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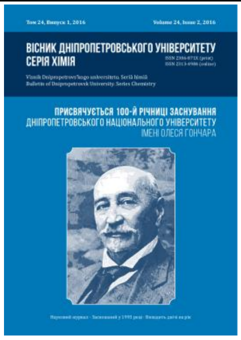

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RADICAL DECOMPOSITION OF 2,4-DINITROTOLUENE AT CONDITIONS OF ADVANCED OXIDATION. COMPUTATIONAL STUDY

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Abstract

At the present time one of the main remediation technologies for such environmental pollutant as 2,4-dinitrotoluene (DNT) is advanced oxidation processes (AOPs). Since hydroxyl radical is the most common active species for AOPs, in particular for Fenton oxidation, the study modeled mechanism of interaction between DNT and hydroxyl radical at SMD(Pauling)/M06-2X/6-31+G(d,p) level. Computed results allow to suggest the most energetically favourable pathway for the process. DNT decomposition consists of sequential hydrogen abstractions and hydroxyl attachments passing through 2,4-dinitrobenzyl alcohol, 2,4-dinitrobenzaldehyde, and 2,4-dinitrobenzoic acid. Further replacement of nitro- and carboxyl groups by hydroxyl leads to 2,4-dihydroxybenzoic acid and 2,4-dinitrophenol, respectively. Reaction intermediates and products are experimentally confirmed. Mostly of reaction steps have low energy barriers, some steps are diffusion controlled. The whole process is highly exothermic.

Keywords: 2,4-dinitrotoluene; hydroxyl radical; Fenton oxidation; DFT; reaction mechanism.

РАДИКАЛЬНЕ РОЗКЛАДАННЯ 2,4-ДІНІТРОТОЛУЕНА В УМОВАХ ПРОГРЕСИВНОГО ОКИСЛЕННЯ. РОЗРАХУНКОВЕ ДОСЛІДЖЕННЯ

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Анотація

У даний час однією з основних технологій для рекультивації такого забруднювача навколишнього середовища, як 2,4-динітротолуена (DNT), є прогресивні процеси окислення (AOPs). Оскільки гідроксильний радикал є найбільш поширеним активним агентом для AOPs, зокрема для окислення Фентона, механізм взаємодії між DNT і гідроксильним радикалом змодельований на SMD(Pauling)/M06-2X/6-31+G(d,p) теоретичному рівні. Розраховані результати дозволяють припустити найбільш енергетично вигідний шлях для процесу. Розкладання DNT складається з послідовних відщеплень Гідрогену і приєднань гідроксилу, що проходять через 2,4-динітробензиловий спирт, 2,4-динітробензойний альдегід і 2,4-динітробензойну кислоту. Подальша заміна нітро- і карбоксильної груп гідроксилом приводить до 2,4-дигідроксибензойної кислоти і 2,4-динітрофенолу відповідно. Проміжні та кінцеві продукти реакції підтверджені експериментально. Більшість стадій реакції мають низькі енергетичні бар'єри, деякі стадії контролюються дифузією. Весь реакційний процес є сильно екзотермічним.

Ключові слова: 2,4-динітротолуен; гідроксильний радикал; окислення Фентона; ТФГ; механізм реакції.

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РАДИКАЛЬНОЕ РАЗЛОЖЕНИЕ 2,4-ДИНИТРОТОЛУОЛА В УСЛОВИЯХ ПРОГРЕССИВНОГО ОКИСЛЕНИЯ. РАСЧЕТНОЕ ИССЛЕДОВАНИЕ

