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KINETICS OF THE AQUEOUS ALKALINE HOMOGENOUS HYDROLYSIS OF HIGH EXPLOSIVE 1,3,5,7-TETRAAZA-1,3,5,7-TETRANITROCYCLOOCTANE (HMX)

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ABSTRACT

In order to get basic data for the design of a novel treatment scheme for high explosives we investigated the kinetics for the aqueous alkaline hydrolysis of 1,3,5,7-tetraaza-1,3,5,7-tetranitrocyclooctane (HMX) and the temperature dependence of the rate constants. We used an HPLC procedure for the analysis of HMX. All experimental data could be fit accurately to a pseudo first-order rate equation and subsequent calculation of second-order rate constants was also precise. Temperature dependence could be modeled with the Arrhenius equation. An increase of 10°C led to an average increase in the second-order rate constants by the 3.16 fold. The activation energy of the second-order reaction was determined to be 111.9 ±0.76 $kJ \cdot mol^{-1}$. We found the alkaline hydrolysis to be rapid (less than 2.5% of the initial HMX-concentration left after 100 minutes) at base concentrations of 23 mmol OH^-/L and elevated temperatures between 60 and 80°C.

KEYWORDS

Alkaline hydrolysis; contaminated water; high explosives; HMX; kinetics; temperature.

INTRODUCTION

Present Situation

Military waste is becoming increasingly important not only because of poorly defined health and environmental hazards, but also because of recent large increases in waste production due to the end of the cold war. Large amounts of waste High Explosives, such as HMX, RDX and TNT, need to be treated from the current stockpile reduction and nuclear weapons dismantling efforts in the U.S.A., Europe and the former Soviet Union. Furthermore contaminated ground- and processwater from closed military bases, former production plants, contaminated soil treatment and weapon dismantling facilities also need to be treated. Byrd *et al.* (in print) report 317,500,000 kg of HE from the U.S.-Department of Defense (DoD) and 50,000 kg HE per year from the U.S.-Department of Energy's (DoE) nuclear weapon dismantlement efforts that need to be disposed. DoE's demilitarization activities are required under the Intermediate-Range Nuclear Forces Treaty (INF) and Strategic Arms Reduction Treaties (START I and II). These activities will generate large amounts of HE-contaminated wastewaters which also must be treated.

Currently HE are still being treated by Open Burning/Open Detonation (OB/OD) (Patterson, in print). Due to environmental concerns, however, this technology is expected to be banned soon (Byrd and Humphreys, in print). HE-laden process- or groundwater from dismantling activities or contaminated sites generally has been treated by adsorption on activated carbon. The exhausted carbon must then be disposed of as hazardous waste, or burned, which has now been banned (Stenstrom *et al.*, 1993).

The heterocyclic nitroorganic compound 1,3,5,7-Tetraaza-1,3,5,7-tetranitrocyclooctane (HMX-High Melting Explosive) is one of the most important High Explosives in the United States and elsewhere. It is a major compound in both DoE-, which uses it as a primer in nuclear weapons, and DoD-formulations, such as plastic bonded explosive *PBX 9404*. Recently HMX has replaced its homolog RDX in importance since it is present in greater quantities in more recent explosive devices (Knezovich, 1993). This is due to the higher safety of HMX against detonation. HMX has adverse effects on the central nervous system (CNS) in mammals (McLellan *et al.*, 1988a), but in higher concentrations than RDX (McLellan *et al.*, 1988b). HMX has also been classified as class D carcinogen by the U.S.-Environmental Protection Agency. Therefore treatment is essential prior to release into the environment.

