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ORGANIC MOLECULES ON METEORITIC SOLID SUBSTRATES

FINAL REPORT

MICHAEL A. SWEENEY

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SANTA CLARA UNIVERSITY
SANTA CLARA, CA
95053

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THE PRODUCTION OF CARBOXYLIC ACIDS VIA THE RADIOLYSIS OF CARBON DIOXIDE AND ALKANE SOLUTIONS

Louis Leos & Michael A. Sweeney

ABSTRACT: The production of C_1-C_3 monocarboxylic acids was investigated by the radiolysis of air-free CO_2 and alkane solutions, utilizing a ^{137}Cs γ-ray source. Samples were first loaded on a vacuum system, irradiated, and then analyzed by the Hewlett Packard model 5890A gas chromatograph. Moreover, the samples were irradiated with and without added ferrous ion.

INTRODUCTION

Carbonaceous chondrites are meteoritic stones embedded with granules abundant in carbon compounds. The organic matter of these particles has been categorized into three separate classes: 1) organic polymers, insoluble in either chloroform or methanol 2) hydrocarbons, soluble in chloroform, and 3) polar organics, soluble in methanol. Isotopic studies in 1982 showed that the methanol soluble organics and the methanol insoluble organic polymers had separate and unique origins (1,2). Studies of the insoluble organic polymer fraction suggest that its formation took place either prior to or during meteoritic development (3,4). As for the soluble hydrocarbons, the accepted hypothesis is that they were synthesized by a Fischer-Tropsch mechanism (5).

Proposals as to the origin of the polar organics, which include the monocarboxylic acids and the amino acids, take into account a recent investigation by Yuen et al. of monocarboxylic acid ^{13}C to ^{12}C ratios (6). This study concluded that as carbon number increases, the decrease in the ^{13}C to ^{12}C ratio is analogous for both the soluble hydrocarbons found on carbonaceous chondrites and the monocarboxylic acids, except that the monocarboxylic acids are richer in ^{13}C. Subsequently, "since the carbonate found on the carbonaceous chondrites is heavier than the hydrocarbons, the simplest hypothesis would be that the CO_2 from the carbonate is added on to the hydrocarbon backbone by some reaction" (7). Furthermore, Hartman at MIT and colleagues have proposed that the polar organics were synthesized during outgassing of the meteors (7), the interiors of which are expected to have contained CO_2, CO, N_2 and NH_3 dissolved in an aqueous medium (8,9). The energy needed for such reactions could have come from radioactive decay, especially from species within the meteors (10).

The conversion of ammonium carbonate into simple amino acids via γ-radiation has been reported by Paschke et al. (11), and more recently by Hartman et al. (7). The present paper focuses on the second component of the polar organics, the monocarboxylic acids.

It has been shown by Garrison et al., in 1951, that CO_2 can be reduced to formic acid upon irradiation of air-free CO_2 solutions, and that in the presence of ferrous ion the yield of product is enhanced (12). In 1960, Getoff, Scholes and Weiss experimentally corroborated these results, and observed that the ferrous ion may protect any formed products from back reaction with any radiation-produced active species by reacting with these species and becoming oxidized to the ferric ion (13). More recently, Kuklin et al. have demonstrated that acetic, formic and propionic acids are the principal products from CO and CH gaseous mixtures exposed to 1MeV electrons (14). Following a similar path, Kurbanov et al. have primarily formed acetic acid along with traces of formic and propionic acids by (γ,n) radiolysis of CH_4 and CO_2 systems (15).

In our investigation, the radiolysis of CO_2 and hydrocarbons was conducted, and the subsequent problems that were encountered in the analysis for monocarboxylic acids is reported herein.

RESULTS AND DISCUSSION

Before irradiation of the solutions, it was observed that sample numbers 40 & 71 contained a brown precipitate and had a yellowish tint. Kropp (16) showed similar findings in solutions of ammonium carbonate and ferrous sulfate that were about to be irradiated. He attributed this phenomenon to the ferrous and/or ferric ions present, but he didn't show that this causes any adverse effects. Sample number 71 was opened and analyzed for any premature Fe(II) oxidation to Fe(III), but results were negative. A new ampule was loaded with identical make-up as the opened sample, and was designated as sample number 71 also.

