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Hydrogen Generation Study:
Preliminary Evaluation of
Alternatives to Formic Acid**

**R. B. King
N. K. Bhattacharyya
V. Kumar**

February 1996

**Prepared for
the U.S. Department of Energy
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**Pacific Northwest National Laboratory
Richland, Washington 99352**

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Summary

Oxalic, glyoxylic, glycolic, malonic, pyruvic, lactic, levulinic, and citric acids as well as glycine have been evaluated as possible substitutes for formic acid in the preparation of feed for the Hanford waste vitrification plant using a non-radioactive feed simulant UGA-12M1 containing substantial amounts of aluminum and iron oxides as well as nitrate and nitrite at 90°C in the presence of hydrated rhodium trichloride. Unlike formic acid none of these carboxylic acids liberate hydrogen under these conditions and only malonic and citric acids form ammonia. Glyoxylic, glycolic, malonic, pyruvic, lactic, levulinic, and citric acids all appear to have significant reducing properties under the reaction conditions of interest as indicated by the observation of appreciable amounts of N₂O as a reduction product of nitrite or, less likely, nitrate at 90°C. Glyoxylic, pyruvic, and malonic acids all appear to be unstable towards decarboxylation at 90°C in the presence of Al(OH)₃. Among the carboxylic acids investigated in this study the α-hydroxy-carboxylic acids glycolic and lactic acids appear to be the most interesting potential substitutes for formic acid in the feed preparation for the vitrification plant because of their failure to produce hydrogen or ammonia or to undergo decarboxylation under the reaction conditions although they exhibit some reducing properties in feed simulant experiments.

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1.0 Introduction

The most promising method for immobilization of highly radioactive nuclear wastes is a vitrification process in which the wastes are incorporated into borosilicate glass logs and the logs are sealed into welded stainless steel canisters for disposal. The current process under consideration for feed preparation for the vitrification process uses formic acid for glass melt redox and melter feed rheology control. In this connection laboratory and pilot scale studies using formic acid for the pretreatment of simulated nuclear wastes have been carried out both at the Westinghouse Savannah River Laboratory (WSRL) and the Pacific Northwest Laboratory (PNL). Of particular significance was the observation in 1988 at PNL of hydrogen generation during treatment of a Neutralized Current Acid Waste (NCAW) feed simulant with formic acid in a laboratory-scale apparatus.¹ Furthermore, in pilot-scale studies at the Savannah River Laboratory (SRL) in 1990 significant levels (three to four times the lower flammability limit) of hydrogen were observed during preparation of a Defense Waste Processing Facility (DWPF) feed simulant.² A further drawback in the use of formic acid for feed preparation is its apparent tendency to reduce nitrate to ammonia in the presence of noble metals thereby presenting a possible ammonium nitrate hazard in the pretreatment plant operation.

These drawbacks in the use of formic acid for feed preparation for the vitrification process raise the question whether a suitable substitute for formic acid can be found which produces neither hydrogen nor ammonia in nitrite/nitrate noble metal systems under the feed preparation conditions. Other criteria in the selection of a formic acid substitute for feed preparation include the following:

- (1) Acidic properties in order to reduce viscosity at high metal concentrations;
- (2) Reducing properties sufficient to minimize foaming in the melter and to prevent loss of ruthenium as volatile RuO_4 from the melter;
- (3) Minimum hydrocarbon content in order to minimize the presence of deleterious carbon in the glass melter, which could cause phase separation by metal reduction and crystal formation;
- (4) Melting point below room temperature and/or high water solubility in order to facilitate addition in a controlled manner;
- (5) Minimum cost and toxicity.

The criterion for acidic properties leads to the consideration of other carboxylic acids as formic acid alternatives. The criterion of minimum hydrocarbon content is translated into hydrocarbon chains of minimum length in order to impart the necessary chemical reactivity.

Important properties of the carboxylic acids of interest are listed in Table 1. The following aspects of the chemical reactivity of these carboxylic acids have been evaluated:

(1) *Hydrogen and ammonia production in feed simulant media:* The acids were added to the full feed simulant UGA-12M1 (Table 2) at 90°C in the presence of hydrated rhodium trichloride, the catalyst precursor shown to be most effective at generating hydrogen from formic acid.³ The formation of hydrogen was monitored by gas chromatography. The formation of ammonia was determined by analysis of the mixture at the end of the reaction using a microammonia electrode.