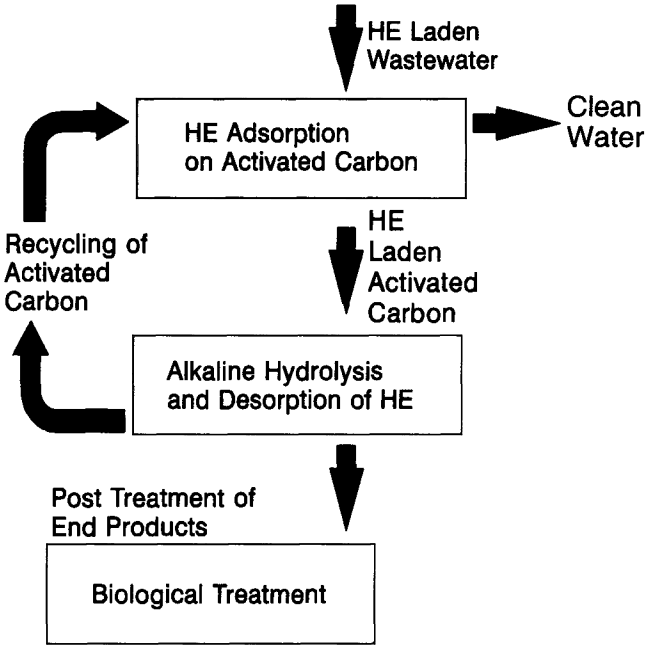

Fig. 1. Novel Treatment Scheme for Water Contaminated with High Explosives

Alkaline Hydrolysis

Alkaline hydrolysis has been identified as an alternative treatment technology for HMX, RDX and other HE by DoE's Lawrence Livermore National Laboratories (LLNL), where it is considered to be a promising 3rd-generation technology (Byrd and Humphreys, in print). Additional basic research is necessary before commercial or industrial facilities can be successfully constructed.

Several researchers have investigated the kinetics of the alkaline hydrolysis of RDX (Epstein and Winkler, 1951; Jones, 1953; Hoffsommer *et al.*, 1977; Croce and Okamoto, 1979). Hoffsommer *et al.* (1977) identified end products and a rate determing E2-elimination as the initial step of the alkaline hydrolysis of RDX. Identified products are NO_2^-, N_2, NH_3, N_2O, $HCOO^-$, CH_2O and H_2. Here the formaldehyde is subject to a *Canizarro*-reaction at the elevated pH and leads to the formation of formate ion (Beyer, 1976). They also confirmed the reaction to be second-order in regard to the RDX- and the OH^--concentration. Second-order rate constants could be calculated from pseudo first-order rate data (for excess OH^-). Less research has been done on the alkaline hydrolysis of HMX; however, we anticipate some similarities to the alkaline hydrolysis of RDX. Epstein *et al.* (1951) concluded that the alkaline hydrolysis of HMX is second-order. Croce *et al.* (1979) emphasized possible rate enhancement effects in the presence of cationic micelles. They proposed that the alkaline hydrolysis of HMX follows the same basic mechanism as RDX, with regard to the almost similar activation parameters for HMX and RDX which were obtained in these rate studies. All these investigations, however, were done at less elevated temperatures (0 to 45°C). Current research is under way at Los Alamos National Laboratories. In the research there the emphasis is on the heterogeneous alkaline hydrolysis of HMX and other high explosives. The objective of these investigations is on the disposal of larger amounts of solid HE (Spontarelli *et al.*, in print).

The objective in our project is to carry out basic research on the alkaline hydrolysis of HE and develop an economical treatment scheme for HMX- and RDX-contaminated waters. HMX-contaminated water contains trace amounts of the compound only due to the low solubility (5mg HMX/L, Rosenblatt *et al.*, 1991). In this project we have identified combined treatment through adsorption of HMX onto granular activated carbon (GAC) and subsequent offline-regeneration of spent GAC through alkaline hydrolysis as a viable process (Fig. 1.). The contaminated water is first cleaned through HMX-adsorption onto GAC, which concentrates the HMX on the carbon and reduces the volume of material to be treated with alkaline hydrolysis. The spent carbon is regenerated with alkaline hydrolysis and can be reused to treat another charge of contaminated water. The end products are thought to be low molecular weight compounds which can easily be degraded in regular wastewater treatment plants with nitrification/denitrification stages. This treatment scheme is complementary to the earlier proposal of Hesselmann *et al.* (1992) which used carbon adsorption with solvent and biological carbon regeneration.

In this manuscript we investigate the chemical kinetics of the alkaline hydrolysis of HMX. Since the rates of the alkaline hydrolysis can be increased significantly through higher temperature or pressure, we investigated the alkaline hydrolysis of HMX at elevated temperatures of 50, 60, 70 and 80°C. The desired pH-value was in the range of 10 to 12.

