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The use of ultra high-performance liquid chromatography for studying hydrolysis kinetics of CL-20 and related energetic compounds

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ABSTRACT

Ultra high-performance liquid chromatography (UHPLC) utilizes columns packed with sub-2-μm stationary-phase particles and allows operation with pressures of up to 15,000 psi to yield increased resolution, speed, and sensitivity versus conventional HPLC. This promising new technology was used for the analysis of energetic compounds (RDX, HMX and CL-20) and a selective method was developed on an Acquity UPLC™. A fast UHPLC method was applied to determine alkaline hydrolysis reaction kinetics of major energetic compounds. Activation energies of alkaline hydrolysis reaction for CL-20, RDX and HMX were comparable to those in literature, however they were determined in a shorter amount of time due to the speed of analysis of the chromatographic method. The use of liophilic salts (KPF_6) as mobile-phase additives for the enhancement of separation selectivity of energetic compounds was demonstrated.

1. Introduction

The search for new energetic materials as potential replacements for currently used explosive and propellant formulations (used in gun and rocket propellants) is an area of intense investigation in military and industrial applications [1–4]. There are three propellant compounds currently attracting much interest: 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12 hexaazaisowurtzitane (HNIW), also known as CL-20, octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine, also known as HMX, and hexahydro-1,3,5-trinitro-1,3,5-triazine, also known as RDX. All three nitramine compounds are structurally related to each other (Fig. 1).

CL-20 is a relatively new compound synthesized for use as an energetic ingredient in propellant formulations [1]. Due to its improved energetic properties (i.e. higher decomposition energy), CL-20 is being considered as a replacement for presently used explosives such as RDX and HMX, which are heavily used in the military and in industry [2]. However, production costs may limit its adaptation. Moreover, CL-20 may likely have pollutants comparable to those of HMX/RDX, therefore its properties, such as solubility and decomposition in aqueous/soil matrices, must be further studied [3,4].

CL-20 consists essentially of a rigid isowurtzitane cage with a nitro group attached to each of the bridging nitrogen atoms. When compared with RDX and HMX, CL-20 has a greater molecular weight, higher heat of formation, more $N–NO_2$ bonds, and greater density (ε polymorph) [5]. It has four distinct polymorphic structures, named α, β, γ, and ε at ambient conditions. The ε-polymorph is the preferred form for use in solid propellants because it has the highest crystal density and solid state stability at ambient conditions [6–10].

CL-20 was recently moved to production and it is now in exploratory and advanced development [11]. Its energetic properties have been comprehensively studied. However, there has been very little research regarding waste by-product treatment of industrial CL-20 production and the potential cleaning of polluted sites. A technology which holds potential for treatment of energetic materials is aqueous alkaline hydrolysis of bulk quantities and contaminated wastewater. Most energetic materials are synthesized in acidic media, so they are susceptible to alkaline hydrolysis. These materials, such as nitrate esters, nitro-aromatics, and nitramines, usually decompose to form nitrates, nitrites, ammonia, nitrogen, hydrogen, organic acids, and formaldehyde [12]. The by-products resulting from alkaline hydrolysis could be either disposed of directly [13], or may undergo additional biological treatment [14].

It is well acknowledged that explosives are vulnerable to bases [13]. The kinetics of the alkaline hydrolysis of energetic compounds has been studied previously [3,4,15–27]. Hoffsommer et al. [17] identified end-products and a rate-determining E2-elimination mechanism as the initial step of the alkaline hydrolysis of RDX.

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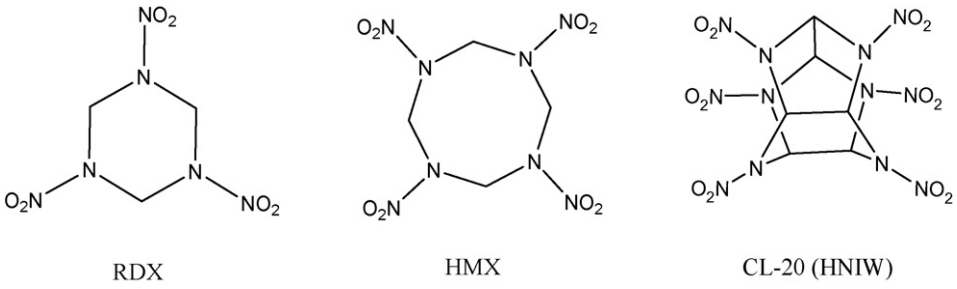

Fig. 1. Structures of RDX, HMX and CL-20.

