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Direct Photolysis of Propyl Nitroguanidine

by RA Pesce-Rodriguez and L Giri

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Acknowledgments

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1. Background/Introduction

Currently, 1-propyl-2-nitroguanidine (PrNQ) is being considered for use as a melt-cast binder for insensitive energetic formulations. As part of an effort funded by the Strategic Environmental Research and Development Program (project #WP18-C3-1299), we reported in 2018 (Pesce-Rodriguez et al. 2018) on properties related to the environmental fate and transport of PrNQ, including water solubility, soil sorption coefficient (K_{oc}), octanol-water partition coefficient (K_{ow}), hydrolysis in neutral water, and vapor pressure. In this follow-up report, we present rates and half-lives for direct photolysis in water. Comparable results for cyclotrimethylenetrinitramine (RDX) are also given.

2. Experimental

Direct photolysis of PrNQ, RDX, and nitroguanidine (NQ) in air-saturated deionized water was performed following Environmental Protection Agency (EPA) fate, transport, and transformation test guidelines provided in OPPTS 835.2210 (“Direct Photolysis Rate in Water by Sunlight”) (EPA 1998). Solutions of PrNQ were exposed to simulated sunlight and then analyzed for concentration changes using a high-performance liquid chromatography (HPLC) with a UV/visible (Vis) detector. Samples were dissolved in aerated, deionized water to achieve a concentration of approximately 50 mg/L and placed in 5-mm-diameter quartz nuclear magnetic resonance (NMR) tubes that were completely filled with solution to eliminate the possibility of evaporation of the analyte or solvent. We conducted the photolysis study using an Atlas Suntest CPS+ solar simulator (Fig. 1), which employs an air-cooled xenon lamp to simulate UV and visible solar radiation in the 300- to 800-nm range. Temperatures at which photolysis was monitored ranged from 35 to 65 °C. A radiative flux (i.e., the amount of light incident on a unit area of a surface) of 765 W/m² was used. At sea level at noon on a cloud-free day, we expect that approximately 1000 w/m² of incident solar radiation will reach the Earth’s surface without being significantly scattered. A solar flux of 765 W/m² is therefore a realistic number for photolysis under ideal weather conditions. The choice of 5-mm quartz tubes as vessels for the photolysis study approximates conditions in a shallow puddle.



Fig. 1 Suntest CPS+ xenon test instrument used to evaluate photolysis of PrNQ in aqueous solution

Because photolysis studies in the literature are conducted under such varying conditions, photolysis of RDX and NQ was studied under conditions identical to those used for PrNQ photolysis so that direct comparison could be made. Because RDX has such a low water solubility, a small amount of acetonitrile (approximately 0.5 mL) was used to dissolve the sample before preparing the aqueous solution.

We measured the analyte concentrations in solution before and after irradiation using an Agilent 1200 series HPLC with a 10-cm C₁₈ column at 22 °C. A 5- μ L sample was introduced into the column by means of an autoinjector. The mobile phase was an isocratic mix of acetonitrile and water (60/40). A UV/Vis detector measured PrNQ absorbance at 270 nm (using 360 nm as a reference). No analysis of phototransformation products was done. Dark samples of PrNQ monitored as controls at 35, 45, 55, and 65 °C proved PrNQ to be stable over the time of the investigation at those temperatures. A similar procedure was used for the analysis of RDX (only the UV detection wavelength differed). Consistent with results given previously (Pesce-Rodriguez et al. 2018), PrNQ was found to be stable in neutral water.

The lowest temperature at which we obtained photolysis rates was 35 °C (the lowest temperature that the solar simulator can maintain). This temperature is within the recommended standard range of test temperatures for photolysis according to ASTM E896-92 (ASTM International 2005), but is higher than is expected in most real-world environments. Consequently, to describe temperature dependence of photolysis rates, we performed direct photolysis at four different temperatures (35, 45, 55, and 65 °C) so that we might be able to extrapolate to ambient temperatures. These data were also used to obtain the energy of activation for the process using

Eq. 1, where the photolysis reaction rate, $k_{\text{photolysis}}$, is a function of temperature, T , and the activation energy of the reaction, E_a :

$$k_{\text{photolysis}} = A e^{-E_a/RT}. \quad (1)$$

3. Results and Discussion

Photolysis results for PrNQ as a function of time are given in Fig. 2 and suggest that the process follows first-order kinetics. The transformation rate constants were estimated by fitting regression lines to plots of the logarithm of PrNQ concentration as a function of time. The regression lines have high correlation coefficients ($R^2 > 0.99$), indicating a good fit and high confidence in the estimated rate constants. The Arrhenius plot given in Fig. 3 shows the photolysis rate to be independent of temperature, suggesting a radical mechanism with a low energy of activation.

