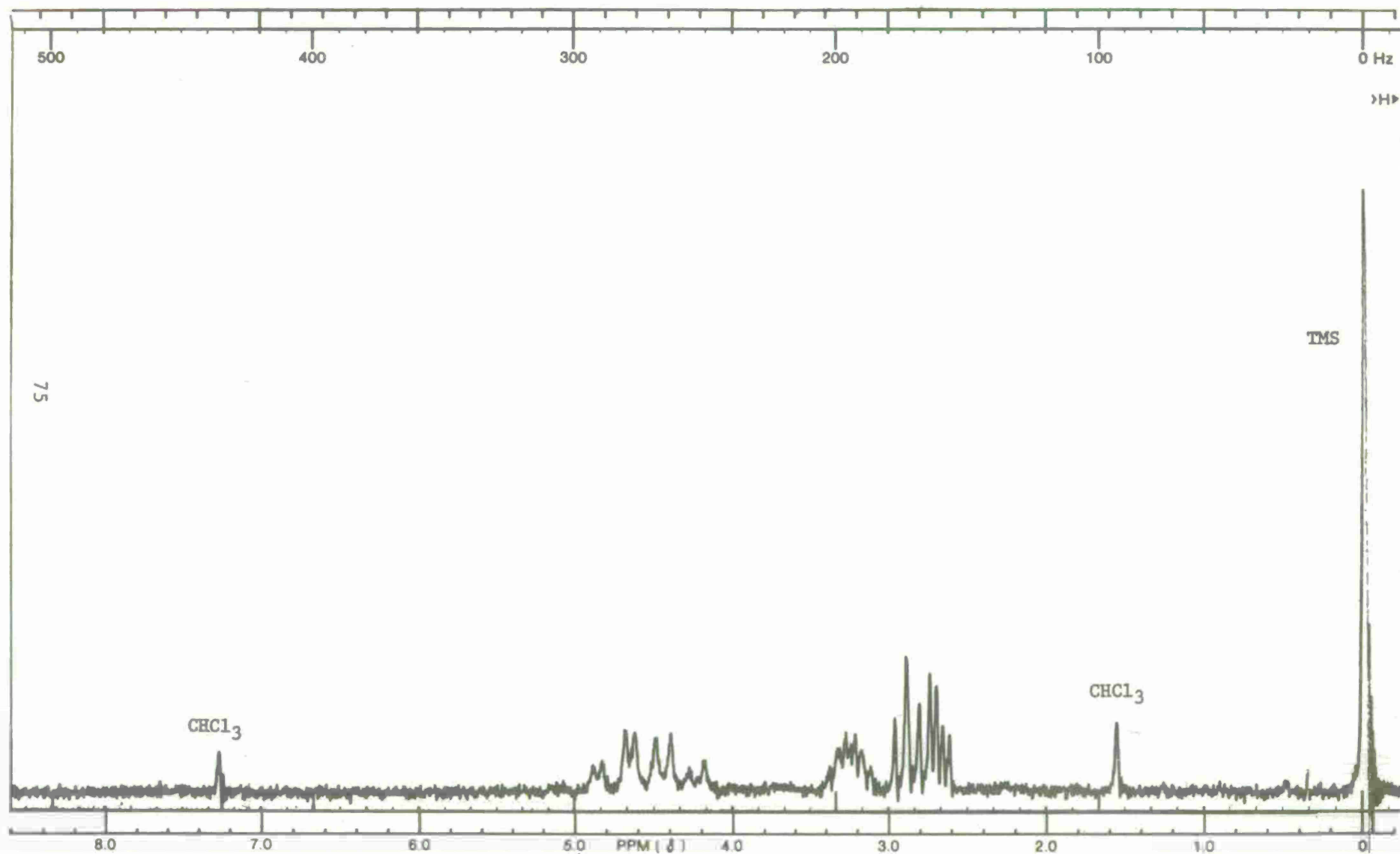


Figure 34. Nuclear magnetic resonance (NMR) spectrum of methylene chloride extract of 1,3-DNG + $\text{Ca}(\text{OH})_2$ reaction mixture dissolved in deuteriochloroform.

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