They identified NO_2^-, N_2, NH_3, N_2O, $HCOO^-$, CH_2O, and H_2 as end-products and by-products. At elevated pH, the formaldehyde is subject to a Canizarro reaction [28] and produces formate [21]. They also established that reaction is second-order with respect to RDX and OH^- reaction components. Rate constants were calculated from pseudo-first-order rate data (for excess OH^-). The alkaline hydrolysis of HMX has not been extensively studied [15]; however, some similarities to the alkaline hydrolysis of RDX are expected. Epstein and Winkler [15] concluded that the alkaline hydrolysis of HMX is second order. In their study, Croce and Okamoto [18] proposed that the alkaline hydrolysis of HMX follows the same basic mechanism as RDX. This proposition was based on the activation parameters for HMX and RDX that were obtained by the Hoffsommer et al. [17] rate studies. Most of these studies investigated the kinetics of the alkaline hydrolysis of HMX and RDX at elevated temperatures (ranging from 50 to 80 °C) with the pH varied from 10 to 12 adjusted by NaOH [4].

Most of the studies on kinetic hydrolysis have used reversed phase HPLC with UV detection as the major analytical technique for determination of the concentration of energetic components in a reaction mixture [1–5]. Researchers often use the U.S. EPA Standard Method 8330 or adapted HPLC methods based on 8330, which was originally developed for the analysis of nitro-aromatic and nitroamine explosives using a Symmetry Shield RP-18 column [2]. The HPLC methods typically used by researchers to study kinetics are isocratic, 40/60% (v/v) acetonitrile/water with elution times of 3.5 and 4.3 min for the major peaks HMX and RDX, respectively [1,4,5]. One drawback of these methods is that CL-20 co-elutes with HMX at the separation conditions described above [3–5].

The introduction of columns packed with sub-2-μm stationary-phase particles in conjunction with ultra high pressure liquid chromatographic systems (UHPLC) is one of the latest contributions towards the trend of developing faster chromatographic methods in the analytical laboratory [29–31]. Shorter analysis times allow for higher sample throughput and reduced solvent consumption and solvent removal costs, which can lead to significant cost savings down the line as a product moves to the production stage [29]. Reducing the column packing material particle diameter yields a lower plate height and allows for greater resolution per unit time for the overall separation [29]. The use of a UHPLC system (operates up to maximum 15,000 psi), and the implementation of "liophilic" mobile-phase additives for enhancement of the chromatographic selectivity for energetic compounds in a fast time scale is demonstrated.

The enhancement of retention of basic compounds is sometimes a challenging task due to their inherent polarity and early elution. One effective approach for enhancement of retention of basic compounds is to add oppositely charged counteranions (liophilic salts) into the mobile phase which interact with the protonated basic compounds. The addition of the salts of hexafluorophosphate (PF_6^-), tetrafluoroborate (BF_4^-) and perchlorate (ClO_4^-) generally provides the greatest changes in retention and only 10–25 mM of the salt is required to produce the desired effect. The benefits of using liophilic salts for the separation of early eluting protonated basic compounds are increased retention, increased apparent efficiency, decreased tailing and increased loading capacity [32–36].

All energetic compounds used in this study have a very low pK_a due to the strong electron-withdrawing nitro groups, and at the pHs studied in this paper the energetic compounds are not positively charged. Even though the compounds are not positively charged the use of liophilic reagents to enhance chromatographic selectivity was investigated and interesting results were obtained. This paper describes the first application of using liophilic salts for the selectivity enhancement of nitramine energetic compounds. The concentration of hexafluorophosphate in the mobile phase was optimized to provide the desired retention/selectivity in the UHPLC method that could be used to monitor the solid state stability of energetic compounds. This method was further optimized and used to monitor the alkaline hydrolysis of CL-20, HMX and RDX.

Alkaline hydrolysis of CL-20 is a minute scale reaction and it is laborious to follow kinetics of this reaction in real time by conventional HPLC method. Therefore, a fast (1 min) UHPLC method for monitoring decomposition of energetic compounds was applied to determine reaction kinetics of alkaline hydrolysis of CL-20, HMX and RDX. The research presented here aims to re-evaluate, using a UHPLC technique, the activation energy of major energetic compounds obtained in prior studies [3,4]. Increased speed of the analysis and significant gains in resolution per unit time for this method were obtained compared to original separations in the literature [3,4] carried out on conventional HPLC (operates at <4000 psi). This method would provide a superior alternative to the U.S. EPA Standard Method 8330.

