



A kinetic model of aqueous-phase alkali hydrolysis of 2,4,6-trinitrotoluene

R. Bajpai^{a,*}, D. Parekh^a, S. Herrmann^b,
M. Popović^b, J. Paca^c, M. Qasim^d

^a Department of Chemical Engineering, University of Missouri, W2061 EBE,
Columbia, MO 65211, USA

^b Studiengang Biotechnologie, FB V, TFH–Berlin, Seestraße 64, D-13347 Berlin, Germany

^c Institute of Chemical Technology, Technická 5, 16628 Prague, Czech Republic

^d US Army Engineer Research and Development Center,
3209 Halls Ferry Road, Vicksburg, MS 39180, USA

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Abstract

Alkali hydrolysis of 2,4,6-trinitrotoluene (TNT) was studied using batch experiments with starting pH values 11 and 12 in glass conical flasks covered with aluminum foil. Isothermal (25 and 40 °C) as well as non-isothermal experiments were conducted. Experiments starting at pH 12 resulted in >95% reduction in the concentration of TNT; those starting at pH 11 had a maximum reduction of 20–25% in TNT concentration. In all the experiments, one major stable intermediate was produced but it could not be identified. The experimental data were used to determine the overall stoichiometry of TNT and hydroxyl ions. Approximately 100 mol (standard deviation 11.4) of hydroxyl ions were consistently consumed per mole of TNT. However, control experiments showed that all but 13 mol (standard deviation 2) of hydroxyl ions were consumed in reactions not related to TNT. A simple kinetic model involving formation of the intermediate was proposed to account for changes in concentrations of TNT and hydroxyl ions. The rate constants and activation energies of the reactions were identified using isothermal data and the kinetic model was then used to predict the experimental data in the non-isothermal experiments reasonably well.

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* Corresponding author. Tel.: +1-314-882-3708; fax: +1-314-884-4940.
E-mail address: bajpair@missouri.edu (R. Bajpai).

1. Introduction

2,4,6-Trinitrotoluene (TNT) has been synthesized and used since the beginning of the last century. The production practices and widespread use of TNT as an explosive have resulted in contamination of large tracts of soils and groundwater almost all over the world [1]. Several efforts have been made to develop technologies for restoration of these contaminated sites. These have included both biological as well as chemical methods [2–6]. Biological methods are considered more desirable, as these are perceived to transform the hazardous molecules to innocuous compounds, environment-friendly, natural, and economical. However, biotransformation of TNT takes place via cometabolism [7] and no naturally occurring microorganism has been found that can utilize TNT as the sole source of carbon and energy. Hence, a primary carbon and energy source must be added to support biodegradation, causing problems of delivery and dosing of the primary substrate in the operation and control of bioremediation processes involving TNT. In addition, microbial metabolization of TNT results in very limited transformation of contaminant carbon to carbon dioxide (mineralization). On the other hand, several mono- and dinitrotoluenes are utilized by a large number of soil microorganisms as carbon and energy sources and are extensively mineralized [8]. Even, 2,4,6-trinitrophenol serves as sole carbon and energy source for some microbes. These results suggest that elimination/substitution of even a single nitro-group from the TNT-ring would enhance its biodegradation and mineralization through a lowering of the steric hindrance by removal of the nitro-group, and also a lowering of the deactivation of the aromatic ring by removal of the strong electron-withdrawing nitro-group.

