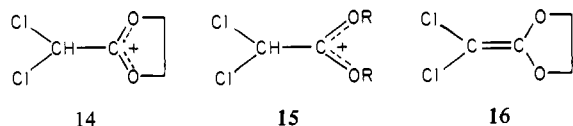


systems such as **8** is relieved by formation of a small ring. It follows from this that the 2-dichloromethyl-1,3-dioxolenium ion, **14**, should be more stable than its acyclic counterparts, **15**, and



that the rate of hydrolysis of 2-dichloromethylene-1,3-dioxolane should be greater than those of corresponding acyclic dichloro-ketene dialkyl acetals such as those studied here. This is in fact

the case:  $k_{H^+}$  for **16** is reported as  $104 \text{ M}^{-1} \text{ s}^{-1}$ ,<sup>2a</sup> which is 20-30 times greater than the rate constants for the acyclic dichloro-ketene acetals determined here.

**Registry No.** **2**, 5634-54-8; **3**, 61543-76-8; **4** (R = CH<sub>3</sub>), 69814-51-3; **4** (R = C<sub>2</sub>H<sub>5</sub>), 54567-93-0; **4** (R = C<sub>3</sub>H<sub>7</sub>), 85390-96-1; H<sub>3</sub>O<sup>+</sup>, 13968-08-6; D<sub>3</sub>O<sup>+</sup>, 24847-51-6; CNCH<sub>2</sub>CO<sub>2</sub>H, 372-09-8; CH<sub>2</sub>ClCO<sub>2</sub>H, 79-11-8; CH<sub>3</sub>OCH<sub>2</sub>CO<sub>2</sub>H, 625-45-6; HCO<sub>2</sub>H, 64-18-6; CH<sub>2</sub>OHCO<sub>2</sub>H, 79-14-1; CH<sub>3</sub>CO<sub>2</sub>H, 64-19-7; D<sub>2</sub>, 7782-39-0; carbon, 7440-44-0.

**Supplementary Material Available:** Tables S1-S8 of hydrolysis rate constants (14 pages). Ordering information is given on any current masthead page.

## Protonation of Diazomethane in Superacid Media<sup>1</sup>

John F. McGarrity\* and D. Phillip Cox

Contribution from the Institut de Chimie Organique, Université de Lausanne, CH-1005 Lausanne, Switzerland. Received October 25, 1982

**Abstract:** Diazomethane is protonated by HOSO<sub>2</sub>F in SO<sub>2</sub>ClF at -120 °C to yield exclusively methanediazonium ion (**1**), which decomposes at -85 °C to yield methyl fluorosulfate. When the more acidic HOSO<sub>2</sub>F/SbF<sub>5</sub> system is used, both **1** and the isomeric methylenediazenium ion (**2**) are formed. These structures are confirmed by experiments using diazomethane labeled with <sup>15</sup>N in each position. The compound **2**, the first example of its class, can be converted into **1** by lowering the acidity of the medium and may be stabilized in the less acidic medium by complexation with SO<sub>2</sub>. The displacement of nitrogen from **1** is nucleophile assisted even in the system HOSO<sub>2</sub>F/SbF<sub>5</sub>/SO<sub>2</sub>ClF.

The existence of alkanediazonium ions as intermediates has been well established in a variety of organic reactions.<sup>2</sup> In particular the methanediazonium ion (**1**) is sufficiently stable in the gas phase under ion cyclotron resonance conditions to allow direct investigation of its deprotonation and nucleophilic substitution reactions.<sup>3</sup> In a recent study of the acid-catalyzed hydrolysis of diazomethane, we were able to generate a protonated diazomethane species at concentrations up to 10<sup>-4</sup> M in THF/water.<sup>4</sup> However on the basis of the kinetic data alone we could not distinguish between structure **1** and that of the isomeric methylenediazenium ion (**2**). Indeed the formation of N-protonated diazoalkanes, such as **2**, has been occasionally proposed to explain anomalous reactions of diazoalkanes with weak acids<sup>5,6</sup> and the role of diazoalkanes as mildly basic catalysts,<sup>7</sup> but the existence of such species has never been proven.

In his pioneering study of protonated diazoalkanes in superacid media, Mohrig was able to examine trifluoroethanediazonium ion and hexafluoropropane-2-diazonium ion, but could not detect any of the N-protonated isomers.<sup>8,9</sup> Similarly, protonation of 1-phenyl-2,2,2-trifluorodiazooethane with fluorosulfuric acid yielded only one species, presumed to be the diazonium ion.<sup>10</sup> In contrast α-diazo ketones are protonated exclusively on oxygen in superacid media.<sup>11-13</sup>

In a preliminary communication on the reaction of diazomethane with fluorosulfuric acid in sulfuryl chlorofluoride, we described two reactive intermediates that decomposed to methyl fluorosulfate **3** on heating.<sup>14</sup> Structure **1** was attributed to the major species and structure **2** was assigned to the minor one. In this paper we correct the latter assignment and describe the conditions necessary for the observation of **2** as well as **1**. Structures **1** and **2** are unequivocally established by use of <sup>15</sup>N-labeled diazomethane.

### Experimental Section

**Materials.** Sulfuryl chlorofluoride was supplied by Aldrich and was purified by refluxing over antimony pentafluoride prior to distillation.<sup>15</sup> Fluorosulfuric acid and [<sup>2</sup>H]fluorosulfuric acid were supplied by Fluka AG (Buchs) and were purified by trap-to-trap distillation on the vacuum line with back distillation of 10% of the distillate. Antimony pentafluoride and hexafluoroantimonic acid were supplied by Aldrich; the former was purified as described for fluorosulfuric acid, and the latter was used as supplied. <sup>15</sup>N-Labeled sodium nitrite and acetamide were used as supplied by Stohler Isotopes (Waltham MA). N-Nitroso-N-methylurea was prepared as described by Vogel.<sup>16</sup>

**Apparatus.** The vacuum line was fitted with Teflon stopcocks lubricated with Kel-F nonvolatile Teflon oil, and Kel-F Teflon grease was used on ground glass joints; both products were supplied by Roth KG (Karlsruhe). <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker WP-60 spectrometer in the FT mode with an internal <sup>19</sup>F lock at 60 and 15.8 MHz, respectively. Chemical shifts (δ) are reported relative to Me<sub>4</sub>Si internal reference.<sup>17</sup> <sup>13</sup>C proton-decoupled spectra were measured

(1) Presented in part: "Abstracts of Papers", Second Chemical Congress of the North American Continent, Las Vegas, 1980; ORGN 036.