Difficulty due to the response of the columns to monocarboxylic acids was encountered. The problems observed are discussed separately and include: adsorption, ghosting of peaks, multiple peaks for acetic acid, difficulty with the aqueous phase, and lack of reproducibility. It must be stated that more extensive reviews on the sources of error in GC analysis of simple monocarboxylic acids exist in the literature, including that of Cochrane (17) and Van Eenaeme et al. (18).

The problems of adsorption and ghosting are closely linked, in that adsorption causes the ghosting of peaks. Secondarily, adsorption generally gives rise to irregular shaped peaks and tailing of peaks. Adsorption occurs when the injected acid sample adheres onto the GC column support material. Subsequently, when this adsorbed acid is eluted by a sufficiently more polar sample, a "ghost" peak is recorded. This can lend uncertainty to many peaks, and is also why the knowledge of a sequence of injections is paramount.

Figures 1, 2 & 3 illustrate the problem of adsorption and its ghosting effect; a Porpak QS packed glass column was used. Figure 1 is a chromatogram of a 1:1 (v/v) neat mixture of acetic and propionic acids (Rt= 1.00min and 2.16min respectively). Figures 2 & 3 show subsequent and consecutive elutions of the acid peaks by injections of the more polar formic acid (injected neat). Ghost peaks were seen for acetic acid in both figures 2 & 3 (Rt= 1.15min and 1.16min respectively), while a propionic acid ghost peak was only observed in figure 2 (Rt= 2.38min). It should be pointed out that a flame ionization detector (FID), which was used throughout all analyses, does not respond to formic acid.

Based on this fact, in 1963 Ackman and Burgher (19) developed an analytical method t overcome any difficulties associated with adsorption. Their supposition was that since formic acid is the strongest acid of the simple monocarboxylic acids (ie., formic acid has a greater dissociation constant), it would strongly bind to any adsorption sites present on the column support material and thus prevent the C_2-C_6 acids from becoming adsorbed. Experimentally, they made the carrier gas, helium, polar by passing it over concentrated formic acid before allowing it to enter the column. Analysis of the C_2 -C_6 monocarboxylic acids carried out in this continually polar atmosphere resulted in symmetrical peaks without ghosting. Both Van Eenaeme et al, (18) and Cochrane (17,20) have confirmed this technique, using both nitrogen and helium as the carrier gas.

Cochrane (17) has also reported a second method for eliminating adsorption. It entails the injection of aqueous formic acid solution (50%, v/v) in between sample injections. However, the ghosting effect could not be completely eliminated. This second method was carried out in the present investigation, with the modification of injecting formic acid neat in between sample injections. Unfortunately, results could not be reproduced, as the response of the acids varied from injection to injection. Accordingly, Van Eenaeme et al. (18) found ghosting to be worse for acetic and propionic acids compared to any higher acids. Cochrane (17) as well has reported that at concentrations lower than 1000ppm, problems of ghosting and tailing increase dramatically if formic acid isn't used in the carrier gas.

Early work on the phenomenon of ghosting by Smith and Gosnell (21), later to be corroborated by Geddes and Gilmour (22), showed that adsorption of C_2-C_6 acids on the glass wool plug and on carbonaceous deposits in the injection port was a major problem, and a leading cause of excessive tailing and ghosting. Smith and Gosnell (21) found that frequent cleaning of the injection port chamber reduced adsorption, whereas Geddes and Gilmour (22) overcame any adsorption problems through the introduction of formic acid vapor into the carrier gas, thereby also confirming the earlier work of Ackman and Burgher (19). In addition, Ottenstein and Bartley (23) have reported the outstanding merits of coating the glass wool plug with H_3PO_4 to minimize adsorption. Only the cleansing of the injection port and the replacement of the septum was undertaken in the present investigation, which resulted in a minimal decrease in adsorption.

Problems were also encountered when analyzing acetic acid in the aqueous phase, including that of replication. This difficulty has also been experience by Kaplanová and Janák (24) in their review of the separation of monocarboxylic acids in aqueous solution. Figures 4, 5 & 6 are chromatograms of acetic acid neat, 10^{-2} M standard, and 10^{-4} M standard respectively; a methyl silicone capillary column was used. Figures 5 & 6 each show a triple peak characteristic for acetic acid in the aqueous phase. Ackman and Burgher (19) occasionally observed two peaks for acetic acid, which appeared to depend upon the amount of water present in the injected sample.