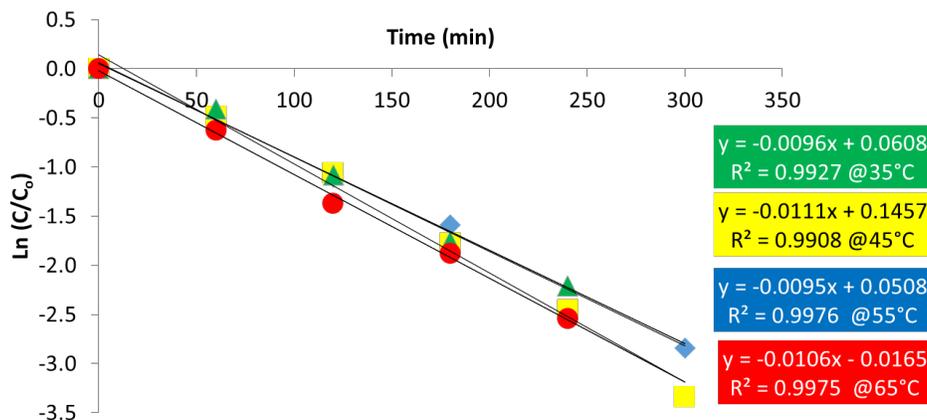


Fig. 2 Photolysis kinetics of PrNQ at 35, 45, 55, and 65 °C.

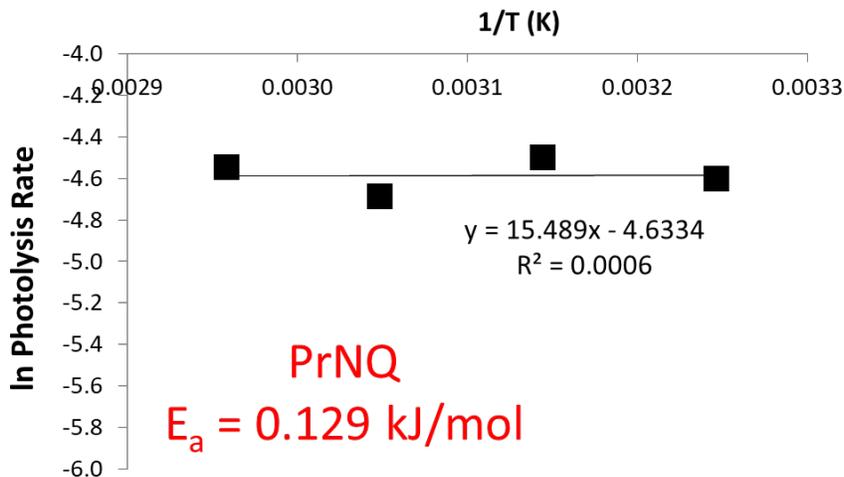


Fig. 3 Arrhenius plot for PrNQ photolysis

The photolysis rates and Arrhenius plot for RDX and NQ obtained under the same conditions used for PrNQ are given in Figs. 4–7. Unlike PrNQ, the photolysis rate of RDX is sensitive to temperature and has an energy of activation that is approximately 50 times higher.