Hydroxyl ions are strong nucleophiles and have a potential for removing nitro-groups (a good leaving group) from TNT molecules. Several researchers have studied reactions of TNT with bases in the past [9–12]. Arienzo [3] has provided a summary of these reactions. Several researchers [13–17] have recently studied kinetics of alkali hydrolysis of TNT. Emmrich [13,14] conducted experiments in aqueous solution of TNT and in TNT-contaminated soil slurries at constant pH values, and proposed a pseudo first-order kinetic model representing disappearance of TNT. However, she discussed neither the kinetics of hydroxyl ions nor the stoichiometry of the reaction. Felt et al. [15,16] conducted their experiments in presence of excess hydroxyl ions. Felt et al. [16] have also proposed an empirical mathematical model to describe the variation of TNT concentration with time. The effect of temperature on the reaction kinetics was investigated [15], but the concentration of hydroxyl ions in the reaction system was not monitored and, therefore, could not be incorporated in their model. The degradation kinetics of TNT included formation of unidentified intermediates whose concentrations were modeled in the form of peak heights in UV-Vis spectra [16]. Karasch et al. [17] reported kinetic data of disappearance of TNT under uncontrolled pH and temperature conditions, but did not discuss the stoichiometry of reaction. Thus, the current state-of-the-art permits estimates of neither the alkali demand in the process nor the dynamics of hydroxyl ion concentration in the reaction. This information is necessary to determine the economics of base-hydrolysis as a potential technology for treatment of TNT-contaminated fluids and solids. Hence, the focus of this work was to establish the stoichiometry of the reaction between TNT and hydroxyl ions, and to present a mathematical framework to explain the observed rates and extent of TNT transformation by alkali. The experiments were conducted using aqueous solutions of TNT in glass containers.

2. Materials and methods

Aqueous solution of TNT was obtained from the US Army Engineer Research and Development Center (USAERDC) in Vicksburg, Mississippi. pH of this solution was 7.0 and the concentration of TNT in the solution was 47 mg/l.

Standard solution of TNT was also obtained from Supelco (Bellefonte, PA) in the form of 1000 $\mu\text{g/ml}$ solutions in acetonitrile. This was diluted with reverse osmosis (RO) grade water to form standards with concentrations of TNT ranging from 1 to 100 mg/l. The standards were injected in HPLC to prepare a calibration curve for TNT.

Alkali solutions used in this study were sodium and calcium hydroxides (NaOH, $\text{Ca}(\text{OH})_2$). 1N sodium hydroxide solution was purchased from Fischer Scientific, New Jersey. 0.1N NaOH solutions were prepared by 1:10 dilution of the 1N stock. 1.0 and 0.1N NaOH solutions were used to adjust pH of TNT solution to 12 and 11, respectively. In some experiments, $\text{Ca}(\text{OH})_2$ was also used to adjust the solution pH. For this purpose, saturated solution of $\text{Ca}(\text{OH})_2$ was prepared by dissolving $\text{Ca}(\text{OH})_2$ pellets in hot deionized water, cooling the solution overnight, and then filtering the crystals off using a 0.2 μm Nylon 66 filter (Cole-Parmer, Illinois). pH of the freshly prepared $\text{Ca}(\text{OH})_2$ solution was 12.5 and it was used to adjust pH of TNT solution to 11 or 12 as desired. The pH meter used in this work was calibrated by a two-point calibration procedure with pH 10 and pH 12 standards.

Experiments were performed in glass conical flasks with 100 ml TNT solution. Requisite amount of TNT stock solution was transferred to a flask and a predetermined amount of alkali solution (NaOH, $\text{Ca}(\text{OH})_2$) was added to adjust the solution pH at the start of each experiment. For uncontrolled-temperature experiments, conducted on a lab-bench, a pH probe and a thermometer probe were suspended in the flask and a magnetic agitator was used to mix contents of the flask. The flasks were covered with aluminum foil to prevent light-induced TNT transformation. Under uncontrolled temperature conditions, the temperature of the reaction mixture varied between 19 and 33 $^{\circ}\text{C}$. Controlled-temperature experiments (25 and 40 $^{\circ}\text{C}$) were conducted in a windowless shaking incubator at 150 rpm. In the incubator, the temperature variation was within ± 1 $^{\circ}\text{C}$ of the set point. Five milliliter samples were collected from the flasks at predetermined times, starting at zero time. Temperature and pH readings were recorded at the time samples were withdrawn from the flasks. A drop of concentrated hydrochloric acid was added to the samples before storing them in a refrigerator pending analysis.

Two control experiments were also performed under isothermal conditions. In these experiments, deionized water was used instead of TNT solution. Everything else including the amount of alkali added was kept same as in the main experiments; analysis of samples was limited to pH measurements.