(2) *Reducing power:* The formation of N₂O by reduction of the nitrite and/or nitrate upon addition of the acid to the full feed simulant in the experiments designed to measure hydrogen and ammonia production can be taken as an indication of some reducing power of the acid in question. The formation of N₂O was also studied in experiments with limited component NaNO₂/NaNO₃/RhCl₃ systems.

(3) *Stability towards decarboxylation:* Organic acids can undergo decomposition through CO₂ loss (decarboxylation)⁴ according to the following equation:

The decarboxylation of simple hydrocarbon organic acids, such as the straight-chain fatty acids C_nH_{2n+1}CO₂H, requires elevated temperatures but the introduction of electronegative substituents adjacent to the carboxyl group can lower drastically the decarboxylation temperatures. The stability of the acids of interest towards decarboxylation was evaluated by adding the acid at 90°C to an Al(OH)₃ slurry and monitoring the formation of CO₂ by gas chromatography.

2.0 Conclusions and Recommendations

The observations concerning other carboxylic acids as possible substitutes for formic acid in feed preparation for the vitrification of high level nuclear wastes can be summarized as follows:

(1) Formic acid is the only acid found to generate H₂ upon addition to the UGA-12M1 feed simulant containing rhodium (Table 3). Therefore, it appears that substitution of any other acid for formic acid should eliminate the rhodium-catalyzed generation of hydrogen.

(2) Formic, malonic, and citric acids generate small quantities of ammonia from the feed simulant UGA-12M1, which apparently arises from nitrite or nitrate reduction (Table 3). This is a distinct drawback because of the potential hazard of the formation of explosive ammonium nitrate from this ammonia and residual nitrate.

(3) Glyoxylic, glycolic, malonic, pyruvic, lactic, levulinic, and citric acids all appear to have significant reducing properties under the reaction conditions of interest as indicated by the observation of appreciable amounts of N_2O as a reduction product of nitrite or, less likely, nitrate in the experiments with the full feed simulant (Table 3). Experiments with limited component systems (Table 5) suggest that the mechanism for the production of N_2O appears not to be the same for all of these acids. For example, α -hydroxycarboxylic acids such as lactic, glycolic, and citric acids fail to give N_2O in a $NaNO_2/NaNO_3/RhCl_3$ system at $90^\circ C$ in the absence of a solid hydroxide such as $Al(OH)_3$. However, the addition of $Al(OH)_3$ to the $NaNO_2/NaNO_3/RhCl_3$ system at $90^\circ C$ gives N_2O , at least in the case of lactic acid (Table 5).

(4) Glyoxylic, pyruvic, and malonic acids all are unstable with respect to decarboxylation to CO_2 at $90^\circ C$ in a pure $Al(OH)_3$ suspension (Table 6).

(5) Oxalic, glycolic, malonic, and citric acids as well as glycine are all solids at room temperature and thus must be dissolved in water before they can be added to the reactor. A larger volume of liquid thus must be added to introduce a given amount of acid into the reactor.

In evaluating these carboxylic acids as possible substitutes for formic acid in the feed preparation of high level nuclear wastes for the vitrification plant, the tendencies to evolve hydrogen, to produce ammonia, and to undergo decarboxylation at $90^\circ C$ all would appear to be undesirable properties. In addition, reducing properties and low carbon content appear to be desirable from the point of the vitrification process. Among the carboxylic acids investigated the α -hydroxy acids glycolic and lactic acids do not have the undesirable properties of hydrogen formation, ammonia formation, and decarboxylation at $90^\circ C$ but are capable of generating N_2O from nitrite and/or nitrate in the presence of a solid support such as $Al(OH)_3$. These two α -hydroxycarboxylic acids thus appear to be interesting candidates for formic acid substitutes in feed preparation for the vitrification plant. Liquid lactic acid has the advantage over solid glycolic acid in ease of controlled addition to the high level nuclear waste in the feed preparation plant and thus merits more detailed investigation. The γ -keto acid levulinic acid, like glycolic and lactic acid, has the advantages of not forming hydrogen and/or ammonia as well as stability towards decarboxylation. However, the higher carbon content of levulinic acid including a $-CH_2CH_2-$ chain in its structure might be deleterious in the glass melter thereby making it less desirable than glycolic or lactic acid in feed preparation.

This preliminary evaluation of possible alternatives to formic acid in the feed preparation for the waste vitrification plant does not address the behavior of possible alternatives to formic acid in the glass melter. The importance of reducing properties for

the acid used for feed preparation in the vitrification process needs to be assessed in greater detail in model experiments. If reducing properties for formic acid substitutes do not prove to be particularly significant in the glass melter, then inexpensive, non-toxic acids with no problems with hydrogen production, ammonia production, or decarboxylation such as acetic acid can be considered for this application.