2. Experimental

2.1. Reagents and chemicals

The CL-20 used was manufactured by A.T.K. Thiokol Propulsion (Brigham City, UT) and supplied by Picatinny Arsenal, NJ. Data provided by Thiokol indicated that the CL-20 had a purity greater than 99% (determined by HPLC), had an ε-polymorph content greater than 98% (determined by Fourier transform infrared spectroscopy), and an average particle size of 2 μm with a uniformity coefficient of 1.47. The RDX used was synthesized and supplied by the U.S. Army TACOM/ARDEC (Picatinny Arsenal, NJ), and had a HMX content of 10% (w/w) as a production related impurity. The acetonitrile was HPLC-grade (Fisher Scientific, Pittsburg, PA). Potassium hexafluorophosphate was obtained from Acros Organics (Morris Plains, NJ). Trifluoroacetic acid and ammonium hydroxide were purchased from Fisher Scientific (Pittsburg, PA). Deionized water was obtained using the Elga Ultra Pure LabWater system (High Wycombe, UK).

2.2. Apparatus

CL-20, RDX and HMX were analyzed using a reverse-phase UHPLC system (Acquity UPLC™, Waters Corp, Milford, MA), equipped with a photodiode array detector with a data frequency acquisition of 80 Hz.

A variable-volume calibrated pipette (1000 μL Pipetman, Gilson Inc, Middletown, WI) was used for the preparation of a reaction mixture of alkaline-aqueous hydrolysis experiments.

2.3. Columns

An Acquity BEH C-18 (2.1 mm × 100 mm) 1.7-μm column with 135-Å pores (Waters, Milford, MA) was used for hydrolysis experiments as well as for method development. An Acquity BEH Shield RP-18 (2.1 mm × 100 mm) 1.7-μm column was used only for method development.

2.4. Conditions for analysis of hydrolysis experiments

The chromatographic conditions for CL-20 consisted of an isocratic binary mobile phase A and B (40:60, v/v) pumped at a flow rate of 0.8 mL/min and spectrophotometric detection at 228 nm. CL-20 eluted as a symmetrical peak with a retention time of 0.85 min. Total run time was 1 min. Mobile phase A consisted of 0.05% trifluoroacetic acid (v/v) (pH 2.2) and 30 mM NH_4PF_6. This mobile phase was filtered using 0.22-μm Millipore filter. Mobile phase B was pure acetonitrile. The column temperature was 45 °C. A 5-μL full loop injection was used. Column pressure was approximately 8500 psi. Due to the less hydrophobic nature of RDX and HMX compared to CL-20, the chromatographic conditions for RDX and HMX analysis were as follows: isocratic binary mobile phase A and B (95:5, v/v) pumped at a flow rate of 1.0 mL/min and spectrophotometric detection at 228 nm. Mobile phases A and B had the same composition as those in the analysis of CL-20. The retention time for RDX was 2.3 min. The retention time for HMX was 2.1 min. Total run time was 3 min. Column temperature was 45 °C. A 3-μL pressure assisted partial loop injection was used. Column pressure was around 9600 psi.

2.5. Conditions for method development experiments

The chromatographic conditions for method development consisted of mobile phases A and B pumped at a flow rate of 0.5 mL/min and spectrophotometric detection at 247 nm. Total run time was 4 min. Mobile phase A consisted of 0.2% trifluoroacetic acid (v/v) with or without addition of 30 mM NH_4PF_6. This mobile phase was filtered using 0.22-μm Millipore filter. Mobile phase B was acetonitrile with addition of 0.2% trifluoroacetic acid. The column temperature was 45 °C. A 5-μL full loop injection was used. The gradient used was: isocratic hold for 1 min at 5% B, then over 0.5 min to 40% B, then over 1.5 min to 95% B, then hold for 0.5 min at 95% B and equilibrate at initial conditions for 0.5 min. Total run time was 4 min. Column pressure at initial was approximately 8300 psi.

2.6. Sample preparation

Sample solutions used for hydrolysis experiments as well as standard solutions of CL-20 and RDX were prepared in 30/70 (v/v) acetonitrile/deionized water. The target concentrations for standards were 0.2 and 0.3 mg/mL respectively. The target concentration for HMX was 0.3 mg/mL. HMX standard solution was prepared in 50/50 (v/v) acetonitrile/deionized water. The detection limit (s/n = 19) for CL-20 was 0.04 mg/L. Since RDX had a HMX content of 10% (w/w), the standard measurements were multiplied by a correction factor of 0.9. The detection limit (s/n = 21) for RDX was 0.05 mg/L.