MATERIALS AND METHODS

Analytical

Dissolved HMX was analyzed using High Performance Liquid Chromatography with a variable wavelength UV-detector (HPLC/UV, Hewlett-Packard Series 1050) set to 236nm. A mobile phase consisting of 40% water, 30% methanol and 30% acetonitrile (v/v/v) was used at a flow rate of 1ml/min. A C18 reversed phase column (Adsorbosphere, Alltech) with pre-filter element and guard column was applied. Peaks were detected at retention times between 3.5 and 3.6 minutes. Linearity occurred between 0 and 5 mg/L. Standards were prepared for 0.5, 1, 2, 4 and 5 mg HMX/L, where the highest concentration was also the solubility limit. We found 100µg HMX/L to be the detection limit with this method. For the external calibration, at least three data points were gathered for each standard concentration. The mean was then used for the calibration curve. All samples were filtered through sterile Acrodisc-13 0.2µm syringe-microfilters (Gelman Sciences, Ann Arbor, MI) before injection.

Experimental

Experiments were performed in a water bath at 50, 60, 70, 80°C and were held at constant temperature for at least one hour prior to the start of a kinetic run. From an HMX stock solution (approximately 4 mg HMX/l) 1000ml were provided into the reaction vessel (1000 ml Erlenmeyer) and heated in the water bath until constant temperature was reached. The mixture was stirred by an overhead motor stirring unit (stainless steel). The appropriate amounts of 1-M NaOH (0.22 mL, 2.1 mL, 23 mL) were provided with an Eppendorf adjustable pipettor (0.22, 2.1 mL) or a common pipette (23 mL). The volume change was evaluated for 23 mL. A precision scientific timer was set simultaneously to the start of a kinetic run. Samples of 1ml were taken at predefined times using 1cc-microsyringes and attached needles; sample collection time was 2 seconds; samples were immediately filtered into cooled (0°C) HPLC vials. In order to check the constant pH (provided through excess OH^--concentration) 10ml-samples were taken with volumetric pipettes and immediately transferred into cooled 30ml-beakers for pH-determination. In order to minimize volume change due to sampling, 10ml-samples were taken only occasionally.

Kinetics

In accordance to previous researchers (Hoffsommer *et al.*, 1977) a second-order rate equation was applied to fit the data:

$$\frac{dc_{HMX}}{dt} = -k_{HMX,2} \cdot c_{HMX} \cdot c_{OH^-} \tag{1}$$

where c_{HMX} is the HMX-concentration, c_{OH^-} the hydroxide ion-concentration and $k_{HMX,2}$ the second-order rate constant. In the case of constant OH^--concentration or negligibly small deviation in concentration provided through excess base, equation-1 can be reduced to a pseudo first-order rate equation:

$$\frac{dc_{HMX}}{dt} = -k_{HMX,1} \cdot c_{HMX} \tag{2}$$

where $k_{HMX,1}$ is the pseudo first-order rate constant. For $t=0$; $c_{HMX}=c_{HMX,0}$ and integration from 0 to t the solution of the differential equation (Equation 2) is:

$$\ln \frac{c_{HMX}}{c_{HMX,t=0}} = -k_{HMX,1} \cdot t \tag{3}$$

Pseudo first-order rate constants can be obtained through a linear least square fit of the sample data to equation-3, where the rate constant is the slope of the graph of the function. The second-order rate constant can then be evaluated from the pseudo first-order rate constants at a constant OH^--concentration using the equation $k_{HMX,2} = k_{HMX,1}/c_{OH^-}$. The kinetic constants were further evaluated with respect to their temperature dependence using the Arrhenius-equation:

$$\ln k_{HMX}(T) = \ln A - \frac{E}{R \cdot T} \tag{4}$$

where A is the empirical Arrhenius-factor or pre-exponential factor; E is the empirical activation energy (must be independent from temperature); R is the gas constant and T the absolute temperature. The Arrhenius-factor A and the constant E/R can be determined from a linear least square fit of the logarithm of the specific rate constants against the reciprocal of the absolute temperature (Benson, 1982). All error determination limits were obtained using standard deviation from the mean.