Table I
Possible Acids for the Processing of Nuclear Wastes for Vitrification
Plants

Acid ^a	Formula	Molecular Weight	mL required for 1 mole acid, wt% ^b	Acidity (K ₁)	Cost from Aldrich ^g for 3 kg
Formic (l)	HCO ₂ H	46	38(88)	1.8×10^{-4}	\$32
Oxalic (s)	HO ₂ C-CO ₂ H	126 ^c	965(13)	3.8×10^{-2}	\$24
Glyoxylic ^d	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}-\text{C}-\text{CO}_2\text{H} \end{array}$	74	113(50)	4.6×10^{-4}	\$84 (50% aq.)
Glycolic (s)	HO-CH ₂ -CO ₂ H	76	152(50)	1.5×10^{-4}	\$595
Acetic (l)	CH ₃ -CO ₂ H	60	57(100)	1.8×10^{-5}	\$42
Glycine (s)	H ₂ N-CH ₂ -CO ₂ H	75	376(20)	2.3×10^{-3}	\$54
Malonic(s)	HO ₂ C-CH ₂ -CO ₂ H	104	174(60)	1.5×10^{-3}	\$175
Pyruvic (l)	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3-\text{C}-\text{CO}_2\text{H} \end{array}$	88	69(98)	5.6×10^{-3}	\$253
Lactic (l)	$\begin{array}{c} \text{H} \quad \text{OH} \\ \diagdown \quad \diagup \\ \text{C} \\ \diagup \quad \diagdown \\ \text{CH}_3 \quad \text{CO}_2\text{H} \end{array}$	90	119(85)	1.4×10^{-4}	\$39
Butyric (l) ^e	CH ₃ CH ₂ CH ₂ CO ₂ H	88	92(100)	1.5×10^{-5}	\$22
Levulinic (l) ^f	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3-\text{C}-\text{CH}_2\text{CH}_2\text{CO}_2\text{H} \end{array}$	116	102(98)	2.5×10^{-5}	\$136
Citric (s)	$\begin{array}{c} \text{CH}_2\text{CO}_2\text{H} \\ \diagup \\ \text{HO}-\text{C} \\ \diagdown \quad \diagup \\ \text{CO}_2\text{H} \quad \text{CH}_2\text{CO}_2\text{H} \end{array}$	192	318(50)	8.4×10^{-4}	\$81

^a(l) = liquid under ambient conditions; (s) = solid under ambient conditions ^bThis assumes that commercial liquid acids are added without dilution. Solid acids are assumed to be dissolved in a minimum amount of water so that they can be added gradually as liquids to the reactor. The concentration of the aqueous solutions or the purities of the commercially available liquid acids are given in weight percent in parentheses. ^cAs the dihydrate H₂C₂O₄·2H₂O. ^dAvailable commercially as a 50% aqueous solution. ^eButyric acid has a repulsive odor so we have not yet studied it. No reducing properties of butyric acid are anticipated. ^fM.p. 30-33°C. ^g1992-1993 catalog from the Aldrich Chemical Company, Milwaukee, Wisconsin.

Table 2
Composition of the Feed Simulant UGA-12M1

Component ^a	Molarity	Source	Amount ^c	Water solubility ^d
Al	0.226	Al(NO ₃) ₃ ·9H ₂ O	84.8 g	63.7 g/100g @ 25°C
Cd	0.03	Cd(NO ₃) ₂ ·4H ₂ O	9.2 g	215 g/100 g @ 25°C
Fe	0.45	Fe(NO ₃) ₃ ·9H ₂ O	181.8 g	"soluble"
Mn	0.0314	{ KMnO ₄ Mn(NO ₃) ₂ ·6H ₂ O	{ 2.0 g 5.4 g	{ 6.38 g/100 g @ 20°C 426.4 g/100 g @ 0°C
Nd	0.0264	Nd(NO ₃) ₃ ·6H ₂ O	11.6 g	152.9 g/100 g @ 25°C
Ni	0.0392	Ni(NO ₃) ₂ ·6H ₂ O	11.6 g	238.5 g/100 g @ 0°C
Si	0.0854	SiO ₂	5.1 g	insoluble
Zr	0.156	ZrO(NO ₃) ₂ ·6H ₂ O	52.9 g	soluble
Na ⁺	0.801 ^b	Na ₂ CO ₃ + NaNO ₃ + NaNO ₂	see below	see below
CO ₃ ²⁻	0.125	Na ₂ CO ₃	13.2 g	7.1 g./100 g @ 0°C
NO ₃ ⁻	0.116	NaNO ₃	9.9 g	92.1 g/100g @ 25°C
NO ₂ ⁻	0.435	NaNO ₂	30.0 g	81.5 g/100 g @ 15°C

