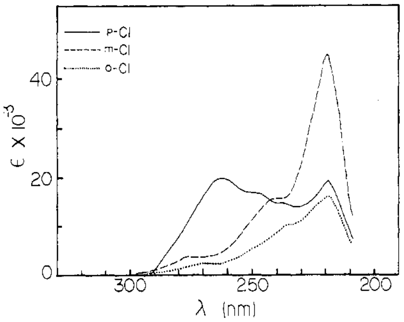

Figure 5. Effect on E_{CT} of chlorine atom substitution in the para, meta, and ortho positions of triphenylgallium.

relatively minor and constant role in the π excited state.

Comparison of the charge-transfer spectra of ortho, meta, and para chloro-substituted compounds in Figure 5 shows the effect caused by moving a common substituent to different positions on the ring. The main charge-transfer band increases in energy as the atom moves closer to the metal. Steric effects alone can account for this trend by causing a progressive increase in the pitch of the rings and hence increasing the gap between the ground and excited states. However attention should also be paid to possible changes in the Ga–C σ bond. It has been noted that ^{69}Ga and ^{71}Ga nuclear quadrupole rersonance frequencies in these same compounds decrease in this series (para, 49.14 MHz; meta, 47.11 MHz; ortho, 46.70 MHz).[4] In order to account for this change in the metal electric field gradient, a decrease in the Ga–C σ-bond covalency is indicated.[4] It is to be noted that decreased π bonding should increase the resonance frequency which is opposite the observed trend. An increase in steric hindrance is most likely the source of the suggested Ga–C bond length increase, but both the bond length increase and a ring pitch increase would lead to the increased charge-transfer energy.

In sum, these data suggest that the spatial requirements of ortho and meta substitution cause structural changes in these compounds that effectively insulate the gallium atom from an active role in the π excited states. Electronic effects involving participation of the gallium atom do seem important in understanding para substituent effects, however.

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Registry No. $(C_6H_5)_3B$, 960-71-4; $(C_6H_5)_3Ga$, 1088-02-4; $(C_6H_5)_3In$, 3958-47-2; $(p\text{-}CH_3C_6H_4)_3Ga$, 18797-37-0; $(p\text{-}CH_3CH_2C_6H_4)_3Ga$, 58448-01-4; $(p\text{-}(CH_3)_3CC_6H_4)_3Ga$, 58447-98-6; $(p\text{-}CH_3OC_6H_4)_3Ga$, 58448-03-6; $(p\text{-}FC_6H_4)_3Ga$, 58448-00-3; $(p\text{-}ClC_6H_4)_3Ga$, 58447-99-7; $(p\text{-}BrC_6H_4)_3Ga$, 18797-36-9; $(m\text{-}CH_3C_6H_4)_3Ga$, 18797-38-1; $(m\text{-}FC_6H_4)_3Ga$, 58448-13-8; $(m\text{-}ClC_6H_4)_3Ga$, 58448-02-5; $(m\text{-}BrC_6H_4)_3Ga$, 58448-14-9; $(o\text{-}ClC_6H_4)_3Ga$, 58448-04-7; $(2,4,6\text{-}(CH_3)_3C_6H_4)_3Ga$, 60607-12-7.

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Aminolysis of Trifluoromethylchlorophosphoranes. Preparation and Characterization of the Trifluoromethyltris(dimethylamino)phosphonium Ion, $CF_3P[N(CH_3)_2]_3^+$

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The new trifluoromethyltris(dimethylamino)phosphonium ion has been prepared from CF_3PCl_4 or $(CF_3)_2PCl_3$ and dimethylamine. The latter case involves substitution of CF_3 by dimethylamine yielding CF_3H. $(CF_3)_2PCl_2[N(CH_3)_2]$ also reacts with dimethylamine yielding CF_3H and the $CF_3P[N(CH_3)_2]_3^+$ ion. The ion is stable in aqueous solution but hydrolyzes in alkaline solution to $OP[N(CH_3)_2]_3$ and CF_3H. Spectroscopic properties of the phosphonium ion are reported.