An interesting and possibly related sidenote is an occurrence reported by Wills (25). He found that the FID response to a constant amount of acetic acid decreases with the increase of water present in the sample. This was attributed to the water-acetic acid hydrate (figure 7b), which wasn't detected. If this water-acetic acid hydrate was detected and responsible for the double peak formation noted by Ackman and Burgher (19), then perhaps the triple peak phenomenon shown in figures 5 & 6 is directly linked. The species that may account for these peaks are shown in figure 7. Speculation as to the third peak may include, among other reasons, the behavior of aqueous acetic acid in the particular capillary column utilized, or the fact that species 7a and 7b diverged into two separate peaks.

When injections of water followed an injection of acetic acid neat, the familiar three peak pattern was again observed. The chromatograms labelled as figures 8, 9 & 10 were obtained on the same capillary column, and exemplify this comportment; the difference in Rt values between figures 5 & 6 and 8, 9 & 10 emphasizes the problem of reproducibility encountered from day to day analysis. The elution of adsorbed acetic acid by water in this fashion may give further credence to the hydrate theory postulated above. No further investigation was made into this phenomenon.

Unfortunately, analysis was attempted for only sample 18 because of the problems already specified. Difficulty was experienced in duplicating any chromatogram characteristic of the sample's component. As part of the analysis, extractions of sample number 18, acetic acid neat and 10^{-2} M acetic acid standard with anhydrous ethyl ether were carried out; the capillary column was used again.

Chromatograms of the ether layers from sample number 18 and acetic acid neat (figures 11 & 13 respectively), resemble one another closely. The extracted aqueous layer for sample number 18 (figure 12) showed four peaks (0.87min, 1.29min, 2.01min and 2.37min), whereas the aqueous layer for acetic acid neat showed only one major peak (1.76min, figure 14). One could try to make a case that the double peak phenomenon previously discussed is actually observed in figure 12 at 2.01min and 2.37min, but this assertion needs more supportive and reproducible data to gain validity.

When 10^{-2} M acetic acid standard and acetic acid neat were extracted and compared, the ether layers of both matched up nicely (figures 15 & 17 respectively). Two peaks were observed in the 10^{-2} M acetic acid standard aqueous layer (2.08min and 2.47min, figure 16), while the corresponding aqueous layer of acetic acid neat furnished a single peak (3.07min, figure 18). An interesting observation is that both figures 12 & 16 show two peaks with similar retention times, the first around two minutes and the second close to two and a half minutes. Although this is certainly not conclusive evidence of any kind, optimistically one could say that the possibility of acetic acid present in sample number 18 gained a bit of corroboration by way of this observation. Further investigation is warranted before any conclusions can be drawn.

EXPERIMENTAL

Water obtained from NASA Ames Research Center (Mountain View, Calif.), purified by ion exchange, active charcoal and reverse osmosis, was de-aerated by the freeze-pump-thaw method on a vacuum system utilizing a General Electric model 1402 vacuum pump. Ferrous sulfate heptahydrate (MCB, A.C.S. reagent grade) was weighed into borosilicate glass ampules, and de-aerated water was then distilled under vacuum into these containers. Methane, ethane and CO_2 (all Mattheson, research grade) were likewise distilled into the ampules. Since CO_2 is readily soluble in water, only low pressures of around 30 torr were needed in order to load this gas. With methane and ethane however, pressures close to 1 atm. were utilized. The ampules were then sealed and weighed. A diaphragm gauge (Mattheson, type 316) along with thermocouple and discharge vacuum gauges (Consolidated Vacuum Corp., type GTC-100 and GPH-100C respectively) were used to obtain all pressure values.

$FeSO_4 \cdot 7H_2O$ weights of 0.0556 gms. and 0.0111 gms., along with sample volumes of 20 ml were planned initially. This would give 0.01 M and 0.002 M ferrous sulfate respectively. But the amount of water distilled into the ampules varied roughly between 10 ml and 20 ml, and so the actual ferrous sulfate concentrations were slightly different than those planned initially. It is interesting to note that two samples were found to be discolored and to contain a brown precipitate (sample numbers 40 and 71). Both had the greatest concentration of ferrous sulfate; this concentration was about 0.02M, twice the amount that was initially considered to be used. Table I shows the contents of each sample.

All samples were irradiated in a 4500 curie (1.7E+14 Becquerel) ^{137}Cs source (J. L. Shepherd Mark I, San Jose State University) at a dose rate of 7E+04 Rad/hr. Sample number 18, which was analyzed, received a total exposure of 1.7 MRad.