RESULTS AND DISCUSSION

All experimental data (Fig. 1, 2 and 3, Table 1) could be fitted accurately using the pseudo first-order model (Equation 2). This is reflected by low error limits (Table 1, ±0.38% to ±2.38%). The correlation coefficients are close to 1 for all experiments. The subsequent calculation of the second-order rate constants from the pseudo first-order rates was also successful (Table 2). Low error limits (±0.09% to ±1.36%) and very good correlation coefficients (0.9998 or >0.9999) reflect that a pseudo first-order model with subsequent calculation of the second-order rate constants is applicable here. As expected, the increase of hydroxide ion led to equivalent increase in the pseudo first-order rates. An increase in the hydroxide-concentration by ten fold corresponds with an increase of the rate by approximately ten fold.

TABLE 1 PSEUDO FIRST-ORDER RATE CONSTANTS AND CORRELATION COEFFICIENTS (R^2) FOR THREE DIFFERENT OH^--CONCENTRATIONS

T	$k_{HMX.1}$ (10^{-3} min^{-1})			T	R^2		
	0.22 mmol OH^-/L	2.1 mmol OH^-/L	23 mmol OH^-/L		0.22 mmol OH^-/L	2.1 mmol OH^-/L	23 mmol OH^-/L
50°C	0.089 ±2.38%	0.99 ±1.46%	10.82 ±0.38%	50°C	0.9972	0.9991	0.9999
60°C	0.35 ±2.82%	3.28 ±0.81%	38.45 ±1.88%	60°C	0.9952	0.9997	0.9979
70°C	1.19 ±1.81%	11.87 ±1.32%	126.53 ±1%	70°C	0.998	0.999	0.9995
80°C	3.62 ±1.51%	39.64 ±0.63%	374.9 ±1.26%	80°C	0.9989	0.9997	0.9995

Fig. 2 shows the kinetic experiments at a hydroxide concentration of 0.22 mmol/L. At 50°C alkaline hydrolysis is very slow. After more than 20 hours more than 90% of the initial HMX was still present. For the intermediate concentration of 2.1mmol OH^-/L and elevated temperatures, alkaline hydrolysis is significantly faster (Fig. 3). In Fig. 4 it can be seen that the alkaline hydrolysis of HMX at 23mmol OH^-/L is quite rapid, particularly for the elevated temperatures of 60, 70 and 80°C, where less than 2.5% of the initial HMX-concentration was present after 100 minutes.

TABLE 2 CALCULATED SECOND-ORDER RATE CONSTANTS AND CORRELATION COEFFICIENTS

T	$k_{HMX.2}$ (L mol^{-1} min^{-1})	R^2
50°C	0.47 ±0.09%	>0.9999
60°C	1.68 ±0.52%	>0.9999
70°C	5.5 ±0.25%	>0.9999
80°C	16.19 ±1.36%	0.9998

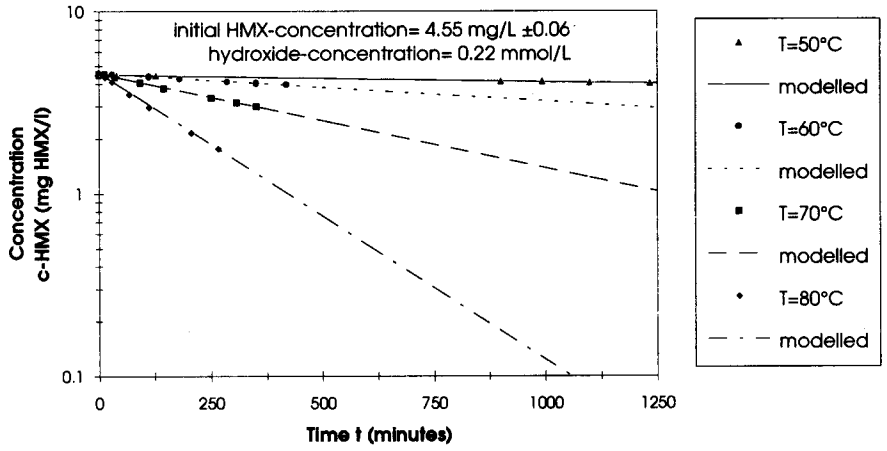

Fig. 2. Experimental data and pseudo first-order model simulation for 0.22 mmol OH^-/L and T=50,60,70,80°C.

