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AMINOSULFUR TRIFLUORIDES: RELATIVE THERMAL STABILITY [1]

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SUMMARY

The fluorinating reagent, DAST (diethylaminosulfur trifluoride, **1b**), has the potential to decompose violently when heated and presents a hazard if not properly handled . This investigation has shown that the decomposition occurs in two steps. First, a non-energetic disproportionation occurs to give sulfur tetrafluoride and bis(diethylamino)sulfur difluoride (**3b**). The less stable difluoride thus formed then undergoes a vigorous exothermic decomposition (detonation). The relative stabilities of DAST and several of its analogs were determined by differential thermal analysis. Morpholinosulfur trifluoride (**1g**, morpho-DAST) was the most stable of the aminosulfur trifluorides examined, and its use in place of the less stable DAST is recommended for fluorinations of alcohols.

INTRODUCTION

DAST (diethylaminosulfur trifluoride, **1b**) has gained widespread popularity as a fluorinating reagent in the last few years as can be seen by more than one hundred references [2] to its use. Although several other dialkylaminosulfur trifluorides have been prepared and some have been shown to be fluorinating agents, most of the work has been done with DAST. This is probably because the early work [3,4] was done primarily with DAST, and DAST was the first of this class of reagents to become commercially available [5].

Even though many fluorinations with DAST have been highly successful, there are some difficulties associated with this reagent. Explosions have been reported [6] in its preparation and use, and in some instances, major amounts of by-products are formed during the fluorinating process [2]. Other known trifluorides, such as dimethylaminosulfur trifluoride, (**1a**, methyl-DAST), and morpholinosulfur trifluoride, (**1g**, morpho-DAST), could possibly be superior to DAST, but comparisons have not been made.

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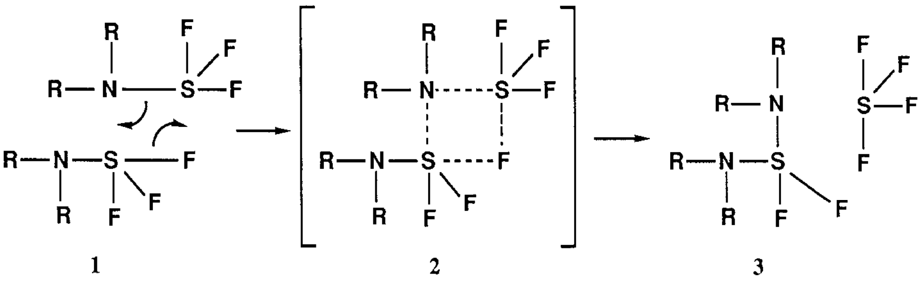
THERMAL STABILITY

We examined the thermal stability of DAST and compared it to the stability of four other known and two new aminosulfur fluorides (*Table I*) in the hope of finding a fluorinating reagent that would be safer to use than DAST. Our observations indicate that the decomposition of the aminosulfur trifluorides (**1**) occurs in two distinct stages. All of the samples examined underwent a slow decomposition at about 90° C, with evolution of sulfur tetrafluoride and formation of a diaminosulfur difluoride (**3**), as illustrated in *Scheme I*. Upon further heating, the samples underwent a catastrophic decomposition (explosion or detonation) at a temperature characteristic for each trifluoride, giving gaseous products and a considerable amount of black char. The detonation temperature does not depend on the bulk of the sample, but it does depend upon the rate at which it is heated Slower heating results in slightly lower detonation temperatures.



Scheme 1

The mechanism for the formation of **3** is believed to be a bimolecular disproportionation as illustrated in *Scheme 1*. An acid catalyzed mechanism for the disproportionation was ruled out when it was demonstrated that addition of hydrofluoric acid to the aminosulfur trifluoride did not change appreciably the detonation temperature.

The pure diaminosulfur difluorides (**3**) undergo a catastrophic decomposition at a temperature considerably below that of the corresponding trifluorides **1**. For example, **3b** detonated at 108° C, whereas DAST detonated 39° higher at 147° C when heated under identical conditions. We believe that the detonation of the trifluorides occurs only after a sufficient concentration of the less stable difluoride has been formed, and it is the very exothermic decomposition of the difluoride that initiates the explosion of the trifluoride. In contrast to the behavior of the trifluorides, the detonation temperature of the difluorides does not change appreciably with the rate at which they are heated. This observation supports the view that the difluorides serve as the detonation trigger for the trifluorides.