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Аннотация

В настоящее время одной из основных технологий для рекультивации такого загрязнителя окружающей среды, как 2,4-динитротолуола (DNT), являются прогрессивные процессы окисления (AOPs). Так как гидроксильный радикал является наиболее распространенным активным агентом для AOPs, в частности для окисления Фентона, механизм взаимодействия между DNT и гидроксильным радикалом смоделирован на SMD(Pauling)/M06-2X/6-31+G(d,p) теоретическом уровне. Рассчитанные результаты позволяют предположить наиболее энергетически выгодный путь для процесса. Разложение DNT состоит из последовательных отщеплений водорода и присоединений гидроксила, проходящих через 2,4-динитробензиловый спирт, 2,4-динитробензойный альдегид и 2,4-динитробензойную кислоту. Дальнейшая замена нитро- и карбоксильных групп гидроксилом приводит к 2,4-дигидроксибензойной кислоте и 2,4-динитрофенолу соответственно. Промежуточные и конечные продукты реакции подтверждены экспериментально. Большинство стадий реакции имеют низкие энергетические барьеры, некоторые стадии контролируются диффузией. Весь реакционный процесс является сильно экзотермическим.

Ключевые слова: 2,4-динитротолуол; гидроксильный радикал; окисление Фентона; ТФП; механизм реакции.

Introduction

2,4-Dinitrotoluene (**DNT**) is used for production of dyes, explosives, organic synthesis and as a propellant additive. It is formed in a large amount during 2,4,6-trinitrotoluene (**TNT**) production and can release into environment. The U.S. Environmental Protection Agency determines **DNT** as a priority pollutant, thus remediation of **DNT** at contaminated sites is required. Alkali hydrolysis, iron reduction and advanced oxidation are actively used to remove **DNT** from environment [1–12]. Advanced oxidation processes (AOPs) are one of the most promising methods for the treatment of soils and waters contaminated by **DNT** [1–12]. Most of these processes are associated with the generation of radical species mainly hydroxyl radical ($OH^{\bullet}$), which is a strong oxidizing agent (E^0=2.8 eV) and can cause rapid decomposition of **DNT**. Fenton's reagent (hydrogen peroxide + ferrous iron) as one of the most common AOPs was used to remove **DNT** from aqueous solutions as well as contaminated soil [1–8]. It was found that Fenton's degradation of DNT followed the first order reaction kinetics [5–7]. The main products for **DNT** primary degradation were suggested as 2,4-dinitrobenzaldehyde, 2,4-dinitrobenzoic acid, 1,3-dinitrobenzene, 3-nitrophenol, 2,4-dinitrophenol [3–6]. The aim of the present paper is to shed more light on the mechanism of the initial steps of the interaction of **DNT** with hydroxyl radical and chemical nature of possible intermediates and products encountered in the oxidation process.

Computational Methodology

All calculations were performed using the Gaussian 09 suite of programs [13]. The M06-2X functional of the Density Functional Theory (DFT) was chosen for the study because it was recommended for applications involving thermochemistry, kinetics, and noncovalent interactions on the base of assessment of its performance over broad amounts of data [14]. SMD model in a combination with Pauling radii was selected as a solvation model for the present study. The relevant stationary points (intermediates, transition states, and products) in aqueous solution were fully optimized at the SMD(Pauling)/M06-2X/6-31+G(d,p) level. Since our computational analysis is based on the values of Gibbs free energy, stationary points were further characterized by calculation of the analytic harmonic vibrational frequencies at the same theory level as geometry optimization.

Results and Discussion

The pathways for the initial steps of the interaction of **DNT** with hydroxyl radical are direct substitution of nitrogroup, attaching hydroxyl radical to C1 atom, and hydrogen abstraction from the methyl group of **DNT** (Fig.). All pathways are exothermic. The first pathway leads to intermediates **INT1** and **INT2**, the second one results in formation of **INT3**. The

