

# **Stability of the Caustic-Side Solvent Extraction (CSSX) Process Solvent: Effect of High Nitrite on Solvent Nitration**

**July 2002**

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**STABILITY OF THE CAUSTIC-SIDE SOLVENT EXTRACTION (CSSX) PROCESS  
SOLVENT: EFFECT OF HIGH NITRITE ON SOLVENT NITRATION**

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## EXECUTIVE SUMMARY

### PURPOSE AND BACKGROUND:

The purpose of this investigation was to determine whether nitrated organic compounds could be formed during operation of the Caustic-Side Solvent Extraction (CSSX) process, and whether such compounds would present a safety concern. The CSSX process was developed to remove cesium from alkaline high-level salt waste stored at the U.S. Department of Energy Savannah River Site (SRS). The solvent is composed of the cesium extractant calix[4]arene-bis-(4-*tert*-octylbenzo-crown-6) ("BOBCalixC6"), a fluorinated alcohol phase modifier, tri-*n*-octylamine (TOA), and an isoparaffinic diluent (Isopar® L). During the CSSX process, the solvent is expected to be exposed to high concentrations of nitrate and nitrite dissolved in the alkaline waste feed. The solvent will also be exposed to dilute (50 mM) nitric acid solutions containing low concentrations of nitrite during scrubbing, followed by stripping with 1 mM nitric acid. The solvent is expected to last for one year of plant operation, and the temperatures the solvent may experience during the process could range from as low as 15 °C to as high as 35 °C. Excursions from standard process conditions could result in the solvent experiencing higher temperatures, as well as concentrations of nitrate, nitrite, and most importantly nitric acid, that exceed normal operating conditions. Accordingly, conditions may exist where nitration reactions involving the solvent components, possibly leading to other chemical reactions stemming from nitration reactions, could occur. To model such nitration reactions, the solvent was exposed to the types of nitrate- and nitrite-containing solutions that might be expected to be encountered during the process (even under off-normal conditions), as a function of time, temperature, and concentration of nitrate, nitrite, and nitric acid. The experiments conducted as part of this report were designed to examine the more specific effect that high *nitrite* concentrations could have on forming nitrated organics. The present set of results supplement those obtained from earlier experiments conducted in FY 2001 [1] in which nitration effects due to nitric acid alone and an average nitrite-containing alkaline simulant were examined.

### NITRATION RESULTS UNDER ALKALINE CONDITIONS:

Continuous contact of the CSSX solvent (containing the Cs-7SB modifier at 0.75 M, BOBCalixC6 at 0.007 M, and TOA at 3 mM) with an alkaline simulant approximating the bulk-constituent composition of SRS waste tank 13-H (2.6 M in nitrite and 0.77 M in nitrate) for 26 days at 60 °C revealed no evidence for the formation of nitrated organic, and no noticeable evidence of solvent decomposition. This result is in agreement with FY 2001 studies [1] using an alkaline simulant containing 0.5 M nitrite and the FY 2001 formulation of the CSSX solvent (modifier at 0.50 M, BOBCalixC6 at 0.010 M, and TOA at 1 mM) in which no evidence of nitrated products were observed following continuous contact for 28 days at 61 °C.

### NITRATION RESULTS UNDER ACIDIC CONDITIONS:

Continuous contact of the CSSX solvent with nitric acid solutions (0.01, 0.05, 0.30, and 1.0 M) both with and without added nitrite revealed that minor solvent degradation takes place only under the most severe (off-normal process) conditions. Small amounts of degradation products were observed to accumulate with increasing time of exposure of the solvent to 1 M nitric acid solutions and 60 °C, with



precipitation of a viscous orange oil taking place after 26 days exposure. For one sample, the components of the oil were separated by chromatography and characterized by multi-nuclear NMR and GC/MS. The oil contained about 88-90% unreacted modifier, with the balance mostly comprised of two main degradation products. *These two degradation products were revealed to be non-nitrated ketone derivatives of the modifier, and not nitrated derivatives [1] as previously believed.* The structures consistent with NMR analysis are aromatic ketone derivatives of the modifier in which the *sec*-butyl group was transformed into in one case an acetyl [ $-\text{C}(=\text{O})\text{CH}_3$ ] group, and in the second case, a propionyl [ $-\text{C}(=\text{O})\text{CH}_2\text{CH}_3$ ] group, with the former predominating at about a 2:1 ratio. The fluorinated alcohol portion of the modifier in these ketone derivatives remains intact. The presence of added nitrite does not appear to alter the product outcome, but only slightly increases the yield of the ketone degradation products. *NMR spectroscopy detected no degradation products of any kind for solvents in contact with nitric acid concentrations below 0.3 M at 60 °C, and below 1 M at 36 °C, even after 30 days continuous contact.*

A possible mechanism of formation of these ketone degradation products may include radical reactions involving the reactive benzylic carbon of the modifier [the  $-\text{CH}$  of the *sec*-butyl moiety  $-\text{CH}(\text{CH}_3)(\text{CH}_2\text{CH}_3)$ ] to form nitrated intermediates such as the nitrate ester [ $-\text{CONO}_2(\text{CH}_3)(\text{CH}_2\text{CH}_3)$ ]. Under acidic conditions, one of the oxygens of the nitro group can be protonated to form a positively charged intermediate [2]. A subsequent synchronous reaction in which either the methyl (slightly favored) or the ethyl substituent of the *sec*-butyl moiety migrates to oxygen with concomitant loss of HONO could give rise to cationic species [ $-\text{C}^+\text{OCH}_3(\text{CH}_2\text{CH}_3)$  or  $-\text{C}^+\text{OCH}_2\text{CH}_3(\text{CH}_3)$ ]. Further reaction with the aqueous phase could result in loss of the methoxy or ethoxy group to produce respectively the ethyl [ $-\text{C}(=\text{O})\text{CH}_2\text{CH}_3$ ] or methyl [ $-\text{C}(=\text{O})\text{CH}_3$ ] ketone species. There is some NMR evidence to suggest that a nitrate ester may be present in very small quantities in the oil as an intermediate that does not appear to accumulate.

On the basis of the data obtained, it appears that reaction of the solvent with nitric acid even up to 1 M at 60 °C for a month does not result in the buildup of observable nitrated organics that could pose a safety risk. Overall, about 7–8% of the modifier was observed to decompose under the most severe conditions of 30 days of continuous contact with 1 M nitric acid containing 0.3 M sodium nitrite at 60 °C, with about 90% of the decomposition giving rise to the two ketone derivatives described above. As the nitric acid concentrations are increased, nitration reactions would be expected to become more significant, and nitrated organic products would be expected to become more prevalent in the solvent. However it is now clear that *the formation of nitrated organics under the conditions the solvent is expected to experience during normal plant operations is essentially nonexistent, or at the very least, insignificant.* There appears to be a considerable safety margin with respect to nitric acid and nitrite concentrations; that is, there is no detectable degradation of the solvent at up to 0.3M nitric acid and 0.3 M sodium nitrite at 36 °C.





## 1. INTRODUCTION

As the Caustic-Side Solvent-Extraction (CSSX) process for cesium removal from alkaline high-level waste moves closer to possible implementation at the U.S. Department of Energy's Savannah River Site [1], safety issues for operation of the facility will become increasingly important. Among these safety issues is the potential production of materials arising from degradation of the solvent during plant operation that may pose a fire or explosion risk.

During the operation of the CSSX process, the solvent will be exposed to conditions in which the potential exists to form nitrated organic materials. The conditions include contact with alkaline feeds containing high concentrations of nitrate (up to 3 M) and nitrite (up to 2 M) during extraction operations, and contact with nitric acid solutions, also potentially containing nitrite, during the scrubbing and stripping operations. Nominal flowsheet conditions call for organic to aqueous (O/A) flow ratios of 0.33 on extraction, and 5.0 on both scrubbing and stripping. Since some nitrated organics are unstable and have the potential to explode, from a safety standpoint it is important to understand the kinds of nitrated organics that could be formed under both the normal operating conditions of the process, as well as abnormal conditions (e.g., higher than normal temperatures or nitric acid concentrations) that may arise from an operational error. It will then be necessary to determine whether any of the nitrated organics so formed pose a safety risk with respect to plant operation. It is also of interest to determine to what extent the presence of nitrite influences the extent of nitration of the solvent components.

The work reported herein represents a study of the effect that contacting the solvent both with simulants containing high (up to 2.6 M) levels of sodium nitrite and with solutions containing nitric acid and sodium nitrite at various concentrations has on the possible formation of potentially hazardous nitrated organics. The study examined conditions that the solvent is likely to encounter in the actual process, and also more severe conditions that may be representative of process upset conditions.



## 2. EXPERIMENTAL SECTION

### 2.1 MATERIALS AND SOLUTION PREPARATIONS

The following Nitrogen-15 enriched reagents were purchased from Aldrich Chemical Co. and were used as received without further purification: a) Nitric- $^{15}\text{N}$  acid, 40 wt% solution in water, 98 atom%  $^{15}\text{N}$  (lot # 22917PI TO); b) sodium nitrite- $^{15}\text{N}$ , 99 atom%  $^{15}\text{N}$  (lot# 17623JO JO); and c) sodium nitrate- $^{15}\text{N}$ , 98 atom%  $^{15}\text{N}$  (lot # 13406AU AU). The following reagents (all natural abundance, 0.37%, in  $^{15}\text{N}$ ) were used as received: a) cesium nitrate, 99.999% (Aldrich lot # 17108DS); b) potassium hydroxide (Aldrich lot # DG00815DG); c) sodium hydroxide, 50% W/W, (VWR lot # 126770/117907); d) sodium nitrite (J.T. Baker, lot # L32624, with no anti-caking agent); e) sodium nitrate, 99.99+%, (Aldrich lot # 05821A1); f) cesium hydroxide, 99.9%, 50 wt% solution in  $\text{H}_2\text{O}$ , (Aldrich lot # 06430KU LU); and g) Ultrex II Ultrapure Nitric acid (J.T. Baker lot # T 19541).

Aqueous simulant and nitric acid solutions were prepared using water from a Barnstead Nanopure purification system (minimum  $18\text{M}\Omega\text{-cm}$  resistivity).

The CSSX solvent used in these experiments was ORNL lot# PVB B000894-87W, containing the Cs-7SB modifier at 0.75 M, the BOBCalixC6 at 0.007, and the tri-*n*-octylamine at 0.003 M.

Table 1. Waste simulant compositions

Designation <sup>a</sup>	[NaOH]	[KOH]	[CsOH]	[Na $^{15}\text{NO}_2$ ]	[NaNO $_2$ ]	[NaNO $_3$ ]	[Na $^{15}\text{NO}_3$ ]
13-H $^{15}\text{Nitrite}$	2.23	0.07	$5.0 \times 10^{-4}$	2.6	0	0.77	0
13-H $^{15}\text{Nitrate}$	2.23	0.07	$5.0 \times 10^{-4}$	0	2.6	0	0.77
26-F	4.65	0.041	$5.0 \times 10^{-4}$	0	0	0	0.956

<sup>a</sup>13-H and 26-F refer to tank numbers.

### 2.2 EXPERIMENTAL MATRIX AND TEST PROTOCOL

#### 2.2.1 Tank Simulant Contacting

Each waste simulant solution was contacted with solvent at an O/A phase ratio of 0.33 (1.6 mL solvent phase, 4.8 mL aqueous phase). Teflon FEP centrifuge tubes (8-mL capacity), cleaned using a standard protocol of rinsing twice each successively with tap water, Barnstead Nanopure water, 95% ethanol, and acetone, followed by air and argon drying, were used for the contacting experiments. Labline Imperial III incubators, Model 305PI, set at  $35 \pm 0.5$  °C (35 °C) and Model 310M set at  $60 \pm 0.5$  °C (60 °C) were used to maintain constant temperatures. The samples were agitated by end-over-end rotation on Glas-Col rugged rotators placed inside the incubators. Manipulations of the solvent and aqueous phases were performed using calibrated Eppendorf pipettes. The simulant contacting experiments were sampled



for Nuclear Magnetic Resonance (NMR) spectral analyses at 13, 20, and 28 days. At the first sampling time (day 13), however, it was discovered that simulant contact no. 26F-15NO<sub>3</sub>/60 °C contained no solvent, as it apparently having leaked out through the cap. The remaining simulant in 26F-15NO<sub>3</sub>/60 °C was measured at 4.15 mL, accordingly 1.383 mL of solvent was added, and the test period for this simulant was begun anew. Simulant 26F-15NO<sub>3</sub>/60 °C was subsequently subsampled for NMR analyses at day 7 and day 15. The general sampling protocol involved the removal of 100-μL samples from both the organic and aqueous phases for NMR analysis. An additional 200 μL of aqueous phase was removed at the time of sampling in order to maintain the 0.33 O/A phase ratio over the course of the contacting period. The aqueous phases were set aside for possible later analysis. For NMR analysis, the organic samples were diluted with 670 μL CDCl<sub>3</sub> containing N-15 enriched acetamide at 0.0115 M, giving an effective concentration of 0.01 M acetamide in the 770 μL final volume. Proton, carbon-13, fluorine-19, and nitrogen-15 NMR analyses were performed as needed.

### **2.2.2 Nitric Acid / Sodium Nitrite Solution Contacting**

Each nitric acid/sodium nitrite-containing aqueous phase was prepared according to the matrix in Table 2 below. The aqueous phases were then contacted with solvent at an O/A phase ratio of 5 (11.0 mL solvent phase, 2.2 mL aqueous phase) in 8-mL Teflon FEP centrifuge tubes in incubators under the same conditions described in Section 2.2.1 above. The solvent and aqueous phases were subsampled as above for NMR analyses, but at intervals of 11, 18, and 26 days.