The samples were analyzed by isocratic high performance liquid chromatography (HPLC) with a reversed-phase C-18 column. The mobile phase was a mixture of 55% methanol and 45% water. It was pumped at a flow rate of 0.6 ml/min. Peaks were detected using a UV detector at 254 nm and integrated using an integrator. The column pressure ranged from 17 to 19 MPa. The samples were not filtered in order to avoid removal of compounds formed during degradation by adsorption in the filter material. The run time was approximately 45 min. Hydroxyl ion concentrations were calculated from measured pH values in the solution at the time of sampling.

3. Results

Results from several typical experiments involving reaction of TNT with alkali in aqueous solution are presented in Figs. 1 and 2. In these figures, the profiles of TNT and hydroxyl ions are presented at two starting pH values (12 and 11 in Figs. 1 and 2, respectively) and where NaOH or Ca(OH)₂ solutions were used to adjust pH. Temperature was not controlled in these experiments. Although the temperature profiles were similar, these were not identical. Each experiment was repeated several times and good reproducibility was observed in all replicate experiments. Experiments conducted on different days were also reproducible within limits of temperature variation. These figures suggest that cations (Na⁺ and Ca²⁺) had

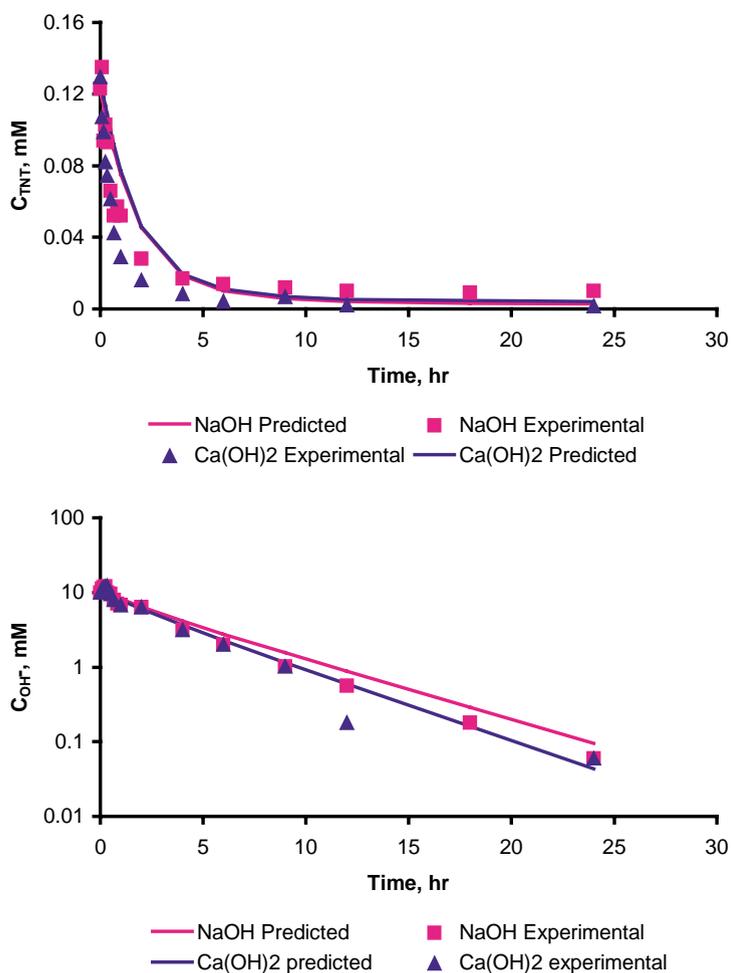


Fig. 1. TNT and hydroxyl ion concentration profiles in uncontrolled temperature experiments. Initial pH = 12. Source of hydroxyl ions: NaOH or Ca(OH)₂.