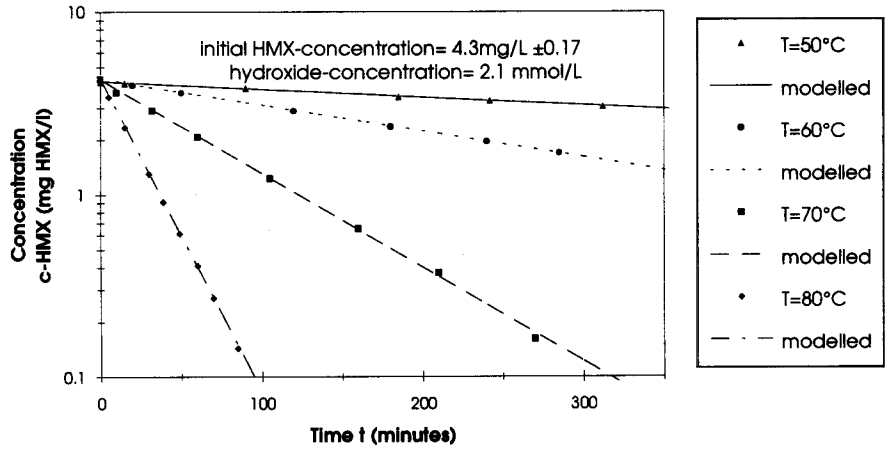

Fig. 3. Experimental data and pseudo first-order model simulation for 2.1 mmol OH^-/L and T=50,60,70,80°C.

We compared the second-order rate constant obtained by Croce *et al.* (1979) at T=25°C (0.3 ±10% $L \cdot mol^{-1} \cdot s^{-1} \cdot 10^{-3}$) with our calculated rate of 0.24 $L \cdot mol^{-1} \cdot s^{-1} \cdot 10^{-3}$ (model data for T=25°C). Even though the rates are of the same magnitude it is possible that the difference of 20% in the rates is due to different assumptions regarding the solubility of HMX in water. Croce *et al.* (1979) report standard solutions containing 6, 9 and 12 mg HMX/L in water, which are all above the solubility limit of 5 mg HMX/L as reported in the literature (Rosenblatt *et al.*, 1991) and which we confirmed. It can be assumed that heterogeneity might have had an impact on the results of Croce *et al.*

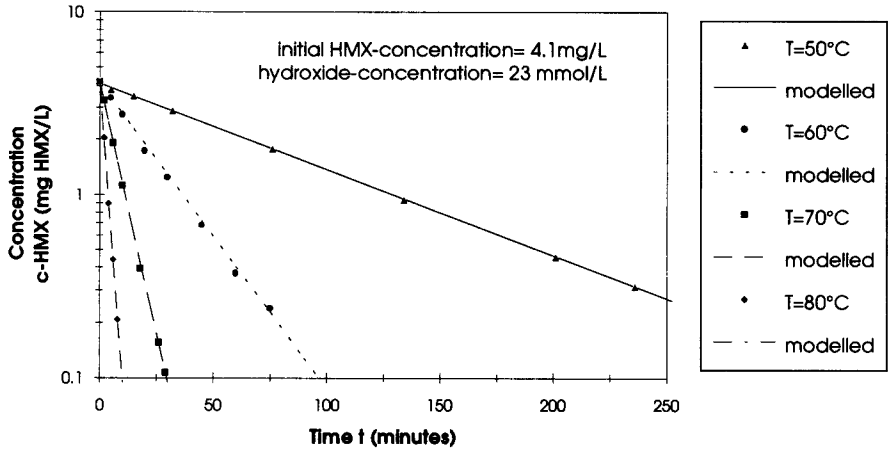

Fig. 4. Experimental data and pseudo first-order model simulation for 23 mmol OH^-/L and T=50,60,70,80°C.

