List of Publications:

(1) *Can Surface Energy be a Parameter to Define Morphological Change of Rock-Salt Crystals with Additives? A First Principle Study*
M. A. S. Khan, and B. Ganguly*, Cryst. Eng. Comm.* **2012***, 15,* 2631*.*

(2) *Origins of Reversing Diastereoselectivity of α,β-dichloro-γ-butenolides and γ-Butyrolactams in Direct Vinylogous Aldol Addition: A Computational Study*

M. A. S. Khan, J. Zhang, K. D. Sarma and B. Ganguly, *RSC Advances,* **2012**, *2,* 8460.

(3) *Assessing the Reactivation Efficacy of Hydroxylamine Anion towards VX-Inhibited AChE: A Computational Study.*
M. A. S. Khan, and B. Ganguly*, J. Mol. Model.,* **2012***, 18,* 1801*.*

(4) *Probing the Simulant Behavior of PNPDPP towards Paraoxon and Parathion: A Computational Study.*
M. A. S. Khan, T. Bandyopadhyay and B. Ganguly*, J. Mol. Graph. Model.* **2012***, 34,* 10.

(5) *Can Nitrilotriacetic Acid (NTA) Act as a Habit Modifier for Rock Salt Crystals? An Answer from Computational and Experimental Studies.*
M. A. S. Khan, A. Singh, S. Haldar and B. Ganguly, *Cryst. Growth Des.,* **2011**, *11,* 1675*. (Published as part of a virtual special issue on Structural Chemistry in India: Emerging Themes)*

(6) *Probing the Reactivation Process of Sarin-Inhibited Acetylcholinesterase with α-Nucleophiles: Hydroxylamine Anion is Predicted to be a Better Antidote with DFT Calculations.*
M. A. S. Khan, R. Lo, T. Bandyopadhyay and B. Ganguly*, J. Mol. Graph. Model., **2011, 29, 1039.*

(7) *Remarkable Effect of Hydroxylamine Anion towards the Solvolysis of Sarin: A DFT Study.*
M. A. S. Khan, M. K. Kesharwani, T. Bandyopadhyay and B. Ganguly, *J. Mol. Struct. (THEOCHEM)* **2010**, *944*, 132. *(Cited in one of the world's top most visited websites, Wikipedia) (http://nl.wikipedia.org/wiki/Sarin_(zenuwgas))*

(8) *Solvolysis Process of Organophosphorus Compound P-[2-(dimethylamino)ethyl]-N,N-Dimethylphosphonamidic Fluoride with Simple and α-Nucleophiles: A DFT Study*
M. K. Kesharwani, **M. A. S. Khan**, T. Bandyopadhyay and B. Ganguly, *Theor. Chem. Acc.* **2010**, *127*, 39.

(9) *Solvolysis of Chemical Warfare Agent VX is More Efficient with Hydroxylamine Anion: A Computational Study*
M. A. S. Khan, M. K. Kesharwani, T. Bandyopadhyay and B. Ganguly, *J. Mol. Graph. Model.*, **2009**, *28*, 177.

(10) *Probing the Influence of pH Dependent Citric Acid towards the Morphology of Rock Salt: A Computational Study.*
M. A. S. Khan, A. Sen and B. Ganguly, *Cryst. Eng. Comm.,* **2009**, *11*, 2660.

Participation in National and International level Symposium and Workshop:

(1) A Computational Study Towards Understanding the Conformations and Destruction of Organophosphorus Nerve Agent GV*;* **M. A. S. Khan**, M. K. Kesharwani and B.Ganguly. 11th CRSI National Symposium in Chemistry held from 6 to 8 February 2009 at National Chemical Laboratory, Pune, India (**Poster presentation**).

(2) Participated in 2nd National level two-day **workshop** on Cheminformatics organized by the departments of biotechnology and bioinformatics, Christ college, Rajkot, on January 7 & 8, 2011.