The new hexamethyleneiminosulfur trifluoride (**1f**) was the least stable of the trifluorides examined, with a detonation temperature of 130° C when a one millimolar sample was heated at 20°/min 4-Morpholinosulfur trifluoride (**1g**, morpho-DAST) was the most stable, with a detonation temperature of 175° C under the same conditions. The di(*n*-alkylamino)sulfur trifluorides all had about the same stability (148°± 5° C), with the larger alkyl groups giving slightly greater stability to the trifluorides. This could result from a slower buildup of the difluoride due to greater steric hindrance in the transition state **2** caused by the larger alkyl groups. The cyclic aminosulfur trifluorides **1d**, **1e**, and **1g**, were considerably more stable than the dialkylamino trifluorides. This could be due to the trifluorides and their corresponding difluorides having a more rigid structure and therefore less "wagging" effect to assist in breaking bonds. However, neither the steric bulk explanation nor the "wagging" effect can account for the unexpected instability of **1f**.

TABLE I

Detonation temperatures of aminosulfur fluorides (**1** & **3**) and yields of fluorocyclohexane (**4**) formed by fluorination of cyclohexanol

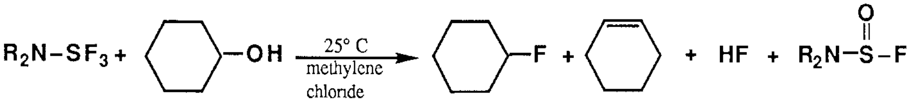
Cpd. No.	Aminosulfur Fluoride	Detonation Temp.,°C*	% Yield **4**†
1a	Dimethylaminosulfur trifluoride	144	31.8
1b	Diethylaminosulfur trifluoride	147	27.1
1c	Dibutylaminosulfur trifluoride	153	18 4
1d	1-Pyrrolodinosulfur trifluoride	156	19.1
1e	1-Piperidinosulfur trifluoride	172	21.1
1f	Hexamethyleneiminosulfur trifluoride	130	17.2
1g	4-Morpholinosulfur trifluoride	175	39.4
3b	*Bis*(diethylamino)sulfur difluoride	108	16.6
3e	*Bis*(1-piperidino)sulfur difluoride	135	17.2
3f	*Bis*(hexamethyleneimino)sulfur difluoride	118	—
3g	*Bis*(4-morpholino)sulfur difluoride	138	10.0

* for a one millimolar sample heated at 20°/min (average of three or more runs).

† from reaction of cyclohexanol with the aminosulfur fluoride at 25°C in methylene chloride solvent.

FLUORINATING ABILITY

The reaction of DAST with most primary alcohols and many secondary and tertiary alcohols gives nearly quantitative yields (before isolation) of the corresponding fluoride [2] However, certain secondary and tertiary alcohols give considerably lower yields of the fluoride due to extensive formation of an olefinic by-product. Cyclohexanol is an example of a simple alcohol that fails to give a satisfactory yield: when it is reacted with DAST at room temperature in methylene chloride, the major product is cyclohexene (73% gc yield), fluorocyclohexane (**4**) being formed in only 27% gc yield (see *Table I* and *Scheme 2*). This low yield of fluorocyclohexane is believed to be due to steric/conformational effects [7]



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Scheme 2

Because of the difficulty in fluorinating cyclohexanol, we considered this alcohol to be a useful model compound to compare the fluorinating ability of the various aminosulfur trifluorides. Each of the trifluorides was reacted with cyclohexanol under identical conditions. *Table I* shows the results of these reactions Although none of the reagents gave high yields of fluorocyclohexane, 4-morpholinosulfur trifluoride (**1g**, morpho-DAST) reproducibly gave the highest yield. The reasons for the higher yields are not clear, but it is probably due to a combination of steric and electronic factors. The diaminosulfur difluorides **3b**, **3e**, and **3g** also reacted with cyclohexanol to give fluorocyclohexane, but in each case, the yields were lower than those obtained with the corresponding trifluorides.

CONCLUSIONS

As a fluorinating reagent, 4-Morpholinosulfur trifluoride (**1g**, morpho-DAST) appears to have advantages over DAST (**1b**) and the other trifluorides that we examined. Not only is it more thermally stable, and therefore safer to handle, but it also gives a slightly higher yield of **4** in the fluorination of cyclohexanol. In addition, it fumes less in laboratory air, and is consequently easier to handle.

EXPERIMENTAL

DAST and methyl-DAST were purchased from Carbolabs, Inc., and the aminosulfur fluorides **1d**, **1e**, **1g**, **3b**, **3e**, and **3g** were prepared by literature procedures [3,4]. The new aminosulfur fluorides were prepared by a modification of these procedures, as follows:

Dibutylaminosulfur Trifluoride (**1c**).

A 20.5-g (0.1 mol) sample of *N,N*-di-*n*-butylaminotrimethylsilane [8] was added dropwise over a period of ten min. to a flask containing 8 mL (*ca* 15 g, 0.14 mol) of sulfur tetrafluoride cooled to -78°. The reaction mixture was slowly warmed to 25° and then distilled under reduced pressure to give 17.6 g (81%) of **1c** as a light yellow liquid, bp 57-59° (0.5 mm). Anal. Calcd for $C_8H_{18}F_3NS$. C, 44.22; H, 8.35. Found: C, 43.99; H, 8.28.