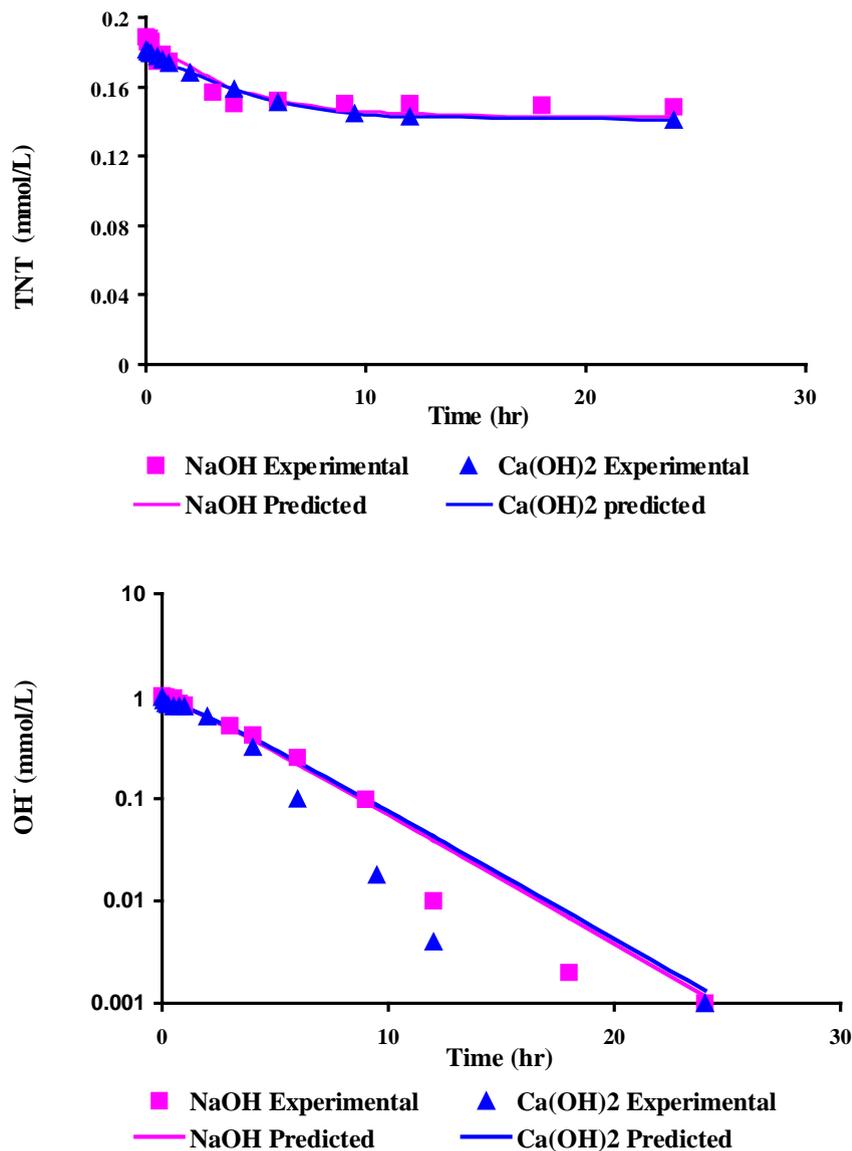


Fig. 2. TNT and hydroxyl ion concentration profiles in uncontrolled temperature experiments. Initial pH = 11. Source of hydroxyl ions: NaOH or Ca(OH)₂.

no effect on the reaction. This was expected but still was tested as preliminary experiments conducted by Karasch et al. [17] had pointed to some effect of cations in solution. Results of the preliminary experiments were, however, not supported by a large number of repeated experiments reported here.

The rate and the extent of disappearance of TNT from solution depended on the starting pH of solution. With starting pH of 12, 85–90% reduction of TNT took place within 5 h, after which a very slow rate of disappearance was observed over the next several hours. The reduction in TNT concentration after 24 h was always in excess of 95%. With starting pH of 11, however, TNT degradation was very slow and the maximum degradation of TNT was only around 20–25%. The rate of disappearance of TNT was strongly correlated to hydroxyl ion concentration in solution and TNT degradation came to a virtual halt when hydroxyl ion concentration dropped below 0.1 moles/L (i.e. pH < 10). The concentration of hydroxyl ions is also plotted in Figs. 1 and 2.