The temperature dependency of the rate constants was evaluated using the Arrhenius equation (Equation 4). The fit of both the pseudo first-order and the calculated second-order rate constants as functions of temperature was accurate (Fig. 5). The correlation coefficients (Table 3) are between 0.9991 and 0.9999. The average values of the parameter *E/R* from the pseudo first-order determinations are very close to that obtained from the calculated second-order rate constants. With respect to our results we consider the activation energy *E* to be temperature independent over the range from 50 to 80°C. The value of the activation energy *E* as obtained from the second-order rate constants (Table 3, 111.9±0.76 kJ·mol^{-1}) is very precise, since deviations of ±4 kJ·mol^{-1} are accepted in common practice (Baerns *et al.*, 1992). In the experiments an average rate increase factor of 3.16 was found corresponding to an increase of 10°C in temperature. This value is in agreement with the investigations of Hoffsommer *et al.* (1977) where a factor of 3.5 was found for the rates of the alkaline hydrolysis of RDX at 25, 35 and 45°C.

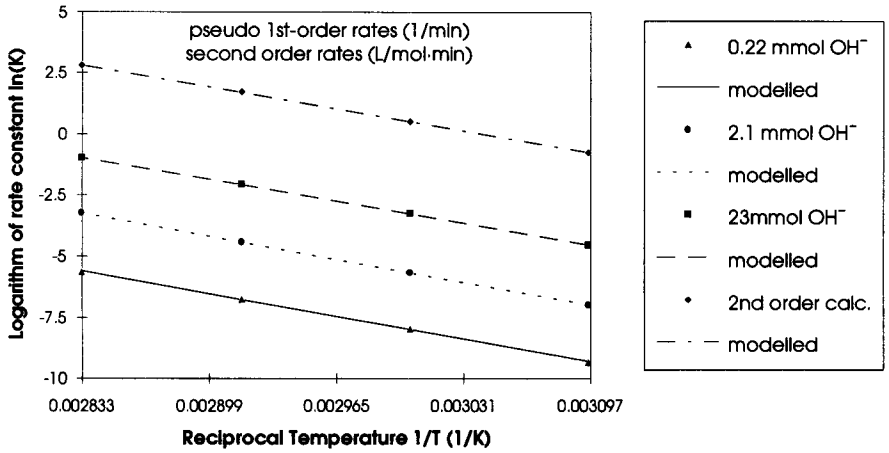

Fig. 5. Arrhenius-plot of pseudo first-order and calculated second-order rate constants

TABLE 3 ARRHENIUS PARAMETER AND CORRELATION COEFFICIENTS FOR PSEUDO FIRST-ORDER AND CALCULATED SECOND-ORDER RATE CONSTANTS

	0.22 mmol OH^-/L	2.1 mmol OH^-/L	23 mmol OH^-/L	second-order rate constant calculated
R^2 of Arrhenius-fit	0.9996	0.9991	0.9999	0.9999
ln*A*	34.31	36.67	37.24	40.93 ±0.67%
$((mol \cdot L^{-1})^{1-n} \cdot min^{-1})$	*reaction order n= 1*			*n= 2*
E/R (K)	-14087	-14096	-13489	-13459 ±0.68%
E ($KJ \cdot mol^{-1}$)				111.9 ±0.76
average *E/R*	-13891 ±2.5%			

CONCLUSIONS

We investigated the aqueous alkaline hydrolysis of HMX to determine basic kinetic data for the design of the treatment scheme as shown in Fig. 1. Base concentrations of 2.1 to 23 mmol OH^-/L and elevated temperatures above 50°C rapidly degraded HMX. The resulting sodium concentrations, since NaOH was used, were between 5.06 and 529 mg Na^+/L and are non-toxic for further (bio)-treatment. We therefore compared the sodium-concentration with a low sodium mineral water (Gerolsteiner-brand, Germany) which carries 45 mg Na^+/L. That is about the Sodium-concentration which is reached with 2.1 mmol NaOH/L.