Hexamethyleneiminosulfur Trifluoride (**1f**).

A mixture of 49.7 g (0.5 mol) of hexamethyleneimine, 80.7 g (0.5 mol) of hexamethyldisilazane, 2 g of ammonium sulfate, and 1 mL of chlorotrimethylsilane was heated under reflux until chromatographic analysis indicated that the reaction was complete (30 hrs.). Distillation gave 51.4 g (60 % yield) of hexamethyleneiminotrimethylsilane as a colorless liquid, bp 186-187°. Anal. Calcd for $C_9H_{21}F_3NSi$: C, 63.08; H, 12.35. Found: C, 63.05; H, 12.40.

A 17.1-g (0.1 mol) sample of hexamethyleneiminotrimethylsilane was added dropwise over a period of 10 min. to a flask containing 8 mL (*ca* 15 g, 0.14 mol) of sulfur tetrafluoride cooled to -78°. The reaction mixture was slowly warmed to 25° and then distilled under reduced pressure to give 14.2 g (85 %) of **1f** as a yellow liquid, bp 50° (0.5 mm). Anal. Calcd for $C_6H_{12}F_3NS$: C, 38.49; H, 6.46. Found: C, 38.28; H, 6.25.

Bis(hexamethyleneimino)sulfur Difluoride (**3f**)

A solution of 2.42 g (90.01 mol) of hexamethyleneiminotrimethylsilane in 30 mL of ether was added dropwise over a period of 5 min. to a solution of 2.59 g (0.01 mol) of **1f** in 30 mL of ether cooled to -78°. The reaction mixture was then warmed to room temperature and the solvent and by-product fluorotrimethylsilane was distilled off at reduced pressure (0.5 mm) to give 2.54 g (95 %) of **3f** as a yellow solid, mp 40-45°. Elemental analyses were not obtained because of the instability of **3f**, but its IR spectrum was very similar to those of the other known difluorides **3b**, **3e**, and **3g**

Thermal Analyses of Aminosulfur Fluorides

Differential thermal analyses were performed in triplicate on each of the aminosulfur trifluorides and diaminosulfur difluorides listed in *Table I* by heating a 1 mmol-sample of the fluoride in a 5 mm thin-walled glass tube at a constant rate of 20°/min in a silicone oil bath The temperature of the oil bath was plotted against the difference in temperature between the sample and the bath. The detonation temperature was recorded as the bath temperature at the time when the differential temperature was the greatest In a few cases, the size of the sample was doubled, and also in a few cases, the rate of heating was slowed to 10°/min. *Chart I* shows examples of these plots.

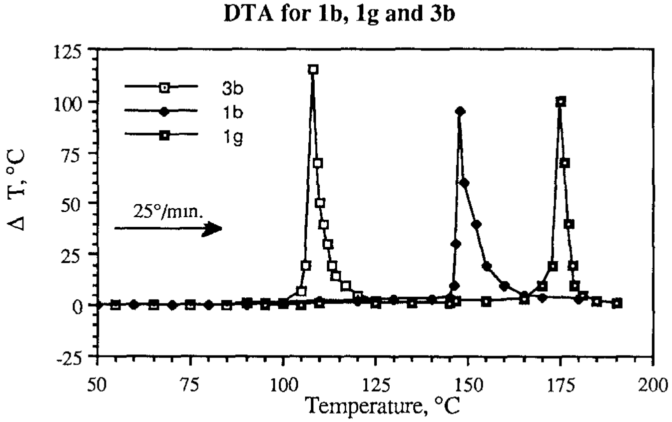

CHART I

Reactions of Aminosulfur Fluorides with Cyclohexanol (see *Table I*).

A solution of 1 mmol of dry cyclohexanol in 4 mL of methylene chloride at 25° was added to 2 mmol of the aminosulfur fluoride fluorinating reagent The reaction mixture was shaken, and then poured into an equal volume of 5% aqueous sodium bicarbonate The organic layer was washed with water, dried ($MgSO_4$), and then analyzed by gas chromatography

Controlled Thermal Decomposition of **1b** to give **3b** and Sulfur Tetrafluoride

A 1.0-g sample of DAST was heated at 110° (by a bath of refluxing toluene) for 90 min and the gas that slowly evolved was condensed in a trap cooled to -78°. The evolved gas was identified as almost pure sulfur tetrafluoride by comparison of its infrared spectrum with that of an authentic sample. The remaining dark residue, after cooling, was identified as a slightly impure sample of **3b** by comparison of its infrared spectrum with that of an authentic sample of pure **3b** [3].

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