2.7. Hydrolysis experiments

Hydrolysis experiments for CL-20 were carried out at five temperatures (5, 10, 15, 20, and 25 °C) (homogeneous alkaline hydrolysis) using NH_4OH at a concentration of 6.2 M. Hydrolysis experiments (homogeneous alkaline hydrolysis) for RDX and HMX were also carried out at five temperatures (15, 20, 25, 30, and 35 °C) using the same NH_4OH concentration. The temperature of the reaction was kept at the target value ±0.5 °C using the autosampler chamber of the Acquity UPLC™.

All sample solutions were equilibrated at the target temperature for at least 1 h before the start of the experiments. Sample solution (0.5 mL) containing dissolved reactant was placed in a 1.5 mL HPLC vial. Next, 0.5 mL of concentrated solution of NH_4OH (6.2 M, pH 12.6) was added to the solution. This mixture was vigorously mixed for 5 s. and placed in the autosampler chamber at the appropriate temperature for UPLC analysis. Samples for CL-20 analysis were injected into the UPLC system every minute without disrupting the temperature regime. Samples for RDX and HMX analysis were also injected in the same manner over a defined period of time: 60 min for 15 °C, 30 min for 20 °C, 20 min for 25 °C, 15 min for 30 °C, and 10 min for 35 °C.

3. Results and discussion

3.1. Method development

Highly efficient separations are critical for the analysis of complex mixtures. The separation of HMX and RDX presents some challenges due to structural similarities of these compounds. These challenges were addressed by using ultra high-performance liquid chromatography in conjunction with liophilic mobile-phase additives.

The use of ultra high-performance liquid chromatography (UHPLC) with columns packed with sub-2-μm stationary phase allows for faster run times (3–5 times faster compared to conventional HPLC) [29–31]. This resulted in development of a chromatographic method with a run time of less than a minute, which is particularly important for CL-20 alkaline hydrolysis experiments in order to obtain data in real time scale. In the first separation on a BEH-C18 column, using isocratic mode with TFA as a mobile-phase additive the selectivity between HMX and RDX was 1.09 and the resolution was less than 2.0 (Table 1). The use of dif-

Table 1
Effect of increasing concentration of liophilic mobile-phase additive on selectivity, resolution, capacity factor and efficiency of HMX and RDX during isocratic separation

Concentration KPF_6 (mM)	Selectivity, α	USP resolution	Capacity factor, HMX k	Efficiency, HMX N	Capacity factor, RDX k	Efficiency, RDX N
0	1.09	1.94	17.70	10,400	19.30	8400
10	1.10	2.21	17.09	10,700	18.83	8570
20	1.11	2.43	16.64	10,700	18.53	8630
30	1.12	2.67	16.16	10,500	18.17	8680