(2) Kirmse, W. *Angew. Chem., Int. Ed.* **1976**, *15*, 251-261.

(3) Foster, M. S.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1972**, *94*, 2425-2431.

(4) McGarrity, J. F.; Smyth, T. *J. Am. Chem. Soc.* **1980**, *102*, 7303-7308.

(5) Closs, G. L.; Goh, S. H. *J. Org. Chem.* **1974**, *39*, 1717-1723.

(6) Griengl, H.; Janoschek, R. *Tetrahedron* **1977**, *33*, 445-448.

(7) Clinging, R.; Dean, F. M. *J. Chem. Soc. C* **1971**, 3668-3671.

(8) Mohrig, J. R.; Keegstra, K. *J. Am. Chem. Soc.* **1967**, *89*, 5492-5493.

(9) Mohrig, J. R.; Keegstra, K.; Maverick, A.; Roberts, R.; Wells, S. J. *J. Chem. Soc., Chem. Comm.* **1974**, 780-781.

(10) Diderich, G. *Helv. Chim. Acta* **1972**, *55*, 2103-2112.

(11) Wentrup, C.; Dahn, H. *Helv. Chim. Acta* **1970**, *53*, 1637-1645.

(12) Avaro, M.; Levisalles, J.; Sommer, J. M. *Chem. Commun.* **1968**, 410-412.

(13) Malherbe, R.; Dahn, H. *Helv. Chim. Acta* **1974**, *57*, 2492-2503.

(14) Berner, D.; McGarrity, J. F. *J. Am. Chem. Soc.* **1979**, *101*, 3135-3136.

(15) Calves, J.-Y.; Gillespie, R. J. *J. Am. Chem. Soc.* **1977**, *99*, 1788-1792.

(16) Vogel, A. I. "A Text-book of Practical Organic Chemistry", 3rd ed.; Longmans, Green and Co.: New York, 1956; p 696.

by using a pulse angle of 23° and a 3-s delay between scans. The proton-coupled spectra were measured by using the "gated decoupling" pulse sequence. Coupling constants ( $J$ ) are given in hertz. Peak areas were measured for quantitative experiments by weighing the cut-outs of the enlarged spectra. MS measurements were performed on a Hewlett-Packard 5980 A instrument coupled to a Hewlett-Packard 5710 GLC.

**Standard Technique for Sample Preparation.** Fluorosulfuric acid was distilled via a short-path bridge on the vacuum line into a 5-mm NMR tube, equipped with a male B-14 ground glass joint, to a depth of 1.4 cm. The acid was partially back-distilled to leave a depth of 1 cm (0.25 g, 2.5 mmol). Sulfuryl chlorofluoride (0.5 mL) was distilled onto the acid (total depth = 5 cm). The NMR tube was transferred under dry nitrogen to another bridge, and antimony pentafluoride, typically 0.22 g (1 mmol, 0.5 cm in a 5-mm NMR tube), was distilled onto the walls just above the  $\text{SO}_2\text{ClF}$ . Pure dry nitrogen was introduced. The NMR tube was capped with a glass tube that could be stoppered and constantly flushed with nitrogen through a side arm and then removed to a Dewar flask containing a methanol/ethanol/liquid  $\text{N}_2$  mixture at  $-100^\circ\text{C}$  in a fume hood. The components of the acid solution were mixed by vigorous manual shaking, under nitrogen and with periodic cooling.

Diazomethane was prepared by the addition of aqueous potassium hydroxide (1 mL, 30%) to a suspension of *N*-nitroso-*N*-methylurea (60 mg, 0.6 mmol) in ethoxybenzene (10 mL) at  $0^\circ\text{C}$ . The mixture was stirred for 10 min, and then the ethereal layer was decanted, dried over KOH pellets for 15 min at  $-10^\circ\text{C}$ , and transferred to a two-necked round-bottomed flask held at  $0^\circ\text{C}$ . A stream of pure, dry nitrogen was directed as a jet onto the stirred diazomethane solution at a flow rate of  $350\text{ mL min}^{-1}$ , then through three gas traps held at  $-78^\circ\text{C}$ , and finally through a glass capillary (i.d. 0.5 mm, length 35 cm). (All glassware and connecting polythene tubing was thoroughly oven-dried at  $100^\circ\text{C}$  before use.) The NMR tube was cooled to a constant temperature of  $-120^\circ\text{C}$ . The stopper of the connecting tube was removed and the nitrogen-carrying capillary was immersed in the acid solution to within 1 cm of the tube bottom. A protective screen was installed.<sup>20</sup> The passage of gas was continued until the ethereal solution became colorless (normally 15 min); the capillary was removed, and the NMR tube was conveyed in the cold bath and under nitrogen to the vacuum line. The solution was degassed by three freeze-pump-thaw cycles at  $-195^\circ\text{C}$  and  $-120^\circ\text{C}$  before sealing under vacuum.

Samples for  $^{13}\text{C}$  NMR experiments were prepared in 10-mm tubes with the above-mentioned quantities multiplied by 4.

The yield of diazomethane transferred by this procedure to an NMR tube containing ether, in a control experiment, was estimated as 60% by back-titration with benzoic acid.

**Experiments with Hexafluoroantimonic Acid.** Hexafluoroantimonic acid (100  $\mu\text{L}$ ) was syringed by using a glass capillary needle onto sulfuryl chlorofluoride cooled to  $-100^\circ\text{C}$  in the NMR tube assembly. Mixing and sample preparation were carried out as described above.

**Proton Exchange Experiments.** Diazomethane was passed into a solution of  $\text{DOSO}_2\text{F}/\text{SbF}_5$  in  $\text{SO}_2\text{ClF}$  as described above. After degassing on the vacuum line  $\text{HOSO}_2\text{F}$  (2.5 mmol) was distilled and frozen onto the walls of the NMR tube just above the solution, before the tube was sealed. Spectra were run of the deuterated sample up to  $-80^\circ\text{C}$  with no observable mixing of the suspended protic acid. The tube was transferred to a cold bath held at  $-100^\circ\text{C}$ , and there the  $\text{HOSO}_2\text{F}$  was completely dissolved by shaking, before the sample was returned to the spectrometer.

