Recycling and Reuse Technology Transfer Center

http://www.rrttc.uni.ed

Gas-Phase Ion-Molecule Reactions of Methyl Tert-Butyl Ether

Publication: 1994 – 021

Scott Peterman, Curtiss D. Hanson

94:021

ANALYTICAL CHEMISTRY

27 STUDY OF DYES ADSORPTION ON ADJU-PHOS AND SURFACE CHARACTERIZATION WITH RESONANCE RAMAN SPECTROSCOPY. Heping Wang and Patricia M. Callahan Department of Chemistry, University of MIssouri-Rolla, Rolla, MO 65401

Mineral vaccine adjuvant's surface property is dependent on environmental conditions. By detecting resonance Raman scattering signals from the adsorbed dye molecules, adjuvant's surface property and its interaction with adsorbed species can be measured. The point of zero charge (PZC) of Adju-Phos an amorpors aluminum phosphate adjuvant, is determined. Surface modification by changing environment, such as pH and ionic strength, were also observed. Adju-Phos surface dissociation model is proposed and the distribution of surface electric potential is discussed.

28 **ASSESSMENT AND MONITORING OF THE DEGRADATIVE PRODUCTS OF PETROLEUM HYDROCARBONS IN DIESEL FUEL.** Lenore M. Koczon, Susan Landon-Arnold and Alan Randa. Northern State University, Department of Mathematics and Natural Sciences, Aberdeen, South Dakota 57401

One of the most significant ground water quality problems in South Dakota is the contamination of public supply wells from accidental releases of chemicals and petroleum. Subsurface contaminated soil can serve as a source of ground water contamination as desorption of organic contaminants occurs. Biodegradation of hydrocarbons by natural populations of microorganisms represents one of the primary mechanisms by which these pollutants are eliminated from the environment. The initial stage of this research was to test in vitro biodegradative capabilities of indigenous microorganisms using a slurry cascade. Assessment of the degree of degradation was monitored using GC/FID analysis. The data from these experiments suggest that as a plug of contaminated soil moves through the cascade recalcitrant components of the fuel are degraded.

29 ANALYTICAL OF HYDROXYPROPYL-β-CYCLODEXTRINS FROM SEPARATE SOURCES. Gregory A. Turner,* Timothy B. Skinner and Evelyn A. Murrill. Midwest Research Institute, Kansas City, Missouri, 64110.

Cyclodextrins and their chemically modified derivatives have been the subject of numerous investigations. Their use has included the area of enzyme modeling and mimetics, in complexation chemistry, as chromatographic stationary phases and enantioselective agents, and as food and drug additives and excipients. Hydroxypropyl-β-cyclodextrin (HP-β-CD) is of considerable interest as a agent for use in drug delivery. This material is normally comprised of a mixture of partially derivatized species. Analysis of HP-β-CDs from different sources in our laboratory was performed to establish their equivalency as drug excipients for regulatory purposes. Elemental, HPLC, NMR, and mass analyses of the native and derivatized HP-β-CDs revealed subtle differences in the samples. The utility of these methods will be presented.

ANALYTICAL CHEMISTRY

30 TWO HPLC METHODS FOR THE ANALYSIS OF PENTAAZAPENTACOSANE. Gregory A. Turner,* Timothy B. Skinner and Evelyn A. Murrill. Midwest Research Institute, Kansas City, Missouri, 64110.

Pentaazapentacosane (1,19-*bis*-(ethylamino)-5,10,15-triazanonadecane, BE-4-4-4-4, BE-4x4), a synthetic aliphatic polyamine analog, is being developed as a potential antineoplastic agent, with selective activity against brain tumors, by the National Cancer Institute. The analysis of BE-4x4 is complicated by its high polarity and lack of UV chromophores. Two stability indicating HPLC methods have been developed and validated for the analysis of BE-4x4. An ion-paired C18 reverse-phase system with refractive index detection is suitable for assay and purity analyses of the bulk compound. An alternate method utilizes trifluoroacetic acid as a volatile pairing agent, on a PRP-1 polymeric column equipped with evaporative light scattering detection (ELSD). The latter method offers superior sensitivity (< 0.01 mg/mL) and is particularly suitable for the ongoing stability and other developmental analyses for this compound. Stability results and the response characteristics of the ELSD for this compound will be presented.