(3) In Silico Approaches towards the Design of Chemical Processes for the Detoxification of Environmentally Hazardous Pesticides and Chemical Warfare Agents; **M. A. S. Khan,** M. K. Kesharwani, T. Bandyopadhyay and B. Ganguly**.** 4th International Congress of Environmental Research held from 15 to 17 December **2011** at Sardar Vallabhbhai National Institute of Technology (SVNIT), Surat, India **(Oral presentation).** *Young environmentalist award for best oral presentation.*

PAPER

Can surface energy be a parameter to define morphological change of rock-salt crystals with additives? A first principles study†

Md Abdul Shafeeuulla Khan and Bishwajit Ganguly*

We have reported that surface energy can be considered as a useful parameter to rationalize the morphology of rock-salt crystals in presence of an impurity. On the basis of first principles DFT calculations of the surface energies before and after the adsorption of surface-capping agent (additive) on the NaCl surfaces, we have shown that the surface energy differences among the three important faces (100), (110) and (111) corroborates the change in character of salt crystals observed experimentally. In accordance with the surface energy calculations, the stability order of the three crystallographic surfaces of NaCl was found to be (100) > (110) > (111) in the absence of additive molecules (*i.e.* clean surfaces). This result is in concurrence with the fact that salt crystals are cubes with (100) surface when grown in aqueous solution. The applied computational methodology towards the determination of surface energies was found to be trustworthy as it has reproduced well the experimental surface energy values of 189 erg cm^{-2} and 445 erg cm^{-2} for (100) and (110) NaCl surfaces, respectively. However, the trend in the decreased surface energy values has been found to be reversed for (100) < (110) < (111) when these surfaces were capped with known additive molecules. This work demonstrates that the change in the thermodynamic quantity (*i.e.*

PAPER

Origins of reversing diastereoselectivity of α,β-dichloro-γ-butenolides and γ-butyrolactams in direct vinylogous aldol addition: a computational study†

Md Abdul Shafeeuulla Khan,[a] Ji Zhang,[b] Koushik Das Sarma*[c] and Bishwajit Ganguly*[a]

Oxygenated five-membered ring compounds are more widespread in nature than the corresponding aza-analogues due to their more interesting biological activity. In our earlier studies, we have reported a simple methodology to synthesize novel synthons like 5-(1'-hydroxy)-γ-butenolide and 5-(1'-hydroxy)-γ-butyrolactam through the direct vinylogous aldol addition reaction. The observed diastereoselectivities for γ-butyrolactones and γ-butyrolactams were not understood in that report. We have reported herein a detailed computational study to understand the observed diastereoselectivity of α,β-dichloro-γ-butenolides and α,β-dichloro-γ-butyrolactams. The transition state calculations performed with B3LYP/cc-pVDZ level of theory to examine the diastereoselectivity of α,β-dichloro-γ-butenolides and α,β-dichloro-γ-butyrolactams have been found to be in good agreement with the observed experimental results. The origin of selectivity is examined by an activation strain model and molecular electrostatic potential (MESP) surfaces. The distortion energies calculated using the activation strain model revealed the origin of diastereoselectivities for butenolides

Probing the simulant behavior of PNPDPP toward parathion and paraoxon: A computational study

Md Abdul Shafeeuulla Khan[a], Tusar Bandyopadhyay[b], Bishwajit Ganguly[a,*]

[a] Analytical Science Discipline, Central Salt & Marine Chemicals Research Institute (Council of Scientific and Industrial Research), Bhavnagar, Gujarat 364002, India
[b] Theoretical Chemistry Section, Chemistry Group, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India