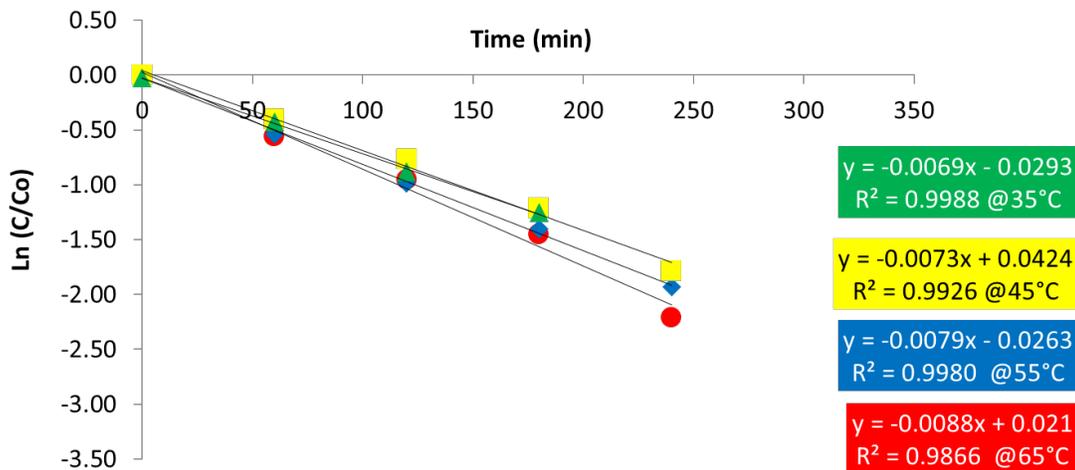


Fig. 4 Photolysis kinetics of RDX at 35, 45, 55, and 65 °C

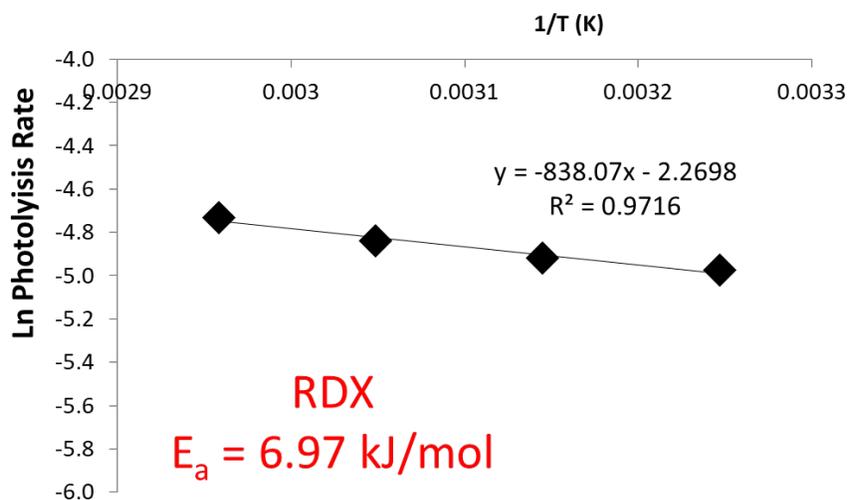


Fig. 5 Arrhenius plot for RDX photolysis

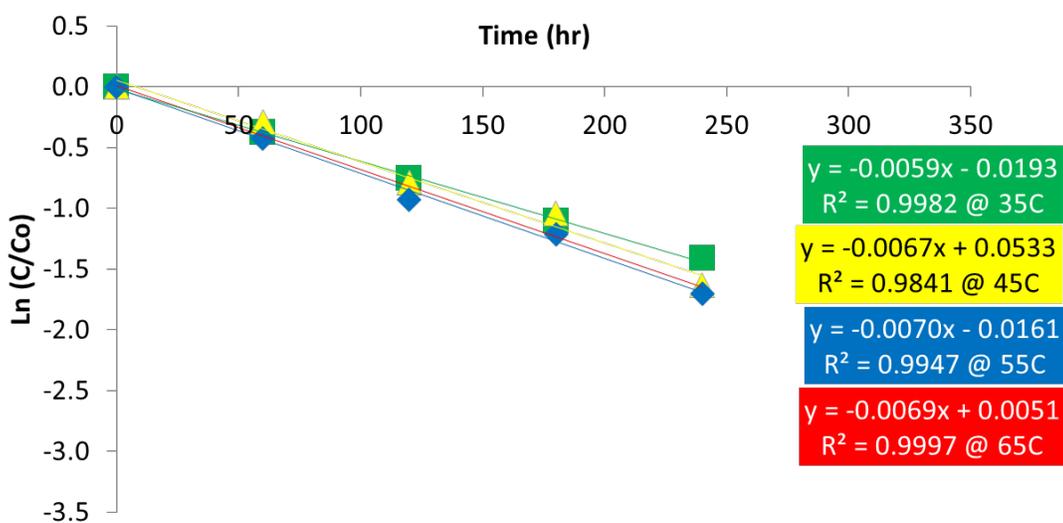


Fig. 6 Photolysis kinetics of NQ at 35, 45, 55, and 65 °C

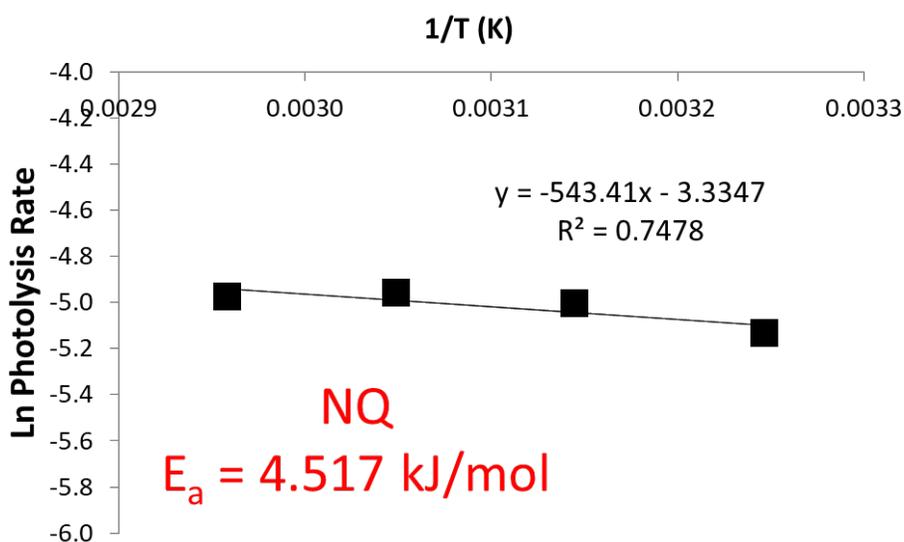


Fig. 7 Arrhenius plot for NQ photolysis

The half-lives for photolysis of PrNQ, RDX and NQ are given in Fig. 8. Also shown are extrapolated values for 20, 25, and 30 °C. Note that the half-life for NQ is significantly shorter than that reported in the literature. For example, Spanggord et al. (1987) report NQ half-life values of 14.4 h in the summer and 55 h in the winter. Of course, such measurements depend on conditions; hence, our inclusion of RDX and NQ values measured under conditions that were identical to those used for PrNQ determination.

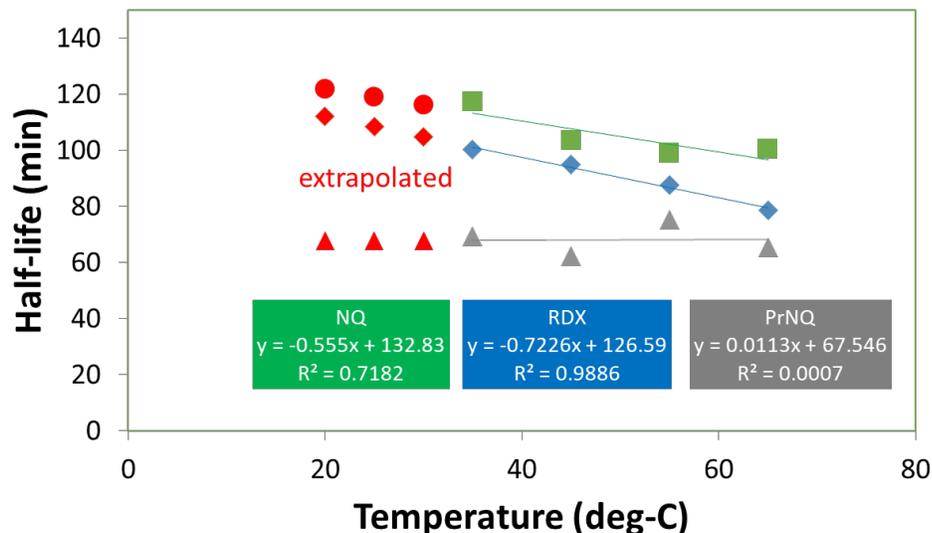


Fig. 8 Photolysis half-lives for PrNQ (gray), RDX (blue), and NQ (green) under identical conditions. Red markers are extrapolated values for 20, 25, and 30 °C.

Despite the fact that the half-lives of RDX and NQ are temperature-dependent and longer than that of PrNQ, the half-lives of all three energetic materials are relatively short, suggesting that they would not linger in the environment if fully dissolved and exposed to sufficient solar radiation. The difference between RDX and both PrNQ and NQ is its limited water solubility (i.e., 6.0×10^{-2} mg/L for RDX vs. $4.40 \times 10^{+3}$ and $1.6 \times 10^{+4}$ mg/L, respectively, for NQ and PrNQ). This means that RDX will photolyze quickly only *after* first dissolving very slowly, while NQ and PrNQ will dissolve and photolyze relatively rapidly.