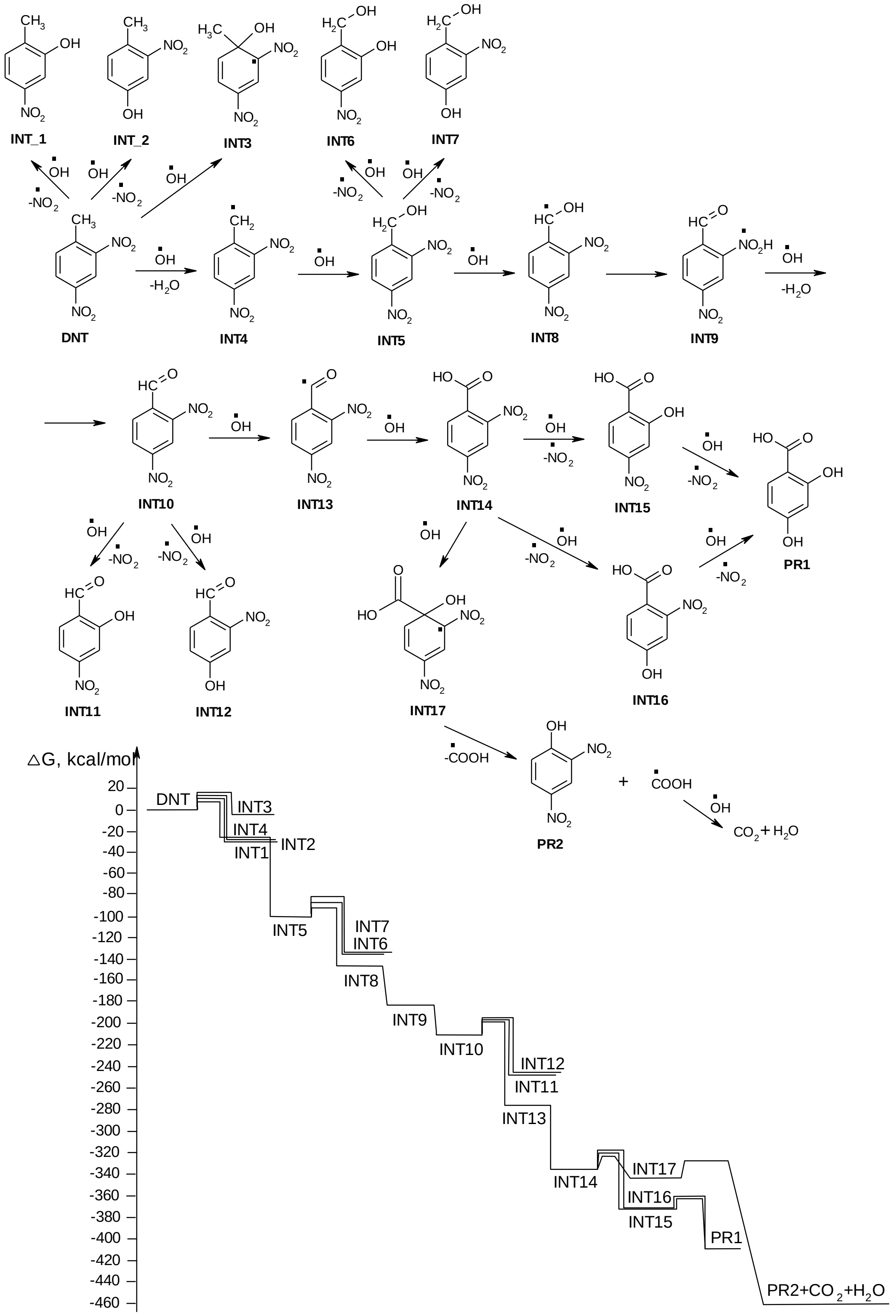

Fig. Computer generated pathway of DNT oxidation with hydroxyl radical, corresponding Gibbs free energy diagram

third one leading to **INT4** is the most kinetically favorable pathway (Table). Therefore we predict that the methyl group transformation will preferable occur at the initial step of **DNT** decomposition. Further **INT4** easy adds hydroxyl radical without energy barrier (diffusion controlled step) and forms 2,4-dinitrobenzyl alcohol (**INT5**). Analysis of possible transformations of **INT5** shows that hydrogen abstraction leading to **INT8** is a dominant pathway as compared with direct substitution of nitrogroup. During optimization **INT8** readily transforms into more stable **INT9**. Elimination of hydrogen from **INT9** passes without energy barrier and results in formation of 2,4-dinitrobenzaldehyde (**INT10**).