^aThe insoluble components are present as Al(OH)₃, Fe(OH)₃, MnO₂, Nd₂O₃, Ni(OH)₂, SiO₂, ZrO₂.

^bThe nominal Na⁺ concentration in the simulant is 0.88 M because of additional Na⁺ from the NaOH precipitant incompletely washed from the oxide/hydroxide precipitates.

^cAmount of source chemical for a one-liter batch.

^dSolubility data were taken from the 50th Edition of the Handbook of Chemistry and Physics.

3.0 Experimental Approach

3.1 Feed Simulant Experiments

The reactions were conducted in glass reaction vessels of ~550 mL total capacity equipped with a threaded plug and O-ring adapter. A pressure gauge was attached to the system. The three side-arms of the vessel near the top were capped with rubber septa through which needles could be inserted to flush the system or to sample the gas phase. The reaction vessel had two thermocouple wells. A thermocouple attached to a cycle heater was placed in one well to maintain a constant temperature. The other well was used to check the temperature of the reaction mixture independently with a second thermocouple. The reaction mixture was stirred magnetically during the course of the experiment.

In typical experiments a reaction vessel of the above type was charged with 50 mL of the feed simulant or other reaction medium and 10 mL of an aqueous solution of rhodium trichloride trihydrate (1.4 mg/mL). After flushing the mixture with argon, the system was closed and the gas phase analyzed using the system described below. The solution was warmed to the desired reaction temperature (typically 90°C) and kept there using a temperature controller. The acid of interest was then added as a neat liquid or concentrated aqueous solution below the surface of the feed simulant from a 10 mL plastic BD disposable syringe driven by a Sage Instruments Model 355 syringe pump set to deliver ~3.87 mL/hr or ~1.15 mL/hr. The setting on the syringe pump to achieve this rate of addition was checked weekly with pure water. The pressure gauge was used to monitor the pressure buildup from the gases produced during the experiment and to assure the absence of leaks. Pressures in excess of 30 psig were frequently found to cause leakage problems and thus were avoided by limiting the amount of feed simulant used. Gas samples were withdrawn periodically at the reaction temperature using a Pressure-Lok syringe inserted into one of the rubber septa; these samples were analyzed immediately by gas chromatography as indicated below.

A summary of all of the experiments of this type is given in Appendix A. Further details are provided as Supplementary Material.

The limited aqueous solubilities of the solid oxalic, malonic, and glycolic acids as well as glycine made it difficult to introduce these acids in reasonable quantities at reasonable rates in aqueous solutions. For this reason in many experiments with these acids the entire portion of the acid was added to the system before closing the apparatus. Some of the gases, particularly CO₂ produced from carbonate, were therefore lost before the system was closed so that an accurate material balance could not be derived.

3.2 Gas Analyses

Hydrogen analyses were performed using a Varian 90P gas chromatograph. The hydrogen was eluted on an 20cm $\times$ 6 mm column packed with a 40/60 mesh 13 $\times$ molecular sieve material obtained from Varian Corporation. Argon was used as the carrier gas. The column temperature was maintained at 80°C. Carbon monoxide, carbon dioxide, nitrous oxide, and nitric oxide were monitored using a Fisher Model 1200 gas partitioner. The gases were separated on the basis of their size and polarity by means of two columns, a 2m 80/100 mesh Columnpak PQ and a 3.3m 13 $\times$ molecular sieve column mounted in series using helium as the carrier gas. The temperatures of both columns were maintained at 50°C. Sensitivity factors were determined from known amounts of pure certified samples of the gases of interest and were rechecked every week. Nitrogen dioxide could not be determined by gas chromatography because of the $\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$ equilibrium.