## **2.3 ANALYSES**

Nuclear Magnetic Resonance Spectrometry. Nuclear Magnetic Resonance spectra were obtained on a Bruker Avance 400 wide-bore spectrometer. Nuclei observed were proton (400.130 MHz), carbon-13 (100.613 MHz), fluorine-19 (376.498), and nitrogen-15 (40.56 MHz). All spectra were obtained in CDCl<sub>3</sub> (99.8 atom % D, obtained from Aldrich Chemical Company). Chemical shifts were referenced against the residual chloroform peak (7.25 ppm) in CDCl<sub>3</sub> for proton spectra, and against the center of the triplet resonance CDCl<sub>3</sub> (77.0 ppm) for proton-decoupled carbon-13 spectra. For fluorine NMR, chemical shifts were referenced against an external reference standard for CClF<sub>3</sub> (set to 0.0 ppm). For the preparation of NMR samples for proton-decoupled nitrogen-15 analysis, a solution of CDCl<sub>3</sub> containing acetamide-<sup>15</sup>N, (99 atom% <sup>15</sup>N, Aldrich lot # 20201CO EO) at a concentration of 0.0115 M was used. The acetamide served as an internal chemical shift reference (−269.6 ppm), as well as providing an approximate integration standard.

The general sampling protocol involved the removal of 100-μL samples from both the organic and aqueous phases. The aqueous phases were set aside for possible later analysis. For NMR analysis each 100-μL organic sample was diluted with 670 μL CDCl<sub>3</sub> containing the N-15 enriched acetamide at 0.0115 M, making for an effective concentration of 0.01 M acetamide in the 770 μL final volume



**Table 2. Nitric acid/sodium nitrite solution compositions**

Series No.	[H <sup>15</sup> NO <sub>3</sub> ]	[HNO <sub>3</sub> ]	[CsNO <sub>3</sub> ]	[Na <sup>15</sup> NO <sub>2</sub> ]	[NaNO <sub>2</sub> ]
1-1	0.01	none	$5.0 \times 10^{-4}$	none	none
1-2	0.05	none	$5.0 \times 10^{-4}$	none	none
1-3	0.30	none	$5.0 \times 10^{-4}$	none	none
1-4	1.00	none	$5.0 \times 10^{-4}$	none	none
2-1	none	0.01	$5.0 \times 10^{-4}$	0.30	none
2-2	none	0.05	$5.0 \times 10^{-4}$	0.30	none
2-3	none	0.30	$5.0 \times 10^{-4}$	0.30	none
2-4	none	1.00	$5.0 \times 10^{-4}$	0.30	none
3-1	0.01	none	$5.0 \times 10^{-4}$	none	0.30
3-2	0.05	none	$5.0 \times 10^{-4}$	none	0.30
3-3	0.30	none	$5.0 \times 10^{-4}$	none	0.30
3-4	1.00	none	$5.0 \times 10^{-4}$	none	0.30
4-1	none	0.01	$5.0 \times 10^{-4}$	0.03	none
4-2	none	0.05	$5.0 \times 10^{-4}$	0.03	none
4-3	none	0.30	$5.0 \times 10^{-4}$	0.03	none
4-4	none	1.00	$5.0 \times 10^{-4}$	0.03	none





On day 26 the sample numbers 1-4, 2-4, 3-4, and 4-4 were observed to have a third layer in the bottom of each respective contacting tube. These viscous orange oil layers were carefully removed from each tube and quantified by volume. The oils were then returned to their respective tubes, and contacting in the incubators continued. Samples of the oil were analyzed by NMR by preparing concentrated solutions in  $\text{CDCl}_3$  (for example, in some cases 350-mg samples of the oil were diluted with 400  $\mu\text{L}$   $\text{CDCl}_3$ ; in other cases 600-mg samples of the oil were diluted with 200  $\mu\text{L}$   $\text{CDCl}_3$  containing the N-15 enriched acetamide.)

Gas Chromatography (GC) and Gas Chromatography/Mass Spectrometry (GC/MS). GC analyses of degradation compounds were performed on a Hewlett Packard HP6850 series GC system using an HP-5MS (crosslinked 5% phenyl methyl siloxane) fused silica capillary column (Agilent Technologies). An inlet temperature of 285 °C and a split ratio of 150:1 were used for all samples. For each run, an initial oven temperature of 50 °C for one minute was used, with a 10 °C/min ramp up to 280 °C. The temperature was held at 280 °C for 10 minutes, followed by a post-run temperature of 300 °C for 3 minutes. GC/MS analyses and spectra were obtained at 70 eV on a HP 5972A MS coupled to HP 5890A Series II GC equipped with a J&W 30 m x 0.25 mm DB-1 dimethylpolysiloxane capillary column (0.25  $\mu\text{m}$  film thickness). The injector and detector were held at 280 °C. The column was heated to 50 °C for 1 min, followed by a ramp at 10 °C/min to 300 °C and held for 20 min.

## 2.4 CHEMICAL SEPARATIONS

An approximately 1-gram sample of the bottom oil, obtained from matrix sample tube number 1-4 following 30 days total continuous contact at 60 °C, was subjected to column chromatography to remove the bulk modifier, and to separate and isolate the individual components. Previous analysis by thin-layer chromatography (TLC) showed that a solvent system comprising hexane/acetone could afford a satisfactory separation of most of the components from both the bulk modifier, and from each other. The sample was loaded onto 50 g of 40-micron flash chromatography silica gel packed in hexane. Compound fractions were eluted with 50-mL runs of solvent using acetone/hexane gradient beginning with 100% hexane and incrementally increasing the acetone concentration. Fractions of 8 mL were collected. The first run was 100% hexane followed by hexane containing acetone at the following volume %: 2%, 4%, 6%, 9%, 12%, 15%, 18%, 22%, 24%, 26%, 28%, 31%, 35%, 40% to 70% in 5% increments, followed by 80%–100% acetone in 10% increments. The column was then stripped with three 50-mL runs of acetone/ethanol solution. The fractions were analyzed by TLC to determine purity and extent of separation. Fractions were pooled, and the eluate solvent removed by rotary evaporation as determined by the TLC analysis. Components were isolated as follows: component #1 in fraction 58; component #2 from pooled fractions 63–66; component #3 from pooled fractions 73–7; and component #4 from pooled fractions 82–85. The individual components were analyzed by NMR and GC/MS.



### 3. RESULTS AND DISCUSSION

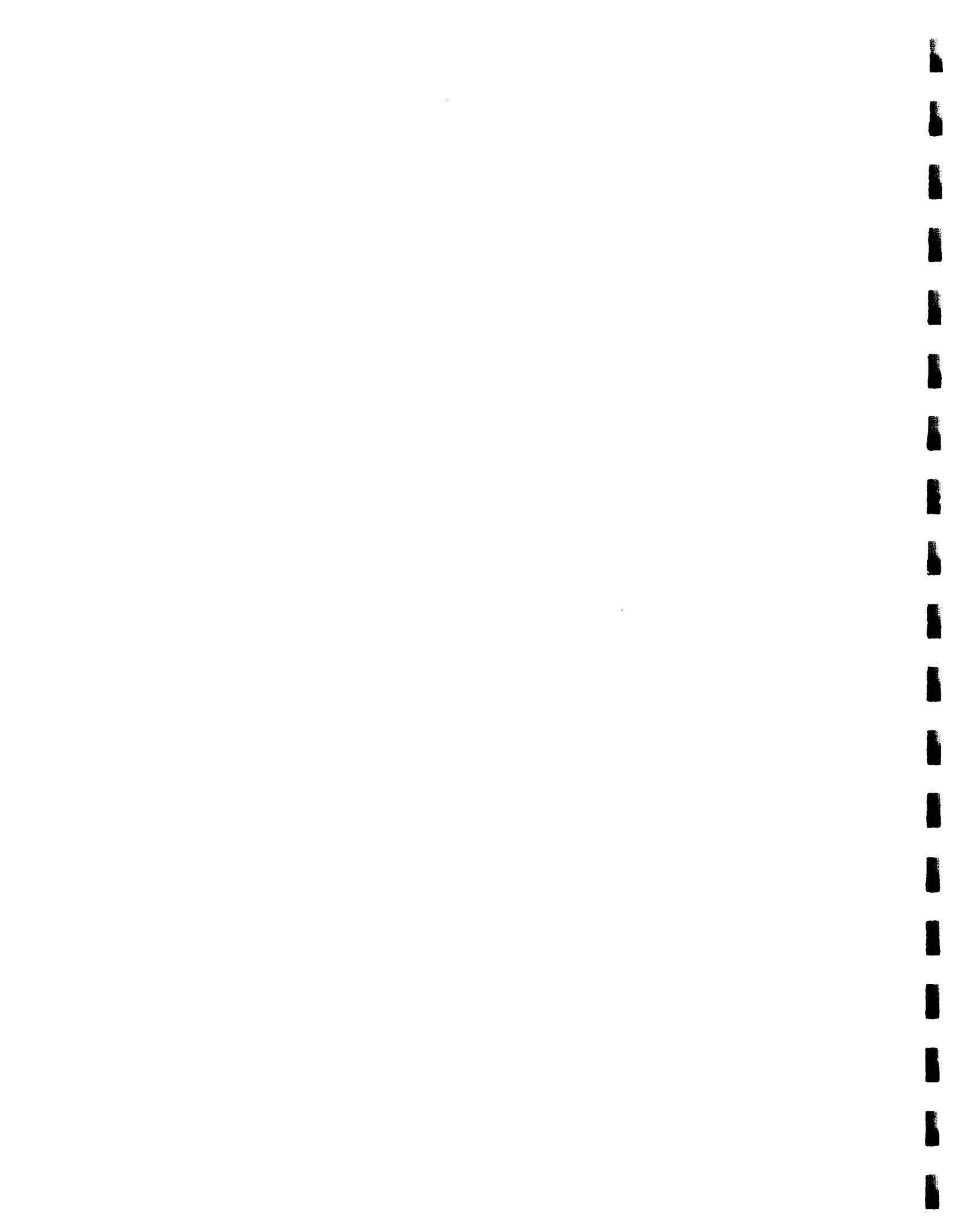
#### 3.1. ALKALINE-SIMULANT STUDIES

*Proton NMR spectral analysis of solvents contacted with each of the simulants noted in Table 1 for 26 days at both 36 °C and 60 °C revealed no detectable ingrowth of degradation products.* There was also no visible color change of the solvent over the course of the experiment. Thus, under alkaline conditions, the presence of high concentrations of nitrite does not appear to lead to the generation of any detectable degradation products. Thermal stability experiments conducted in FY 2000 and FY 2001 [1] between the baseline waste simulant and the previous solvent formulation (0.5 M modifier, 0.01 M BOBCalixC6, 0.001 M TOA) also showed no detectable signs of solvent degradation.

#### 3.2. NITRIC ACID STUDIES

The new solvent [3] (0.75 M modifier, 0.007 M BOBCalixC6, 0.003 M TOA in Isopar L) was contacted with the aqueous solutions containing variable nitric acid and sodium nitrite concentrations as shown in Table 2, at an O/A ratio of 5. Contacting was performed by end-over-end rotation in 30-mL Teflon FEP centrifuge tubes in 36 °C and 60 °C incubators (temperatures verified using a calibrated thermometer). The four nitric acid concentrations employed (0.01, 0.05, 0.30, and 1.0 M) were selected to cover a reasonable range of 0.01 to 0.30 M that the solvent may possibly experience in the process. Since previous studies [1] revealed that the most noteworthy changes to the solvent occurred at nitric acid concentrations of 1 M, this concentration was again examined as an extreme condition. The more rapid formation of degradation products would also facilitate their isolation and identification. To determine what effect the presence of nitrite might have on nitration reactions, three different concentrations of sodium nitrite were examined for each nitric acid concentration: none (control), 0.03 (the highest amount of nitrite that is reasonably expected to be in a scrub solution based on partition data), and 0.30 M nitrite (an extreme case). Two temperatures were again examined, with 36 °C being an expected upper operating limit, and 60 °C being an extreme case. The “extreme cases” were examined to gain an understanding of the type of solvent degradation that might occur during conditions representing possible process upset conditions. Unlike the previous studies [1], in which the nitric acid solutions contained no cesium, all solutions in these studies contained cesium nitrate at a concentration of  $5.0 \times 10^{-4}$  M. This would better simulate process conditions, in which counteranions present (such as nitrate and nitrite) to the BOBCalixC6-cesium cationic complex would be present in the solvent phase.

Results from nitric acid thermal-stability studies conducted in FY 2000/FY 2001 [1] revealed that only minor amounts of degradation product (3.5% of the modifier) were observed during the most severe case of 28 days continuous contact of the solvent with 1 M nitric acid at 61 °C. Even with the addition of nitrite, it was not anticipated that extreme degradation would be observed in the present studies. Thus, an anticipated challenge of the present study would be the ability to visualize, identify, and quantify the small amounts of nitration and other degradation products that might form, particularly in a solvent that is



now 0.75 M in modifier. Nitration of an aromatic nucleus causes the protons on the aromatic carbon atoms adjacent to the carbon connected to a nitro group to exhibit a downfield chemical shift in the proton NMR spectrum, away from the protons on the modifier, thus allowing those protons to be visualized. However, it was possible that other types of nitration products could be formed that would not be easily visualized in the presence of the modifier. Nitrogen-15 NMR is a good way to determine whether nitrogen compounds are being formed, and the chemical shifts are sufficiently sensitive to differentiate between nitroaromatic, nitroaliphatic, and nitrosoaromatic compounds. Nitrogen-14 NMR was also considered a possibility, due to its high natural abundance (99.63%), but due to its spin of unity ( $I = 1$ ), and the correspondingly large nuclear quadrupole moment, the peak linewidths would be very broad, and resolution would be compromised. This was especially a concern since the resonances for nitroaliphatics and nitroaromatics cover a narrow range of only about 40 ppm (20 ppm to -20 ppm relative to nitrate set to 0 ppm), and the linewidth for N-14 can exceed 40 ppm [4]. In contrast, N-15 has a spin of 1/2, and does not possess a quadrupole moment. But since nitrogen-15 has a very low natural abundance (0.37%), it was necessary to use nitric acid and sodium nitrite that are highly enriched ( $\geq 98$  atom%) in nitrogen-15, in order to obtain N-15 spectra in a reasonable amount of time. Though there is some equilibration between nitrate and nitrite, rather than have both the nitrite and the nitrate (from nitric acid) enriched with N-15, we chose one or the other, in an attempt to determine if there would be any discernable differences in the N-15 NMR spectra that might indicate how much of the nitrated products were due to reaction with nitrite vs. nitric acid. Thus, as shown in Table 2, the enrichment was split between nitric acid and nitrite, with series 2 and 3 being the mirror images of each other, with nitrite being enriched in series 2, and the nitric acid being enriched in series 3.