Hydrogen abstraction from aldehyde group is the most energetically favourable transformation of **INT10**. This pathway has about 5 kcal/mol smaller free energy barrier than the replacement of nitrogroup by hydroxyl. Formed **INT13** captures hydroxyl radical and transforms into more stable 2,4-dinitrobenzoic acid (**INT14**). Further, the substitution of nitrogroup by hydroxyl radical occurs in **INT14**. Formation of 2-hydroxy-4-nitrobenzoic acid (**INT15**) and 4-hydroxy-2-nitrobenzoic acid (**INT16**) has close free energy barriers and free reaction energies, therefore these processes may occur simultaneously. The replacement of the second nitrogroup by hydroxyl radical leads to 2,4-dihydroxybenzoic acid (**PR1**). Hydroxyl attaching to C1 of **INT14** leads to formation of **INT17**. The latter transforms into 2,4-dinitrophenol (**PR2**) by elimination of carboxyl radical, which readily undergoes decomposition to carbon dioxide losing hydrogen by interaction with hydroxyl radical.

The process of **DNT** transformation, depicted in Fig. is highly exothermic. The release of approximately 460 kcal/mol energy is predicted. The rate limited step is 2,4-dinitrophenol formation. It should be noted that decarboxylation of 2,4-dinitrobenzoic acid with formation of 1,3-dinitrobenzene was found to be energetically unfavourable process requiring more than 30 kcal/mol free activation energy. We suggest that other than hydroxyl radical reactive species may be responsible for 1,3-dinitrobenzene formation.

Table

SMD(Pauling)/M062x/6-31+G(d,p) level calculated Gibbs free activation energies and Gibbs free energy of reactions for DNT oxidation with hydroxyl radical

Reaction	$\Delta G_{\mathrm{act.}}$, kcal/mol	$\Delta G_{\mathrm{reac.}}$, kcal/mol	Reaction	$\Delta G_{\mathrm{act.}}$, kcal/mol	$\Delta G_{\mathrm{reac.}}$, kcal/mol
$\mathrm{DNT+OH^{\bullet}\rightarrow INT1+NO_2^{\bullet}}$	12.90	-36.14	$\mathrm{INT10+OH^{\bullet}\rightarrow INT12+NO_2^{\bullet}}$	14.42	-38.35
$\mathrm{DNT+OH^{\bullet}\rightarrow INT2+NO_2^{\bullet}}$	13.06	-32.07	$\mathrm{INT10+OH^{\bullet}\rightarrow INT13}$	8.82	-66.37
$\mathrm{DNT+OH^{\bullet}\rightarrow INT3}$	13.82	-12.91	$\mathrm{INT13+OH^{\bullet}\rightarrow INT14}$	–	-59.84
$\mathrm{DNT+OH^{\bullet}\rightarrow INT4+H_2O}$	8.85	-29.27	$\mathrm{INT14+OH^{\bullet}\rightarrow INT15+NO_2^{\bullet}}$	13.88	-39.19
$\mathrm{INT4+OH^{\bullet}\rightarrow INT5}$	–	-71.20	$\mathrm{INT14+OH^{\bullet}\rightarrow INT16+NO_2^{\bullet}}$	13.99	-36.23
$\mathrm{INT5+OH^{\bullet}\rightarrow INT6+NO_2^{\bullet}}$	14.00	-37.13	$\mathrm{INT15+OH^{\bullet}\rightarrow PR1+NO_2^{\bullet}}$	14.12	-36.27
$\mathrm{INT5+OH^{\bullet}\rightarrow INT7+NO_2^{\bullet}}$	13.62	-34.43	$\mathrm{INT16+OH^{\bullet}\rightarrow PR1+NO_2^{\bullet}}$	12.68	-39.23
$\mathrm{INT5+OH^{\bullet}\rightarrow INT9}$	8.71	-46.52	$\mathrm{INT14+OH^{\bullet}\rightarrow INT17}$	13.66	-14.37
$\mathrm{INT9+OH^{\bullet}\rightarrow INT10}$	–	-63.93	$\mathrm{INT17\rightarrow PR2+CO_2+H_2O}$	20.73	-108.33
$\mathrm{INT10+OH^{\bullet}\rightarrow INT11+NO_2^{\bullet}}$	13.67	-41.71			