31 DETERMINATION OF THE REACTION THRESHOLD FOR THE ION-MOLECULE REACTIONS OF CYCLOPROPENYL. Curtiss D. Hanson, Samantha Franck, Michelle D. Hammer, Michaela L. Rich; Department of Chemistry, University of Northern Iowa, Cedar Falls, IA 50614-0423

The $C_3H_3^+$ cation has been extensively studied as a precursor ion to the formation of soot in the pyrolysis of fuels and other hydrocarbons. Studies involving soot nucleation in flames point to an ionic mechanism, versus a neutral free radical mechanism, driving the formation of aromatic hydrocarbons. These studies show that the the $C_3H_3^+$ cation is critical to this transformation. Two forms of $C_3H_3^+$ are observed: i) the propargyl isomer, which has been determined to be highly reactive, and ii) an unreactive cyclopropenyl isomer. Because the cyclopropenyl isomer is the predominate isomer (>90%), reactions of the cyclic form are important to an understanding of the pyrolysis process. Direct observation of the gas-phase reactions of c-$C_3H_3^+$ with conjugated dienes has been accomplished using Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). This technique permits the determination of both the product distribution and the reaction threshold for these reactions.

32 GAS-PHASE ION-MOLECULE REACTIONS OF METHYL TERT-BUTYL ETHER. Scott Peterman and Curtiss D. Hanson, Department of Chemistry, University of Northern Iowa, Cedar Falls, IA 50614-0423.

Methyl tert-butyl ether (MTBE) has recently been introduced as an additive used to increase the octane rating of fuels. MTBE, a petroleum-based non-renewable hydrocarbon has recently been implicated in causing health problems in Alaska and its environmental fate has not been adequately addressed. The environmental impact of MTBE is further complicated by secondary by-products formed by its vapor phase chemistry. Secondary products formed from uncombusted fuel and MTBE in the gas-phase can potentially result in the production of unknown compounds, that if released into the atomosphere unnoticed and without proper identification might cause a great concern to the air pollution in the future. To address the potential impact of the secondary by-products formed from the gas-phase reactions of MTBE, the ion-molecle reactions of MTBE and its reactive fragments have been studied by Fourier transform ion-cyclotron-resonance mass spectrometry.

94:021

27 STUDY OF DYES ADSORPTION ON ADJU-PHOS AND SURFACE CHARACTERIZATION WITH RESONANCE RAMAN SPECTROSCOPY. Heping Wang and Patricia M. Callahan Department of Chemistry, University of MIssouri-Rolla, Rolla, MO 65401

Mineral vaccine adjuvant's surface property is dependent on environmental conditions. By detecting resonance Raman scattering signals from the adsorbed dye molecules, adjuvant's surface property and its interaction with adsorbed species can be measured. The point of zero charge (PZC) of Adju-Phos an amorpors aluminum phosphate adjuvant, is determined. Surface modification by changing environment, such as pH and ionic strength, were also observed. Adju-Phos surface dissociation model is proposed and the distribution of surface electric potential is discussed.

28 ASSESSMENT AND MONITORING OF THE DEGRADATIVE PRODUCTS OF PETROLEUM HYDROCARBONS IN DIESEL FUEL. Lenore M Koczon, Susan Landon-Arnold and Alan Randa Northern State University, Department of Mathematics and Natural Sciences, Aberdeen, South Dakota 57401.

One of the most significant ground water quality problems in South Dakota is the contamination of public supply wells from accidental releases of chemicals and petroleum Subsurface contaminated soil can serve as a source of ground water contamination as desorption of organic contaminants occurs. Biodegradation of hydrocarbons by natural populations of microorganisms represents one of the primary mechanisms by which these pollutants are eliminated from the environment The initial stage of this research was to test in vitro biodegradative capabilities of indigenous microorganisms using a slurry cascade Assessment of the degree of degradation was monitored using GC/FID analysis. The data from these experiments suggest that as a plug of contaminated soil moves through the cascade recalcitrant components of the fuel are degraded

29 ANALYSIS OF HYDROXYPROPYL-β-CYCLODEXTRINS FROM SEPARATE SOURCES. Gregory A. Turner,* Timothy B. Skinner and Evelyn A. Murrill. Midwest Research Institute, Kansas City, Missouri, 64110.

