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PNNL-32032

Experimental Studies of the Dynamics of Adsorbed and Condensed Phase iodine Species Formed in Severe Reactor Accidents

September 2021

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U.S. DEPARTMENT OF ENERGY

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Abstract

We have studied the chemical transformations of semi-volatile organic iodide species (RI) in the condensed phase as well as adsorbed onto the surfaces of environmentally relevant particles, e.g., soot (carbon) and dust (silica) under real-world conditions. The combination of chosen experimental methods provide a molecular-level insight into the chemical dynamics of organic iodides. Throughout this project, we have developed new experimental, quantum chemistry, and data analysis capabilities. All experimental work was performed with ^{127}I.

As of September 2021, we have three manuscripts in preparation concerned with: i) following of the condensed phase (DABCO and alkyl iodide) kinetics experiments using NMR spectroscopy, ii) identifying the morphology of carbon particles created by a spark discharge generator and used to study adsorption of RI, and iii) ascertaining adsorption and chemical transformation kinetics of butyl iodide on the carbon particles. Collected data will also contribute to the prospective fourth manuscript that describes the deconvolution of NMR spectra using mathematical algorithms developed by William Rosenthal.

During FY21 we submitted two concept papers to DOE/NA-22 related to this LDRD project. One paper involved examining the chemistry of alkyl iodides on abiotic surfaces. This concept did not move forward, but was relayed to another US government agency, and we are still waiting to hear about its fate. The second concept paper involves using our aerosol measurement capabilities for monitoring the chemistry of headspace gases in chemical reactors. This proposal has been funded by NA-22 for the next three years.

FY2021 is the last year of our LDRD. No new LDRD research is planned for FY2022.

Acknowledgments

This research was supported by the Chemical Dynamics Initiative (CDI), under the Laboratory Directed Research and Development (LDRD) Program at Pacific Northwest National Laboratory (PNNL). PNNL is a multi-program national laboratory operated for the U.S. Department of Energy (DOE) by Battelle Memorial Institute under Contract No. DE-AC05-76RL01830.

Condensed Phase Iodine Chemistry

Previous studies have described adsorbents such as Activated Carbon (AC) impregnated with DABCO (1,4-diazabicyclo[2.2.2]octane), to trap volatile alkyl iodides compounds during reprocessing of spent fuels. Yet, little is known about the chemical transformations of the adsorbed species under real-world conditions.

The kinetics of the condensed phase second order nucleophilic substitution (S_N2) reactions between DABCO and methyl iodide, or butyl iodide, in protic and aprotic solvents have been examined using Nuclear Magnetic Resonance (NMR). DABCO, which has two nucleophilic amine sites, can sequentially form bonds with two alkyl groups. The first substitution takes place rapidly and has been studied in the past, while kinetics of the second substitution has not been reported. The individual steps of the substitution reactions are shown below.

k_1: DABCO + BuI $\rightarrow$ [DABCOBu$^+$] [I$^-$]

k_2: [DABCOBu$^+$] [I$^-$] + BuI $\rightarrow$ [BuDABCOBu^{+2}] [I$^-$]$_2$

A plot of concentration (M) *vs*. time (seconds) for the first reaction is shown in Fig.1. Because of the difficulties with performing the NMR experiment – especially at higher temperatures: i) data points were missed at the beginning of the reaction due to the speed of the reaction, ii) there was incomplete mixing, iii) precipitate formation, iv) reactants partially in the vapor phase instead of the condensed phase, etc., a sophisticated analysis of obtained data is warranted. A Markov Chain Monte Carlo (MCMC) approach was used to determine rates from the time dependent change in concentration of starting materials and products as determined by ^{1}H NMR spectroscopy. The MCMC approach allows us to obtain a statistically balanced “chain” of possible kinetics parameter values to test and utilize a distribution of samples used to predict parameter values and uncertainties. For example, the rate of the k_1 reaction at 50.9 °C of BuI with DABCO in acetonitrile was determined to be 0.02856(38) M^{-1} sec^{-1}, as compared to a k_1 value of 0.03073 M^{-1} sec^{-1} determined by the differential equation solver. The k_2 rate is approximately one thousand times slower. We have measured the rates of these reactions at 30, 50 and 70 ºC and used Arrhenius and Eyring analyses to obtain activation barriers and thermodynamic parameters.

One added benefit of the MCMC approach is its ability to extrapolate or interpolate concentrations of chemical products forward and backward in time. This would allow, for example, researchers to determine the time and place of a chemical release into the environment, or the degradation rate of these chemicals on environmental surfaces.