HPLC analyses of samples suggested formation of intermediates, but these could not be identified from the retention times of several suspected intermediates (2,4,6-trinitrophenol, trinitrobenzene, mono- and dinitrotoluenes, different dinitrotoluenes). UV-Vis spectra (presented earlier by Karasch et al. [17]) also showed formation of intermediates, but efforts to identify the intermediate using mass spectroscopy did not succeed there either. Karasch et al. [17] observed temporary absorption peaks at 360, 398 and 450 nm. These peaks were common to the absorption peaks of trinitrobenzene and trinitrophenol. The peak at 398 nm is potentially attributable to loss of a nitro-group and/or gain of a hydroxyl group. Further, the disappearance of peak at 450 nm coincides with appearance of another peak at around 360 nm where trinitrophenol absorbs. Felt et al. [16] have also made similar observations without identifying the intermediates.

3.1. Stoichiometry of alkali consumption

Alkali consumption per mole of TNT disappearance was calculated using mass balance between initial and final data points. This mode of calculation gave the most consistent results. Using all the experimental data, the mean value of moles of hydroxyl ions consumed per mole of TNT was found to be 100 (standard deviation of 11.2). Assuming that hydroxyl ions substitute nitro-groups on the aromatic ring, we expected consumption of 1–3 mol hydroxyl ions per mole of TNT. Even assuming role of hydroxyl ions in further splitting of the aromatic ring, the observed consumption of 100 mol per mole of TNT is huge.

Results from two control experiments (in which no TNT was present in aqueous alkali solution, but otherwise identical conditions) are presented in Fig. 3. These show rapid and significant consumption of hydroxyl ions even in absence of TNT. This consumption of hydroxyl ions is perhaps due to reactions with glass. The order of magnitude reduction in concentration of hydroxyl ions is similar to that in TNT hydrolysis experiments (Fig. 1), suggesting that most of the consumption of hydroxyl ions takes place due to reactions unrelated to TNT. In order to subtract the effect of these extraneous reactions from hydrolysis experiments, a modeling approach was employed.

Assuming that the reaction of OH⁻ with glass is mass transfer controlled, a first-order reaction kinetics was utilized to represent the consumption of hydroxyl ions in control flasks.



With the assumption of a first-order kinetics, semi-log plots of experimental data should yield a straight line with slope equal to negative of the rate constant. Such plots are presented

