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13. ABSTRACT (Maximum 200 words)

The effect of inorganic species alone and on organic reactions at hydrothermal conditions was being investigated. The method involves the use of real-time IR spectroscopy in a windowed flow reactor. The specific studies were directed at the water gas shift reaction below the critical temperature of water; the kinetics of decomposition of nickel tetracarbonyl, sodium tetracarbonylcobaltate, and cyclopentadienyl cobalt dicarbonyl at hydrothermal conditions; decarboxylation and defluorination of trifluoroacetate and fluoroform; and the decomposition of an organoazide and sodium azide at hyrothermal conditions.

14. SUBJECT TERMS
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The objective of this program was to advance understanding of hydrothermal reaction mechanisms and kinetics. The application to Army needs is through the demilitarization of chemical agents and explosives by supercritical water oxidation. In such processes a complex mixture of organic and inorganic species are present. As such, there is a need to understand how the reactions of organic species are affected by inorganic components. The work herein is intended to be applied in the heat up stage before the oxidation process begins. All of the research in this report is available in published or manuscript form. Therefore, only abstracts of the work are given here.

I. The Effects of Cations on the Decarboxylation Kinetics of Trifluoroacetate, Cyanoacetate, Propiolate and Malonate Ions

The effect of Group 1 counter ions on the decarboxylation rate of four carboxylate ions (trifluoroacetate, propiolate, cyanoacetate, and malonate) was determined in water at 140-280°C and 275 bar. The decarboxylation kinetics were determined in real time by using IR spectroscopy and a titanium cell flow-reactor with sapphire windows. The complexity of the reaction of $CF_3CO_2^-$ necessitated additional post-reaction studies by ^1H and ^{19}F NMR spectroscopy and F^- ion electrochemistry. Batch mode reactions in a titanium tube reactor were employed for the latter studies. The CF_3H product of $CF_3CO_2^-$ decomposed liberating F^- ions. The cation effect for $CF_3CO_2^-$ is caused primarily by the reaction of F^- with the Group 1 cations in the order $Li^+ > Na^+ > K^+$.., which changed the ionic strength. The rate of decarboxylation of cyanoacetate was unaffected by the cation, whereas the Li^+ ion slowed the rate of decarboxylation of propiolate, perhaps because of complexation with propiolate. These results were compared with the previously investigated malonate system. Where a cation effect was observed, the effect could be attributed to some form of ion pairing, but in each case the details of the interaction slightly differ.

II. Kinetics of the Surface-Catalyzed Water-Gas Shift Reaction with Inadvertent Formation of $Ni(CO)_4$

The rate constants and Arrhenius parameters for the reaction of CO in H_2O were determined at 230-270°C and 27.4 MPa by the use of a titanium flow reactor with real-time detection by infrared spectroscopy through sapphire windows. These rate measurements appear to be the first below the critical temperature of water. The zeroth-order kinetics model produced an Arrhenius activation energy of 32±3 kcal/mol, which is in the range of previously reported values at higher temperatures, but the pre-exponential factor ln(A, mol kg^{-1} s^{-1}) of 20.5 is much larger. The higher over all reaction rate is consistent with heterogeneous catalysis by the reactor surfaces based on 1) the zeroth-order kinetics, 2) the high A factor; 3) the activation energy in the range of the water-catalyzed reaction; and 4) the previously determined dependence of the decomposition rate of the putative formic acid intermediate on the metal used to construct the cell. Extremely toxic $Ni(CO)_4$ was observed to form as a result of extraction of Ni from slightly corroded 316 stainless steel tubes that connected the cell/reactor to the flow control system. $Ni(CO)_4$ formed at somewhat limited conditions, but its occurrence forewarns of the potential hazard of hydrothermal processing when a high CO concentration might be present in a nickel-containing reaction vessel.

III. Decomposition Reactions and Kinetics of $Ni(CO)_4$, $Co(CO)_4^-$ and $(\eta^5\text{-}C_5H_5)Co(CO)_2$ in High Temperature Water

The decomposition behavior of aqueous $Ni(CO)_4$, $NaCo(CO)_4$ and $(\eta^5\text{-}C_5H_5)Co(CO)_2$ was studied by infrared spectroscopy using a titanium flow reactor with sapphire windows. A pressure of 275 bar was applied to prevent gas-liquid phase separation. $Ni(CO)_4$ was investigated in the 50-270°C range with selected partial pressures of CO in the 0-60 bar range. Without added CO, the Arrhenius parameters were $E_a = 10.4 \pm 1.3$ kcal/mol and $\ln(A, s^{-1}) = 10.4 \pm 1.9$ in the 50-90°C range where a first-order rate law was followed. Complete decomposition took place at 170°C within 23 s. The addition of excess CO raised the decomposition temperature. Aqueous $Ni(CO)_4$ could be detected for at least 5 s at 270°C with a 60 bar partial pressure of CO. The isoelectronic ion $Co(CO)_4^-$ was found to be more stable than $Ni(CO)_4$. Its decomposition was characterized in the 200-240°C range without added CO. A first-order rate law was followed up to 50% decomposition, and yielded $E_a = 29.9 \pm 3.7$ kcal/mol and $\ln(A, s^{-1}) = 25.9 \pm 3.8$. The greater robustness of $Co(CO)_4^-$ compared to $Ni(CO)_4$ is attributable to the strength of the metal-carbon bond. η^5-$C_5H_5)Co(CO)_2$ decomposed in the 220-240°C range to $Co(CO)_4^-$ and a considerable amount of insoluble residue. Decomposition reactions for the three studied metal carbonyls were formulated.