3.3 Ammonia Analyses

After completion of the treatment of the feed simulants with the acid of interest, the resulting reaction mixture was analyzed for ammonium ion produced by nitrate or nitrite reduction. In this connection a 0.5 mL sample of the reaction mixture was diluted with 0.5 mL of distilled water and then made strongly basic with 1 to 2 drops of 10 N sodium hydroxide in order to convert NH_4^+ to NH_3 . The ammonia concentration was then determined using a MI-740 microammonia obtained from Microelectrodes, Inc., Londonderry, New Hampshire. This electrode is designed to measure ammonia gas and to record the ammonia concentration as millivolts on a standard pH meter; an Orion 290A portable pH meter was used for these studies. The ammonia electrode was calibrated before each analysis using 0.1 N, 0.01 N, and 0.001 N NH_4Cl solutions made basic with 10 N sodium hydroxide.

3.4 Limited Component System Studies

The reducing power of the acids as well as their stabilities towards decarboxylation were studied in limited component systems. The formation of N_2O , which is an indicator of the reducing power of the acid, was studied by titrating a mixture of 1.5 g of NaNO_2 , 0.5g of NaNO_3 , and 10 mL of a 1.4 mg/mL aqueous solution of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ in 50 mL of H_2O with the acid of interest at 90°C. In some experiments the suspensions of $\text{Fe}(\text{OH})_3$ or $\text{Al}(\text{OH})_3$ containing the same concentration of iron or aluminum as in the feed simulant were used instead of pure water in order to evaluate the effects of these solid phases on the reducing power of these acids since previous work showed that these solid phases sometimes affected the reactivity of formic acid. The decarboxylation of organic acids was

studied by using the organic acid to titrate 50 mL of an $\text{Al}(\text{OH})_3$ suspension. This $\text{Al}(\text{OH})_3$ suspension was made by dissolving 8.5 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 50 mL of H_2O and then titrating to a pH of 7-7.5 using 10 M NaOH) to 90°C. The evolution of gases was studied using gas chromatography in the usual manner.

The samples from these limited component systems were also analyzed using ^{13}C nuclear magnetic resonance spectroscopy (NMR).⁵ All the NMR experiments were performed in a Bruker 250 or 300 MHz NMR spectrometer using aqueous solutions with D_2O or CDCl_3 in a capillary tube as an external lock. The solutions were filtered using glass wool prior to the experiment. The number of NMR scans on the sample depended on its concentration. Chemical shifts (designated as δ) are quoted in parts per million (ppm) downfield from tetramethylsilane as an internal standard.

4.0. Results and Discussion

4.1 Feed Simulant Studies

Table 3 summarizes the production of CO_2 , N_2O , H_2 , and NH_3 from the UGA-12M1 feed simulant upon titration with the organic acids of interest at 90°C in the presence of rhodium trichloride. Formic acid is the only acid observed to produce any H_2 under these conditions. Formic, glyoxylic, glycolic, malonic, pyruvic, lactic, levulinic, and citric acids all produced some N_2O indicating some ability to reduce nitrite or nitrate under feed simulant conditions. Excess elemental nitrogen was generated in the reaction with glycine apparently owing to diazotization of the glycine followed by decomposition of the diazonium derivative $[\text{N}_2\text{CH}_2\text{CO}_2\text{H}]^+$ according to the following reaction sequence:

Small amounts of ammonia (≤ 0.5 mmoles) were detected in the reaction mixtures from the experiments using formic, malonic, and citric acids.

Glycolic, lactic, and citric acids were evaluated in more detail as possible alternatives to formic acid in the treatment of wastes in the HWVP plant. In this connection a mixture of 50 mL of the UGA-12M1H feed simulant, 10 mL of water, the noble metal compound, and 85 mmoles of the acid were heated to $90 \pm 1^\circ\text{C}$ for 400 minutes. The entire portion of the solid glycolic and citric acids were added at the beginning of the experiments whereas the liquid lactic acid was added at the reaction temperature using the syringe pump. Studies were done with all three noble metals of interest, namely Rh, Ru, and Pd. The results are summarized in Table 4.

Table 3
Products Formed by Titration of the UGA-12M1 Feed Simulant with
Various Acids at 90°C in the Presence of Rhodium Trichloride

Acid	mmoles CO ₂	mmoles N ₂ O	mmoles NO	mmoles H ₂	mmoles NH ₃
Formic	19.2	6.2	3.4	0.8	0.5
Oxalic	+	0	+	0	
Glyoxylic	32.3	9.5	3.3	0.0	
Glycolic	9.4	2.4	8.7	0.0	0.0
Glycine	+	0.0	0.0†	0.0	
Malonic	19.7	5.2	4.6	0.0	0.4
Pyruvic	45.9	3.5	0.0*	0.0	
Lactic	10.9	4.5	8.9	0.0	0.0
Levulinic	12.6	3.8	3.0	0.0	0.0
Citric	25.3	1.8	2.0	0.0	0.5

+ Substantial CO₂ and/or NO was produced but not measured quantitatively because of losses of some of the gases between the time of addition of the solid acid and closure of the apparatus.