Analysis was done on the Hewlett Packard model 5890A gas chromatograph fitted with an FID, incorporating helium as the carrier gas and nitrogen as the auxiliary gas. Peak areas were determined by the model 3392A integrator, also from Hewlett Packard. Both packed and capillary columns were used. The

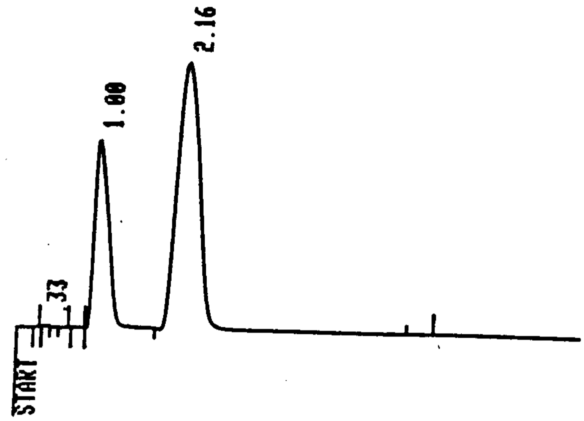

Figure 1. Mixture of 1:1 (v/v) of acetic and propionic acids neat. Attn 2^{21}

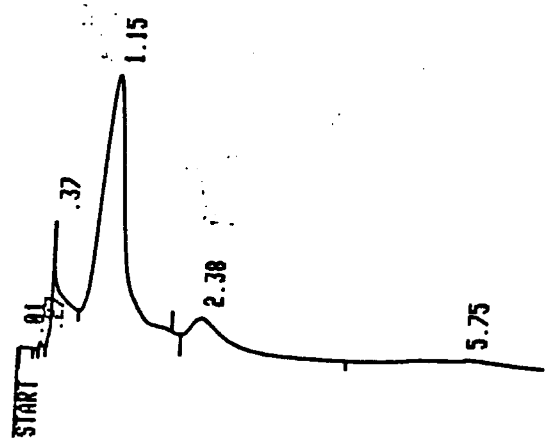

Figure 2. Elution of acetic and propionic acids by formic acid neat injection. Attn 2^{14}

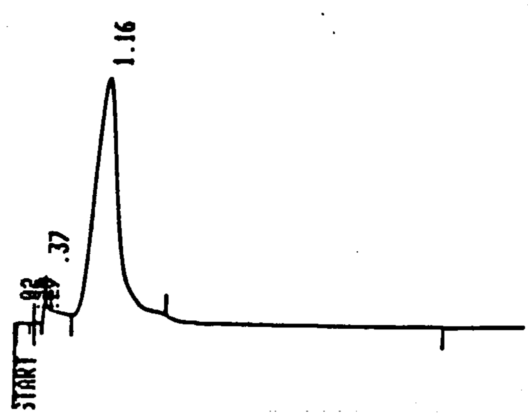

Figure 3. Elution of acetic acid by formic acid neat injection. Attn 2^{14}

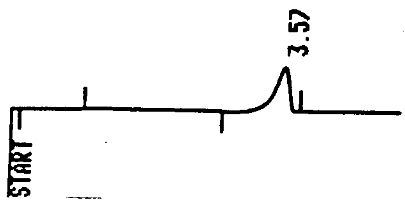

Figure 4. Acetic acid neat.
Attn 2^{18}

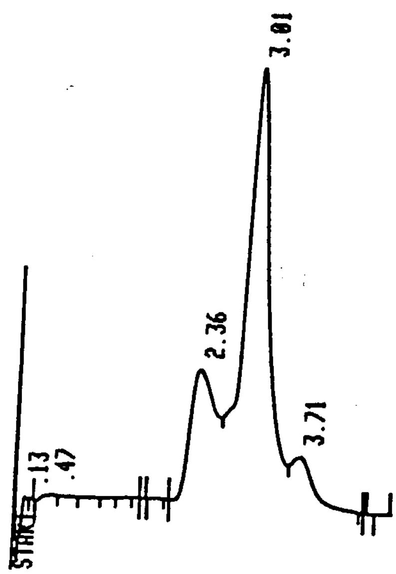

Figure 5. Acetic acid,
.01 M standard, showing
multiple peak characteristic.
Attn 2^{4}

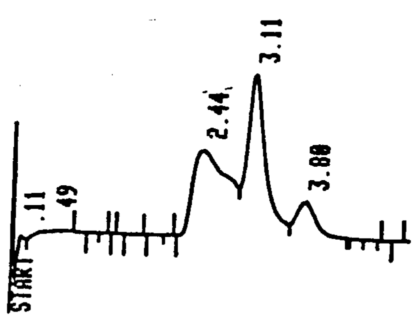

Figure 6. Acetic acid,
10^{-4} M standard, showing
multiple peak characteristic.
Attn 2^{4}