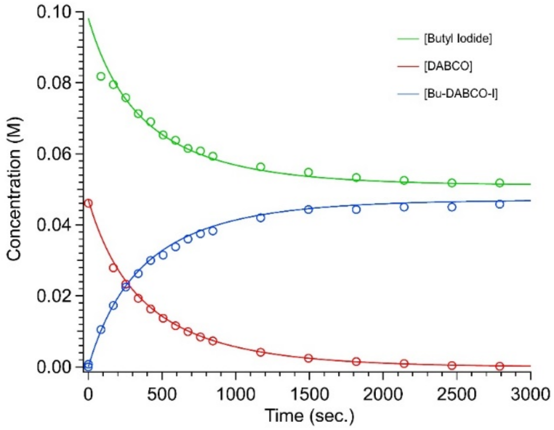

Figure 1. Concentration (M) *vs.* time (sec) plot for DABCO + 1.5 BuI in acetonitrile at 51 °C. The open circles represent collected experimental data. The solid traces are the numerical differential equation solver fit to the data.

In addition to experimental measurements of the reaction rates, we have used quantum chemistry calculation methods to estimate their reaction energies and activation barriers (Table 2). We have noted that the activation barriers are reduced in polar solvents when compared to vacuum due to the preferential stabilization of a more polar of transition state. The first substitution of DABCO with BuI has a 6 $kJmol^{-1}$ greater activation energy than MeI, which corresponds to an order of magnitude slower rate constant, consistent with experimentally obtained results. The second alkylation with MeI also has a 6 $kJmol^{-1}$ greater activation energy and is less exothermic than first alkylation.

In addition to the DABCO alkyl iodide reaction system, we have begun experiments on reactions between MeI and histidine in water. Again, we were using ^{1}H NMR to follow the reaction kinetics. The challenges with these systems include the lower solubility of MeI and histidine in solvents other than water, and the seeming propensity of MeI for attacking atoms other than the amine sites of the histidine. This work will be important in moving the research forward to understand the reactions of methyl iodide with compounds found in nature – aqueous suspensions of biotic and abiotic soils, plant structures, etc.

Dynamics of Particulate-Bound Alkyl-Iodides

We have quantified the adsorption of butyl iodide vapor interacting with activated and graphitic carbon particles. The graphitic carbon particles are generated by a commonly used spark discharge approach. These particles were characterized using the one-of-a-kind Single Particle Mass Spectrometer (miniSPLAT), which provides capabilities for determining particle size, morphology (shape, porosity, etc.) as well as chemical composition of individual particles (see Fig. 2). miniSPLAT analysis of the graphitic carbon particles revealed the presence of two distinct types graphitic carbon particles: fractal and more compact agglomerates of nanoparticles. Given that these carbon particles are commonly used as proxy for fractal combustion soot particles, these findings represent an important new discovery. We demonstrated that more compact agglomerates, comprising up to 20% of particle number concentration, can dominate particles mass loadings, and need to be considered when used for instruments' calibration, and studies of soot reactivity, inhalation toxicity, and optical properties.

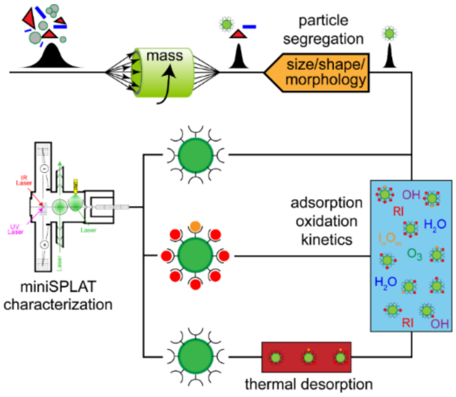

Figure 2. Schematic of experimental set-up used to study adsorption, desorption, and chemical transformations of RI species on the surfaces of particles with precisely controlled properties.

In another series of experiments, the fractal graphitic carbon particles, generated by the spark discharge generator, were injected into a 100 L Teflon reaction chamber, where they were exposed to butyl iodide vapor at room temperature and characterized by miniSPLAT as a function of exposure time. The kinetics of the physisorption of butyl iodide on the surfaces of the fractal carbon particles (surface area of 310 m^2/g) were quantified by measuring temporal evolution of I^+ or Bu^+ ions and changes in particle mass and density.

The mass spectra of the fractal carbon particles (black) and of the fractal carbon particles exposed for 89 min to gas-phase butyl iodide (red) are shown in Fig. 3a. Figure 3b shows that the intensity of I^+ and the butyl fragment ions exhibit identical temporal evolution, as a function of the adsorption time. We have demonstrated that the mass of adsorbed BuI is proportional to carbon particle mass, consistent with their fractal structures (Figure 4). We find that after extended exposure (1200 minutes), the fractal carbon particles adsorbed approximately four monolayers of butyl iodide onto their surface, providing the direct measure of the amount of organic material these particles can accrete.