**Deprotonation Experiments.** Diazomethane was protonated as described above in a solution containing  $\text{HOSO}_2\text{F}$  (2 mmol)/ $\text{SbF}_5$  (2 mmol). The sample was allowed to partially decompose at  $-72^\circ\text{C}$  for 140 min, after which time the singlet at 4.75 ppm had diminished by 70%

(17) We found that  $\text{Me}_4\text{Si}$  was stable up to  $-80^\circ\text{C}$  in  $\text{HOSO}_2\text{F}/\text{SO}_2\text{ClF}$  solutions but decomposed immediately in the presence of  $\text{SbF}_5$ . For such cases the peak of the hydronium ion has been recommended as an internal reference;<sup>18</sup> however, its chemical shift was found to be too temperature dependent for our purpose. The solvent lock signal was used as an external reference; the  $^1\text{H}$  chemical shift of **1** was found to be unchanged. In a control experiment with the  $\text{CH}_3\text{F}/\text{SbF}_5(4:1)/\text{SO}_2\text{ClF}$  system,<sup>19</sup> the spectrum was measured, and then the  $\text{MeOSOCIF}$  species was quenched with acetone before addition of  $\text{Me}_4\text{Si}$ . The identity of the chemical shift of the remaining  $\text{CH}_3\text{F}$  with internal and external references was thus confirmed.

(18) Rimmelin, P.; Schwarz, S.; Sommer, J. *Org. Magn. Reson.* **1981**, *16*, 160-163.

(19) Olah, G. A.; Donovan, D. J. *J. Am. Chem. Soc.* **1978**, *100*, 5163-5169.

(20) In some early experiments explosions destroyed the NMR tube due to the condensation of diazomethane on the inside of the cooled capillary. Adherence to the stipulated flow rate, capillary dimensions, temperature control, and drying conditions consistently prevents these explosions; however, an efficient protective shield is recommended.

Table I.  $^1\text{H}$  and  $^{13}\text{C}$  NMR Data for Protonated Diazomethanes

species	$\delta^a$ $^1\text{H}$	$\delta$ $^{13}\text{C}$
$\text{CH}_3\text{N}_2^+$ ( <b>1</b> )	4.75 s	44.5 q, $^1J_{\text{CH}}^b = 162.6$
$\text{CH}_2\text{DN}_2^+$	4.73 t, $^2J_{\text{HD}} = 2.30$	44.5 t, $^1J_{\text{CD}} = 24.7$
$\text{CH}_2=\text{N}^+=\text{NH}$ ( <b>2</b> )	7.22 d, $^4J_{\text{HH}} = 11.1$ 14.1 t, $^4J_{\text{HH}} = 11.1$	76.6 dt, $^1J_{\text{CH}} = 210$ . $^3J_{\text{CH}} = 14$
$\text{CH}_2=\text{N}^+=\text{ND}$	7.25 t, $^4J_{\text{HD}} = 1.6$	
$\text{CH}_3\text{OSO}_2\text{F}$ ( <b>3</b> )	4.18 <sup>c</sup> s,	65.2, $^c$ $^1J_{\text{CH}} = 155.5$
$\text{CH}_2\text{DOSO}_2\text{F}$	4.20 t, $^2J_{\text{HD}} = 1.6$	
$\text{CH}_3\text{OSO}_2\text{F}/\text{SbF}_5$ ( <b>4</b> )	4.52 s,	70.7
$\text{CH}_3\text{OS}^+\text{O}^-\text{SbF}_6^-$ ( <b>6</b> )	5.14 s, (5.50 <sup>d</sup> )	74.9, <sup>d</sup> $^1J_{\text{CH}} = 162.9$
$\text{CH}_3\text{OS}^+\text{OCIF}^-$	5.19 s, (5.63 <sup>d</sup> )	81.8, <sup>d</sup> $^1J_{\text{CH}} = 165.8$
$\text{SbF}_6^-$ ( <b>7</b> )		
$\text{CH}_2=\text{N}_2$	3.28, <sup>e</sup> $^2J_{\text{HH}} = 4.6$	23.3, <sup>f</sup> $^1J_{\text{CH}} = 195.1$
$\text{CH}_2=\text{C}=\text{CH}_2$	4.55, <sup>g</sup> $^4J_{\text{HH}} = 7.0^g$	74.0, <sup>h</sup> $^1J_{\text{CH}} = 168^g$

<sup>a</sup> Chemical shifts are reported in parts per million relative to internal  $\text{Me}_4\text{Si}$  shift = 0. <sup>b</sup> Coupling constants were measured in hertz.

<sup>c</sup> These chemical shifts were slightly solvent dependent. <sup>d</sup> Reference external  $\text{Me}_4\text{Si}$ , ref 19. <sup>e</sup> Reference 24. <sup>f</sup> Reference 25.

<sup>g</sup> Reference 26. <sup>h</sup> Reference 27.

of its original intensity (see Table III). The tube was removed to a cold bath at  $-100^\circ\text{C}$  in a fume hood and opened. A solution of acetone (50  $\mu\text{L}$ ) in  $\text{SO}_2\text{ClF}$  (50  $\mu\text{L}$ ) was cooled to  $-100^\circ\text{C}$  and slowly added to the acid solution via a cooled syringe. The solution was mixed at  $-100^\circ\text{C}$  and returned to the spectrometer at  $-100^\circ\text{C}$ . After measurement of the spectrum a second addition of acetone was carried out in the same manner.

**Kinetic Experiments.** Diazomethane was protonated by  $\text{HOSO}_2\text{F}/\text{SO}_2\text{ClF}$  (1:4) at  $-120^\circ\text{C}$ . The requisite amount of  $\text{SbF}_5$  was distilled onto the solution before the tube was sealed, and the sample was thoroughly mixed from  $-120$  to  $-100^\circ\text{C}$  before spectra were run.

**Experiments Involving Sulfur Dioxide.** In the standard experiments diazomethane was passed into a solution of  $\text{HOSO}_2\text{F}$  or  $\text{HOSO}_2\text{F}/\text{SbF}_5$  in  $\text{SO}_2\text{ClF}/\text{SO}_2$  (4:1) as described above. The experiments involving protonation of diazomethane and subsequent addition of  $\text{SO}_2$  to the  $\text{SbF}_5$ -containing solution, or of  $\text{SbF}_5$  to the  $\text{SO}_2$ -containing solution, were carried out by the suspension technique described for "Proton Exchange Experiments".