We conclude that the alkaline hydrolysis of HMX in presence of intermediate base concentrations and elevated temperatures would be a feasible regeneration process as part of the treatment scheme (Fig. 1) as mentioned before. In particular the application of a much smaller regeneration process water volume compared with the original wastewater volume is an advantage compared to direct alkaline treatment of the contaminated water. That means that the original wastewater volume which is purificated through adsorption on activated carbon does not need to be contacted with the regenerative base solution. The amount of base needed can be significantly decreased through this separation of the two processes. Even though the alkaline hydrolysis of HMX has been investigated at less elevated temperatures by previous researchers, none has investigated the possibility of combining adsorption on activated carbon and alkaline hydrolysis.

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REFERENCES

Baerns, M., Hofmann, H., Renken, A. (1992). *Chemische Reaktionstechnik*. 2.ed., Thieme, Stuttgart, Germany

Benson, Sidney W. (1982). *The Foundations of Chemical Kinetics*. Updated and corr. ed. Krieger, Malabar, Florida

Beyer, Hans (1976). *Lehrbuch der Organischen Chemie*, 18th ed., Hirzel, Stuttgart, Germany

Byrd Jr., J., Humphreys, J. (in print). Demilitarization: Overview of Problem. *Proceedings of the 12th (1993) International Incineration Conference*, Knoxville, Tennessee, May 3rd-7th

Croce, M., Okamoto, Y. (1979). Cationic micellar catalysis of the aqueous alkaline hydrolysis of 1,3,5-triaza-1,3,5-trinitrocyclohexane and 1,3,5,7-tetraaza-1,3,5,7-tetranitrocyclooctane. *J. Org. Chem.*, **44** (13), 2100-2103

Epstein, S., Winkler, C. A. (1951). Studies on RDX and related compounds. *Canadian Journal of Chemistry*, **29**, 731-733

Hesselmann, R. P. X., Alatriste-Mondragon, F., Babcock, R. W., Knezovich, J. P., Daniels, J. I., Mah, R. A., Stenstrom, M. K. (1992). Presented at the *1992 Waste Management and Environmental Sciences Conference*, San Juan, Puerto Rico, April 9th-11th

Hoffsommer, J. C., Kubose, D. A., Glover, D. J. (1977): Kinetic isotope effects and intermediate formation for the aqueous alkaline homogeneous hydrolysis of 1,3,5-triaza-1,3,5-trinitrocyclohexane (RDX). *J. Phys. Chem.*, **81** (5), 380-385

Jones, W. H. (1953). Mechanism of the homogeneous alkaline decomposition of cyclotrimethylenetrinitramine: Kinetics of consecutive second- and first-order reactions. A polarographic analysis for cyclotrimethylenetrinitramine. *J. Am. Chem. Soc.*, **76**, 829-835

Knezovich, J. (1993). Personal Communication. *UCLA - Lawrence Livermore National Laboratories*

McLellan, W., Hartley, W. R., Brower, M. (1988a). *Health advisory for octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazine*. Office of Drinking Water, U.S.-Environmental Protection Agency, Washington, DC

McLellan, W., Hartley, W. R., Brower, M. (1988b). *Health advisory for hexahydro-1,3,5-tetranitro-1,3,5-triazine*. Office of Drinking Water, U.S.-Environmental Protection Agency, Washington, DC

Patterson, E. (in print). Thermal Treatment of High Explosives at the Pantex Plant. *Proceedings of the 12th (1993) International Incineration Conference*, Knoxville, Tennessee, May 3rd-7th

Rosenblatt, David H., Burrows, Elizabeth P., Mitchell, Wayne R., Parmer, David L. (1991). Organic Explosives and Related Compounds. In: *The Handbook of Environmental Chemistry*, Vol.3, part G, Springer, Berlin

Spontarelli, T., Buntain, G. A., Sanchez, J. A., Benziger, T. M. (in print). Destruction of Waste Energetic Materials Using Base Hydrolysis. *Proceedings of the 12th (1993) Incineration Conference*, Knoxville, Tennessee, May 3rd-7th

Stenstrom, M. K., Heilmann, H. M., Wilkie, J. A. (1993). Novel Treatment Developed for Explosive. *UCLA-Center for Clean Technology Bulletin*, Spring