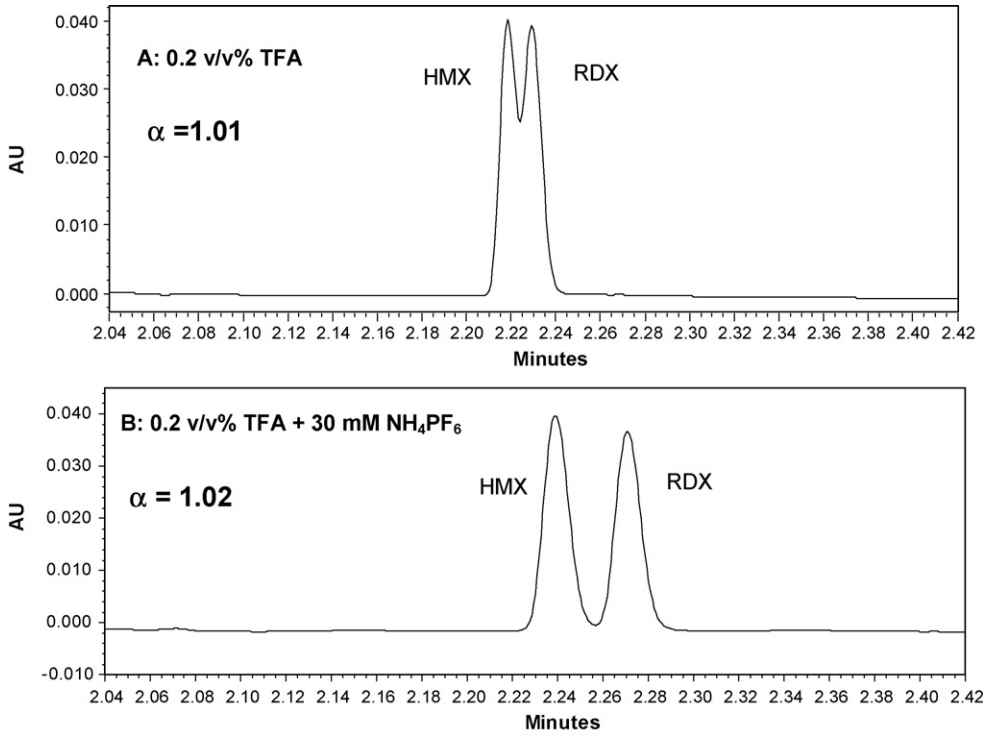

Fig. 2. Effect of liophilic mobile-phase additive in gradient mode on the selectivity enhancement of HMX and RDX. Column: Acquity BEH C-18, 1.7 μm; 2.1 mm × 100 mm; flow rate, 0.5 mL/min; temperature, 45 °C; inj., 5 μL full loop; run time, 4 min; detection, 247 nm; strong wash: 0.1% NH_4OH 50/50 MeCN/H_2O; weak wash: 90/10 H_2O/MeCN; mobile-phase A: (A) 0.2% (v/v) TFA or (B) 0.2% (v/v) TFA + 30 mM NH_4PF_6; mobile-phase B: MeCN 0.2% (v/v) TFA; initial back pressure: ~8300 psi; gradient: isocratic hold for 1 min at 5% B, then over 0.5 min to 40% B, then over 1.5 min to 95% B, the hold for 0.5 min at 95% B and equilibrate at initial conditions for 0.5 min.

ferent columns, changes in organic composition, pH of the mobile phase, and addition of liophilic mobile-phase additives could also be used to achieve the desired chromatographic selectivity.

In order to further enhance the separation on the BEH-C18 column the use of liophilic additives (hexafluorophosphate, PF_6^-) was investigated. These negatively charged counter anions are adsorbed on the stationary-phase surface. For the studied energetic compounds they were not present in ionized positively charged form at pH 2, so no increase in retention was expected upon interaction with the liophilic ions. However, a trend of decreasing retention time (exhibited by a decrease in capacity factor), and enhanced selectivity and resolution for these compounds was

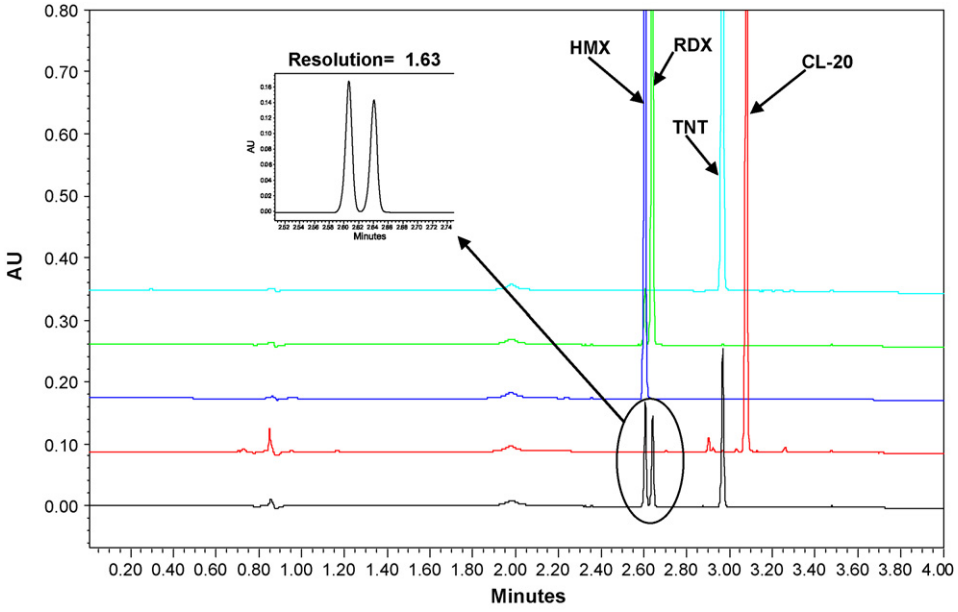

Fig. 3. Separation of major energetic compounds in 4 min run on a BEH-RP18 column. Column: Acquity BEH Shield RP-18 1.7 μm; 2.1 mm × 100 mm; flow rate 0.5 mL/min; Temperature, 45 °C; inj., 5 μL full loop; run time, 4 min; detection, 247 nm; strong wash: 0.1% NH_4OH 50/50 MeCN/H_2O; weak wash: 90/10 H_2O/MeCN; mobile-phase A: 0.2% (v/v) TFA + 30 mM NH_4PF_6; mobile-phase B: MeCN 0.2% (v/v) TFA; initial back pressure: ~8300 psi; gradient: isocratic hold for 1 min at 5% B, then over 0.5 min to 40% B, then over 1.5 min to 95% B, the hold for 0.5 min at 95% B and equilibrate at initial conditions for 0.5 min.