Aliquots of solvent were collected and analyzed by proton NMR at intervals of 11, 18, and 26 days, and compared with the proton NMR spectra of aliquots of solvent collected just after mixing the solvent with the appropriate aqueous phase, but before incubation was started. Nitrogen-15 NMR and carbon-13 NMR were recorded for selected samples where it was evident from the proton NMR that some reaction was occurring. No detectable change in the solvent (as indicated by changes in the proton NMR spectra) was observed for samples exposed to up to 0.3 M nitric acid and up to 0.3 M sodium nitrite for 26 days continuous contact at 36 °C, although the samples containing nitrite at 0.30 M did exhibit a pale yellow hue after this length of time. Nitrogen-15 NMR spectra were also obtained on the samples with the highest nitrite concentrations (sample numbers 3-3 and 2-3), but despite the pale yellow hue of the solvent, no new peaks were detectable. It has been estimated that 26 days continuous contact time corresponds to 7–9 months exposure time in a centrifugal contactor running continuously under processing plant conditions [5]. This estimate took into account the volume of solvent in the scrub section of the contactor cascade vs. the total volume of solvent inventory. Thus, under the conditions that the solvent would be expected to experience during actual processing conditions, no detectable evidence of nitration, or of other solvent degradation products, was observed.

By contrast, the samples exposed to 1 M nitric acid with added nitrite at 36 °C showed a slow ingrowth of the same set of resonances in the proton NMR (most notably a pair of “doublets”, one centered at 7.93 ppm, and the other centered at 6.93 ppm) that were observed in the FY 2001 contacting experiments with 1 M nitric acid alone after 28 days exposure at 60 °C. These doublets appear to possess



the AA'BB' pattern typical of the four aromatic protons on a 1,4-disubstituted aromatic ring. The resonances centered at 7.93 ppm exhibit a downfield chemical shift relative to the protons on the modifier adjacent to the *sec*-butyl group centered at 7.12 ppm. This shift is indicative of a change in the electron-withdrawing ability of the *sec*-butyl group, possibly including its replacement by a different substituent (e.g., a nitro group), or conversion to a different functionality. It appears in these samples that the addition of nitrite somewhat enhances the formation of this 1,4-disubstituted product. The amount observed in the solvent as a percent of the modifier concentration is shown in Table 3.

With the higher contacting (reaction) temperature of 60 °C came a higher extent of reaction. After 26 days exposure at 60 °C, the solvent exposed to the 0.30 M nitric acid solutions that contained added nitrite, and the solvent exposed to all the 1 M nitric acid solutions, showed the presence of this new 1,4-disubstituted product. Furthermore, between 18 and 26 days exposure of the solvent to all the 1 M nitric acid solutions at 60 °C, an orange oily third phase was observed to form. When the tubes were removed from the incubator and allowed to stand during the sampling period, this phase settled to the bottom of the tube, below the aqueous phase. These oils were found to be composed of mostly unreacted modifier (at concentrations of approximately 1.6 to 2.4 M, depending on the sample). In addition, the new 1,4-disubstituted product was found to be present at 9–12 mol% of the unreacted modifier (approximately 0.14 to 0.26 M, depending on the sample), with the balance being mostly Isopar® L (see Figure 1 for proton NMR on the oil from sample number 1-4.) The higher concentration of the material(s) responsible for the resonance centered at 7.93 ppm resulted in an improved signal-to-noise ratio, and closer examination of this signal indicated that it may actually be two overlapping “doublets”, due to the presence of two separate species with very similar chemical shifts. It appeared that the more upfield doublet, centered close to 7.92 ppm, was about twice the intensity of the more downfield doublet centered near 7.94 ppm. Table 3 summarizes the percentage of the two 1,4-disubstituted products as calculated by integration of the proton NMR resonances for the overlapping doublet peaks at 7.95-7.91 ppm against the proton NMR resonances for the modifier centered at 7.12 ppm, for all samples. For the samples where the orange oily third phase was observed, data is provided for both the solvent and the oil.

The amount of 1,4-disubstituted products formed for all the 60 °C/1-M nitric acid exposure samples was found to increase over the period of 11–26 days, although the increase over the 11-day to 18-day increment was barely measurable. Table 4 shows these results, and also an estimated calculation of the total amount of modifier that decomposed to give rise to the amount of the new 1,4-disubstituted products in each case. After 26 days, all the 60 °C sample tubes were returned to the 60 °C incubator for an additional 4 days, after which time the contacting was permanently halted at 30 days total exposure time.





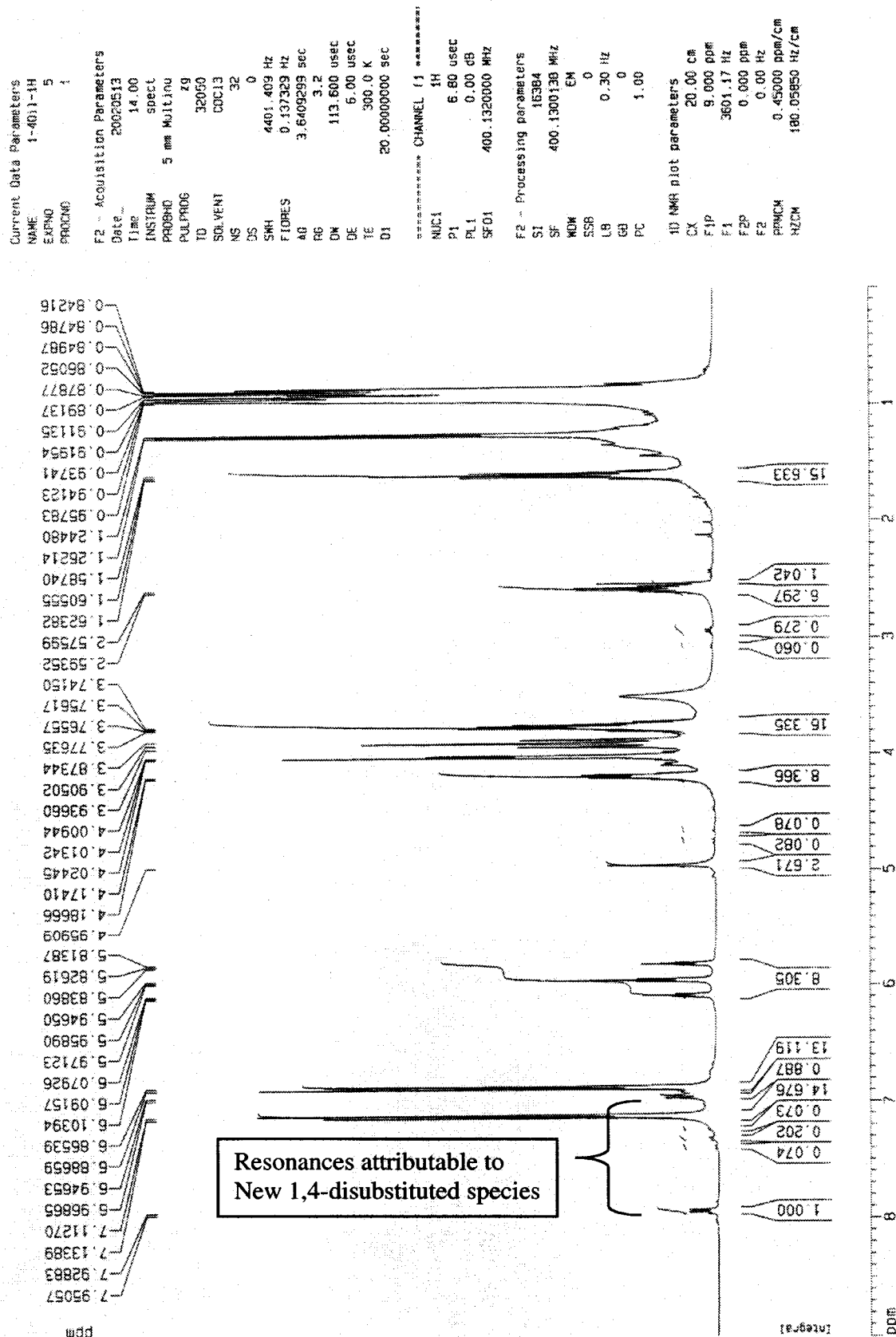


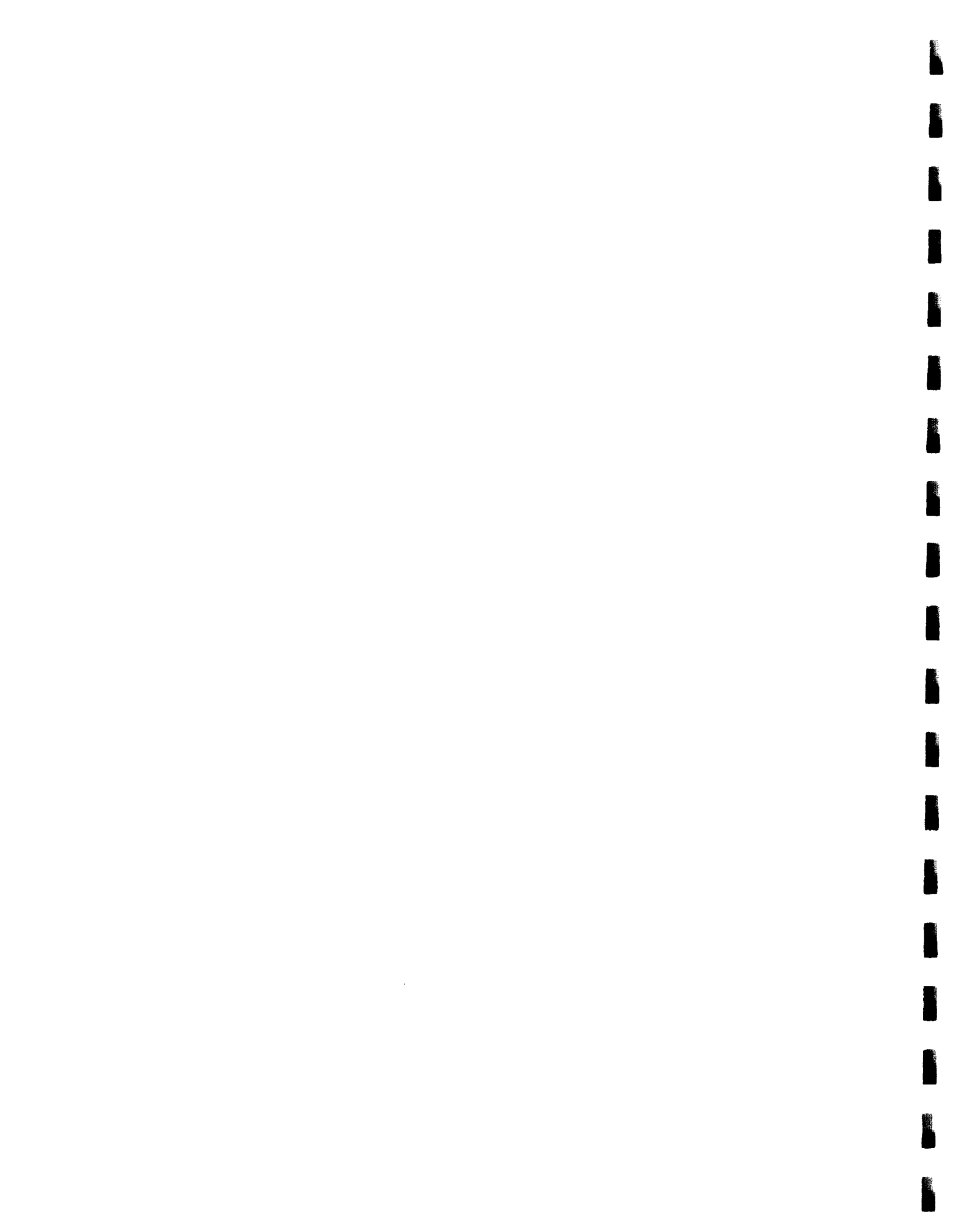
Figure 1. Proton NMR of orange oil from sample #1-4.



**Table 3. Percentage (relative to unreacted Cs-7SB modifier) of 1,4-disubstituted modifier degradation products present in solvent samples following 26 days continuous contact with nitric acid / sodium nitrite solutions at 36 °C and 60 °C.**

Sample ID	[HNO <sub>3</sub> ], M	[NaNO <sub>2</sub> ], M	% (relative to unreacted modifier) <sup>a</sup> 1,4-di-substituted products present at 36 °C	% (relative to unreacted modifier) <sup>a</sup> 1,4-di-substituted products present at 60 °C	Phase separation?
1-1	0.01( <sup>15</sup> N)	None	None	None	No
4-1	0.01	0.03 ( <sup>15</sup> N)	None	None	No
3-1	0.01( <sup>15</sup> N)	0.30	None	None	No
2-1	0.01	0.30 ( <sup>15</sup> N)	None	None	No
1-2	0.05 ( <sup>15</sup> N)	None	None	None	No
4-2	0.05	0.03 ( <sup>15</sup> N)	None	None	No
3-2	0.05 ( <sup>15</sup> N)	0.30	None	None	No
2-2	0.05	0.30 ( <sup>15</sup> N)	None	None	No
1-3	0.30 ( <sup>15</sup> N)	None	None	None	No
4-3	0.30	0.03 ( <sup>15</sup> N)	None	0.58	No
3-3	0.30 ( <sup>15</sup> N)	0.30	None	0.40	No
2-3	0.30	0.30 ( <sup>15</sup> N)	None	0.47	No
1-4	1.0 ( <sup>15</sup> N)	None	None	Top: 3.2; oil: 9.1	Yes (60 °C)
4-4	1.0	0.03 ( <sup>15</sup> N)	0.15	Top: 2.7; oil: 9.6	Yes (60 °C)
3-4	1.0 ( <sup>15</sup> N)	0.30	0.30	Top: 2.6; oil: 12.2	Yes (60 °C)
2-4	1.0	0.30 ( <sup>15</sup> N)	0.22	Top: 2.7; oil: 11.7	Yes (60 °C)

<sup>a</sup>Uncertainty is 5%.