Cyclodextrins and their chemically modified derivatives have been the subject of numerous investigations. Their use has included the area of enzyme modeling and mimetics, in complexation chemistry, as chromatographic stationary phases and enantioselective agents, and as food and drug additives and excipients. Hydroxypropyl-β-cyclodextrin (HP-β-CD) is of considerable interest as a agent for use in drug delivery. This material is normally comprised of a mixture of partially derivatized species. Analysis of HP-β-CDs from different sources in our laboratory was performed to establish their equivalency as drug excipients for regulatory purposes. Elemental, HPLC, NMR, and mass analyses of the native and derivatized HP-β-CDs revealed subtle differences in the samples. The utility of these methods will be presented.

30 TWO HPLC METHODS FOR THE ANALYSIS OF PENTAAZAPENTACOSANE. Gregory A. Turner,* Timothy B. Skinner and Evelyn A. Murrill. Midwest Research Institute, Kansas City, Missouri, 64110.

Pentaazapentacosane (1,19-*bis*-(ethylamino)-5,10,15-triazanonadecane, BE-4-4-4-4, BE-4x4), a synthetic aliphatic polyamine analog, is being developed as a potential antineoplastic agent, with selective activity against brain tumors, by the National Cancer Institute. The analysis of BE-4x4 is complicated by its high polarity and lack of UV chromophores. Two stability indicating HPLC methods have been developed and validated for the analysis of BE-4x4. An ion-paired C18 reverse-phase system with refractive index detection is suitable for assay and purity analyses of the bulk compound. An alternate method utilizes trifluoroacetic acid as a volatile pairing agent, on a PRP-1 polymeric column equipped with evaporative light scattering detection (ELSD). The latter method offers superior sensitivity (< 0.01 mg/mL) and is particularly suitable for the ongoing stability and other developmental analyses for this compound. Stability results and the response characteristics of the ELSD for this compound will be presented.

31 DETERMINATION OF THE REACTION THRESHOLD FOR THE ION-MOLECULE REACTIONS OF CYCLOPROPENYL. Curtiss D. Hanson, Samantha Franck, Michelle D. Hammer, Michaela L. Rich; Department of Chemistry, University of Northern Iowa, Cedar Falls, IA 50614-0423

The $C_3H_3^+$ cation has been extensively studied as a precursor ion to the formation of soot in the pyrolysis of fuels and other hydrocarbons. Studies involving soot nucleation in flames point to an ionic mechanism, versus a neutral free radical mechanism, driving the formation of aromatic hydrocarbons. These studies show that the the $C_3H_3^+$ cation is critical to this transformation. Two forms of $C_3H_3^+$ are observed: i) the propargyl isomer, which has been determined to be highly reactive, and ii) an unreactive cyclopropenyl isomer. Because the cyclopropenyl isomer is the predominate isomer (>90%), reactions of the cyclic form are important to an understanding of the pyrolysis process. Direct observation of the gas-phase reactions of c-$C_3H_3^+$ with conjugated dienes has been accomplished using Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). This technique permits the determination of both the product distribution and the reaction threshold for these reactions.

32 GAS-PHASE ION-MOLECULE REACTIONS OF METHYL TERT-BUTYL ETHER. Scott Peterman and Curtiss D. Hanson, Department of Chemistry, University of Northern Iowa, Cedar Falls, IA 50614-0423.

Methyl tert-butyl ether (MTBE) has recently been introduced as an additive used to increase the octane rating of fuels. MTBE, a petroleum-based non-renewable hydrocarbon has recently been implicated in causing health problems in Alaska and its environmental fate has not been adequately addressed. The environmental impact of MTBE is further complicated by secondary by-products formed by its vapor phase chemistry. Secondary products formed from uncombusted fuel and MTBE in the gas-phase can potentially result in the production of unknown compounds, that if released into the atomosphere unnoticed and without proper identification might cause a great concern to the air pollution in the future. To address the potential impact of the secondary by-products formed from the gas-phase reactions of MTBE, the ion-molecle reactions of MTBE and its reactive fragments have been studied by fourier transform ion-cyclotron-resonance mass spectrometry.