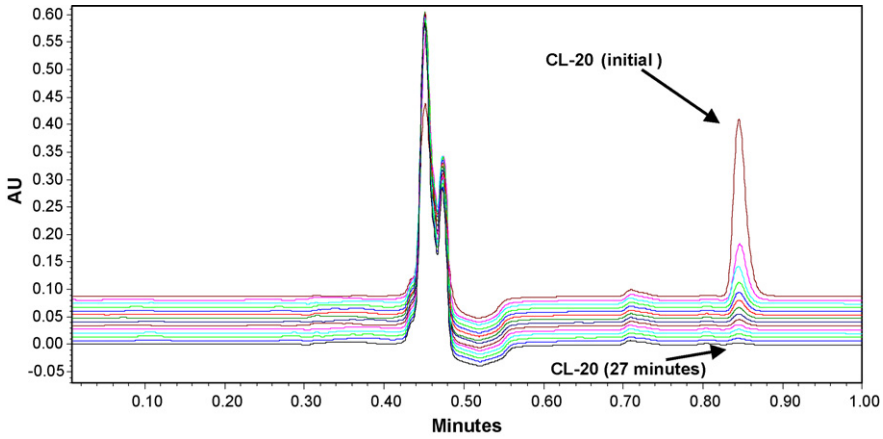

Fig. 4. CL-20 hydrolysis at 5 °C (initial to 27 min). Column: Acquity BEH C-18 1.7 μm; 2.1 mm × 100 mm; flow rate 0.8 mL/min; temperature, 45 °C; inj., 5 μL full loop; run time, 1 min; detection 228 nm; strong wash: 0.1% NH_4OH 50/50 MeCN/H_2O; weak wash: 90/10 H_2O/MeCN; mobile-phase A: 0.05% (v/v) TFA + 30 mM NH_4PF_6; mobile-phase B: MeCN; initial back pressure: ~8500 psi; isocratic: A/B, 40%/60%.

observed with an increase in liophilic additive concentration (see Table 1).

The energetic compounds possess a delocalized negative charge on the oxygen atom. Since these molecules possess a partial negative charge, upon their approach to the stationary phase, which contains adsorbed negatively charged liophilic counter anions, it could be envisioned that a coulombic repulsion occurs. Upon increase of the liophilic additive concentration, there is an increased adsorption of PF_6^- ions onto the stationary phase, leading to further reduction in retention of HMX and RDX (Table 1). The increase in resolution upon increased liophilic additive can be attributed to an increase in selectivity as per the master resolution Eq. (1) where k is the capacity factor, N is efficiency, and α is selectivity. The efficiency did not change upon increasing the liophilic anion concentration, but small changes in selectivity will have a greater effect on change in the resolution (R):

$$R = \frac{\alpha - 1}{\alpha} \frac{k_2}{1 + k_2} \frac{\sqrt{N}}{4} \quad (1)$$

Efficiency (N) and selectivity (α) are complementary descriptors that are dependent on different sets of chromatographic parameters. Efficiency is more dependent on the quality of the column packing, particle size, flow rate, and on instrumental optimization, while selectivity is more dependent on the stationary-phase properties, the nature of the analytes themselves and the interactions with stationary-phase/mobile-phase components.

Enhancement of the resolution between a critical pair of analytes then could be pursued in two different ways: by either increasing the efficiency, or by improving the selectivity. This example emphasizes that the main efforts when developing a separation should be directed towards the achievement of highest possible selectivity first. Therefore, selection of the proper stationary phase and optimization of mobile-phase conditions (additives) is very crucial. In this example the addition of 30 mM PF_6^- lead to the greatest resolution between the critical pair. Further method development experiments used 30 mM PF_6^- concentration in the aqueous portion of the mobile phase.

Leveraging on the knowledge gained from the effect of liophilic additive addition upon the resolution of the critical pair (HMX and RDX) in isocratic mode, a gradient mode separation was investigated for the separation of all the energetic compounds used in this study which have different relative hydrophobicities ($\log P$). Fig. 2 shows effect of addition of liophilic agent on selectivity changes and consequent resolution improvement during gradient mode of separation of HMX and RDX.

This method could also be used as a stability indicating method. Using gradient conditions and liophilic mobile-phase additives, several energetic compounds were successfully resolved during a 4 min run. Resolution between HMX and RDX was 1.5 which is conventionally considered the minimal level for adequate resolution in a chromatographic separation.