**Table 4. Percentage (relative to unreacted Cs-7SB modifier) of 1,4-disubstituted modifier degradation products present in solvent samples following 11, 18, and 26 days continuous contact with 1 M nitric acid / sodium nitrite solutions at 60 °C.**

Sample ID	[HNO <sub>3</sub> ], M	[NaNO <sub>2</sub> ], M	% (relative to unreacted modifier) <sup>a</sup> 1,4-di-substituted products present at 36 °C	% (relative to unreacted modifier) <sup>a</sup> 1,4-di-substituted products present at 60 °C	Approx. total % of modifier decomp. at 60 °C	Approx. vol % separated from solvent (60 °C)
			11Days	11 Days		
1-4	1.0 ( <sup>15</sup> N)	None	None	2.3	2	NA
4-4	1.0	0.03 ( <sup>15</sup> N)	None	1.9	2	NA
3-4	1.0 ( <sup>15</sup> N)	0.30	None	1.6	1.5	NA
2-4	1.0	0.30 ( <sup>15</sup> N)	None	2.0	2	NA
			18 Days	18 Days		
1-4	1.0 ( <sup>15</sup> N)	None	None	2.4	2	NA
4-4	1.0	0.03 ( <sup>15</sup> N)	None	2.1	2	NA
3-4	1.0 ( <sup>15</sup> N)	0.30	None	2.2%	2	NA
2-4	1.0	0.30 ( <sup>15</sup> N)	None	2.1%	2	NA
			26 Days	26 Days		
1-4	1.0 ( <sup>15</sup> N)	None	None	Top: 3.2; oil: 9.1	5	12
4-4	1.0	0.03 ( <sup>15</sup> N)	0.15	Top: 2.7; oil: 9.6	5	12
3-4	1.0 ( <sup>15</sup> N)	0.30	0.30	Top: 2.6; oil: 12.2	6	14
2-4	1.0	0.30 ( <sup>15</sup> N)	0.22	Top: 2.7; oil: 11.7	6	13

<sup>a</sup>Uncertainty is 5%.



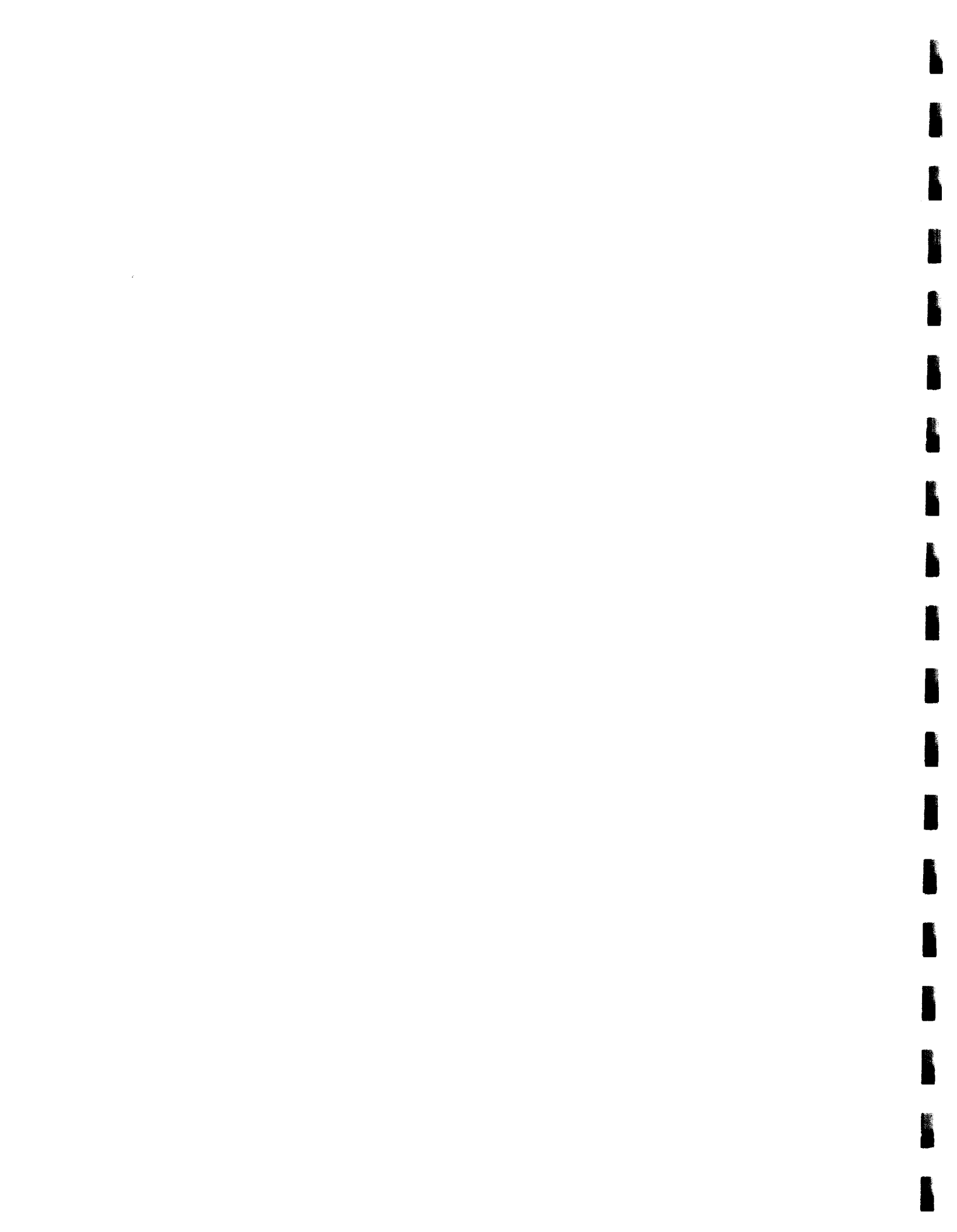
### 3.3. ANALYSIS OF THE “BOTTOM ORANGE OIL”

Since the major decomposition products formed under the most severe exposure conditions of 1 M nitric acid (variable nitrite) and 60 °C get concentrated in an oil that separates out from the solvent, there was the possibility that under milder conditions but longer exposure times the decomposition products could still be generated, separate out, and collect somewhere in the process equipment in a concentrated form. Thus, from a safety perspective it was important to identify these compounds and determine whether they are nitrated and pose any safety risks.

#### 3.3.1. Identification of Major Components

Samples of the oil were directly analyzed by proton, C-13, F-19, and N-15 NMR, as well as GC/MS. As previously stated, the orange oil is composed of mostly modifier, as well as 9–12 mol% (relative to unreacted modifier) of the unknown 1,4-disubstitution products, and lesser amounts of other unknown degradation products. The proton NMR spectra of the bottom oils of the four samples comprising series 4 (sample numbers 1-4 through 4-4) at 60 °C were essentially the same, except for slightly higher amounts of the 1,4-disubstitution products in the samples containing 0.3 M sodium nitrite (Tables 3 and 4).

Carbon-13 NMR analysis of the bottom oils from sample #1-4, and also from sample 60-F (the FY 2000/FY 2001 sample [1] that contained the bottom oil, and that was archived) revealed a key unexpected feature: in both cases the spectra exhibited two resonances between 196 and 200 ppm (see Figure 2 for the C-13 NMR spectrum of the 1-4 oil), in the region one would expect to find ketone carbonyl carbon resonances. Another unusual resonance was found at about 84 ppm. In the spectrum of the #1-4 sample (exposed to N-15 enriched nitric acid), the peak appeared as a small doublet centered at 84.115 ppm with 7.5 Hz coupling (very small peak in Figure 2). In the 60-F sample (exposed to nitric acid with natural abundance N-15), the peak showed up as a small singlet at 84.115 ppm. Both signals were much smaller in intensity than the carbonyl peaks. This could be indicative of a branched aliphatic nitrate (such as  $R_3C-NO_2$ , with typical shifts ~85 ppm), where in the case of the N-15 enriched nitric acid, there would be coupling between the C-13 and the N-15 (the coupling constant is appropriate for a nitroaliphatic). Also present in the C-13 spectra for both the 60-F and #1-4 oil samples is a single peak at 75.7 ppm (slightly greater in intensity than the peak at 84 ppm). This peak might be attributable to nitrate esters of type  $R_2CH-ONO_2$  or  $R_3C-ONO_2$ , as C-13 chemical shifts for nitrate esters of type  $RCH_2-ONO_2$  in the 70-73 ppm range have been reported [6], and branching (substituting the protons with alkyl substituents) tends to push the chemical shifts further downfield. An ester of type  $R_2CH-ONO_2$  could arise from nitration of the modifier alcohol, whereas an ester of type  $R_3C-ONO_2$  could arise from radical reactions involving the  $-CH$  of the *sec*-butyl group (benzylic carbon) and nitric acid. The resonance peak at 75.7 ppm might also be attributable to secondary or tertiary alcohols (alcohol alpha-carbons with chemical shifts typically at 68–75 ppm [7]), including a benzyl alcohol derivative of the modifier, in which the *sec*-butyl methine proton is replaced by a hydroxyl group. Nitrates and nitrate esters could be formed through radical reactions [8-10] involving the reactive benzylic position of the *sec*-butyl group of the modifier, and a benzylic alcohol can be an intermediate in the formation of the nitrate ester.





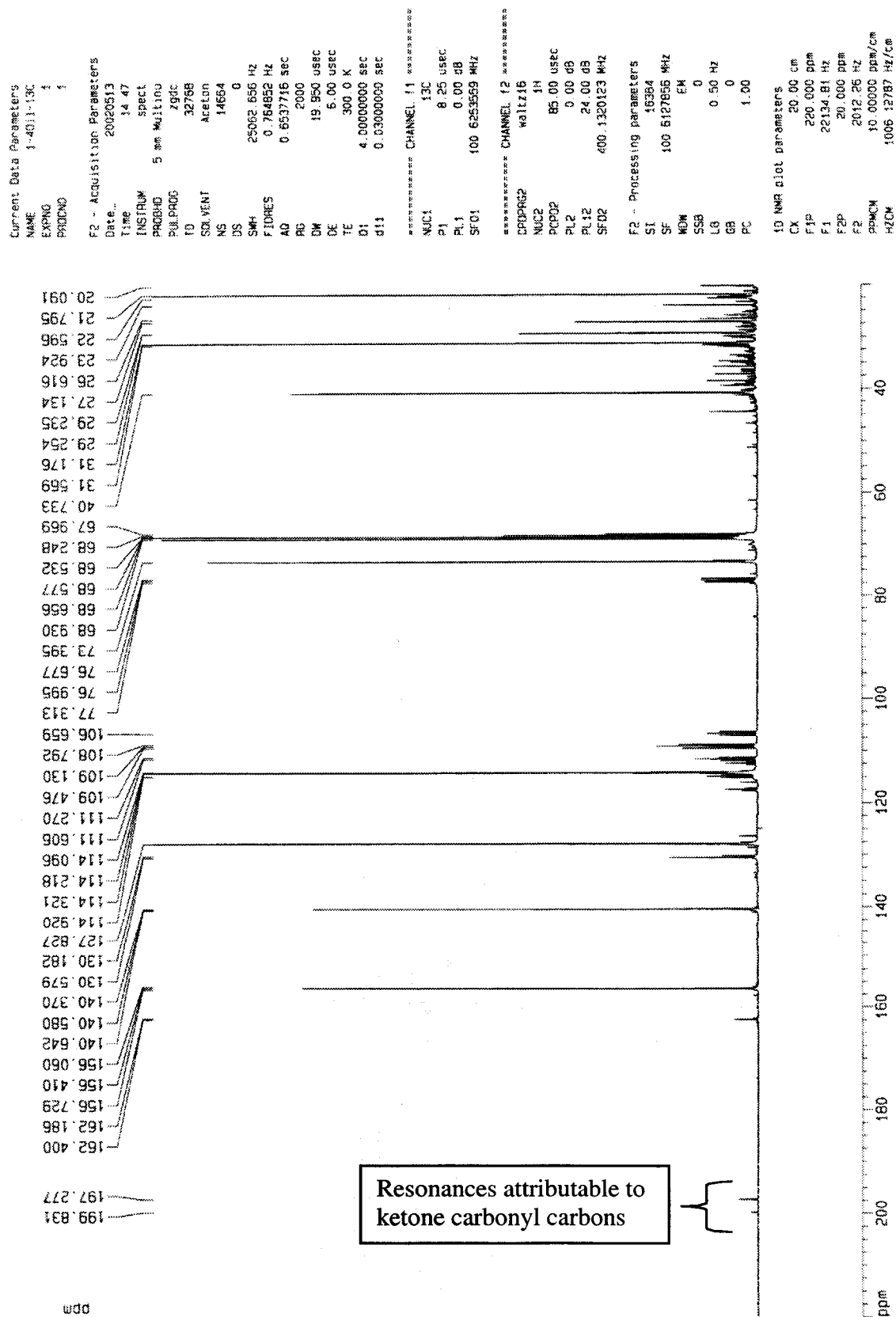


Figure 2. Carbon-13 NMR spectrum of orange oil from sample #1-4.