ARTICLE INFO

ABSTRACT

The extreme toxicity of organophosphorus nerve agents and pesticides mandates to employ models or simulants in place of the actual compounds in the laboratory. The importance of simulants is known, however, their efficacy for direct comparison with the toxic organophosphorus compounds is not well documented. We have examined the potential energy surfaces (PES) for the alkaline hydrolysis of pesticides like paraoxon (diethyl 4-nitrophenyl phosphate), parathion (O,O-diethyl O-4-nitrophenyl phosphorothioate) and PNPDPP (4-nitrophenyl diphenyl phosphate), a simulant with MP2/6-311+G*//B3LYP/6-311+G* + ΔG_{solv} (HF/6-31+G*) level of theory. The effect of aqueous solvation was considered with the Integral Equation Formalism Polarizable Continuum Model (IEF-PCM). The alkaline hydrolysis of these organophosphorus compounds reveals that the reaction proceeds through the attack of hydroxide ion at the phosphorus center to form a pentacoordinate intermediate. The calculated free energies of activation for the alkaline hydrolysis of paraoxon and parathion are in good agreement with the available experimental activation free energies. The computed results show that the reaction profiles for the alkaline hydrolysis of paraoxon, parathion and PNPDPP are largely similar; however, the rate of hydrolysis of parathion may be higher than that of paraxon and PNPDPP. Such difference arises due to the less electrophilic nature of the phosphorus atom of parathion molecule as observed in the charge analysis study. The conceptual DFT analysis also showed the similar trend for the alkaline hydrolysis of paraoxon, parathion and PNPDPP with hydroxide anion. This computational study provides a quantitative support toward the use of PNPDPP as a simulant for organophosphorus compounds, which cannot be used directly for the laboratory purposes.

ORIGINAL PAPER

Assessing the reactivation efficacy of hydroxylamine anion towards VX-inhibited AChE: a computational study

Md Abdul Shafeeuulla Khan · Bishwajit Ganguly

Abstract Oximate anions are used as potential reactivating agents for OP-inhibited AChE because of they possess enhanced nucleophilic reactivity due to the α-effect. We have demonstrated the process of reactivating the VX– anion were also found to be low. The calculated results suggest that V-series compounds can be more toxic than G-series compounds, which is in accord with earlier experimental observations.

Probing the reactivation process of sarin-inhibited acetylcholinesterase with α-nucleophiles: Hydroxylamine anion is predicted to be a better antidote with DFT calculations

Md Abdul Shafeeuulla Khan[a], Rabindranath Lo[a], Tusar Bandyopadhyay[b], Bishwajit Ganguly[a,*]

[a] Analytical Science Discipline, Central Salt & Marine Chemicals Research Institute (Council of Scientific and Industrial Research), Bhavnagar, Gujarat 364 002, India
[b] Theoretical Chemistry Section, Chemistry Group, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India

ARTICLE INFO

ABSTRACT

Inactivation of acetylcholinesterase (AChE) due to inhibition by organophosphorus (OP) compounds is a major threat to human since AChE is a key enzyme in neurotransmission process. Oximes are used as potential reactivators of OP-inhibited AChE due to their α-effect nucleophilic reactivity. In search of more effective reactivating agents, model studies have shown that α-effect is not so important for dephosphylation reactions. We report the importance of α-effect of nucleophilic reactivity towards the reactivation of OP-inhibited AChE with hydroxylamine anion. We have demonstrated with DFT [B3LYP/6-311G(d,p)] calculations that the reactivation process of sarin–serine adduct 2 with hydroxylamine anion is more efficient than the other nucleophiles reported. The superiority of hydroxylamine anion to reactivate the sarin-inhibited AChE with sarin–serine adducts 3 and 4 compared to formoximate anion was observed in the presence and absence of hydrogen bonding interactions of Gly121 and Gly122. The calculated results show that the rates of reactivation process of adduct 4 with hydroxylamine anion are 261 and

---

CRYSTAL GROWTH & DESIGN

Can Nitrilotriacetic Acid (NTA) Act as a Habit Modifier for Rock Salt Crystals? An Answer from Computational and Experimental Studies