Further enhancement of resolution was achieved by changing the column type from BEH-C18 to BEH Shield RP-C18 (Fig. 3). The BEH RP-C18 stationary phase contains polar embedded groups and may offer a different selectivity than the BEH C18 column. The resolution of 1.63 was obtained for the critical pair of peaks, HMX and RDX.

The usage of liophilic mobile-phase additives was sufficient for the separation enhancement of HMX and RDX. Moreover, this

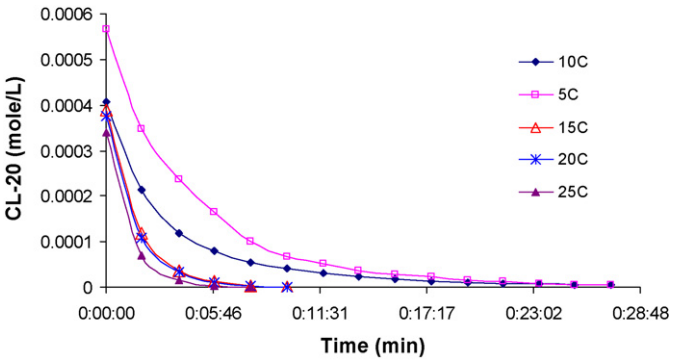

Fig. 5. CL-20 Degradation as a function of temperature.

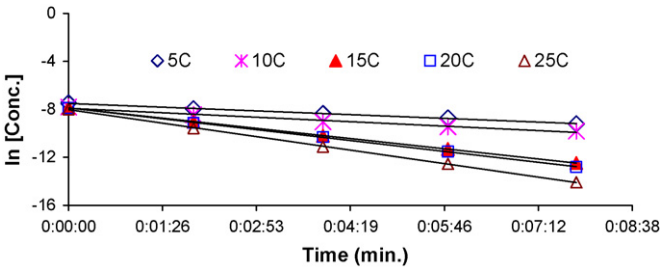

Fig. 6. Determination of rate constant for CL-20 alkaline hydrolysis at different temperatures.

Table 2
Homogeneous alkaline hydrolysis: influence of temperature on the rate constant (k') of CL-20, HMX and RDX decomposition

T (°C)	CL-20, k' (min^{-1})	CL-20, R^2	HMX, k' (min^{-1})	HMX, R^2	RDX, k' (min^{-1})	RDX, R^2
5	312.6	1.00	–	–	–	–
10	371.1	0.98	–	–	–	–
15	850.0	1.00	0.02	0.67	2.10	0.99
20	906.5	1.00	0.16	0.91	4.14	0.99
25	1123.7	1.00	0.08	0.89	5.35	0.99
30	–	–	0.37	0.71	10.02	0.99
35	–	–	0.54	0.99	15.72	0.99

approach of using liophilic additives in a UHPLC method can be used as an alternative to the current EPA 8330 HPLC method for separation of energetic compounds. Validation of this new UHPLC method is ongoing, and will be a subject of a future paper.

3.2. Reaction kinetics

The resulting concentration of energetic compounds obtained upon base hydrolysis at different temperatures could be used for determination of activation energy. By using a concentration of base in large excess compared to the energetic compounds, the amount of base that gets consumed is insignificant and one can equate the whole process to pseudo-first order kinetics:

$$\ln \frac{A}{A_0} = -k't \quad (2)$$

According to Eq. (2) a plot of ln [A], where is A is the concentration of energetic compound (area determined by HPLC) versus reaction time (t) would produce a straight line with a slope of k' (rate constant). The slope of the line should increase with temperature. The relationship between the rate constant k and the temperature is given by the Arrhenius equation:

$$\ln k' = \frac{-E_a}{RT} + \ln C \quad (3)$$

where E_a is the activation energy, R is the gas constant, ln C is a constant and T is the temperature (K). According to Eq. (3) a plot of ln k' (rate constant) versus the reciprocal of the absolute temperature defines a straight line of slope, $-E_a/R$ and the intercept ln C. The activation energy in kJ/mol is obtained from the slope of this linear dependence.