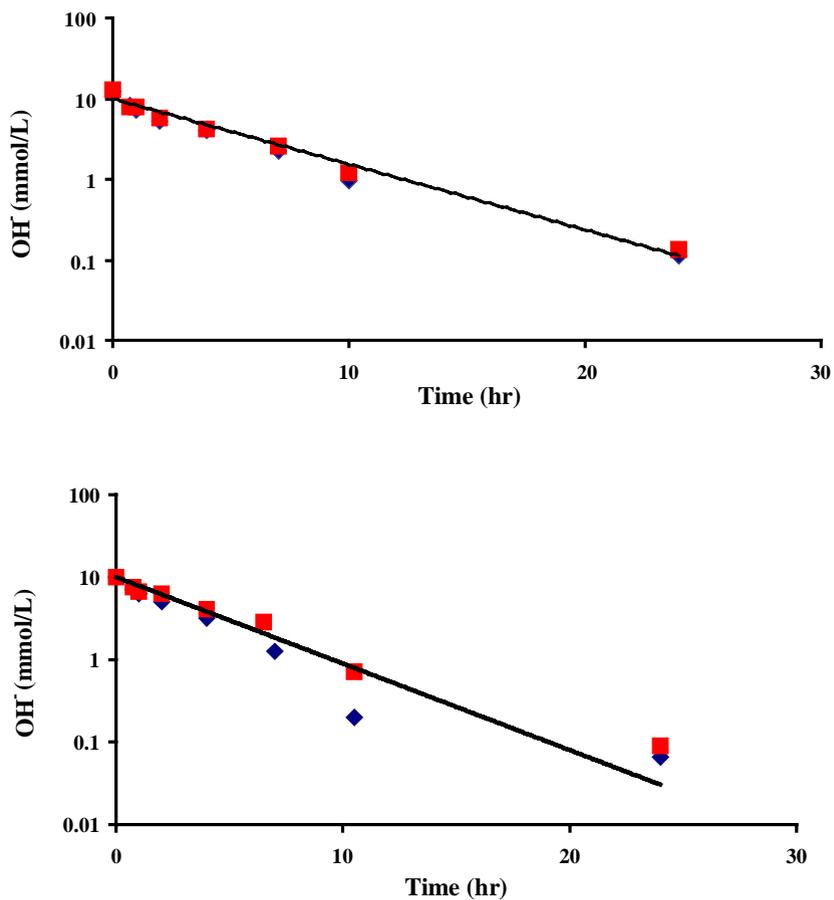


Fig. 3. Consumption of hydroxyl ions in control experiments at 25 and 40 °C. (■) and (◆) represent measurements from replicate experiments. Solid lines represent first-order decay pattern. Initial pH = 12.

in Fig. 3. The first-order reaction rate constants obtained from these plots were:

$$k_1 = 0.185 \text{ h}^{-1} \quad \text{at } 25^\circ\text{C}, \quad \text{and}$$

$$k_1 = 0.20 \text{ h}^{-1} \quad \text{at } 40^\circ\text{C}.$$

These could be represented in the form of the following Arrhenius function

$$k_1 = 0.894 e^{(-965.4/RT)} \text{ h}^{-1} \quad (2)$$

The calculated activation energy value (965.4 cal/g mol) suggests a diffusion-control regime for reactions in the control flasks, justifying the assumed first-order kinetics. The

reduction in concentration of hydroxyl ions due to reactions extraneous to TNT can be calculated as $\{C_{\text{OH}^-}^0(1 - e^{-k_1 t})\}$ and it can be deducted from total consumption of hydroxyl ions in flasks containing TNT to calculate the number of moles of OH^- ions consumed per mole of TNT as

$$m = \left\{ \frac{(\text{mmol OH}^- \text{ consumed})_{\text{flask}} - (\text{mmol OH}^- \text{ consumed})_{\text{control}}}{(\text{mmol TNT consumed})_{\text{flask}}} \right\}_{\text{final}} \quad (3)$$

When these calculations were performed with data from isothermal experiments, a mean value of $m = 13$ (with standard deviation of 2.0) was obtained. Since the two numbers in the numerator of Eq. (3) were large, the value of m calculated this way could still have substantial error. Still, a value of 13 mol hydroxyl ions per mole of TNT was a significant improvement over 100. A more accurate estimate of stoichiometry of hydroxyl ion consumption can be obtained by conducting experiments in inert containers under nitrogen.

3.2. Mathematical model for alkali hydrolysis of TNT

Hydroxyl ions are strong nucleophiles. As a result, these are expected to attack the aromatic ring in TNT. The mathematical model hypothesized that TNT reacts with hydroxyl ions in multiple steps. Since only one intermediate was prominent in the HPLC analysis of samples (this work and that of Karasch et al. [17]) and in the UV-Vis data of samples [16,17], a two-step reaction mechanism was considered. The first step involves nucleophilic reaction between a TNT molecule and a hydroxyl ion. It is assumed that this would already transform the TNT molecule such that the product of this reaction would be detected by HPLC as a new identity (i.e. having different retention time). This step can be written as



Here, C is an unidentified intermediate produced from the first reaction of TNT and a hydroxyl ion. It is further assumed that the intermediate reacts with more hydroxyl ions producing more reactive intermediates. But, since significant amounts of only one intermediate were noted in HPLC and UV-Vis analyses, all the subsequent interactions between the intermediate (C) and hydroxyl ions were lumped together in the second reaction as:



The stoichiometric constant (n) represents the number of hydroxyl ions that participate in the subsequent reactions. Assuming that D represents all the products of subsequent reactions and further since the concentration of residual intermediate C is negligible at the end of the experiment, the total number of hydroxyl ions (B) consumed per molecule of TNT would be $(n + 1)$. Hence,

$$m = n + 1 \rightarrow n = 12$$

Assuming reaction order of each of the species in both the steps as one, the governing equations for a batch system can then be written as

$$\begin{aligned} \frac{dC_A}{dt} &= -k_2 C_A C_B \\ \frac{dC_B}{dt} &= -k_2 C_A C_B - nk_3 C_C C_B - k_1 C_B \\ \frac{dC_C}{dt} &= k_2 C_A C_B - k_3 C_C C_B \end{aligned} \tag{6}$$