Published as part of a virtual special issue on Structural Chemistry in India: Emerging Themes
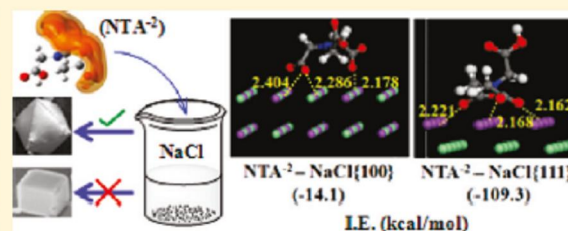
Md Abdul Shafeeuulla Khan,[†] Ajeet Singh,[†] Soumya Haldar,[‡] and Bishwajit Ganguly[*,†]

[†] Analytical Science Discipline, Central Salt & Marine Chemicals Research Institute (Council of Scientific and Industrial Research), Bhavnagar, Gujarat, India-364 002

[‡] Discipline of Marine Biotechnology and Ecology, Central Salt & Marine Chemicals Research Institute (Council of Scientific and Industrial Research), Bhavnagar, Gujarat, India-364 002

Ⓢ Supporting Information

ABSTRACT: It has been reported that nitrilotriacetic acid (NTA) has no effect on the growth habit of sodium chloride. We report here that NTA acts as a habit modifier for rock salt. The concentration of NTA required to influence the habit of salt crystals from cubic to octahedron is much less compared to the concentrations of other organic additives used for this purpose. The influence of NTA under different pH conditions toward the morphology of sodium chloride crystals has been investigated by experimental and computational methods. Prior to any

Remarkable effect of hydroxylamine anion towards the solvolysis of sarin: A DFT study

Md Abdul Shafeeuulla Khan [a], Manoj K. Kesharwani [a], Tusar Bandyopadhyay [b], Bishwajit Ganguly [a,*]

[a] *Analytical Science Discipline, Central Salt & Marine Chemicals Research Institute (Council of Scientific and Industrial Research), Bhavnagar, Gujarat 364 002, India*
[b] *Theoretical Chemistry Section, Chemistry Group, Bhabha Atomic Research Centre Trombay, Mumbai 400 085, India*

ARTICLE INFO

ABSTRACT

The reaction of the nerve agent sarin with hydroperoxide (HOO^-) and hydroxylamine anion (NH_2O^-) has been studied with a correlated molecular orbital and density functional theory. The profound effect was found for α-nucleophiles on the solvolysis process of sarin compared to alkaline hydrolysis. The enthalpy of activation calculated at MP2/6-31+G*//MPW1K/MIDI!+ΔG_{solv} (HF/6-31+G*) level of theory for the reaction of hydroxylamine anion with sarin is 5.2 kcal/mol lower than the barrier for alkaline hydrolysis. The charge descriptions of the α-nucleophiles seem to correlate well with their reactivity towards this organophosphorus compound. Conceptual DFT analysis also showed the similar trend for the solvolysis of sarin with these nucleophiles. The importance of intermolecular hydrogen bonding was also examined with the topological properties of electron density distributions for ($-X–H\cdots O$, $X = O$, N) using Bader's theory of atoms in molecules (AIM) and natural bond orbital (NBO) methods.

REGULAR ARTICLE

Solvolysis process of organophosphorus compound *P*-[2-(dimethylamino)ethyl]-*N*,*N*-dimethylphosphonamidic fluoride with simple and α-nucleophiles: a DFT study

Manoj K. Kesharwani · Md. Abdul Shafeeuulla Khan · Tusar Bandyopadhyay · Bishwajit Ganguly