IV. Observation and Kinetics of Alkylazide Decomposition Channels and N_3^- Behavior in Water above 200°C at 275 Bar

The hydrothermolysis of the water-soluble alkyl azide dimethyl-2-azidoethylamine (2-DAMEZ) was studied at 200-250°C and 275 bar in real time by flow reactor FTIR spectroscopy. The kinetics of 2-DAMEZ decomposition and N_3^- formation represent a minor channel (8% at 250°C). The main channel is loss of N_2 whose presence was determined by mass spectrometry. The Arrhenius parameters for decomposition by the two routes are $E_a = 14.1$ kcal/mol and $\ln(A, s^{-1}) = 10.7$ for the N_2 channel, and $E_a = 17.4$ kcal/mol and $\ln(A, s^{-1}) = 11.8$ for the N_3^- channel. Because of further reactions the organic products could not be identified, but $(CH_3)_3N$ appears to be a major product. The N_3^- ion was found to be stable in water at least to 340°C. However hydrolysis of N_3^- to form HN_3 was pH dependent. ΔH values for the reaction were calculated from a van't Hoff plot. It was found that changes in the bulk dielectric constant affect the equilibrium more than do changes in K_w in the 300-340°C range. Ion pairing of NaN_3 and LiN_3 were also spectrally observed.

V. Summary of significant findings

1. Alkyl fluorides release fluoride ions at hydrothermal conditions.

2. Group 1 and 2 ions have a measurable effect on the decarboxylation kinetics of acids, but each acid has it own characteristics.

2. The water-gas shift reaction can take place at far lower temperatures than previously recognized. Since hydrogen is one of the components, embrittlement of metal vessels is possible.

3. The presence of CO in high concentrations can result in its extraction of Ni from alloys and the production of highly toxic nickel tetracarbonyl. This is a well known reaction but had not be recognized before in a hydrothermal reactor.

4. The azide group in an organo azide decomposes by two channels leading to nitrogen and azide ion. The resulting azide ion is stable in solution up to at least 340°C.

VI. Publications

1. T. B. Brill, "Geothermal Vents and Chemical Processing: The Infrared Spectroscopy of Hydrothermal Reactions," J. Phys. Chem. A, **104**, 4343 (2000) (Invited Feature Article).
2. T. B. Brill, D. Miksa, and N. Gunawardena " Spectroscopy Studies of Hydrothermal Reactions of Organic-Inorganic Mixtures" Proc. Joint ISHR&ICSTR, Kochi, Japan, July, 2000. p. 68 (Invited Keynote Lecture)
3. T. B. Brill, "The Infrad Spectroscopy of Hydrothermal Reactions" Proc. Internat. Symp. Solvothermal Reast., Takamatsu, Japan, July,2000 p. 19 (Invited Plenary Lecture).

4. T. B. Brill, A. J. Belsky, D. Miksa and N. Gunawardena, "Hydrothermal Reactions of Simple Molecules by Real-Time IR Spectroscopy," High Press. Res., **20**, 429 (2001) (invited).

5. D. Miksa and T. B. Brill, "Spectroscopy of Hydrothermal Reactions 17. Kinetics of the Water Gas Shift Reaction Below the Critical Temperature and Inadvertent Formation of $Ni(CO)_4$" Ind. Eng. Chem. Res. **40**, 3098 (2001).

6. D. Miksa and T. B. Brill, "Spectroscopy of Hydrothermal Reactions 21. Reactions and Kinetics of $Ni(CO)_4$, $Co(CO)_4^-$ and $(\eta^5\text{-}C_5H_5)Co(CO)_2$ in High Temperature Water," Ind. Eng. Chem. 41, 5151 (2002).

7. D. Miksa, J. Li, and T. B. Brill, "Spectroscopy of Hydrothermal Reactions 22. The Effects of Group 1 Cations on the Decarboxylation Kinetics of Trifluoroacetate, Propiolate, Cyanoacetate, and Malonate, J. Phys. Chem. A, in press.

8. D. Miksa and T. B. Brill "Spectroscopy of Hydrothermal Reactions 25. Kinetics of Alkylazide Decomposition Channels and N_3^- Behavior in Water above 200°C at 275 Bar", J. Phys. Chem. A. submitted.

VII. Participants

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Davide Miksa (Defending Ph.D. dissertation Nov. 6, 2002)

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VIII. Inventions

None