4. Conclusions

The photolysis of PrNQ was found to be a relatively rapid process. Under the experimental conditions used in this study, the half-life was on the order of 1 h faster than both RDX and NQ under identical conditions. The photolysis of PrNQ was found to have a very low activation energy (more than an order of magnitude lower than that of RDX and NQ) and to be insensitive to temperature, suggesting that it proceeds through a radical mechanism.

No identification of phototransformation products was made.

5. References

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- Spanggord RJ, Chou TW, Mill T, Haag W, Lau W. Environmental fate of nitroguanidine, diethyleneglycol dinitrate, and hexachloroethane smoke. Army Medical Research and Development Command (US); 1987 Sep. Report No.: ADA200324.

List of Symbols, Abbreviations, and Acronyms

| | |
|-------------------------|--|
| E_a | activation energy of the reaction |
| EPA | Environmental Protection Agency |
| HPLC | high-performance liquid chromatography |
| K_{oc} | soil sorption coefficient |
| K_{ow} | octanol-water partition coefficient |
| $k_{\text{photolysis}}$ | photolysis reaction rate |
| NMR | nuclear magnetic resonance |
| NQ | nitroguanidine |
| PrNQ | 1-propyl-2-nitroguanidine |
| RDX | cyclotrimethylenetrinitramine |
| T | temperature |
| UV | ultraviolet |
| Vis | visible |

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