Abstract Density functional theory (DFT) has been used to study the solvolysis process of the organophosphorus compound *P*-[2-(dimethylamino)ethyl]-*N*,*N*-dimethylphosphonamidic fluoride (GV) with simple nucleophile [hydroxide (HO^-)] and α-nucleophiles [hydroperoxide (HOO^-) and hydroxylamine anion (NH_2O^-)]. The lowest energy conformer of GV used for the solvolysis process was identified with Monte Carlo conformational search (MCMM) algorithm employing MMFFs force field followed by DFT calculations. The profound effect was found for α-nucleophiles toward the solvolysis of GV compared to normal alkaline hydrolysis. Incorporation of solvent (water) employing SCRF (PCM) model at B3LYP/6-31+G* showed that solvolysis of GV with hydroperoxide in solvolysis of GV affects the activation barriers; however, the hydroperoxidolysis remains the preferential process. The topological properties of electron density distributions for ($-X–H\cdots O$, $X = O$, N) intermolecular hydrogen bonding bridges have been analyzed in terms of Bader theory of atoms in molecules (AIM). Further, the analysis was extended by natural bond orbital (NBO) methods for the strength of intermolecular hydrogen bonding in the transition state geometries. This study showed that the reactivity of these α-nucleophiles toward the solvolysis of GV is a delicate balance between the nucleophilicity and hydrogen-bond strength. Solvation governs the overall thermodynamics for the destruction of GV, which otherwise is unfavored in the gas phase studies.

Probing the influence of pH dependent citric acid towards the morphology of rock salt: a computational study†

Md Abdul Shafeeuulla Khan, Anik Sen and Bishwajit Ganguly*

The influence of citric acid under different pH conditions towards the morphology of sodium chloride was investigated employing DFT calculations. Prior to any analysis, conformational search of citric acid and its three dissociated forms was performed with molecular mechanics MM2* and DFT (B3LYP/6-31+G*) methods in the gas and aqueous phase. The low energy conformers generated in the aqueous phase were found to be in good agreement with the available crystal structures. The calculated higher composition of citric acid at natural pH = 0.75 $i.e.$, $\alpha_0 = 0.99$ is not effective for the habit modification of sodium chloride. Quantum chemically derived molecular electrostatic potential (MESP) showed the possible sites of citric acid and its dissociated forms with the estimated deepest V_{min} values and their magnitudes provide an insight for their interaction with the crystal surfaces of sodium chloride. The composition analysis and MESP derived data suggest that the dissociated forms of citric acid at higher pH values are responsible for the change in habit of sodium chloride from cubes to octahedrons. Further, slab model calculations performed to mimic the surfaces of sodium chloride with DFT methods using a conductor-like screening model in the aqueous phase (COSMO) for the interactions of citric acid and dihydrogen citrate validates that there is no preference for the {111} plane of NaCl with citric acid. However, a significant preference was seen with dihydrogen citrate, which quantifies the MESP analysis and corroborates the dependence of morphology on the pH of the solution.

Contents lists available at ScienceDirect

Journal of Molecular Graphics and Modelling

journal homepage: www.elsevier.com/locate/JMGM

Solvolysis of chemical warfare agent VX is more efficient with hydroxylamine anion: A computational study

Md Abdul Shafeeuulla Khan [a], Manoj K. Kesharwani [a], Tusar Bandyopadhyay [b], Bishwajit Ganguly [a,*]

[a] Analytical Science Discipline, Central Salt & Marine Chemicals, Research Institute (Council of Scientific and Industrial Research), G.B. Marg, Bhavnagar 364002, Gujarat, India
[b] Theoretical Chemistry Section, Chemistry Group, Bhabha Atomic Research Centre Trombay, Mumbai 400085, India

ARTICLE INFO

ABSTRACT

The reaction of the chemical warfare agent VX with hydroxylamine anion (NH_2O^-) has been studied using a combination of correlated molecular orbital and density functional theory. It has been found that the hydroxylamine anion leads to predominant formation of non-toxic products for solvolysis of VX. The calculated activation barrier for the rate determining step of hydroxylamine anion with VX was found to be lower than that of hydroperoxidolysis and suggesting a more facile solvolysis with the former α-nucleophile. The conformational search was performed for VX using Monte Carlo search method with Merck Molecular force fields (MMFFs), which lead to a more stable conformation than reported. The anomeric effect operates in the lowest energy conformation of VX and contributes towards its stabilization. The reactivity of the α-nucleophiles towards VX was correlated well with the corresponding charges on nucleophilic oxygen atoms.