* A maximum of 4.1 mmoles of NO was produced in this experiment but this was all consumed before the end of the experiment.

† 2.9 mmoles of N₂ was also produced in this experiment but no NO.

Table 4
A Comparison of the Gases Produced upon Treatment of the UGA-12M1H
Feed Simulant With Glycolic, Lactic, and Citric Acids

Acid	Noble Metal(mg)	mmol CO ₂	mmol N ₂ O	mmol NO	mmol NH ₃	Final pH
Glycolic	RhCl ₃ ·3H ₂ O(14)	2.3	1.2	10.4	0.0	4.1
Glycolic	"RuCl ₃ ·3H ₂ O"(15)	1.4	1.1	8.3	0.0	4.1
Glycolic	PdCl ₂ (14)	1.6	1.4	5.3	0.0	3.9
Lactic	RhCl ₃ ·3H ₂ O(14)	8.8	2.8	8.6	0.0	3.9
Lactic	"RuCl ₃ ·3H ₂ O"(14)	9.0	3.0	8.3	0.0	4.0
Lactic	PdCl ₂ (14)	8.8	2.6	8.2	0.0	3.8
Citric	RhCl ₃ ·3H ₂ O(14)	15.8	2.9	3.1	0.9	2.3
Citric	"RuCl ₃ ·3H ₂ O"(15)	16.3	3.2	5.5	0.0	2.3
Citric	PdCl ₂ (16)	16.1	2.7	2.5	1.3	3.4

The following points of interest can be noted from the data presented in Table 4:

- (1) All of the acids produce NO from nitrous acid disproportionation according to the equation

- (2) The only acid producing NH_3 is citric acid. The tendency for noble metals to catalyze NH_3 production from citric acid reduction of nitrate or nitrite is $\text{Pd} > \text{Rh} \gg \text{Ru}$.
- (3) The tendency for oxidation of the acid to CO_2 is citric > lactic > glycolic acid.
- (4) The tendency for reduction of nitrite to N_2O is citric $\approx$ lactic > glycolic acid.

4.2 Limited Component Studies of N_2O Formation

Table 5 summarizes the production of N_2O upon titration of a solution of NaNO_2 , NaNO_3 , and $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ in 50 mL of water with the acid of interest. Malonic, pyruvic, and levulinic acids were found to have enough reducing power to produce N_2O in the absence of a solid support. Lactic acid required the presence of $\text{Al}(\text{OH})_3$ in concentrations similar to those found in the feed simulant to give N_2O .

Table 5
Production of N_2O in Limited Component Experiments with
 $\text{NaNO}_2/\text{NaNO}_3/\text{RhCl}_3$ in Water or $\text{Al}(\text{OH})_3$

Acid	mmoles of N_2O
Formic	5.7 in H_2O without NaNO_3
Oxalic	0.0 in H_2O
Glyoxylic	6.8 with $\text{Al}(\text{OH})_3$; 7.1 with $\text{Fe}(\text{OH})_3$
Glycolic	0.0 in H_2O
Malonic	5.8 in H_2O
Pyruvic	1.7 in H_2O
Lactic	0.0 in pure water; 5.1 with $\text{Al}(\text{OH})_3$
Levulinic	3.0 in H_2O
Citric	0.0 in H_2O

4.3 Stability of Carboxylic Acids Towards Decarboxylation

The stabilities of the carboxylic acids towards decarboxylation under the reaction conditions of interest were evaluated by titrating a 0.45 M $\text{Al}(\text{OH})_3$ suspension with the carboxylic acid of interest at 90°C (Table 6). Acids with a carbonyl group directly linked to the carboxyl group (e.g., glyoxylic and pyruvic acids) as well as malonic acid with an electronegative HO_2CCH_2- group directly linked to the carboxyl group showed the greatest instability towards decarboxylation.

Table 6
Stability of the Carboxylic Acids Towards Decarboxylation in an $\text{Al}(\text{OH})_3$
Suspension at 90°C

Acid	mmoles of CO_2
Oxalic	+
Glyoxylic	2.2
Glycolic	0.0
Glycine	+
Malonic	15.1
Pyruvic	14.1
Lactic	0.2
Levulinic	0.0
Citric	0.0

+ Substantial CO_2 was produced but not measured quantitatively because of losses of some of the gases between the time of addition of the solid acid and closure of the apparatus.