Introduction

Dimethylamine reacts with $(CF_3)_3PCl_2$ to form $(CF_3)_3PCl[N(CH_3)_2]$ and $(CF_3)_3P[N(CH_3)_2]_2$ according to the amount of amine used.[1] $(CF_3)_2PCl_3$ however reacts in a more complicated fashion giving, in addition to the analogous $(CF_3)_2PCl_2[N(CH_3)_2]$, the phosphonium salt $CF_3P[N(CH_3)_2]_3^+Cl^-$ by elimination of CF_3H.

Experimental Section

$(CF_3)_2PCl_3$ and CF_3PCl_4 were prepared as described[2-4] by adding chlorine to the chlorophosphines $(CF_3)_2PCl$ and CF_3PCl_2,[5] respectively, which were prepared by reaction of mercury(II) chloride[6] with iodophosphines prepared from CF_3I and red phosphorus.[5] Commercial dimethylamine was vacuum distilled before use. All other chemicals were reagent grade products and were used without purification.

Infrared spectra of solids were obtained on Nujol and Fluorolube mulls using Perkin-Elmer 457 or 421 instruments. Volatile compounds were contained in a 9-cm cell with KBr windows. NMR spectra were obtained with Varian A56/60 or HA 100 or Bruker HFX-90 instruments. Where necessary samples were prepared in a dry atmosphere using carefully dried solvents. Capillaries of 5% TMS in CCl_3F were added to provide external reference for ^{1}H or ^{19}F chemical shift measurements. ^{1}H spectra were measured at 60 or 100 MHz and ^{19}F at 56.4 or 94.1 MHz except in the case of the Bruker in-

Table I. Reaction Products of $(CF_3)_2PCl_3$ with $(CH_3)_2NH$[a]

Initial $(CH_3)_2NH$ (mol)/initial $(CF_3)_2PCl_3$ (mol)	0.8	2.0	2.9	4.2	5.7	8.5	12.4
Reacted $(CH_3)_2NH$ (mol)/reacted $(CF_3)_2PCl_3$ (mol)	2.3	2.6	2.8	2.9	3.6	3.9	4.5
Products							
(1) % $(CH_3)_2NH$ recovered	0	23.2	27.3	35.0	36.5	54.9	64.1
(2) % $(CF_3)_2PCl_3$ recovered	65.6	41.0	24.0	4.4[b]	0	0	0
(3) % $(CF_3)_2PCl_2N(CH_3)_2$	22.5	39.1	47.0	31.0	25.6	22.5	21.9
(4) % CF_3H (=% $CF_3P[N(CH_3)_2]_3{}^+$)	2.9	7.4	12.0	22.5	35.5	44.4	64.5
(5) % unknown $(CF_3)_2P$ species[c]	2.9	2.5	4.5	8.5	8.5	6.0	0
% total CF_3P species[d]	93.9	90.0	87.5	66.4	79.6	72.9	86.4

[a] Short reaction time (30 min) as described in Experimental Section. [b] Quantity involved here is small and the value is consequently less reliable. [c] Obtained from percent CF_3H and NMR spectra of solid residues as described in the text. [d] Obtained by adding percent values in rows (2)-(5).

strument where measurements were made at 84.7 MHz. The ^{31}P spectrum was also obtained with the Bruker instrument at 36.4 MHz and referenced to a P_4O_6 (capillary) standard.[8] Microanalyses were done by the Department of Chemistry, University of Alberta, or Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