**Table 5. Results of proton-decoupled Nitrogen-15 NMR spectral analyses of bottom orange oils from sample numbers 1-4, 2-4, and 3-4.**

Sample	N-15 resonances (relative to acetamide at -269.6)	Approx. conc. (mM)	Comments
Bottom oil from sample 1 - 4 (exposure to 1 M N-15 enriched nitric acid only for 30 days at 60 °C)	5.14 ppm	7.2	Possibly nitroaliphatic
	-0.13 ppm	2.5	Possibly free nitrate, nitric acid, nitrate ester, or nitroaliphatic
	-0.85 ppm	2.1	Possibly free nitrate, nitric acid, nitrate ester, or nitroaliphatic
	-2.97 ppm	4.8	Possibly free nitrate, nitric acid, nitrate ester, or nitroaliphatic
	-10.78 ppm	0.7	Possibly nitroaromatic
	-11.88 ppm	4.9	Possibly nitroaromatic
	-360.97 ppm	3.6	Possibly tertiary amine (Can't be TOA unless exchange occurred)
Bottom oil from sample 2 - 4 (exposure to 1 M nitric acid plus 0.30 M N-15 enriched sodium nitrite for 30 days at 60 °C)	5.21 ppm	3.0	Possibly nitroaliphatic. Note: All peaks small relative to 1-4 sample. The -360 ppm peak is absent.
	-2.95	1.1	Possibly free nitrate, nitric acid, nitrate ester, or nitroaliphatic
	-11.88	0.5	Possibly nitroaromatic
Bottom oil from sample 3 - 4 (exposure to 1 M N-15 enriched nitric acid plus 0.30 M un-enriched sodium nitrite for 30 days at 60 °C)	5.14 ppm	5.3	Possibly nitroaliphatic. Note: spectrum very similar to that of sample 1-4, except a few additional peaks.
	-0.05 ppm	3.4	Possibly free nitrate, nitric acid, nitrate ester, or nitroaliphatic
	-0.78 ppm	1.6	Possibly free nitrate, nitric acid, nitrate ester, or nitroaliphatic
	-2.97 ppm	4.5	Possibly free nitrate, nitric acid, nitrate ester, or nitroaliphatic
	-3.92 ppm	1.0	Possibly free nitrate, nitrate ester, or nitroaliphatic
	-10.78 ppm	0.4	Possibly nitroaromatic
	-11.88 ppm	2.0	Possibly nitroaromatic
	-361.0 ppm	3.8	Possibly tertiary amine (Can't be TOA unless exchange occurred)



The N-15 NMR spectra were obtained on sample numbers 1-4, 2-4, and 3-4 by mixing 600–610 mg (approximately 550  $\mu\text{L}$ ) of each oil in a 5-mm NMR tube with 200  $\mu\text{L}$  of  $\text{CDCl}_3$  containing N-15 enriched acetamide at 0.0115 M (the acetamide concentration would be approximately 0.003 M in the approximately 750  $\mu\text{L}$  total volume). These spectra showed a series of peaks in the regions associated with both aliphatic nitrate species and aromatic nitrate species. There was no evidence of either nitrosoaromatic of type  $\text{Ar}-\text{NO}$  (N-15 chemical shifts  $\sim 550$  ppm) or aliphatic nitrite esters of type  $\text{R}-\text{ONO}$  (N-15 chemical shifts typically  $-35$  to  $-40$  ppm) being present. The N-15 NMR results are summarized in Table 5, which includes an estimate of their concentration in the oil, based on the concentration of the acetamide in the solution. The most prevalent N-15 peak in all the samples has a chemical shift of 5.1–5.2 ppm (nitroaliphatic region) and a concentration of approximately 7.2 mM in the #1-4 oil sample. The concentration of this species is lower in the #2-4 and #3-4 samples, likely owing to dilution of the N-15 with N-14, as would be expected from equilibration between nitrate and nitrite. The concentration of the 1,4-disubstituted products in these oils is more than 20 times greater than the concentration of this most abundant N-15 containing material, indicating that the 1,4-disubstituted degradation products likely do not contain nitrogen.

The N-15 NMR analysis indicates that both nitroaliphatics (which usually show up in the 0 to 15 ppm range; e.g., nitromethane is at about 0 ppm, and nitroethane is at about 12 ppm) and nitroaromatics (which usually show up in the 0 to  $-15$  ppm range; e.g., nitrophenol is at  $-7$  ppm) [4] are present in the oils, and thus are decomposition products. As stated above, nitrite esters of type  $\text{R}-\text{ONO}$  are not observed. It is not clear whether nitrate esters ( $\text{R}-\text{ONO}_2$ ) are present, as it has been difficult to find N-15 chemical-shift data on these materials in the literature. It is quite possible, however, that the N-15 chemical shift for a nitrate ester will be similar to that of nitrate, that is, near zero ppm. Hence, any peaks near zero ppm could be due to nitrate esters. The peak at about  $-361$  is unusual, as this is in the area where amines, particularly tertiary amines, appear (when run as a concentrated sample, TOA appears at  $-332$  ppm). However, all these species appear to be present at very low concentrations overall. Extrapolating the approximate concentrations in the oil to what the concentrations would be in the solvent prior to phase separation (about an 8-fold dilution), the concentrations of each species would be well under 1 mM. For the #1-4 sample, assuming each species has a single nitrogen, the total concentration of nitrogen-containing species in the oil is about 26 mM, which extrapolates to slightly above 3 mM in the solvent. (Also, two of the peaks near 0 ppm are likely due to free extracted nitric acid and extracted nitrate; curiously, we did not see indications of extracted nitrite in the #2-4 sample, but this may be due to its conversion to nitrate – see below). *Thus, the total amount of nitrogen-containing materials generated following exposure to 1 M nitric acid for 30 days at 60 °C appears to be no greater than about 3 mM. If all these nitrogen-containing species were arising from the modifier, they would represent only 0.4% decomposition.*

Analysis of the aqueous phases associated with oil sample numbers 1-4 through 3-4 showed only a peak near zero, representing nitrate. The nitrite signal, which should normally appear at 233 ppm, was not present, even in the #2-4 sample, which was prepared to contain unenriched nitric acid, and enriched nitrite. Thus, the nitrite is apparently converted to one or more different species, perhaps by some sort of disproportionation reaction. Of interest is that when natural-abundance nitric acid is added to a solution of N-15 enriched sodium nitrite at 0.30 M in deuterium oxide (to afford a nitric acid concentration of 1 M),



colorless bubbles are quickly evolved from the solution, and a N-15 NMR spectrum obtained about 10 minutes after the addition of the nitric acid shows no peak at 233 ppm, but instead a peak a near zero ppm, indicating that the N-15 previously associated with nitrite is now associated with nitrate. Thus, it is possible that nitrite is not stable in the presence of 1 M nitric acid, and that no nitrite was formally present at the start of the experiment.

Analysis of some of the oils (#2-4, #3-4, and also the 60-F oil from FY 2000/FY 2001) directly by GC/MS showed the modifier as the major peak on the chromatogram, eluting at 18.3 min (top of peak), plus two other substantial peaks in about a  $1.5 \pm 0.3$  to 1 ratio, eluting at 19.9 and 20.6 min, respectively. The largest masses ( $m/z$ ) recorded in the MS for these two peaks were 324 for the peak eluting at 19.9 min and 338 for the peak eluting at 20.6 min (these may or may not be the molecular ion peaks). There were also a number of smaller peaks with longer retention times (22–24 min), indicating that these species may have higher molecular weights, though that is not always the case, as it depends on the relative affinity of the compound for the stationary phase.

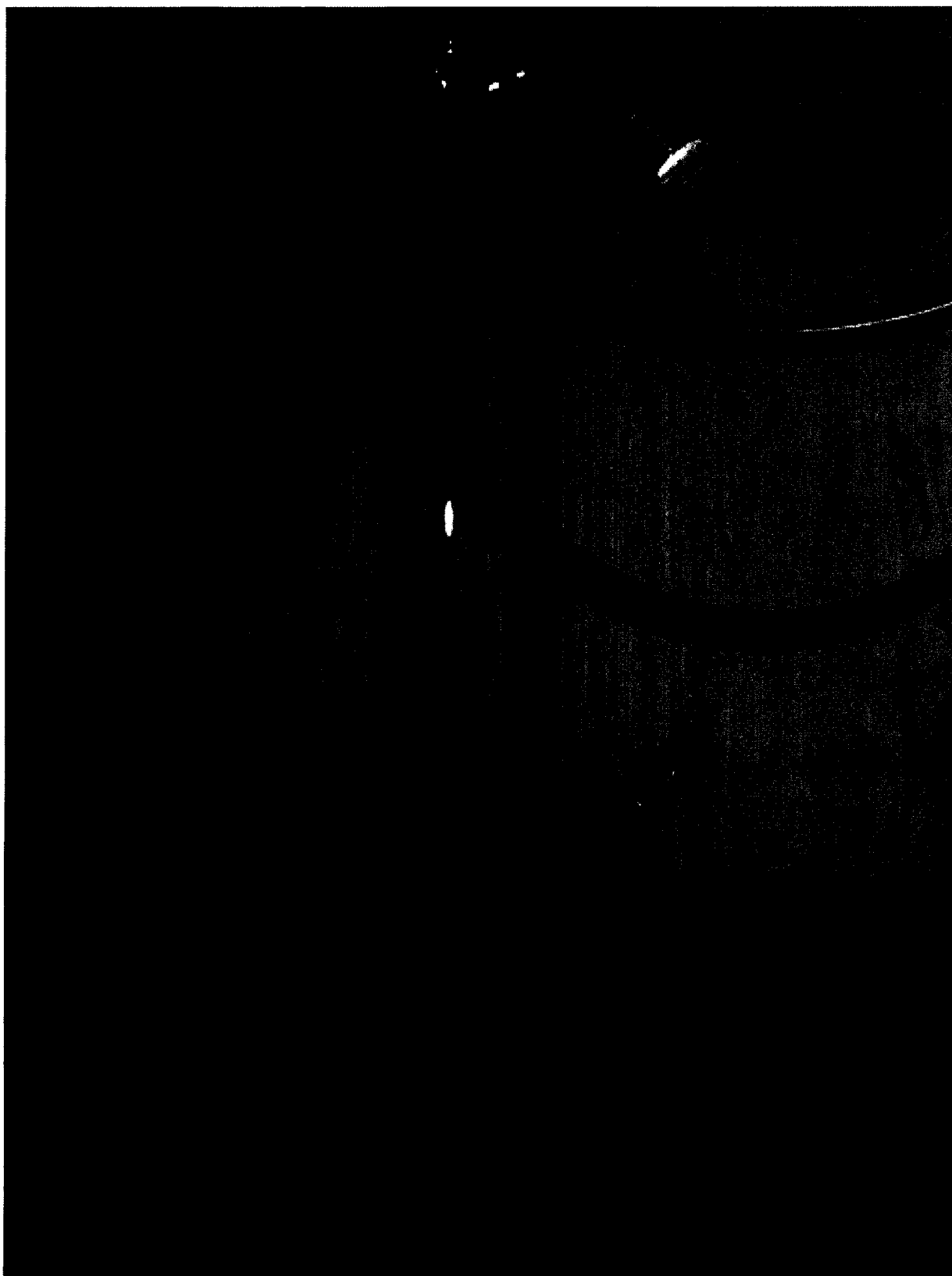
Thus, it appears that the 1,4-disubstituted products being formed are the major decomposition products, and, based on the N-15 NMR, that these materials likely do not contain nitrogen. However, positive identification of these materials could not be accomplished unless they were separated from the oil, or at that the very least, the modifier would need to be removed from the oil.

To better facilitate the positive identification of the main 1,4-disubstituted species, and to try to identify some of the other species present in the oils, an approximately 1-g sample of the bottom orange oil (recovered from the Series #1-4 sample following 30 days continuous contact at 60 °C) was subjected to column chromatography. The sample was eluted using acetone/hexanes gradient, starting with pure hexanes and increasing the percentage of acetone incrementally (see Experimental Section). The sample separated into a series of colored bands that separated further upon migration down the column (Figure 3). The modifier ran ahead of the colored bands and was the first major material to be eluted from the column.

The eluate was collected in 8-mL fractions. The fractions were analyzed by TLC to determine the purity and extent of separation. On the basis of the TLC results, the fractions were pooled, and the eluate solvent removed by rotary evaporation. Four major components were isolated from the column: component 1 in fraction #58; component #2 from pooled fractions #63–66 (1st main yellowish band in Figure 3); component #3 from pooled fractions #73–75 (2<sup>nd</sup> yellowish band), and component #4 from pooled fractions #82–85 (orange band near the top of the column). The individual components were analyzed by NMR and GC/MS.







**Figure 3. Column chromatography of 1-g sample of orange oil from sample #1-4.**



Proton NMR analysis revealed component #1, consisting of only a few mg of sample, to be comprised of mostly unreacted BOBCalixC6. Some BOBCalixC6 in the solvent might have been trapped or solubilized in the material that oiled out. Proton NMR analysis of component #2 (about 30 mg isolated, see Figure 4) revealed it to contain mostly a material possessing the aromatic resonances attributable to the 1,4-disubstituted product (centered at 7.94 and 6.93 ppm). Component #3 (about 20 mg isolated, see Figure 5) was found to contain a material with nearly identical aromatic resonances centered at 7.92 and 6.93 ppm. In both cases, all the resonances attributable to the fluorinated alcohol portion of the modifier were present, however resonances attributable to an intact *sec*-butyl group were absent. In place of the *sec*-butyl group, for component #2 there appeared a quartet centered at about 2.95 ppm and a triplet centered at 1.18 ppm, consistent with an ethyl group alpha to a carbonyl. For component #3, there was a singlet present at 2.55 ppm, consistent with a methyl group alpha to a carbonyl. The proton spectrum for component #2 (Figure 4) also contains minor resonances from unidentified materials (likely other decomposition products) that co-eluted with the main material. These can be seen as resonances in the aromatic region of 7.2–7.7 ppm, additional peaks in the aliphatic region upfield of 2 ppm, and a smaller quartet at 3.1 ppm (about 25% of the main quartet centered at 2.95 ppm). Component #3 appears to be reasonably pure, with the proton spectrum (Figure 5) showing only a small number of extra peaks, mostly in the aliphatic region between 0.85 and 1.7 ppm, from unidentified material. In further discussions below, component #2 refers to the major material in the collected fraction, and likewise for component #3.

The NMR spectral data of components #2 and #3 were compared with literature spectral data for acetophenone and propiophenone [7] and with experimentally-determined spectral data for the model compounds 4-nitrophenol and 4'-methoxy acetophenone. Based on this comparison, the structure of component #2 is consistent with a material formed from the modifier in which the *sec*-butyl group was transformed into a propionyl [ $-\text{C}(=\text{O})\text{CH}_2\text{CH}_3$ ] group. Similarly, the structure of component #3 is consistent with a material formed from the modifier in which the *sec*-butyl group was transformed into an acetyl [ $-\text{C}(=\text{O})\text{CH}_3$ ] group. The proton NMR results, including the chemical shifts for model compounds, are shown in Figure 6. The carbon-13 spectra obtained for components #2 (Figure 7) and #3 (Figure 8) also confirm these structures, with component #2 having a carbonyl carbon appearing at 199.5 ppm, and component #3 having a carbonyl carbon appearing at 196.8 ppm. These C-13 chemical shifts are in very good agreement with chemical shifts of similar compounds (Figure 9).