**Quenching Experiments.** The acid solutions were rapidly poured into a suspension of  $\text{NaHCO}_3$  (500 mg) in methanol (10 mL) at  $-90^\circ\text{C}$ . The mixture was allowed to warm to  $-30^\circ\text{C}$  and then the solvent was trap-trap distilled on a high-vacuum line. The distillate was analyzed by GC/MS on a Carbowax column (20%, 3 m,  $20^\circ\text{C}$ ); retention times: dimethyl ether and methyl chloride 0.8 min, methanol 2.2 min.

## Results and Discussion

**Protonation with  $\text{HOSO}_2\text{F}$ : Formation of the Methanediazonium Ion.** Conventional methods of sample introduction into superacid media are inapplicable to preparations involving diazomethane. On the one hand it decomposes instantly in  $\text{SO}_2\text{ClF}$  even at  $-120^\circ\text{C}$  to yield a polymeric material; furthermore it is extracted very rapidly from a dichloromethane matrix by the acid solution at  $-120^\circ\text{C}$ , and again polymerization occurs. However very clean samples may be obtained by bubbling the diazomethane gas, diluted in a nitrogen stream, through the acid solution at  $-120^\circ\text{C}$ . This procedure allows gradual addition of the substrate and efficient mixing by the bubbling action, thus avoiding the high local concentrations that lead to oligomerization.

The  $^1\text{H}$  NMR spectrum of diazomethane protonated by  $\text{HOSO}_2\text{F}$  in  $\text{SO}_2\text{ClF}$  at  $-120^\circ\text{C}$  shows one singlet at 4.75 ppm attributed to **1**, accompanied by a small amount (5%) of the singlet of methyl fluorosulfate **3** at 4.18 ppm (identical with an authentic sample). On heating to  $-85^\circ\text{C}$  this peak becomes more intense at the expense of the former, and at  $-80^\circ\text{C}$  the decomposition is complete within 1 h. The use of  $\text{DOSO}_2\text{F}$  led to a broadened resonance for **1-d**, which became resolved into a triplet ( $J = 2.3\text{ Hz}$ ) on heating to  $-80^\circ\text{C}$ . The methyl fluorosulfate formed also contained only one deuterium atom.

The chemical shift of the resonance at 4.75 ppm is invariant for samples prepared with  $\text{HOSO}_2\text{F}$ ,  $\text{HOSO}_2\text{F}/\text{SbF}_5$ , and  $\text{HF}/\text{SbF}_5$ , so no counterion effect is discernible. Furthermore the  $^{19}\text{F}$  spectrum of a sample prepared with  $\text{HOSO}_2\text{F}$  showed no resonance attributable to a covalently bound fluorosulfate species. Samples prepared with mono  $^{15}\text{N}$ -labeled diazomethane show

Table II.  $^{15}\text{N}$ - $^1\text{H}$  and  $^{15}\text{N}$ - $^{13}\text{C}$  Coupling Constants<sup>a</sup> for Protonated Diazomethanes

species	$^1J_{\text{NH}}$	$^2J_{\text{NH}}$	$^3J_{\text{NH}}$	$^1J_{\text{NC}}$	$^2J_{\text{NC}}$
$\text{CH}_2=\text{N}_2$		0.14	1.10	-23.9	
$\text{CH}_3\text{N}^+\equiv\text{N}$ (1)		3.7	1.84	4.5	4.5
$\text{CH}_2=\text{N}^+=\text{NH}$ (2)	65.5	3.2(HCN)	2.75	32.2	<2
		7.8(NNH)			
$\text{CH}_3\text{N}^+\equiv\text{C}$		+3.2 <sup>b,c</sup>		-9.8	
				( $\text{CH}_3\text{N}$ ) <sup>b,c</sup>	
$\text{CH}_3\text{N}^+\equiv\text{CCH}_3$		+3.8 <sup>c,d</sup>			

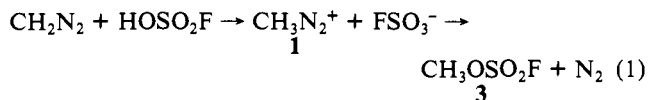
<sup>a</sup> No algebraic sign is specified when it has not been determined.

<sup>b</sup> Reference 28. <sup>c</sup> Calculated by multiplying  $J_{\text{H}^{14}\text{N}}$  by  $\gamma(^{15}\text{N})/\gamma(^{14}\text{N}) = 1.4$ . <sup>d</sup> Reference 29.

$^{15}\text{N}$ -H coupling with coupling constants of 3.66 Hz to the  $\alpha$  nitrogen and 1.8 Hz to the  $\beta$  one. Therefore the observed species contains both the original nitrogen atoms of the diazomethane.

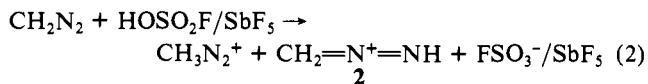
The proton-coupled  $^{13}\text{C}$  spectrum of this species consists of a quartet ( $J = 163$  Hz). On the basis of these observations we attribute to it structure 1. The complete spectra data and those for comparison products are listed in Tables I and II.

In our preliminary communication we also reported the formation of a minor species containing a methylene group and tentatively assigned structure 2 to it. We have since found that the formation of this compound, now considered to be 5 (vide infra), depends on the presence of  $\text{SO}_2$  in the solvent. When  $\text{HOSO}_2\text{F}$  in  $\text{SO}_2\text{ClF}$ , purified as recommended by Gillespie,<sup>15</sup> is employed as the acid system, *N*-protonated diazomethane is not observed.



**Protonation with  $\text{HOSO}_2\text{F}/\text{SbF}_5$ : Formation of the Methylenediazenium Ion.** When diazomethane is protonated by the more strongly acidic system  $\text{HOSO}_2\text{F}/\text{SbF}_5$  at  $-120$  °C, the resonance of 1 at 4.75 ppm is accompanied by a doublet (two H) at 7.22 ppm coupled to a triplet at 14.1 ppm<sup>21</sup> (one H). As the temperature is raised to  $-70$  °C the triplet broadens without concomitant broadening of the doublet. Hence one can conclude that the triplet resonance is due to an N-H proton subject to  $^{14}\text{N}$  quadrupolar relaxation. Accordingly when either of the diazomethane nitrogens is labeled with  $^{15}\text{N}$  the low-field resonance appears as a doublet of triplets (Figure 1). The coupling constant to the terminally labeled nitrogen is 65.5 Hz, whereas that to the centrally labeled nitrogen is 7.8 Hz. Consequently it is apparent that the second species contains a terminal N-H group and that no nitrogen scrambling occurs.