The governing equations presented above account for consumption of hydroxyl ions in the extraneous sink reactions as well as in those with TNT. C_A , C_B , and C_C are the concentrations of TNT, hydroxyl ions, and the unidentified intermediate in the flasks. These equations were

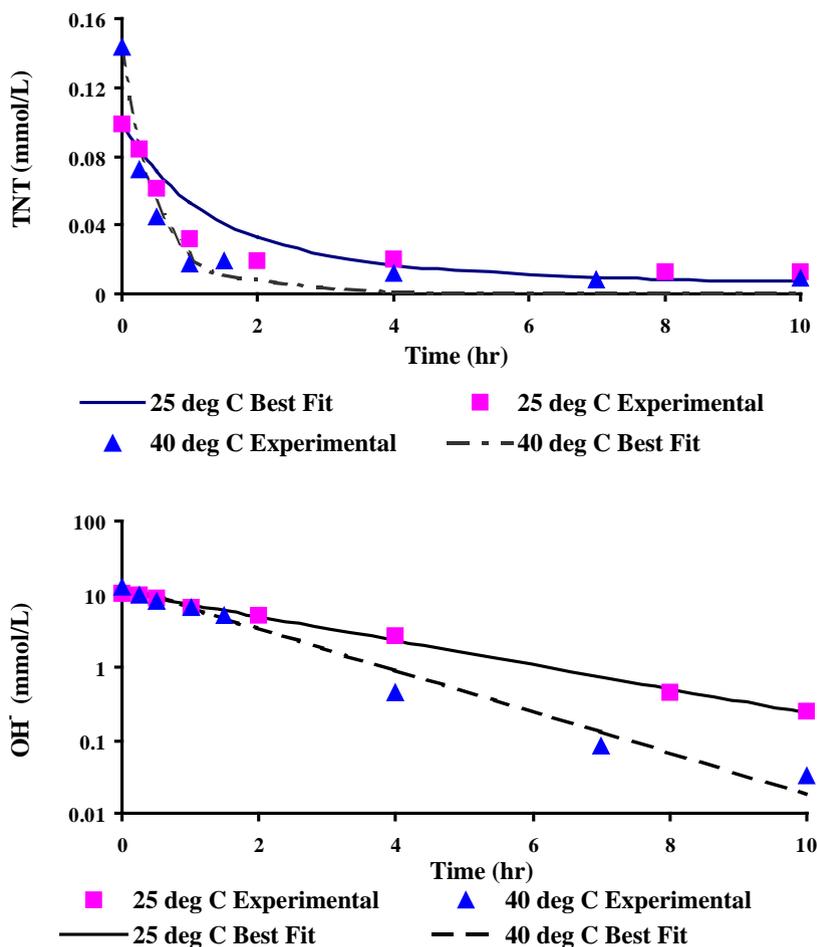


Fig. 4. TNT and hydroxyl ion concentration profiles in controlled temperature experiments. Initial pH = 12. Source of hydroxyl ions: NaOH.

solved in Visual FORTRAN programming language using Adams–Moulton’s method. The parameters (k_2 and k_3) were estimated by fitting the solution of governing equations to the constant temperature experimental data (shown in Fig. 4) using Quasi-Newton/finite-difference gradient method and the following values were obtained:

$$k_2 = 0.066 \left(\frac{\text{L}}{\text{mmol h}} \right) \quad \text{and} \quad k_3 = 0.172 \left(\frac{\text{L}}{\text{mmol h}} \right) \quad \text{at } 25^\circ\text{C}$$

and

$$k_2 = 0.17 \left(\frac{\text{L}}{\text{mmol h}} \right) \quad \text{and} \quad k_3 = 0.278 \left(\frac{\text{L}}{\text{mmol h}} \right) \quad \text{at } 40^\circ\text{C}$$