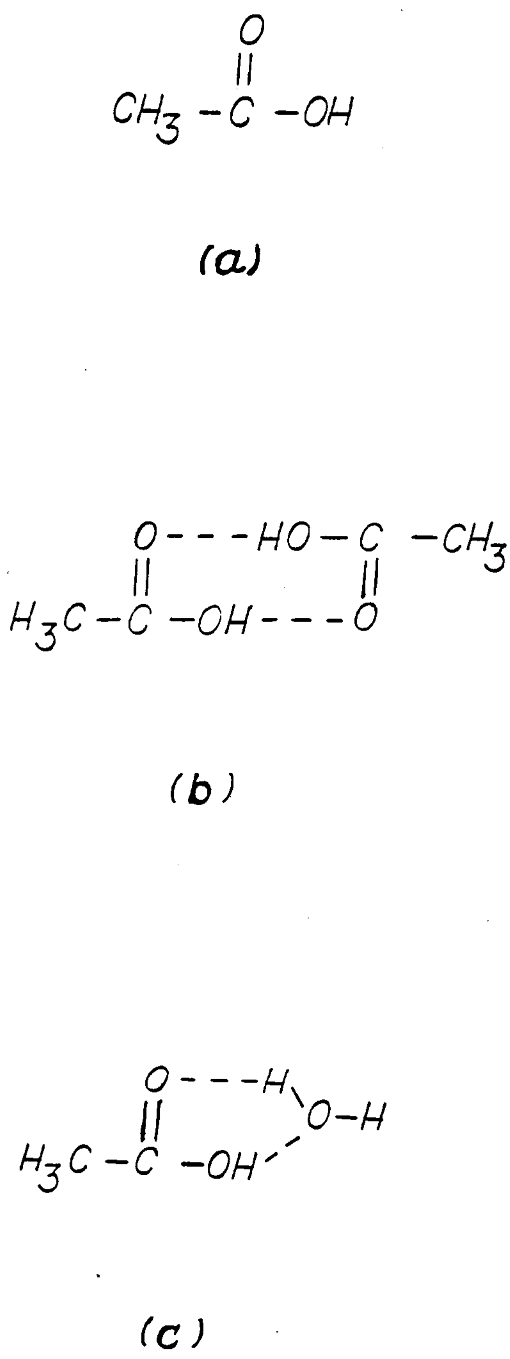

Figure 7.