In the proton-coupled  $^{13}\text{C}$  spectrum of diazomethane protonated by  $\text{HOSO}_2\text{F}/\text{SbF}_5$ , the resonance of 1 is accompanied by a triplet of doublets ( $J = 210, 15$  Hz) with a chemical shift of 76.6 ppm. On the basis of these and the above  $^1\text{H}$  NMR data we assign structure 2 to the second species.



(21) This chemical shift was found to vary slightly with temperature and acidity.

(22) The data for 2 correct those already published,<sup>14</sup> which are now attributed to the  $\text{SO}_2$ -complexed species 5.

(23) Dean, P. A. W.; Gillespie, R. J. *J. Am. Chem. Soc.* **1969**, *91*, 7260-7264.

(24) Jacobsen, J. P.; Schaumberg, K.; Nielsen, J. T. *J. Magn. Reson.* **1974**, *13*, 372-378.

(25) Albright, T. A.; Freeman, W. J. *Org. Magn. Reson.* **1977**, *9*, 75-79.

(26) Whipple, E. B.; Goldstein, J. H.; Stewart, W. E. *J. Am. Chem. Soc.* **1959**, *81*, 4761-4764.

(27) Spiesscke, H., personal communication quoted in: Stothers, J. B. "Carbon 13 NMR Spectroscopy"; Academic Press: New York, 1972; p 75.

(28) Schulman, J. M.; Venanzi, T. *J. Am. Chem. Soc.* **1976**, *98*, 4701-4705.

(29) Olah, G. A.; Kiovsky, T. E. *J. Am. Chem. Soc.* **1968**, *90*, 4666-4672.

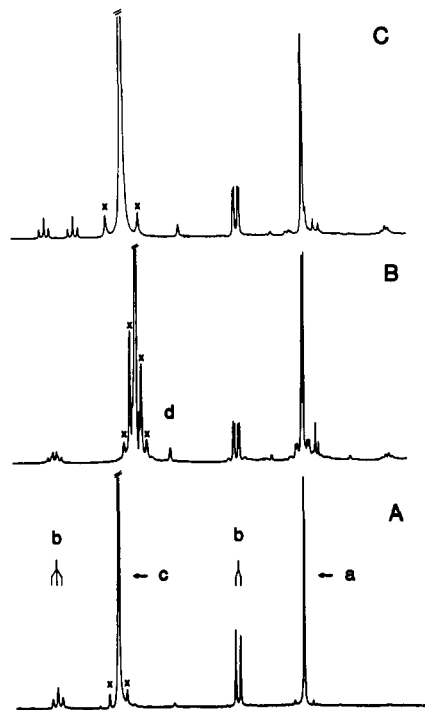


Figure 1.  $^1\text{H}$  NMR spectra of diazomethane protonated by  $\text{HOSO}_2\text{F}/\text{SbF}_5/\text{SO}_2\text{ClF}$  at  $-100$  °C; (A)  $\text{CH}_2=\text{N}=\text{N}$ ; (B)  $\text{CH}_2=^{15}\text{N}=\text{N}$ ; (C)  $\text{CH}_2=\text{N}^{15}\text{N}$ . (a) 1; (b) 2; (c)  $\text{HOSO}_2\text{F}$ ; spinning side bands are marked x.

In all samples prepared with  $\text{SbF}_5$ , decomposition of 1 commenced around  $-75$  °C; however, 2 remained relatively stable until  $-60$  °C. The final product from both species was 3, accompanied by its complex with  $\text{SbF}_5$ . The identity of this complex was established in a blank experiment by adding  $\text{SbF}_5$  to authentic methyl fluorosulfate in  $\text{SO}_2\text{ClF}$ . No information is available for the stoichiometry or constitution of this complex, to which we refer for convenience as  $\text{CH}_3\text{OSO}_2\text{F}/\text{SbF}_5$  (4) by analogy with the  $\text{CH}_3\text{SO}_2\text{F}/\text{SbF}_5$  complex.<sup>23</sup> The ratio of free to complexed product is of course proportional to the concentration of  $\text{SbF}_5$ .

**NMR Parameters for 1 and 2.** The complete spectral data for 1 and 2 and those for relevant comparison products are presented in Tables I and II.

The  $^1\text{H}$  chemical shift of 1 correlates well with those of other methyl groups attached to strongly electron-withdrawing substituents. The difference in the geminal  $^2J_{\text{HH}}$  coupling constants for 1 and 3 of  $(-15.0$  Hz and  $(-10.5$  Hz, respectively (derived from multiplying the observed  $^2J_{\text{HD}}$  constant by  $\gamma(\text{H})/\gamma(\text{D}) = 6.55$ ) results from two contributions. Firstly, in 3 there is a positive increment due to the inductive effect of the electron-withdrawing substituent<sup>30</sup> (cf.  $^2J_{\text{HH}}$  in  $\text{CH}_4 = -12.4$  Hz); this effect should also exist in 1 but is offset by the negative contribution of each of the two  $\pi$  bonds of the diazonium group<sup>31</sup> (cf. for  $\text{H}_3\text{C}\equiv\text{N}$   $^2J_{\text{HH}} = -16.9$  Hz).

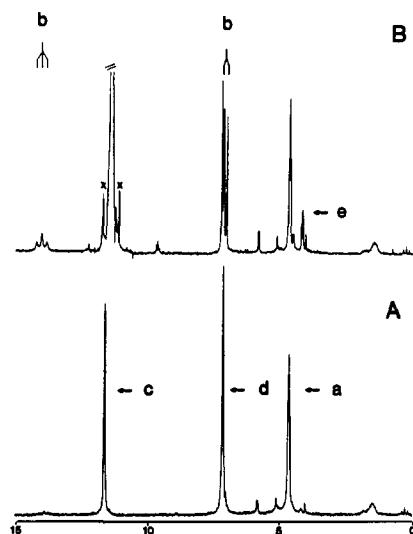
The  $^1J_{\text{CH}}$  coupling constant of 1 is similar to those of other highly reactive methylating agents in Table I; however, the  $^{13}\text{C}$  chemical shift of 1 is 20-30 ppm upfield from those of its analogues although 20 ppm downfield from the diazomethane resonance. Roberts has already indicated the unreliability of the  $^{13}\text{C}$  chemical shift as a measure of electron density on carbon in neutral diazo compounds.<sup>32</sup> The shielding provided by the diazo group appears to persist in the methanediazonium ion.