Finally, GC/MS spectra obtained on components #2 and #3 confirmed that the peak eluting at 19.9 min is the acetyl component #3 with a MW and molecular ion peak of 324, and that the peak eluting at 20.6 min is the propionyl component #2 with a MW and molecular ion peak of 338. The fragmentation patterns were also consistent with the structures (Figure 10).



Component #2 (fractions 63-66) following column chromatography.  
 ~900 mg of Bottom oil from sample 1-4 (combined 600 and 310 mg)  
 after 30 days at 50 deg C, 1 M nitric acid)  
 Proton NMR rerun after re-isolated compound after GC/MS analysis

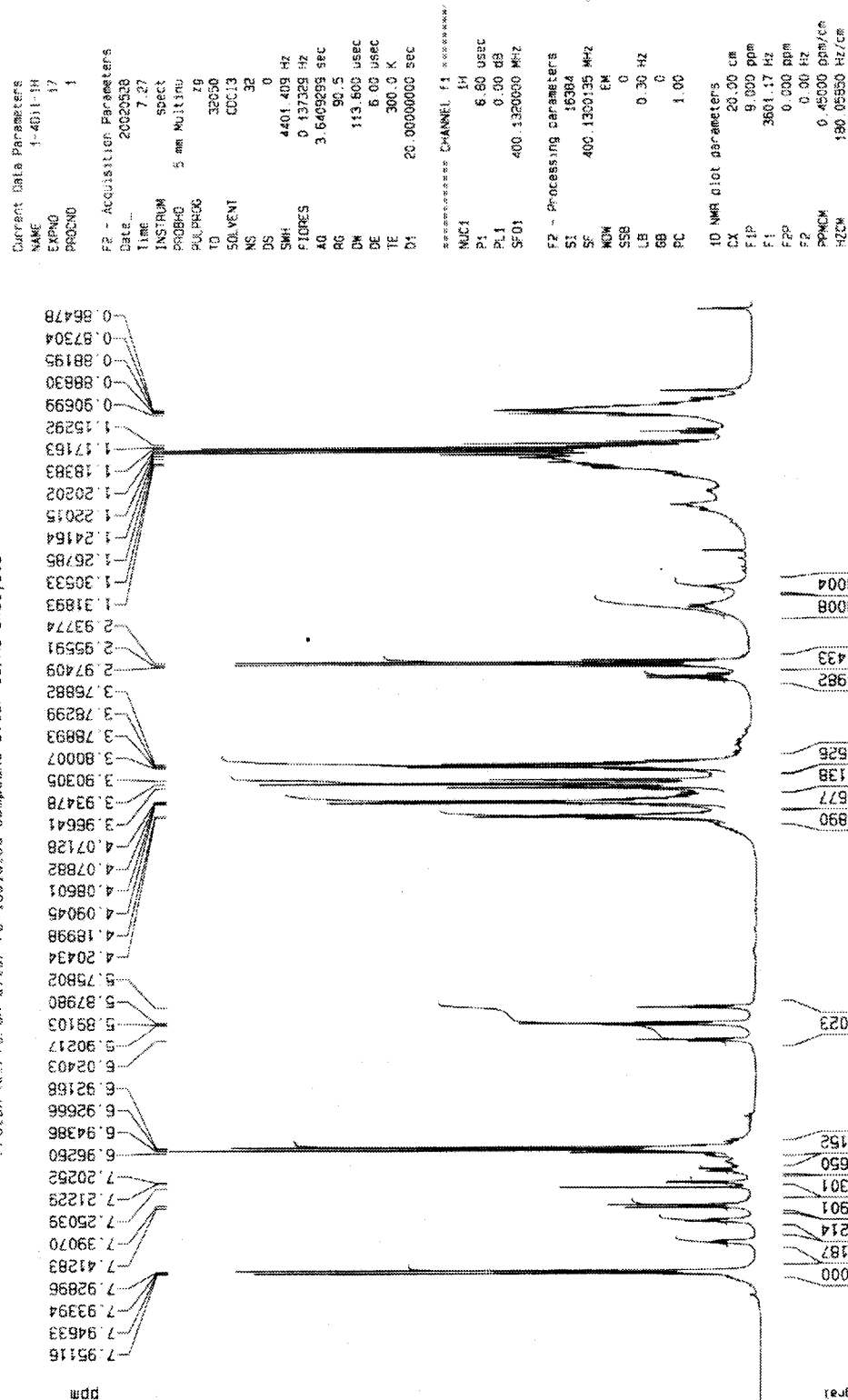


Figure 4. Proton NMR of component #2 from chromatography of sample #1-4 oil.



Component #3 (fractions 73-75) following column chromatography,  
 ~900 mg of Bottom oil from sample 1-4 (combined 600 and 310 mg)  
 (after 30 days at 60 deg C; 1 M N-15 enriched nitric acid)

Proton NMR

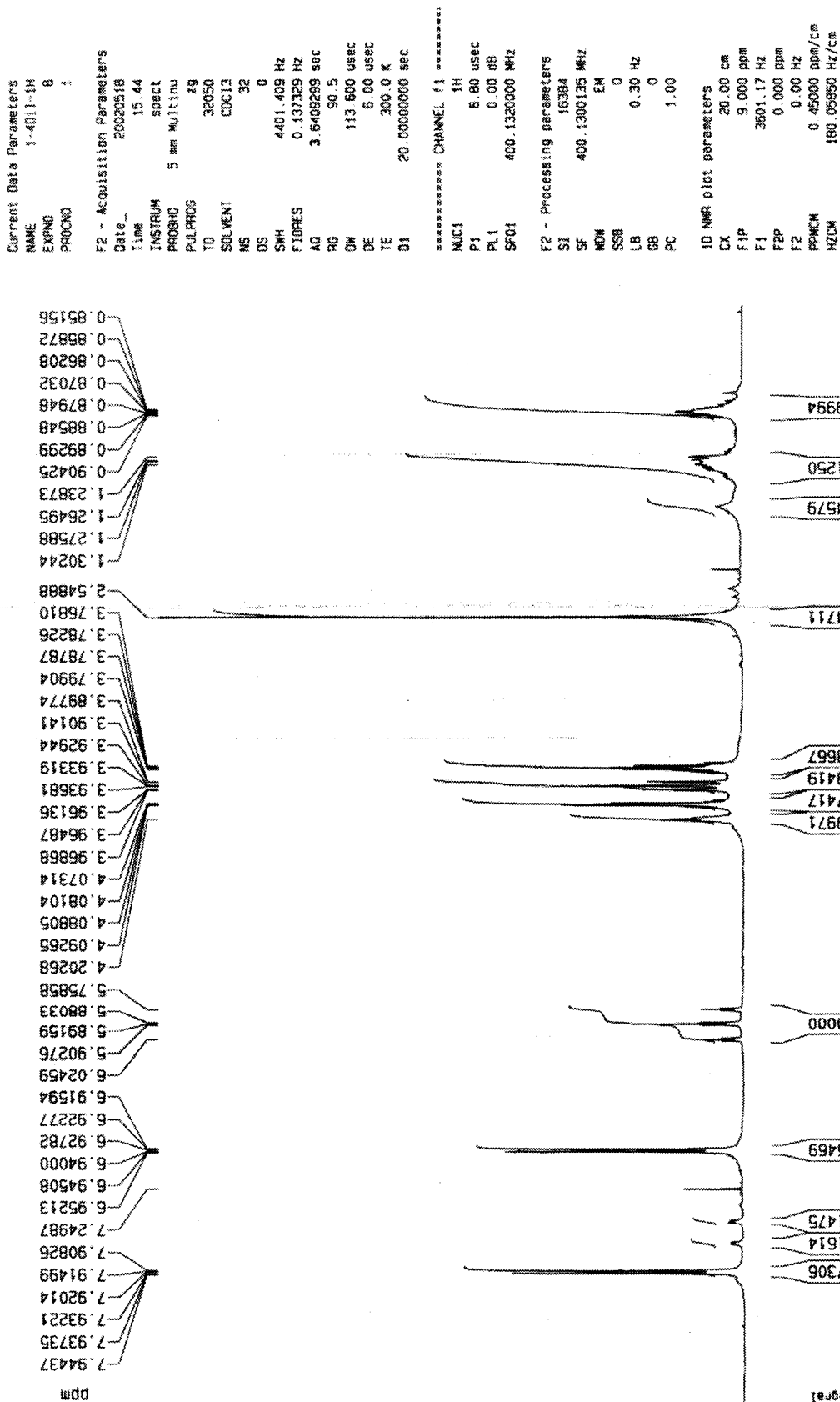
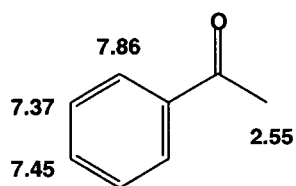


Figure 5. Proton NMR of component #3 from chromatography of sample #1-4 oil.

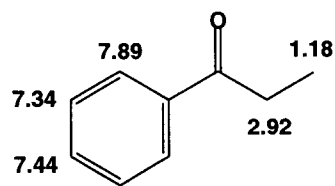




### Literature (Reference) Compounds

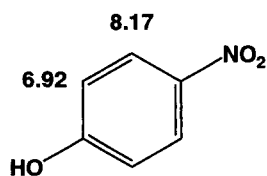


acetophenone

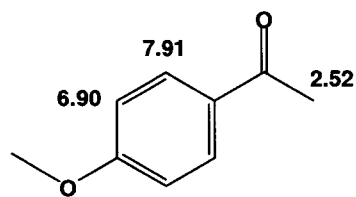


propiophenone

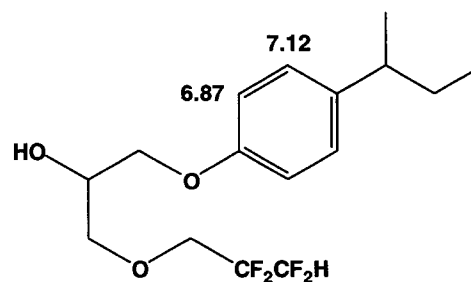
### Model Compounds



4-nitrophenol

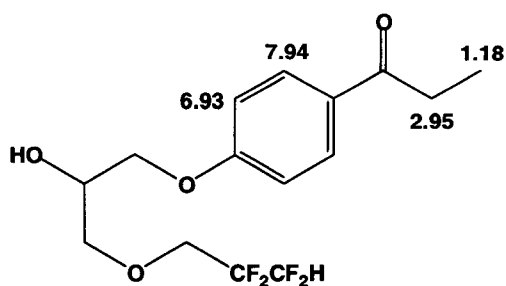


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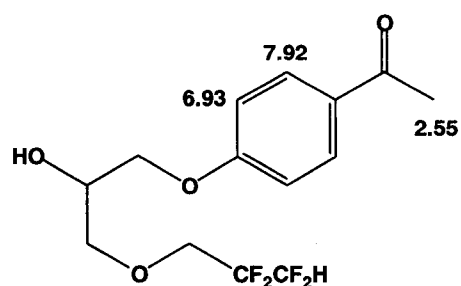


Cs-7SB Modifier

### Identified Main Components of Oil



Component #2



Component #3

Figure 6. Proton NMR chemical shifts of reference and model compounds, and the two main degradation components of the oil. All chemical shifts were obtained in  $\text{CDCl}_3$ .



Component 2 (fractions 63-66 following column chromatography)  
 ~900 mg of Bottom oil from sample 1-4 (combined 600 and 310 mg)  
 (after 30 days at 60 deg C; 1 M N-15 enriched nitric acid)  
 13 C NMR.

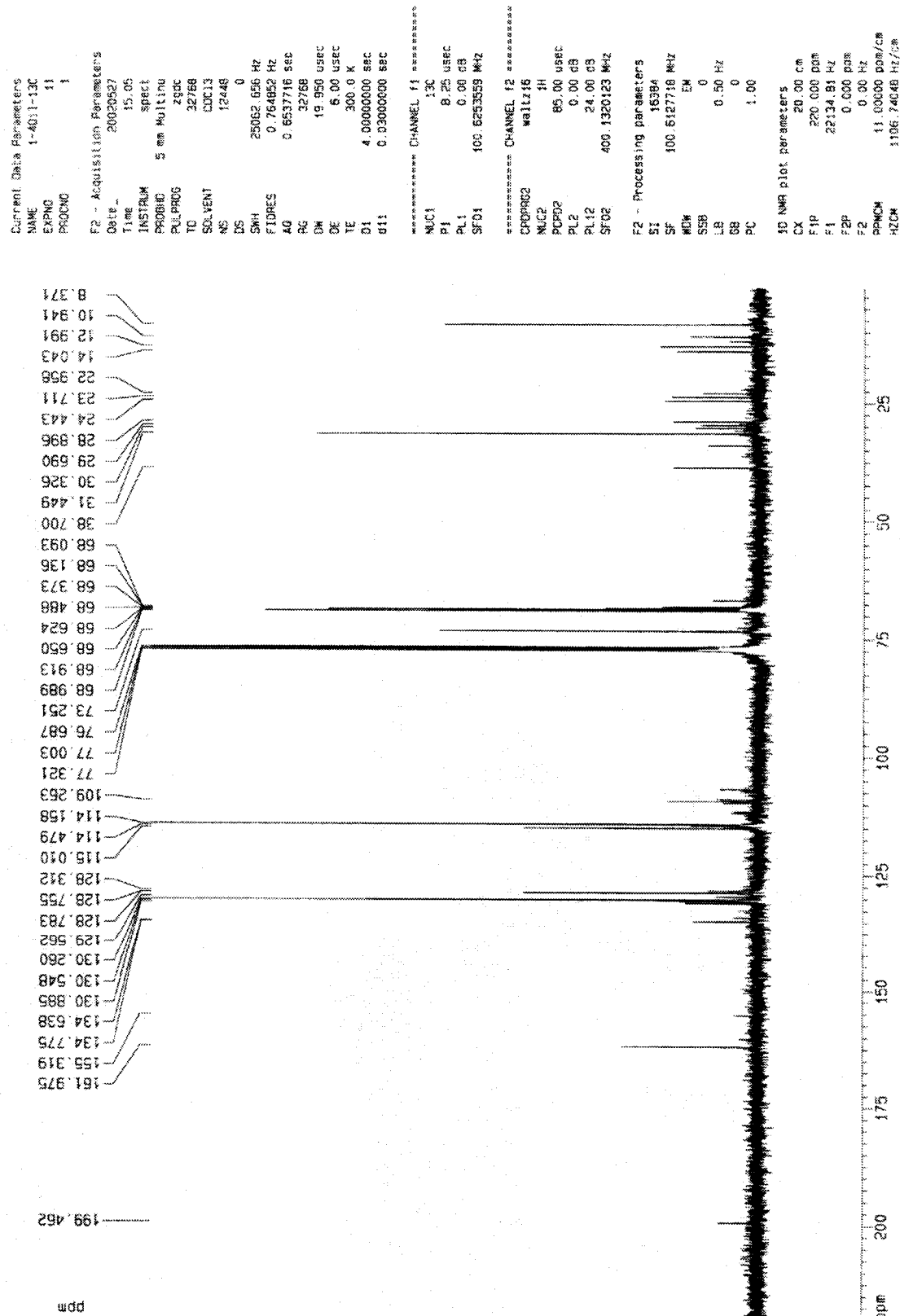


Figure 7. Carbon-13 NMR of component #2 from chromatography of sample #1-4 oil.