4.4 Carbon-13 NMR Studies

Carbon-13 NMR spectroscopy⁵ was investigated as an analytical method for identifying the non-volatile organic degradation products obtained from reactions of the carboxylic acids of interest in the aqueous media used for these experiments. The carbon-13 NMR data that have been obtained to date are summarized in Table 7. The following points are of interest:

- (1) In the aqueous media studied the non-carboxylic carbonyl groups in glyoxylic acid and acetaldehyde appear to undergo essentially complete hydration to $\text{C}(\text{OH})_2$ groups. For example, a resonance at δ 88.7 from the sp^3 carbon of a $\text{HC}(\text{OH})_2-$ group is observed in glycolic acid but no resonance around δ 200 from the sp^2 carbon of a $\text{HC}(\text{=O})-$ group.

(2) The carbon-13 NMR data (Table 6) suggest that reaction of glyoxylic acid with a mixture of $\text{Al}(\text{OH})_3$, NaNO_2 , and NaNO_3 produces glycolic, acetic, and oxalic acids.

Table 7
Carbon-13 NMR Data on Carboxylic Acids in Aqueous Solution

Acid	Condition	$-\text{CH}(\text{OH})_n$	$-\text{CH}_2-$	$-\text{CH}_3$	$>\text{C}=\text{O}$	$-\text{CO}_2\text{H}$
Formic	pure					169.2
Oxalic	pure					164.8
Oxalic	with $\text{Al}(\text{OH})_3$					164.5, 167.8
Glyoxylic	pure	88.7				175.3
Glyoxylic	with $\text{Al}(\text{OH})_3$	88.7				175.7
Glyoxylic	$\text{Al}(\text{OH})_3/\text{NO}_2^-/\text{NO}_3^-/\text{Rh}$	89.3	62.1	22.9		167.8, 169.1, 176.9, 179.3
Glycolic	pure		61.7			178.7
Acetic	pure			22.8		178.9
CH_3CHO	pure	100.5		22.9		
Malonic	pure		43.0			173.5
Malonic	$\text{NO}_2^-/\text{NO}_3^-/\text{Rh}$		43.2			176.3, 168.1
Pyruvic	pure			27.9	197.3	164.3
Lactic	pure	69.0		21.9		180.5
Lactic	$\text{Al}(\text{OH})_3/\text{NO}_2^-/\text{NO}_3^-/\text{Rh}$	69.1, 71.6		21.2		178.4, 182.4
Levulinic	pure		31.6, 40.1	31.1	212.0	179.7
Levulinic	$\text{Al}(\text{OH})_3/\text{NO}_2^-/\text{NO}_3^-/\text{Rh}$		31.6, 40.5	31.1	216	180.7

* Chemical shifts of the indicated carbon atoms are given as ppm relative to internal $(\text{CH}_3)_4\text{Si}$ (δ).

5.0 Literature References

- (1) K. D. Wiemers, *Evaluation of Process Off-Gases Released During the Forming of Simulated HWVP Feed*, presented at the American Institute of Chemical Engineers 1988 Summer National Meeting, Denver, Colorado, August, 1988.

- (2) N. D. Hutson, *Integrated DWPF Melter System (IDMS) Campaign Report*, Hanford Waste Vitriification Plant (HWVP) Process Demonstration, WSRC-TR-0403, Rev. O, UC-721.
 - (3) King, R. B.; King, A. D., Jr.; Bhattacharyya, N. K.; King, C. M.; Landon, L. F., results presented at the Symposium on *Chemical Pretreatment of Nuclear Wastes for Disposal* held in conjunction with the Fall 1992 National Meeting of the American Chemical Society, Washington, D. C., August, 1992, abstract I&EC 0119; symposium volume in press (eds., Schulz, W. W.; Horwitz, E. P., Plenum, New York).
 - (4) Clark, L. W., *The Decarboxylation Reaction*, in *The Chemistry of Carboxylic Acids and Esters*, Patai, S., ed., Interscience, 1969, pp 589-622.
 - (5) Levy, G. C., ed., *Topics in Carbon-13 NMR Spectroscopy*, Wiley, New York, 1984.
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Appendix A **Summary of Experiments Discussed in this Report***