Based on the calculated data the most favourable reactive channel may be described as follow. Firstly, replacement of hydrogens of the methyl group by hydroxyl occurs. The process consists of the sequence elimination of hydrogen from the methyl group and addition of hydroxyl radical. The most stable intermediates are 2,4-dinitrobenzyl alcohol, 2,4-dinitrobenzaldehyde, 2,4-dinitrobenzoic acid. As soon as methyl group transforms into carboxyl group the substitution of nitrogroup by hydroxyl starts. Sequence substitution of two nitrogroups by hydroxyls leads to 2,4-dihydroxybenzoic acid. At the same time the replacement of carboxyl group by hydroxyl may occur. This process results in formation of 2,4-dinitrophenol. It should be noticed that we studied the earlier steps of interaction of **DNT** with hydroxyl radical. The species depicted in Fig. are intermediates and not the final products of the reaction. Additional chemical reactions are necessary to full mineralization of DNT. The suggested mechanism of **DNT** primary decomposition, based on DFT calculations, is confirmed by experimentally detected products for Fenton oxidation of **DNT** [3–6].

Conclusion

Reaction of **DNT** with hydroxyl radical was modeled at SMD(Pauling)/M06-2X/6-31+G(d,p) level. Calculations show that decomposition of **DNT** starts from methyl group transformation into hydroxymethyl, carbonyl, and carboxyl groups. Then displacement of nitro- or carboxyl group by hydroxyl occurs. The calculated main products (2,4-dinitrobenzyl alcohol, 2,4-dinitrobenzaldehyde, 2,4-dinitrobenzoic acid, and 2,4-dinitrophenol) are experimentally observed during Fenton oxidation of DNT. The process has low Gibbs free activation energies and high exothermicity. We hope that this paper will help to understand the mechanism of degradation process of **DNT** with hydroxyl radical, and promote the improvement of AOPs technologies for removal of **DNT** and other nitroaromatic compounds from environment.

Bibliography

[1] Oh S. Y. Reductive removal of 2,4-dinitrotoluene and 2,4-dichlorophenol with zero-valent iron-included biochar / S. Y. Oh, Y. D. Seo, K. S. Ryu // Bioresource Technol. – 2016. – Vol. 216. – P. 1014–1021. Way of Access : http://dx.doi.org/10.1016/j.biortech.2016.06.061

[2] Degradation Effect and Mechanism of Dinitrotoluene Wastewater by Magnetic Nano-Fe_3O_4/H_2O_2 Fenton-like / S. Jiang [et al.] // Ozone: Sci. Engin. – 2016. – Vol. 38, N 3. – P. 225–232. Way of Access : http://dx.doi.org/10.1080/01919512.2015.1115716

[3] Ho P. C. Photooxidation of 2,4-dinitrotoluene in aqueous solution in the presence of hydrogen peroxide / P. C. Ho // Environ. Sci. Technol. – 1986. – Vol. 20, N 3. – P. 260–267. Way of Access : http://dx.doi.org/10.1021/es00145a007

[4] Effects of surfactants on reduction and photolysis (>290 nm) of nitroaromatic compounds / R. A. Larson [et al.] // Environ. Sci. & Technol. – 2000. – Vol. 34, N 3. – P. 505–508. Way of Access : http://dx.doi.org/10.1021/es990891e

[5] Fenton oxidation of 2,4- and 2,6-dinitrotoluene and acetone inhibition / Y. He [et al.] // Front. Environ. Sci. Engin. China – 2008. – Vol. 2, N 3. – P. 326–332. Way of Access : http://dx.doi.org/10.1007/s11783-008-0038-4

[6] Mohanty N. R. Oxidation of 2,4-dinitrotoluene using Fenton's reagent: Reaction mechanisms and their practical applications / N. R. Mohanty, I. W. Wei // Hazard. Waste Hazard. Mater. – 1993. – Vol. 10, N 2. – P. 171–183. Way of Access : http://dx.doi.org/10.1089/hwm.1993.10.171