The  $^2J_{\text{NH}}$  coupling constant for 1 is intermediate between those for methyl isocyanide and the methylacetoneitrilium ion (we assume that it is positive as the proton is not near to a nitrogen lone pair<sup>33</sup>)

(30) Pople, J. A.; Bothner-By, A. A. *J. Chem. Phys.* **1965**, *42*, 1339-1349.

(31) Barfield, M.; Grant, O. M. *J. Am. Chem. Soc.* **1963**, *85*, 1899-1904.

(32) Duthaler, R. O.; Forster, H. G.; Roberts, J. D. *J. Am. Chem. Soc.* **1978**, *100*, 4974-4979.



**Figure 2.**  $^1\text{H}$  NMR spectra of proton exchange experiments: (A)  $\text{CH}_2\text{N}_2 + \text{DOSO}_2\text{F}/\text{SbF}_5$  before addition of  $\text{HOSO}_2\text{F}$ ; (B) same solution as (A) after addition of  $\text{HOSO}_2\text{F}$ . (a)  $\text{CH}_2\text{DN}_2^+$ ; (b)  $\text{CH}_2\text{N}_2^+\text{H}$ ; (c)  $\text{HOSO}_2\text{F}/\text{SbF}_5$ ; (d)  $\text{CH}_2\text{N}_2^+\text{D}$ ; (e)  $\text{CH}_2\text{DOSO}_2\text{F}$ ; spinning side bands are marked x.

but is markedly different from that of diazomethane. The  $^1J_{\text{CN}}$  coupling constant of **1** also differs significantly from those of diazomethane and ethyl diazoacetate for which the coupling is apparently dominated by the Fermi contact term.<sup>34</sup> In this respect it resembles the  $^1J_{\text{CN}}$  constants for the isoelectronic acetonitrile and methyl isocyanide systems where substantial positive contributions arise from orbital and spin dipolar terms.<sup>35</sup>

The  $^1\text{H}$  chemical shifts of **2** are appropriate for the proposed structure; on the other hand the observed  $^4J_{\text{HH}}$  coupling of 11.1 Hz is remarkable compared to the corresponding constant of 7 Hz for allene and that of 2 Hz for methyldiazene ( $\text{CH}_3\text{N}=\text{NH}$ ).<sup>36</sup> At present no other reasonable data for comparison seem to exist.<sup>37</sup> The  $^{13}\text{C}$  chemical shift of **2** is very similar to that of the terminal carbon in allene. The former shift could reasonably have been predicted to be by far the greater, if one assumes that the electron density is considerably lower on the diazenium carbon, as is consistent with its much greater  $^{13}\text{C}$ - $^1\text{H}$  coupling constant (by 42 Hz). So again the  $^{13}\text{C}$  shielding effect of the diazo-derived group is apparent.

The one-bond  $^1J_{\text{NH}}$  constant measured for **2** is substantially less than would be predicted from the Binsch relation for a trigonal nitrogen.<sup>38</sup> However similar anomalously low  $^1J_{\text{NH}}$  constants have been previously noted for ketimines<sup>38</sup> (e.g.,  $^1J_{\text{NH}} = 51$  Hz) and have been rationalized as being due to contributions from the electron orbital motion in the lone pair; accordingly the apparent anomaly was removed by protonation of the imine.<sup>38</sup> The increase in the absolute magnitude of the  $^1J_{\text{CN}}$  constant due to N-protonation is certainly worthy of note, but again lack of sufficient comparison data prevents further analysis.

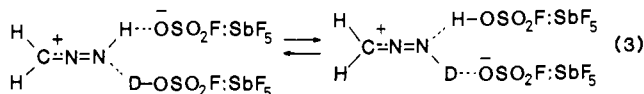
**Proton Exchange Experiments.** When  $\text{DOSO}_2\text{F}$  is employed as an acid, either alone or accompanied by  $\text{SbF}_5$ , only one deuterium atom is incorporated into the methanediazonium ion and into the final product methyl fluorosulfate. Hence protonation of diazomethane on the carbon atom is irreversible in this highly acidic medium. This was to be expected as the same phenomenon exists in aqueous acidic solution.<sup>4</sup> The coupling observed between

**Table III.** Relative Concentration of Species (%) Present before and after Addition of 50- $\mu\text{L}$  Aliquots of Acetone

	$\text{CH}_3\text{N}_2^+$	$\text{CH}_2\text{N}_2^+\text{H}$	$\text{CH}_3^-/\text{OSO}_2\text{F}$	$\text{CH}_3\text{OSO}_2\text{F}/\text{SbF}_5$
before	12.9	37.6	32.8	16.6
1st injection	21.8	18.5	47.4	12.2
2nd injection	24.7	3.3	65.4	6.5

the N-H and methylene protons of **2** excludes a rapid proton exchange on nitrogen; however, an exchange slow on the NMR time scale is conceivable, and was demonstrated in the following manner. A sample of diazomethane in  $\text{DOSO}_2\text{F}/\text{SbF}_5/\text{SO}_2\text{ClF}$  was prepared as usual and degassed, but before the NMR tube was sealed  $\text{HOSO}_2\text{F}$  (1 equiv relative to  $\text{DOSO}_2\text{F}$ ) was distilled into it and condensed on the walls above the sample solution. The tube was then sealed, and in subsequent operations care was taken to maintain its temperature below  $-100^\circ\text{C}$  to prevent melting and admixture of the protic acid. The  $^1\text{H}$  NMR spectrum run on this sample at  $-100^\circ\text{C}$  showed 1-d and 2-d (Figure 2A). The tube was placed in a cold bath at  $-100^\circ\text{C}$  and shaken to dissolve the protic acid. The spectrum of the mixed solution, Figure 2B, showed both the N-protonated and N-deuterated species. As expected no change was observed in the resonance of **1**.

The exchange of the N-H proton cannot occur by a deprotonation reprotonation mechanism via the free conjugate base, as the competing irreversible protonation on carbon would ensure complete conversion to the diazonium ion. An attractive (but not unique) alternative would be proton exchange within a hydrogen-bonded complex, e.g., eq 3. No information is available



concerning the order or the concerted nature of the individual proton transfers.