The concentration of base and the starting concentration of energetic compound influence the reaction rate of hydrolysis of energetic materials under alkaline conditions. It was suggested that the alkaline hydrolysis of the nitramines HMX and RDX proceeds via an E2-elimination mechanism, and follows second-order kinetics [17,18,20]. In this experiment, ammonium hydroxide was used as the base to initiate the reaction. Since it is difficult to measure the consumption of NH_4OH accurately during the course of the reaction, determining the second-order rate constant directly is not trivial. However, a pseudo-first-order rate constant can be obtained by adjusting the conditions of the experiment. This can be done by maintaining a constant excess of NH_4OH during the reaction, at a concentration high enough that any change in the concentration of the base would be insignificant compared to the change in concentration of energetic compound. Under such conditions the reaction would follow the pseudo-first order rate equation. A series of reactions for the homogeneous energetic alkaline hydrolysis were run with an initial CL-20 concentration of 0.2 mg/mL (0.45 mM), an HMX concentration of 0.015 mg/mL (0.05 mM), an RDX concentration of 0.15 mg/mL (0.5 mM) and a NH_4OH concentration of 3.1 M.

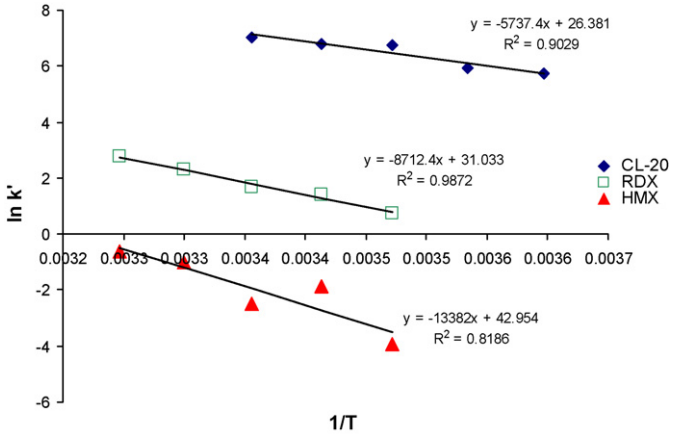

Fig. 7. Activation energy determination of CL-20, RDX and HMX using the Arrhenius equation.

The experiments were performed at 5, 10, 15, 20, and 25 °C for CL-20. The molar ratio of NH_4OH to CL-20 was 6889 in these studies. An isocratic HPLC method was used for these determinations. Fig. 4 shows an overlay of representative chromatograms of CL-20 hydrolysis at 5 °C.

The time–concentration dependence in all studied experiments agreed with the assumption that the energetic compound disappearance follows first-order behavior with respect to energetic compound concentration (Figs. 5 and 6).

Also, a set of experiments was run at 15, 20, 25, 30, and 35 °C to determine the kinetics of HMX and RDX alkaline hydrolysis. Hydrolysis reactions of HMX and RDX were run together in one reaction mixture. HMX was present as a 10% impurity in RDX and both were monitored simultaneously in one run. An initial RDX concentration of 0.15 mg/mL (0.5 mM) was used for this experiment. In these experiments, the NH_4OH concentration was 3.1 M, corresponding to the molar ratio 6078 of NH_4OH to the sum of RDX and HMX. Relevant kinetic parameters for homogeneous alkaline hydrolysis were obtained by applying linear regression analysis using analyte concentration–time dynamics. Table 2 presents the computed pseudo-first order rate constants (k') and the corresponding correlation coefficients (R^2) for these energetic compounds.

Fig. 7 shows the data obtained from a linear least-squares fit of the Arrhenius plot of the natural logarithm of the apparent rate constants (ln k') versus the reciprocal of the absolute temperature ($1/T$) at five temperatures for the three energetic compounds.

The data correlates closely to the pseudo-first order kinetic model with acceptable correlation coefficients. Table 3 presents the

Table 3
Activation energy of alkaline hydrolysis for CL-20, RDX and HMX

	E_a/R	Our data E_a (kJ/mol)	Data from literature E_a (kJ/mol)	References
CL-20	5737.4	47.7	55.7	[3]
RDX	8712.4	72.4	99.9; 58.6	[4,15]
HMX	13382	111.3	111.9; 104.7	[4,15]

calculated activation energy for the HMX, RDX and CL-20 hydrolysis as well as their corresponding values obtained from literature.

The disparity between literature data and our data for the activation energy could be attributed to the alkali strength in the reaction. A noticeable difference was reported by Karakaya et al. [26] for alkaline hydrolysis at different concentrations of NaOH at constant temperature and initial concentration of CL-20.

4. Conclusions

Selective methods for analysis of energetic compounds have been developed on a UHPLC system using columns packed with sub-2-μm stationary-phase particles in combination with the usage of liophilic salts (KPF_6) as mobile-phase additives. The enhancement of separation selectivity of energetic compounds by using liophilic additives was demonstrated. A fast method for reaction monitoring was developed and applied to determine hydrolysis kinetics of three major energetic compounds. Values of activation energies obtained for CL-20, RDX and HMX were comparable to those in literature, however were obtained in a shorter amount of time.

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