Component 3 (fractions 73-75 following column chromatography).  
 ~900 mg of Bottom oil from sample 1-4 (combined 800 and 310 mg)  
 (after 30 days at 60 deg C, 1 M N-15 enriched nitric acid)  
 13 C NMR.

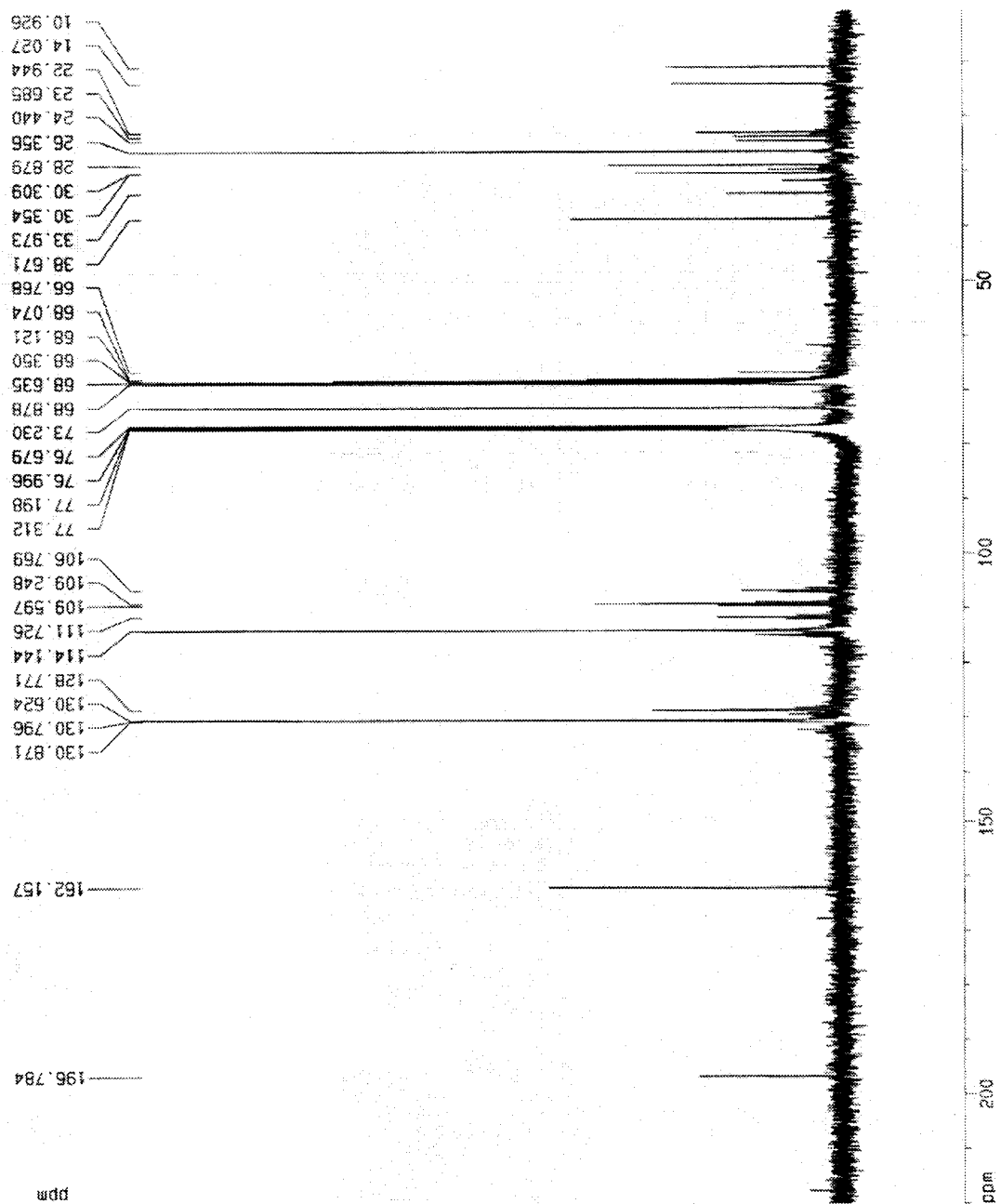
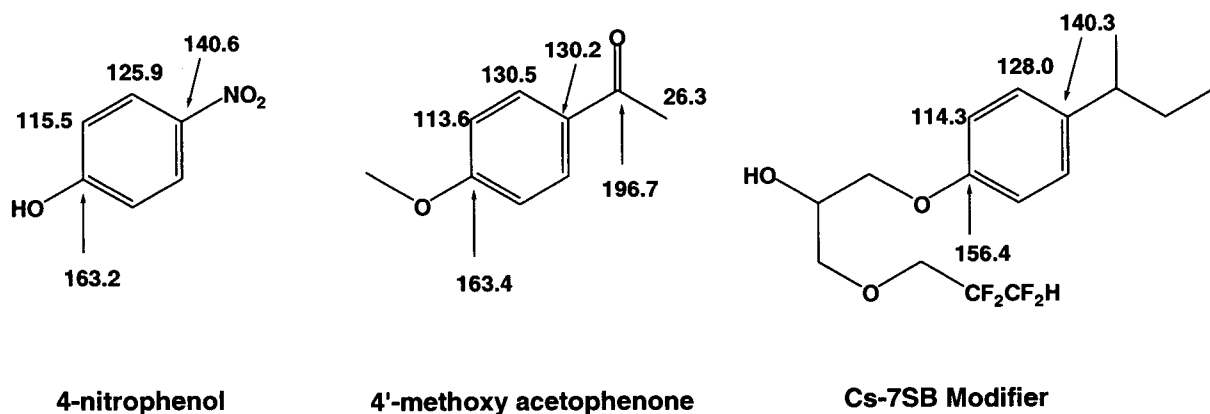


Figure 8. Carbon-13 NMR of component #3 from chromatography of sample #1-4 oil.



## Model Compounds



## Identified Main Components of Oil

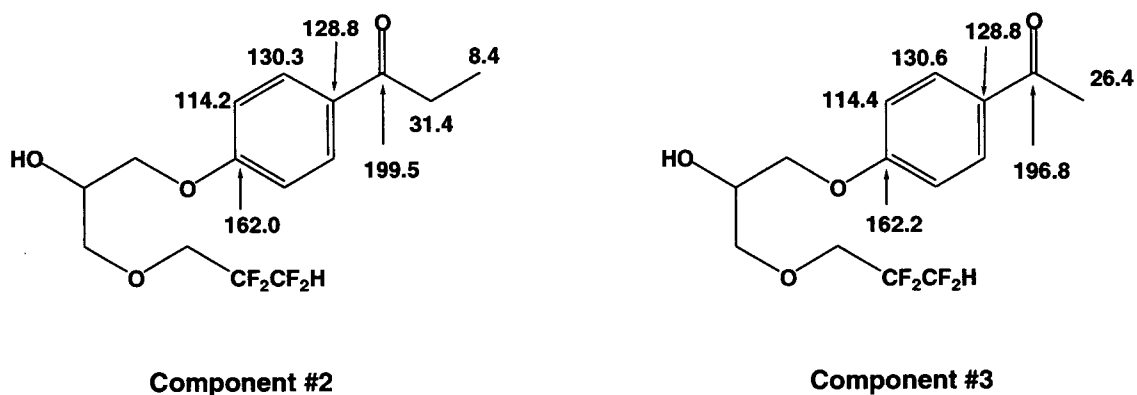
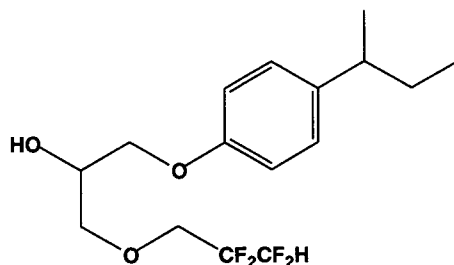


Figure 9. Carbon-13 NMR chemical shifts of known model compounds and the two main degradation components of the oil. All chemical shifts were recorded in CDCl<sub>3</sub>, except for 4-nitrophenol (acetone-<sub>d</sub><sub>6</sub>).



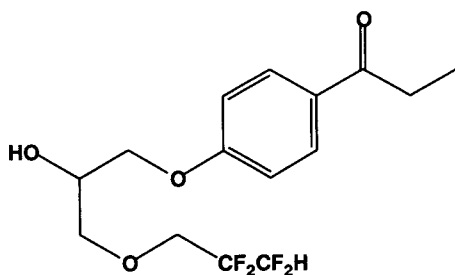


**GC/MS of Modifier in 2-4, 3-4, and 60-F oils**



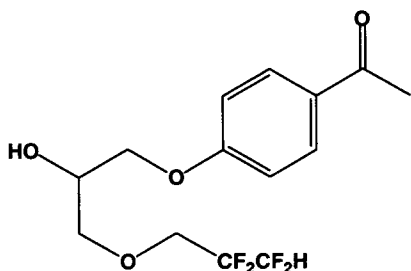
**C<sub>16</sub>H<sub>22</sub>F<sub>4</sub>O<sub>3</sub>: MW = 338.34**  
**Molecular ion peak at m/z = 338 observed**  
**m/z = 323 (loss of methyl)**  
**m/z = 309 (loss of ethyl)**  
**m/z = 291 (loss of sec-butyl)**

**GC/MS analysis of component #2 from column, and 2nd large peak eluting after modifier in 2-4, 3-4, and 60-F oils in GC:**



**C<sub>15</sub>H<sub>18</sub>F<sub>4</sub>O<sub>4</sub>: MW = 338.30**  
**Molecular ion peak at m/z = 338 observed**  
**m/z = 309 (loss of ethyl)**  
**m/z = 291 (loss of COCH<sub>2</sub>CH<sub>3</sub>)**

**GC/MS analysis of component #3 from column, and 1st large peak eluting after modifier in 2-4, 3-4, and 60-F oils in GC:**



**C<sub>14</sub>H<sub>16</sub>F<sub>4</sub>O<sub>4</sub>: MW = 324.27**  
**Molecular ion peak at m/z = 324 observed**  
**m/z = 309 (loss of methyl)**  
**m/z = 291 (loss of COCH<sub>3</sub>)**

**Figure 10. Results of GC/MS analysis of modifier and two main degradation components present in the oil.**



Analysis of the orange component #4 (total about 10 mg from pooled fractions) revealed it to be a mixture of materials that move the same on TLC. During preparation of the proton NMR sample in  $\text{CDCl}_3$ , it was discovered that the most orange-colored component did not dissolve; this was instead dissolved in deuterioacetone. Proton NMR analysis of components #4C (yellow  $\text{CDCl}_3$  solution), and #4A (orange deuterioacetone solution) showed no AA'BB' quartets in the aromatic region for either component, but instead showed one small doublet, plus some complicated splitting that cannot be readily interpreted. The spectrum also revealed a complicated region for the fluorinated portion of the molecule. Fluorine-19 NMR revealed a very "messy" spectrum, indicating that significant changes (and decomposition) of the fluorinated portion of the molecule had occurred (in contrast, the F-19 NMR spectra for components #2 and #3 were very clean and were the same as that of the Cs-7SB modifier except for a slight difference in the chemical shift). The N-15 NMR spectrum on #4C did show a single peak at  $-12.6$  ppm, suggestive of a nitrated aromatic. The N-15 NMR spectrum on #4A did not show anything, but this may have been a concentration problem. The C-13 NMR spectrum for #4C did indicate a substituted aromatic, possibly a nitroaromatic; the #4A sample was too dilute to obtain a useful C-13 spectrum. GC/MS was also inconclusive, as there were several small peaks that appeared to give only a few small fragments; based on the retention times on the column the masses of these fragments, all below  $m/z = 200$ , did not appear to be molecular ion peaks.

It was thus not possible to identify materials comprising the minor orange component #4 coming off the column, but it was clear that extensive degradation of the modifier had occurred. It also appeared that the materials responsible for the N-15 peaks observed in the #1-4 oil (Table 5) either do not survive the column or are volatile enough to be lost during evaporation of the solvent from the eluted fractions.

### 3.3.2. Discussion of Possible Mechanism of Formation

The pathway(s) by which the two ketone materials are formed from the modifier by contact with 1 M (and to a lesser extent 0.3 M) nitric acid may involve nitrated intermediates. Review of the literature and discussion with colleagues [2] suggests that there is precedent [8-10] for the formation of ketones and other oxidized organics from reaction of alkylaromatics with dilute nitric acid. The oxidized products can be formed via nitrated alkyl intermediates, with the benzylic carbon position of the alkyl chain being especially reactive [8-10]. The nitrated intermediates may include nitroaliphatics ( $\text{R-NO}_2$ ), nitrate esters ( $\text{R-ONO}_2$ ), and perhaps nitrite esters ( $\text{R-ONO}$ ) [2,8-10]. The nitrated intermediates may in turn have been formed from benzylic alcohol intermediates. The C-13 and N-15 NMR data indicate that the nitroaliphatics and nitrate esters may form in very small quantities; no evidence of nitrite esters was detected. It appears that if present, the nitro aliphatics and nitrate esters do not build up but instead react to form the more stable ketone products. Nitrate esters in particular are not very stable, so this is not unreasonable.