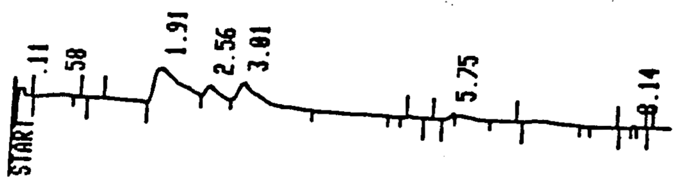

Figure 8. Elution of acetic acid by water. Attn 2^5

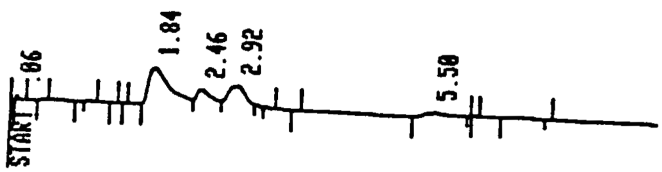

Figure 9. Elution of acetic acid by a second water injection. Attn 2^5

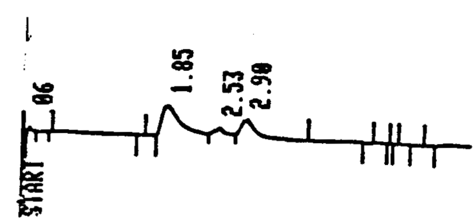

Figure 10. Elution of acetic acid by a third water injection. Attn 2^5

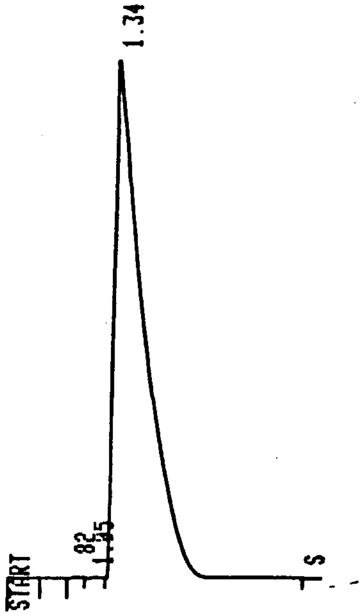

Figure 11. Ether layer from extracted sample number 18. Attn 2^{21}

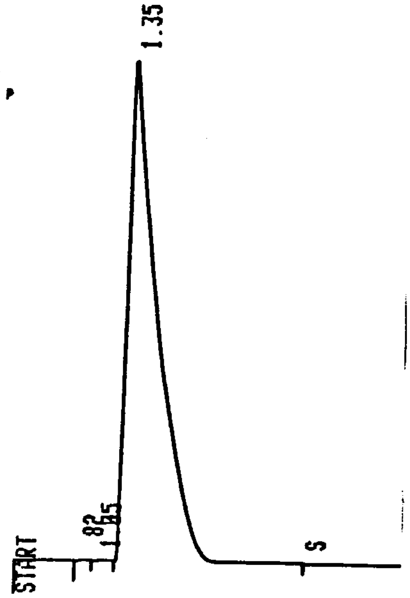

Figure 13. Ether layer from extracted acetic acid neat. Attn 2^{21}

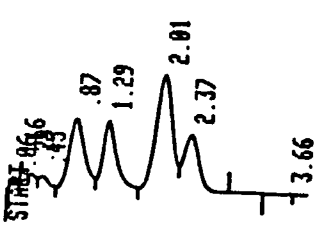

Figure 12. Aqueous layer from extracted sample number 18. Attn 2^{11}

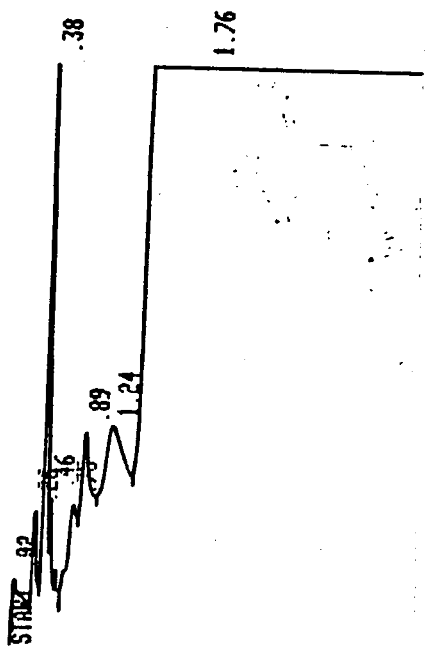

Figure 14. Aqueous layer from extracted acetic acid neat. Attn 2^{5}

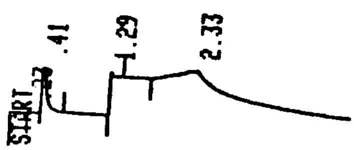

Figure 15. Ether layer from extracted .01 M acetic acid standard. Attn 2^{14}

Figure 17. Ether layer from extracted acetic acid neat. Attn 2^{13}

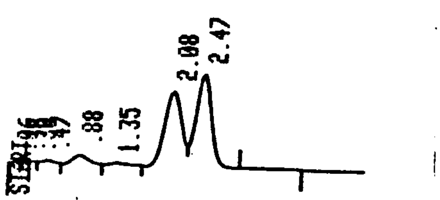

Figure 16. Aqueous layer from extracted .01 M acetic acid standard. Attn 2^{9}

Figure 18. Aqueous layer from extracted acetic acid neat. Attn 2^{15}

—TABLE I—

SAMPLE	CO_2 (mol)	CH_4 (mol)	CH_3CH_3 (mol)	H_2O (ml)	$FeSO_4$ (g.)	approx. Molarity	ppt obs.
18	5E-06	3E-05	—	19.8	.0558	.01	—
34	8E-06	2E-05	—	11.2	.0110	.001	—
35	1E-05	—	—	10.4	—	—	—
36	1E-05	—	—	11.8	.0125	.001	—
37	1E-05	2E-05	—	10.4	—	—	—
40	2E-05	2E-05	—	10.9	.0595	.02	√
71	—	—	—	12.7	.0584	.02	√
74	1E-05	2E-05	NA	13.6	.0114	.001	—

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