**Deprotonation of the Methylenediazenium Ion.** The remarkable effect of increasing the acid strength (from pure  $\text{HOSO}_2\text{F}$  to  $\text{HOSO}_2\text{F}/\text{SbF}_5$  (1:1)) on the ratio of C-protonation to N-protonation could be interpreted in two ways. Firstly, protonation on nitrogen could be intrinsically slower than on carbon and become competitive only with stronger acids. In diazomethane, protonation of either terminus will involve rehybridization and electron reorganization, and these factors, allied to the overall exothermicity of the reaction, are chiefly responsible for determining the rate of proton transfer.<sup>39</sup> However, C-protonations of diazoalkanes have been shown to have low intrinsic barriers in the Marcus formalism,<sup>40,41</sup> and in this particular case the reaction will be extremely exoenergetic (the  $\text{pK}_a$  of **1** = 10).<sup>4</sup> Hence the Brønsted  $\alpha$  should be very small and any extra thermodynamic drive provided, e.g., by use of  $\text{HOSO}_2\text{F}/\text{SbF}_5$ , will have little effect on the activation free energy in the forward sense. The same situation must exist for N-protonation if it is sufficiently rapid to compete with protonation on carbon.

An alternative explanation is that protonation on nitrogen occurs at a rate comparable to that on carbon, but leads to a thermodynamically less stable species. Subsequently the fluorosulfate anion may be sufficiently basic to deprotonate **2** and convert it irreversibly into **1**. However when complexed to  $\text{SbF}_5$  the  $\text{FSO}_3^-$  anion may have its basicity sufficiently reduced that it deprotonates **2** only above  $-70^\circ\text{C}$ , at which temperature any diazonium ion formed is decomposed more rapidly into fluorosulfate product. Here all the free energy of stabilization of the complexed anion is translated into free energy of activation for deprotonation ( $\alpha = 1$ ) and so can have important kinetic consequences.

(39) Kresge, A. *J. Acc. Chem. Res.* **1975**, *8*, 354-360.

(40) Alberly, W. J.; Conway, C. A.; Hall, J. A. *J. Chem. Soc., Perkin Trans. 2* **1976**, 473-477.

(41) Kreevoy, M. M.; Oh, S. W. *J. Am. Chem. Soc.* **1972**, *94*, 2425-2431.

(33) Levy, G. C.; Lichter, R. L. "Introduction to  $^{15}\text{N}$  Nuclear Magnetic Resonance Spectroscopy"; Wiley: New York, 1979; p 114.

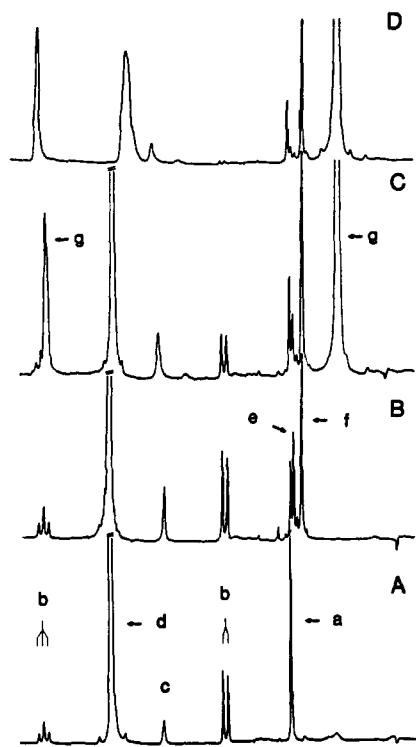
(34) Lichter, R. L.; Srinivasan, P. R.; Smith, A. B., III; Dieter, R. K.; Denney, C. T.; Schulman, J. M. *J. Chem. Soc., Chem. Commun.* **1977**, 366-368.

(35) Schulman, J. M.; Venanzi, T. *J. Am. Chem. Soc.* **1976**, *98*, 4701-4705.

(36) Tsuji, T.; Kosower, E. M. *J. Am. Chem. Soc.* **1971**, *93*, 1992-1999.

(37) We have also succeeded in preparing the homologue of **2**,  $\text{CH}_3\text{CH}=\text{N}^+=\text{NH}$ , and found  $^4J_{\text{HH}} = 10.2$  Hz.

(38) Binsch, G.; Lambert, J. B.; Roberts, B. W.; Roberts, J. D. *J. Am. Chem. Soc.* **1964**, *86*, 5564-5570.



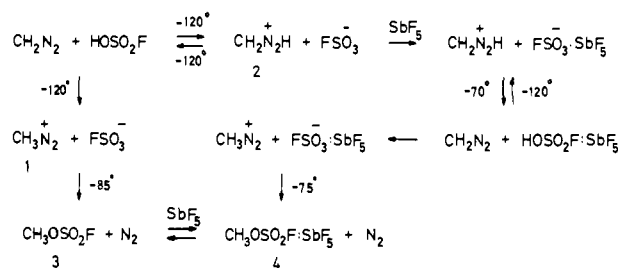
**Figure 3.**  $^1\text{H}$  NMR spectra of selective deprotonation experiments: (A)  $\text{CH}_2\text{N}_2 + \text{HOSO}_2\text{F}/\text{SbF}_5$  at  $-100^\circ\text{C}$ ; (B) same solution as (a) after standing at  $-72^\circ\text{C}$  for 140 min; (C) same solution as (B) after first addition of acetone at  $-100^\circ\text{C}$ ; (D) same solution as (C) after second addition of acetone. (a)  $\text{CH}_3\text{N}_2^+$ ; (b)  $\text{CH}_2\text{N}_2^+\text{H}$ ; (c)  $\text{H}_3\text{O}^+$ ; (d)  $\text{HOSO}_2\text{F}/\text{SbF}_5$ ; (e)  $\text{CH}_3\text{OSO}_2\text{F}/\text{SbF}_5$ ; (f)  $\text{CH}_3\text{OSO}_2\text{F}$ ; (g)  $(\text{CH}_3)_2\text{C}^+\text{-OH}$ .