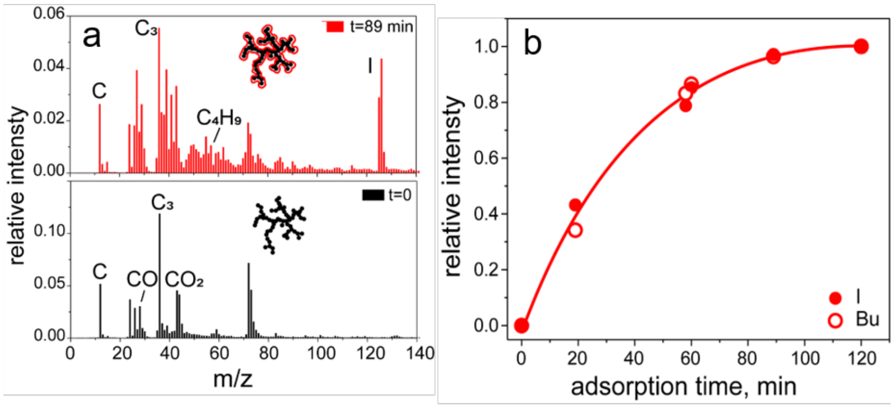

Figure 3. (a) Mass spec of graphitic carbon particles before (black) and after exposure to butyl iodide (red); (b) The adsorption rate for physisorbed butyl iodide on fractal graphitic carbon particles.

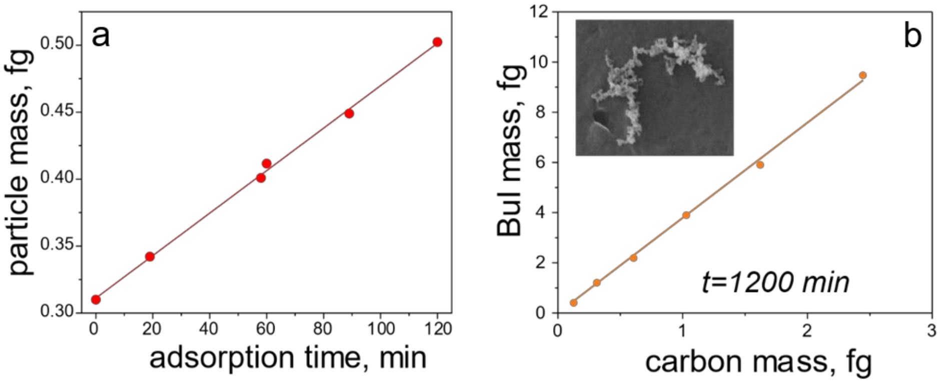

Figure 4. Increase in measured particle mass as a function of BuI exposure time (a); and the mass of BuI adsorbed after 1200 min as a function of fractal carbon particle mass (b).

When the 150 nm (0.32 fg) fractal carbon particles are first impregnated by DABCO and then exposed to gas-phase butyl iodide, the mass spectral data indicate both chemisorption and physisorption. The mass spectra for this exposure experiment are shown in Fig. 5a and the rate of uptake of butyl iodide is shown in Fig. 5b. These results are new and important because they give us an estimate of the sorption rate of organic iodides onto aerosol particles, including the rate of formation of non-volatile particle -bound mono-substituted DABCO-C_4H_9 (*m/z* = 169).

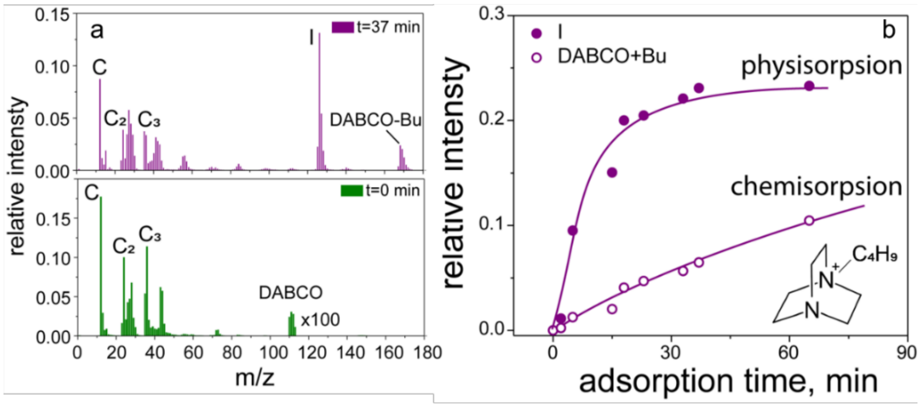

Figure 5. (a) The mass spectra of DABCO impregnated fractal graphitic carbon particles before (green) and after the exposure to butyl iodide for 37 minutes; (b) The adsorption rate of butyl iodide on fractal carbon particles impregnated with DABCO.