[7] Electrochemical Reduction of 2,4-Dinitrotoluene in Aprotic and pH-Buffered Media / E. J. Olson [et al.] // J. Phys. Chem. C. – 2015. Vol. 119, N 23. – P. 13088–13097. Way of Access : http://dx.doi.org/10.1021/acs.jpcc.5b02840

[8] Jho E. H. Different fate of Pb and Cu at varied peroxide concentrations during the modified Fenton reaction in soil and its effect on the degradation of 2,4-dinitrotoluene / E. H. Jho, J.-W. Jung, K. Nam // J. Chem. Technol. Biotechnol. – 2013. – Vol. 88, N 8. – P. 1481–1487. Way of Access : http://dx.doi.org/10.1002/jctb.3991

[9] Comprehensive Investigations of Kinetics of Alkaline Hydrolysis of TNT (2, 4, 6-Trinitrotoluene), DNT (2, 4-Dinitrotoluene), and DNAN (2, 4-Dinitroanisole) // L. Sviatenko [et al.]// Environ. Sci. Technol. – 2014. – Vol. 48, N 17. – P. 10465–10474. Way of Access : http://dx.doi.org/10.1021/es5026678

[10] Evaluation of remediation processes for explosive-contaminated soils: kinetics and Microtox® bioassay / S. Y. Oh [et al.]// J. Chem. Technol. Biotechnol. – 2016. – Vol. 91. – P. 928–937. Way of Access : http://dx.doi.org/10.1002/jctb.4658

[11] Mahbub P. Application of photo degradation for remediation of cyclic nitramine and nitroaromatic explosives / P. Mahbub, P. N. Nesterenko // RSC Adv. – 2016. – Vol. 6. – P. 77603–77621. Way of Access : http://dx.doi.org/10.1039/C6RA12565D

[12] Chen W.-S. Mineralization of dinitrotoluenes in industrial wastewater by electro-activated persulfate oxidation / W.-S. Chen, Y.-C. Jhou, C.-P. Huang // Chem. Eng. J. – 2014. – Vol. 252. – P. 166–172. Way of Access : http://dx.doi.org/10.1016/j.cej.2014.05.033

[13] Gaussian 09, Revision A.02 / M. J. Frisch [et al.] – Gaussian, Inc.: Wallingford CT, 2009.

[14] Zhao Y. The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functional / Y. Zhao, D. G. Truhlar // Theor. Chem. Account – 2008. – Vol. 120. – P. 215–241. Way of Access : http://dx.doi.org/10.1007/s00214-007-0310-x

References

[1] Oh, S.-Y., Seo, Y.-D., & Ryu, K.-S. (2016). Reductive removal of 2,4-dinitrotoluene and 2,4-dichlorophenol with zero-valent iron-included biochar. *Bioresource Technol.*, 216, 1014–1021. doi: 10.1016/j.biortech.2016.06.061

[2] Jiang, S., Zhu, J., Ding, Y., Bai, S., Guan, Y., & Wang, J. (2016). Degradation Effect and Mechanism of Dinitrotoluene Wastewater by Magnetic Nano-Fe_3O_4/H_2O_2 Fenton-like. *Ozone: Sci. Engin.*, *38*(3), 225–232. doi: 10.1080/01919512.2015.1115716

[3] Ho, P. C. (1986). Photooxidation of 2,4-dinitrotoluene in aqueous solution in the presence of hydrogen peroxide. *Environ. Sci. Technol.*, *20*(3), 260–267. doi: 10.1021/es00145a007

[4] Larson, R. A., Jafvert, C. T., Bosca, F., Marley, K. A., & Miller, P. L. (2000). Effects of surfactants on reduction and photolysis (>290 nm) of nitroaromatic compounds. *Environ. Sci. & Technol.*, *34*(3), 505–508. doi: 10.1021/es990891e