These two explanations could be tested by generating both **1** and **2** and then reducing the acidity with the aim of converting **2** into **1**. Diazomethane was protonated as usual by  $\text{HOSO}_2\text{F}/\text{SbF}_5/\text{SO}_2\text{ClF}$ , and the tube was sealed. The sample was then allowed to stand at  $-72^\circ\text{C}$  for 140 min. During this time the concentration of **1** diminished from 46% to 13% (percentage of the total sum [**1**] + [**2**] + [**3**] + [**4**]), whereas [**2**] changed only from 43% to 38% (Table III). The tube was then cooled in liquid nitrogen, opened, and then transferred to a cold bath at  $-100^\circ\text{C}$ . Acetone was added cautiously as a precooled solution in  $\text{SO}_2\text{ClF}$ . When acetone is protonated, it liberates a stoichiometric equivalent of fluorosulfate anion, and if this is formed in excess of the  $\text{SbF}_5$  concentration, then the basicity is increased and both **1** and **2** are converted more rapidly into **3**. Successive additions led to a decrease in the concentration of **2** and an increase in that of the diazonium ion and methyl fluorosulfate (Figure 3). The proportions of the species observed are given in Table III. The proportion of  $\text{CH}_3\text{OSO}_2\text{F}/\text{SbF}_5$  decreases predictably with the addition of acetone and gives a convenient monitor of the amount of  $\text{SbF}_5$  uncomplexed by  $\text{FSO}_3^-$ .

Hence the methylenediazonium ion is the thermodynamically less stable isomer and its formation in the more acidic media is a kinetically controlled process. The effect of temperature on the distribution of protonated diazomethanes was examined by preparing two samples with the same acid solution at different temperatures. At  $-127^\circ\text{C}$  the ratio [**1**]/[**2**] was 71:29; at  $-80^\circ\text{C}$  it was 84:16. So the effect is not very marked but does indicate a small increase in the kinetically controlled product at lower temperature, as would be expected. There is a noticeable increase in the proportion of **2** formed as the ratio  $[\text{SbF}_5]/[\text{HOSO}_2\text{F}]$  increases. This could result from the increasingly efficient trapping by  $\text{SbF}_5$  of the  $\text{FSO}_3^-$ , which is liberated by protonation with free  $\text{HOSO}_2\text{F}$ . The various reactions revealed by the above experiments are summarized in Scheme I.

**Reactions in the Presence of Sulfur Dioxide.** When the diazomethane is protonated by  $\text{HOSO}_2\text{F}$  in  $\text{SO}_2\text{ClF}$  containing up to 20%  $\text{SO}_2$ , the methanediazonium ion peak in the  $^1\text{H}$  NMR

Scheme I



spectrum is accompanied by another broad resonance at 6.01 ppm with the same peak area. This peak was previously observed as a minor species in earlier experiments where the  $\text{SO}_2\text{ClF}$  was less rigorously purified and was attributed to **2** on the basis of its chemical shift, apparent exchange broadening, and  $^{13}\text{C}$  spectral data ( $\delta$  73.3, broad triplet,  $J = 176.0$  Hz). On heating of this solution to  $-80^\circ\text{C}$  decomposition occurs to give methyl fluorosulfate (**3**) as the major (80%) product, accompanied by a variety of unidentified peaks. Quenching of a sample in methanol at  $-100^\circ\text{C}$  leads to no identifiable products containing sulfur. When  $\text{SbF}_5$  is added gradually to a solution of diazomethane in  $\text{HOSO}_2\text{F}/\text{SO}_2/\text{SO}_2\text{ClF}$  the peak at 6.01 ppm is shifted downfield to 6.71 ppm, remaining nevertheless a broad singlet. When  $\text{SO}_2$  was added to the preformed mixture of **1** and **2** in  $\text{HOSO}_2\text{F}/\text{SbF}_5/\text{SO}_2\text{ClF}$  the methylene doublet of **2** at 7.2 ppm was converted into the broad singlet resonance at 6.71 ppm. Furthermore the triplet resonance at 14.1 ppm disappeared on the addition of  $\text{SO}_2$ . We conclude that in the absence of  $\text{SbF}_5$ ,  $\text{SO}_2$  traps the unstable diazenium species **2** to give an addition complex formulated as **5**. Such complexation of strong alkylating agents by  $\text{SO}_2$  and to a much lesser extent  $\text{SO}_2\text{ClF}$  has been well documented by Olah,<sup>19</sup> Gillespie,<sup>42</sup> and Peterson.<sup>43</sup> The broadening of the resonances observed in both the  $^1\text{H}$  and  $^{13}\text{C}$  spectra could then be a consequence of the rapid proton exchange on the terminal nitrogen, and a higher proportion of the dicationic conjugate acid in the presence of  $\text{SbF}_5$  could account for the observed downfield shift.

Several control experiments were carried out to ensure that the  $\text{SO}_2$ -containing species did not result from electrophilic attack on the  $\text{SO}_2$  on diazomethane itself. The diazoalkane was passed into a solution of  $\text{SO}_2/\text{SO}_2\text{ClF}$ , with subsequent addition of  $\text{HOSO}_2\text{F}$ . A complicated array of peaks was observed, none of which corresponded to the previously observed peak at 6.01 ppm. Furthermore when diazomethane was passed into a solution of  $\text{HOSO}_2\text{F}$  in  $\text{SO}_2/\text{SO}_2\text{ClF}$  (4:1), only methyl fluorosulfate was observed; no intermediates nor the decomposition products systematically formed from **5** could be observed.

The ratio of species [**5**]/[**1**] of 3:2 then would indicate that protonation on nitrogen is faster than on carbon. However, given the tentative nature of the assignment of structure **5**, this result should be taken as a corroboration rather than a confirmation of the overall scheme.

Sulfur dioxide also plays a role in the decomposition of **1**. In those solutions containing both  $\text{SO}_2$  and  $\text{SbF}_5$ , the major decomposition product of **1** is no longer methyl fluorosulfate but rather a product with a proton chemical shift of 5.11 ppm. Evidence is presented below that this is methylated  $\text{SO}_2$ , **6**. The decomposition of **5** in the same solutions is complex and has not been clarified. The transformations involving  $\text{SO}_2$  are outlined in Scheme II.

**Rate of Decomposition of the Methanediazonium Ion.** Whereas in the samples free of  $\text{SbF}_5$  the decomposition of **1** is complete in 1 h at  $-80^\circ\text{C}$ , no reaction is noticeable at this temperature in the more acidic solutions. The influence of the solution basicity, and hence nucleophilicity, on the decomposition rate of **1** was examined in more detailed with samples A, B, and C containing

(42) Gillespie, R. J.; Riddell, F. G.; Sim, D. R. *J. Am. Chem. Soc.* **1976**, *98*, 8069-8072.

(43) Peterson, P. E.; Brockingham, R.; Vidrine, D. W. *J. Am. Chem. Soc.* **1976**, *98*, 2660-2661.