Acid	mmoles	Reaction	Date	mmoles CO ₂	mmoles N ₂ O	mmoles NO†	mmoles H ₂	mmoles NH ₃
Glyoxylic	87	UGA-12M1	7/14/93	32.3	9.5	3.3(4.1)	0.0	
Glyoxylic	85	RhCl ₃ /NaNO ₂ /NaNO ₃	7/27/93	12.4	6.5	4.5	0.0	
Glyoxylic	86	Al(OH) ₃ /RhCl ₃ /NaNO ₂ /NaNO ₃	7/28/93	19.6	6.8	4.0(6.3)	0.0	
Glyoxylic	90	Fe(OH) ₃ /RhCl ₃ /NaNO ₂ /NaNO ₃	7/29/93	20.7	7.1	3.8	0.0	
Glyoxylic	86	Al(OH) ₃	8/6/93	2.2	0.0	0.0	0.0	
Glycolic	85	UGA-12M1	8/31/93	9.3	2.4		0.0	
Glycolic	85	RhCl ₃ /NaNO ₂ /NaNO ₃	7/8/93	0.0	0.0	13.5	0.0	
Glycolic	85	Al(OH) ₃	9/9/93	0.0	0.0	0.0	0.0	
Glycolic	85	UGA-12M1/PdCl ₂	9/28/93	1.6	1.4	5.3(7.3)	0.0	0.0
Glycolic	85	UGA-12M1/RuCl ₃	9/29/93	1.4	1.1	8.3(10.0)	0.0	0.0
Glycolic	85	UGA-12M1/RhCl ₃	9/30/93	2.4	1.2	10.4(13.4)	0.0	0.0
Malonic	45	UGA-12M1	8/24/93	19.7	5.2	4.6	0.0	
Malonic	45	RhCl ₃ /NaNO ₂ /NaNO ₃	8/25/93	19.6	5.8	4.6(5.0)	0.0	
Malonic	43	Al(OH) ₃	8/26/93	15.1	1.9	0.0	0.0	
Pyruvic	85	UGA-12M1	7/13/93	45.9	3.5	0.0(4.1)	0.0	
Pyruvic	88	RhCl ₃ /NaNO ₂ /NaNO ₃	8/20/93	9.2	1.7	10.1(13.1)	0.0	
Pyruvic	86	Al(OH) ₃	8/5/93	14.1	0.0	0.0	0.0	
Lactic	89	UGA-12M1	2/24/93	11.0	4.4	8.9(9.3)	0.0	
Lactic	81	Al(OH) ₃ /RhCl ₃ /NaNO ₂ /NaNO ₃	7/23/93	0.0	5.1	9.8(10.5)	0.0	
Lactic	75	Al(OH) ₃	8/10/93	0.2	0.0	0.0	0.0	
Lactic	85	UGA-12M1/PdCl ₂	9/22/93	8.8	2.6	8.3(9.0)	0.0	0.0

Acid	mmoles	Reaction	Date	mmoles CO ₂	mmoles N ₂ O	mmoles NO	mmoles H ₂	mmoles NH ₃
Lactic	85	UGA-12M1/RuCl ₃	9/23/93	9.0	3.0	8.3(8.7)	0.0	0.0
Lactic	85	UGA-12M1/RhCl ₃	9/24/93	8.8	2.8	8.6(8.8)	0.0	0.0
Levulinic	88	UGA-12M1	8/11/93	12.6	3.8	3.0(3.4)	0.0	
Levulinic	80	RhCl ₃ /NaNO ₂ /NaNO ₃	8/19/93	5.6	3.0	6.7(7.1)	0.0	
Levulinic	85	Al(OH) ₃	8/18/93	0.0	0.0	0.0	0.0	
Citric	28	UGA-12M1	8/12/93	25.3	1.8		0.0	
Citric	28	Al(OH) ₃	8/17/93	0.0	0.0	0.0	0.0	
Citric	85	UGA-12M1/RhCl ₃	9/16/93	15.8	3.0	3.1(7.7)	0.0	0.9
Citric	85	UGA-12M1/PdCl ₂	9/17/93	16.1	2.7	2.5(6.2)	0.0	1.3
Citric	85	UGA-12M1/RuCl ₃	9/21/93	16.3	3.2	5.5(7.0)	0.0	0.1

*All of these experiments were performed at 90°C. The indicated compositions are those found at the end of the reaction period. See the Experimental Section for a detailed discussion of the reaction conditions and experimental methods.

†The maximum amount of NO is given in parentheses.