From these, the following frequency factors and the activation energies were calculated:

$$\begin{aligned} k_2 &= 2.66 \times 10^7 \exp \left(-\frac{11740}{RT} \right) \frac{\text{L}}{\text{mmol h}} \\ k_3 &= 3.77 \times 10^3 \exp \left(-\frac{5920}{RT} \right) \frac{\text{L}}{\text{mmol h}} \end{aligned} \quad (7)$$

The activation energies are in cal/mol. The governing equations (Eq. (6)) were solved with parameters k_1 , k_2 , and k_3 from Eqs. (2) and (7) to predict the concentrations of TNT and hydroxyl ions in different experiments. Since the measured data from temperature-controlled experiments (Fig. 4) were used to estimate the parameters, predictions of TNT and hydroxyl ion profiles were made for the uncontrolled temperature experiments. These predictions are shown in Figs. 1 and 2 as solid lines. For temperature variations during the experiments, the measured temperature profiles were used and linear interpolations were made between successive temperature readings. The agreement between experimental data and model predictions is quite good.

4. Discussion

Emmerich [13] has conducted isothermal experiments (20°C) under iso-pH conditions in aqueous solutions of TNT and in contaminated soil slurries. Since the experiments were conducted at constant pH and since Emmerich [13,14] reported no accounts of alkali consumption from her data, it is not possible to calculate the stoichiometry of alkali consumption. In fact, in our knowledge, the current manuscript is the first reported attempt to account for alkali consumed per mole of TNT consumed. As reported earlier, significant amounts of alkali can be consumed by reactions unrelated to TNT and these can adversely affect the economic viability of using alkali to transform TNT in environmental systems. On the other hand, the consumption of hydroxyl ions in reactions extraneous to TNT does not stop as pH drops (as does TNT consumption), this might even be considered fortuitous. One can start with high pH for high TNT-disappearance rate and yet end up with relatively neutral pH at distances not far from the point of injection.

On the basis of her experiments, Emmerich [13] proposed a reaction-kinetics with first-order reaction order both with respect to TNT as well as hydroxyl ions. From the

homogeneous reaction pseudo-first-order rate constants reported by her at different pH values, the value of second order rate constant for disappearance can be calculated to be 0.036 L/(mmol h) at reaction temperature of 20 °C. The value of rate constant k_2 representing disappearance of TNT in this work (Eq. (7)) comes out to be 0.044 L/(mmol h) at 20 °C. Although not exactly same, this value is of the same order of magnitude as that calculated from the work of Emmerich [13]. There is no other published work that can be used to compare the energy of activation found in this work. In this work, experiments were conducted at only two isothermal temperatures. As a result, an error bound could not be assigned to the activation energy values reported here and work at several other temperatures is desired for better estimates of the rate parameters.

The two-step model proposed in this work can be considered as a second-generation model. This adds one additional parameter (compared to Emmerich's model) in the kinetic analysis of the reaction. It was, however, done with an eye to reconcile the modeling effort with the experimental observation of one major intermediate that is produced in significant quantities during the course of reaction. Felt et al. [16] have reported a similar effort on the basis of peak heights in UV-Vis spectra observed during this reaction. These authors have proposed multi-step reaction mechanisms involving four components and first-order and/or second-order reactions. These authors used analysis suggested by Friedlander et al. [18] to estimate the rate constants, but did not propose any discrimination between the models. One problem with the modeling effort of Felt et al. [16] is that this effort attempts to predict number of intermediates from the variations in height of a single peak. It disregards the variations in molar absorptivities of the components (intermediates) and their transition states enveloped in the peak. As a result, a prediction of number of intermediates from peak height is questionable at best.

5. Conclusions

The experimental data presented here suggest that consumption of hydroxyl ions for reactions unrelated to TNT are significant and must be accounted for in order to have an accurate accounting of alkali needs for hydrolysis of TNT in aqueous solutions. The simple schematic and mathematical model was shown to represent the experimental observations quite satisfactorily and might be used for designing treatment units.

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