[5] He, Y., Zhao, B., Hughes, J. B., & Han, S. S. (2008). Fenton oxidation of 2,4- and 2,6-dinitrotoluene and acetone inhibition. *Front. Environ. Sci. Engin. China*, *2*(3), 326–332. doi: 10.1007/s11783-008-0038-4

[6] Mohanty, N. R., & Wei, I. W. (1993). Oxidation of 2,4-Dinitrotoluene Using Fenton's Reagent: Reaction Mechanisms and Their Practical Applications. *Hazard. Waste Hazard. Mater.*, *10*(2), 171–183. doi: 10.1089/hwm.1993.10.171

[7] Olson, E. J., Isley III, W. C., Brennan, J. E., Cramer, C. J., & Buhlmann, P. (2015). Electrochemical Reduction of 2, 4-Dinitrotoluene in Aprotic and pH-Buffered Media. *J. Phys. Chem. C*, *119* (23), 13088–13097. doi: 10.1021/acs.jpcc.5b02840

[8] Jho, E. H., Jung, J.-W., & Nam, K. (2013). Different fate of Pb and Cu at varied peroxide concentrations during the modified Fenton

reaction in soil and its effect on the degradation of 2,4-dinitrotoluene. *J. Chem. Technol. Biotechnol.*, *88*(8), 1481–1487. doi: 10.1002/jctb.3991

[9] Sviatenko, L., Kinney, C., Gorb, L., Hill, F. C., Bednar, A. J., Okovytyy, S., & Leszczynski, J. (2014). Comprehensive Investigations of Kinetics of Alkaline Hydrolysis of TNT (2,4,6-Trinitrotoluene), DNT (2, 4-Dinitrotoluene), and DNAN (2,4-Dinitroanisole). *Environ. Sci. Technol.*, *48* (17), 10465–10474. doi: 10.1021/es5026678

[10] Oh, S.-Y., Yoon, H.-S., Jeong, T.-Y., & Kim, S. D. (2016). Evaluation of remediation processes for explosive-contaminated soils: kinetics and Microtox® bioassay. *J. Chem. Technol. Biotechnol.*, *91*, 928–937. doi: 10.1002/jctb.4658

[11] Mahbub, P., & Nesterenko, P. N. (2016). Application of photo degradation for remediation of cyclic nitramine and nitroaromatic explosives. *RSC Adv.*, *6*, 77603–77621. doi: 10.1039/C6RA12565D

[12] Chen, W.-S., Jhou, Y.-C., & Huang, C.-P. (2014). Mineralization of dinitrotoluenes in industrial wastewater by electro-activated persulfate oxidation. *Chem. Eng. J.*, *252*, 166–172. doi: 10.1016/j.cej.2014.05.033

[13] Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Scalmani, G., Barone, V., Mennucci, B., Petersson, G. A., Nakatsuji, H., Caricato, M., Li, X., Hratchian, H. P., Izmaylov, A. F., Bloino, J., Zheng, G., Sonnenberg, J. L., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., Montgomery, Jr., J. A., Peralta, J. E., Ogliaro, F., Bearpark, M., Heyd, J. J., Brothers, E., Kudin, K. N., Staroverov, V. N., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A., Burant, J. C., Iyengar, S. S., Tomasi, J., Cossi, M., Rega, N., Millam, J. M., Klene, M., Knox, J. E., Cross, J. B., Bakken, V., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R. E., Yazyev, O., Austin, A. J., Cammi, R., Pomelli, C., Ochterski, J. W., Martin, R. L., Morokuma, K., Zakrzewski, V. G., Voth, G. A., Salvador, P., Dannenberg, J. J., Dapprich, S., Daniels, A. D., Farkas, Ö., Foresman, J. B., Ortiz, J. V., Cioslowski, J., & Fox, D. J. (2009). Gaussian 09 (Revision A.02) [Computer software]. Gaussian Inc., Wallingford CT.

[14] Zhao, Y., & Truhlar, D. G. (2008). The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functional. *Theor. Chem. Account*, *120*, 215–241. doi: 10.1007/s00214-007-0310-x