Additional experiments were conducted during FY2021 in which we examined the photolysis of particle-bound and gas-phase butyl iodide.

In the first series of experiments, fractal 0.5 fg carbon particles adsorbed 0.043 fg of butyl iodide during 45 minutes of exposure in a Teflon chamber. The gas and particles in the chamber were then irradiated by 14, 40-watt black lamps, which are intended to simulate solar radiation (see Fig. 6). This photolysis process resulted in a large change of particle mass, composition, and number density (see Fig. 7). The average mass spectrum of the particles is shown in Fig. 8 and indicates the presence of I, I_2, IO_{1-4}, I_2O_{2-5}, $C_{2-3}H_3O$, etc. ions.

Figure 6. Teflon chamber with carbon particles and butyl iodide exposed to black lamp light.

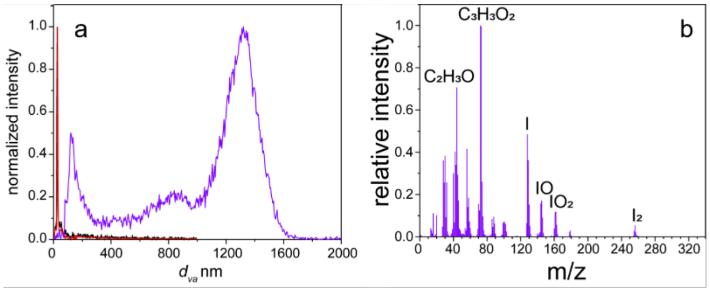

Figure 7. Photolysis of gas-phase and particle-bound BuI resulted in large change in particle size, mass, composition, and number concentrations. The latter indicates new particle formation due to nucleation of gas-phase BuI photolysis products.

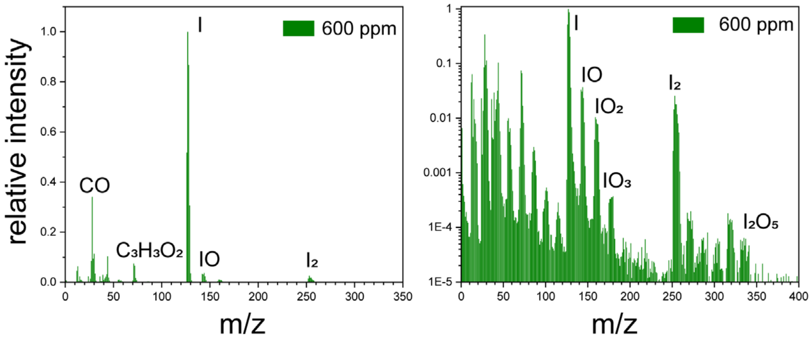

Figure 8. The average mass spectrum of particles produced by photolysis of 600 ppm of gas-phase butyl iodide.

Further cycles of light and dark for the aerosol system in the Teflon bag showed further particle coagulation and chemistry. This work highlights the complexity of iodine chemistry in the atmosphere, particularly related to diurnal effects. This is a topic that needs further investigation with follow-on funding.

Impact

Our LDRD project has given us the opportunity to explore several aspects of iodine chemistry in the condensed phase and on aerosols, and these results are invaluable in understanding iodine chemistry in the environment. We believe we can leverage our unique results to pursue funding on these topics in the future and, in fact, have received funding to understand the role of aerosols in reprocessing chemistry.

Condensed phase measurements of DABCO/alkyl iodide reactions have given us detailed information on the kinetic and thermodynamic properties of these systems. We have developed new data analysis tools for processing incomplete or imperfect kinetic data sets that allow us to predict the concentrations of chemical products and reactants forward and backward in time. We have measured the rates of the second alkylation step for methyl and butyl iodide reacting with DABCO for the first time. We have used quantum chemistry calculation methods to determine the thermodynamic properties of these S_N2 reactions.

Using single particle mass spectrometry (miniSPLAT), we discovered the presence of two distinct types of graphitic carbon particles created in an electrical discharge: fractal and compact agglomerates. We have measured the rate at which butyl iodide physisorbs onto the fractal particles, and we have determined their sorption capacity. This is a new and important result because it informs researchers studying reactor accidents of the amount of material that might be taken up by these types of particles. We have measured the rate at which butyl iodide is chemisorbed and physisorbed onto fractal graphitic soot particles that have been impregnated with DABCO. This is a new and important result because it demonstrates the nature (and rate) of chemical sorbtion to these types of particles.

We have examined the photolysis of gas- phase alkyl iodides and observed complex nucleation and growth of particles composed of iodine pentoxide with co-condensed organic iodine-free compounds. This work is important for understanding the chemistry of iodine chemistry in the atmosphere.

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