It is known [9,10] that alkylbenzenes can react with even dilute nitric acid to form nitroalkyl benzenes, and that these nitration reactions are often accompanied by oxidation side-reactions; however the conditions need to be somewhat forcing. The early work of Konovalov in particular showed that dilute



(1%) nitric acid was capable of nitrating the benzylic carbon of propylbenzene when conducted in a sealed tube at 100–105 °C for 90 hours. Factors affecting nitration included nitric acid concentration (which determines the concentration of NO<sub>2</sub>, the *de facto* nitrating agent [9]), temperature, pressure, and duration of the reaction. The reactivity of C–H bonds in the alkyl side-chain of the alkylbenzene generally showed the reactivity ordering of tertiary > secondary > primary, with the benzylic position being particularly reactive [9]. It is noteworthy that in the present work, the experiments were conducted in tightly closed Teflon tubes at 60 °C for ~600 hours, and that products from oxidative side-reactions appear to dominate over products of nitration. This appears to be consistent with Konovalov's observations.

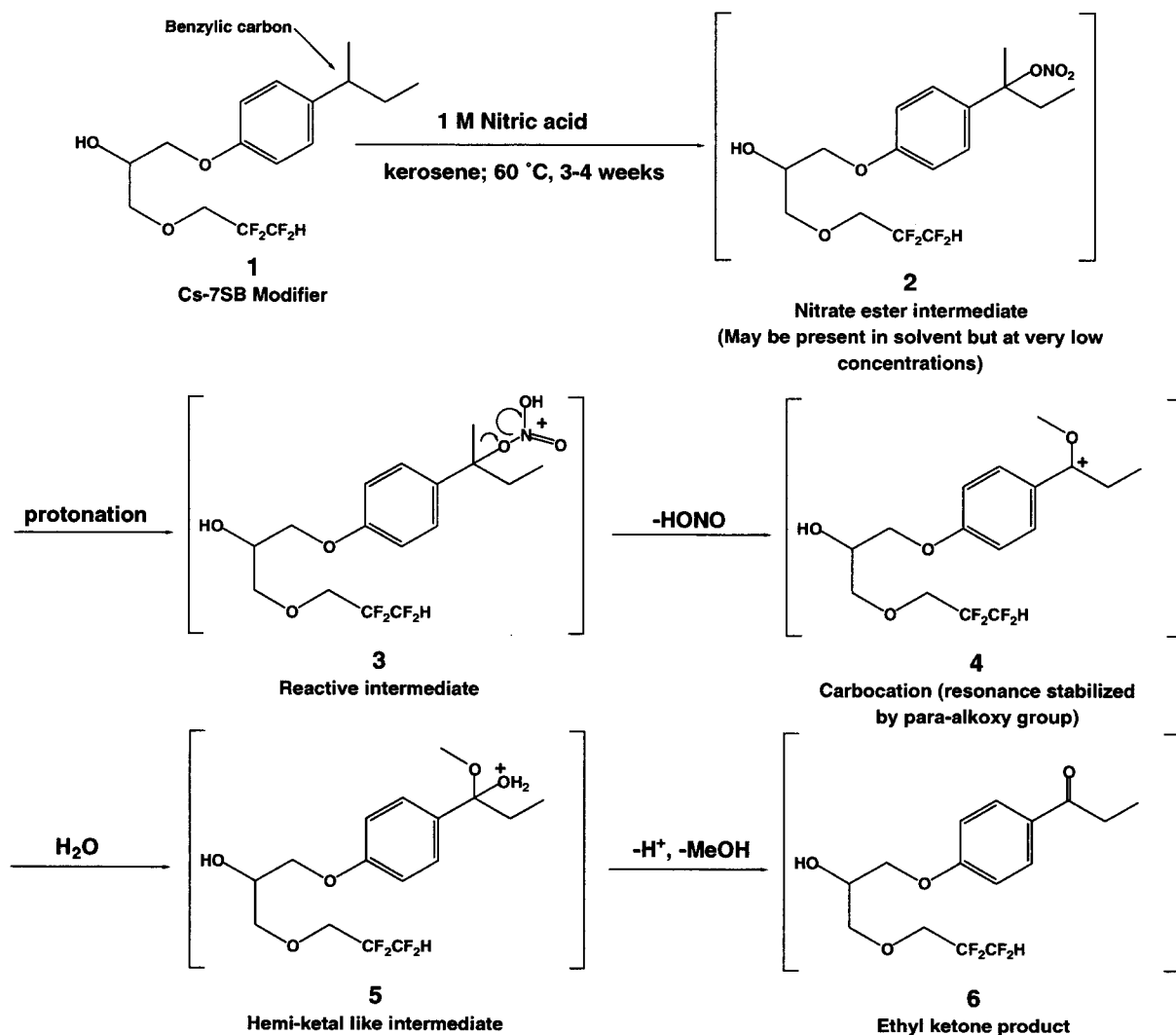
A possible mechanism of formation of these two ketone products is shown in Figure 11 [2]. The benzylic hydrogen (on the *sec*-butyl chain) of the modifier could form the nitrate ester through radical reactions [8]. Subsequent protonation of an oxygen on the nitro group would form a positively charged intermediate. A subsequent synchronous reaction in which either the methyl or ethyl substituent of the *sec*-butyl moiety migrates to oxygen with concomitant loss of HONO could give rise to cationic species as shown in Figure 11 [2]. Methyl migration is generally more favorable, and in fact the methyl derivative was observed to be the more prevalent ketone product in the oil and in the solvent.

The carbocations so formed from alkyl-group migration can be resonance-stabilized by the oxygen from the para alkoxy group of the modifier (RO–, where R contains the fluorinated alcohol moiety of the modifier). Reaction of these carbocations with water could lose (presumably through a hemi-ketal type of intermediate) the methoxy or ethoxy group to produce respectively the ethyl [–C(=O)CH<sub>2</sub>CH<sub>3</sub>] or methyl [–C(=O)CH<sub>3</sub>] ketone species.

The aromatic group could in principle also migrate and be eliminated to give in a similar fashion methyl ethyl ketone (MEK) as a degradation product. It is possible that this reaction may occur to a minor extent, but MEK would not be expected to be present in the solvent, due to its volatility and aqueous solubility, and no evidence for MEK was observed via NMR. The other fragment of this reaction would be the fluoroalcohol phenol *para*-RO-Ar-OH, where R again is the fluorinated alcohol portion of the modifier. Evidence for the presence of this species as a degradation product is inconclusive.



Nitrate esters may result from radical reactions involving the reactive benzylic position:



Similarly, the ethyl group can migrate to oxygen to give the ethoxy cation which can lead to the methyl ketone

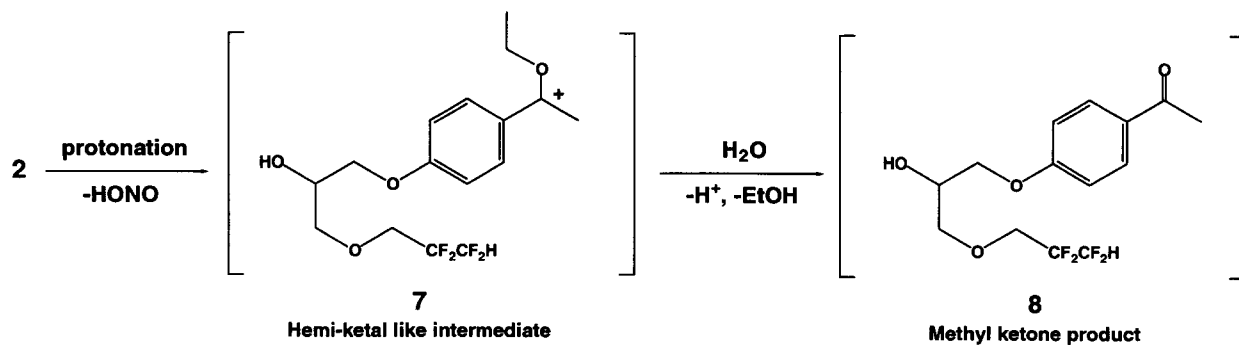


Figure 11. Possible mechanism of formation of ketone products from reaction of modifier with nitric acid.





#### 4. CONCLUSIONS

In summary, the risk of forming nitrated organics that can build up in the solvent during operation of the CSSX process during exposure of the solvent to acidic nitrate solutions both with and without added nitrite appears to be negligible. Furthermore, nitration of the solvent in response to exposure of the solvent to alkaline simulants containing nitrate and nitrite appears to be nonexistent. Under severe acidic conditions, well outside the envelope of expected operating conditions, there is NMR evidence suggesting that nitrated organics (nitroaromatics, nitroaliphatics, and nitrate esters) *might* be formed in very low quantities. The major degradation products that slowly accumulate during prolonged exposure of the solvent to nitric acid are stable (non-explosive) ketone derivatives of the modifier. However, these only form under conditions that are much more severe (1 M nitric acid, 0.3 M sodium nitrite, 60 °C) than would be expected to be encountered in the process. Only small amounts (about 5–6%) of these ketone derivatives of the modifier were formed under the most severe test conditions of continuous contact of the solvent with 1 M nitric acid for 26 days at 60 °C. It is possible that nitroaliphatics and/or nitrate esters are involved as reactive intermediates during the formation of these ketones, as plausible reaction mechanisms showing the intermediacy of these nitrated materials can be written. Under experimental test conditions that are closer to the operating conditions expected for the process (0.05 M nitric acid, 0.03 M nitrite, 36 °C), no detectable evidence for solvent degradation was observed after 26 days.

In principle, nitration of the aromatic ring of the modifier (and also BOBCalixC6) could occur. From the N-15 NMR data, there was some evidence that very small quantities of nitrated aromatics were being formed, but the amounts corresponded to no more than 0.4% degradation of the modifier. This is not unreasonable, as previous work [10] suggests that more concentrated nitric acid solutions are required for nitration of the aromatic ring to proceed at a rate that would be cause for concern.

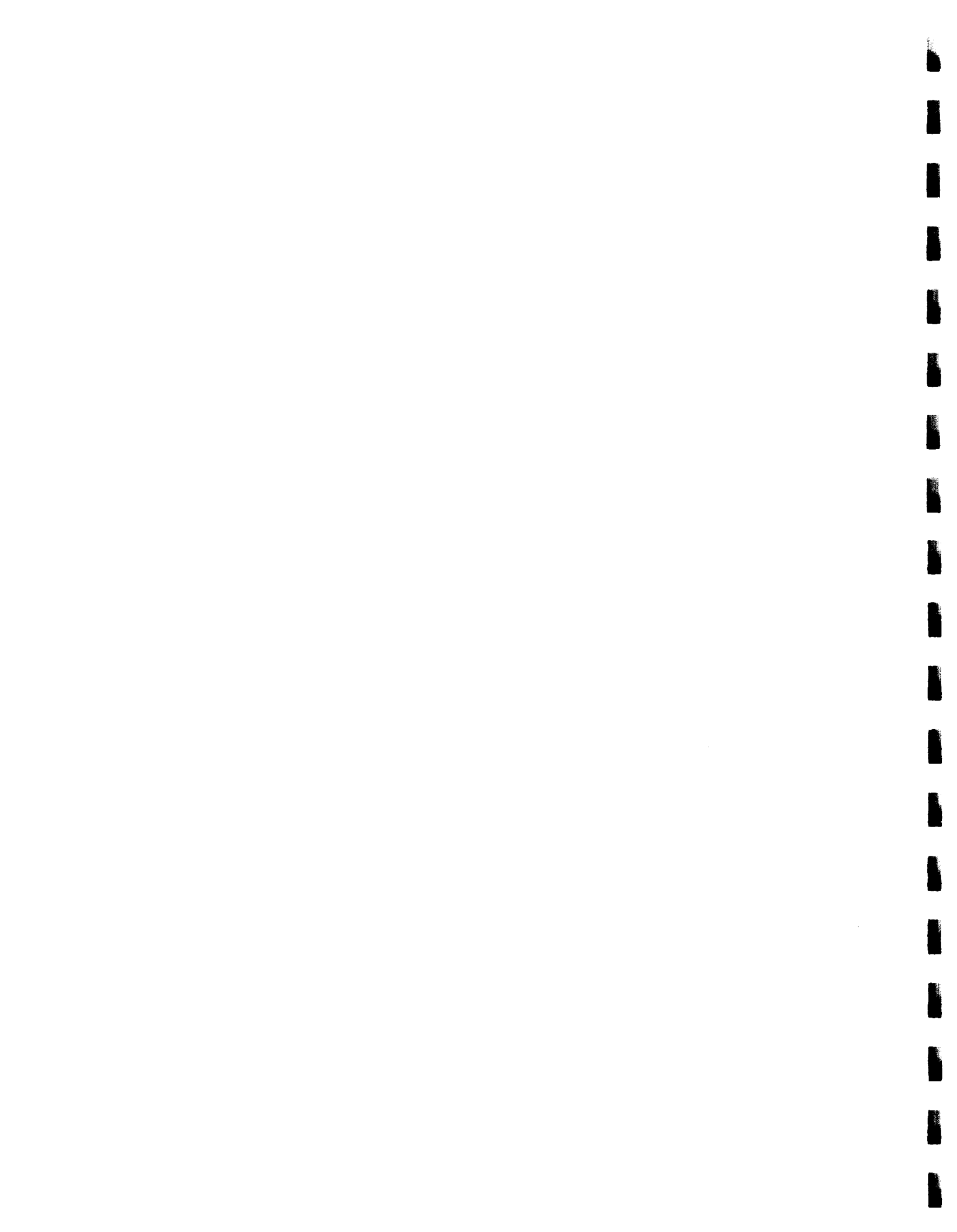


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