Reaction of $(CF_3)_2PCl_3$ with Dimethylamine. (a) Reaction of Long Duration. A sample of $(CF_3)_2PCl_3$ (1.077 g, 3.91 mmol) was allowed to react with $(CH_3)_2NH$ (1.081 g, 24.02 mmol) for 4 days at room temperature. Vacuum fractionation of the volatile products gave $(CH_3)_2NH$ (0.185 g, 4.11 mmol; collected at −116 °C) and CF_3H (0.283 g, 4.04 mmol; collected at −196 °C). The white involatile solid which remained in the reaction tube was identified as a mixture of $CF_3P[N(CH_3)_2]_3{}^+Cl^-$ and $(CH_3)_2NH_2{}^+Cl^-$ salts as described below. Other species which could not be identified were present in small concentrations in the solid product as indicated by ^{19}F NMR (ϕ 59.8 ppm, $^2J_{PF}$ = 116 Hz; ϕ 66.4 ppm, $^2J_{PF}$ = 207 Hz) on solutions in CD_3CN and $CDCl_3$; however, the species giving rise to these signals did not persist in aqueous solutions. The latter of these two species appeared to be a $(CF_3)_2P$ species according to the ^{31}P NMR spectrum (δ = +119.3 vs. P_4O_6, $^2J_{PF}$ = 207 Hz, septet) of the solid in CD_3CN solution, a conclusion which is further substantiated by the observation that neutral hydrolysis of the salt mixture leads to the disappearance of the J = 207 Hz (as well as the J = 116 Hz) signal and the appearance of a ^{19}F signal due to[9] $(CF_3)_2PO_2{}^-$. As indicated below $CF_3P[N(CH_3)_2]_3{}^+$ is water stable and the signal arising therefrom remains unchanged upon hydrolysis.

(b) Short-Duration Reaction series. By use of the apparatus described elsewhere,[1] various amounts of $(CF_3)_2PCl_3$ were reacted with dimethylamine at room temperature for 30 min. The amount of amine used throughout the series was kept relatively constant to minimize the effect of its partial pressure on the reaction mechanism. Typically a quantity of dimethylamine (~20 mmol) was condensed into a side arm and isolated by closing the stopcock. Next a weighed quantity of $(CF_3)_2PCl_3$ (3-5 mmol) was condensed into the reaction vessel and allowed to warm to room temperature. Dimethylamine, also at room temperature, was admitted through the intervening stopcock whereupon immediate reaction with $(CF_3)_2PCl_3$ ensued. After 30 min the volatile products were separated giving $(CF_3)_2PCl_2[N(CH_3)_2]$[1] containing traces of unreacted $(CF_3)_2PCl_3$ in the −45 °C trap (relative proportions were deduced by ^{19}F NMR), unreacted $(CF_3)_2PCl_3$ (if any) at −96 °C, unreacted dimethylamine at −116 °C, and CF_3H at −196 °C. The solid residues were dissolved in CH_3CN and analyzed by ^{19}F NMR spectroscopy showing, in addition to $CF_3P[N(CH_3)_2]_3{}^+$, variable proportions of the species with J = 207 Hz mentioned above. The quantity of this species was estimated by multiplying the percent CF_3H value (equal to percent $CF_3P[N(CH_3)_2]_3{}^+$) by the relative proportion of the J = 207 Hz species to $CF_3P[N(CH_3)_2]_3{}^+$ ion in the NMR spectrum, assuming the former to contain two CF_3 groups. Results are given in Table I and plotted in Figure 1. The unknown species was not plotted.

Reaction of $(CF_3)_2PCl_2[N(CH_3)_2]$ with Dimethylamine. $(CF_3)_2PCl_2[N(CH_3)_2]$ (0.276 g, 0.972 mmol) and $(CH_3)_2NH$ (0.082 g, 1.83 mmol) were condensed into a tube which was allowed to warm slowly over a 1-h period to room temperature. The recovered products were CF_3H (0.024 g, 0.34 mmol) excess $(CH_3)_2NH$ (0.016 g, 0.36 mmol), and an involatile white solid, which was identified by its ^{19}F NMR spectrum in CD_2Cl_2 as a mixture of unreacted $(CF_3)_2PCl_2[N(CH_3)_2]$ (ϕ_F 66.6 ppm, $^2J_{PF}$ = 158 Hz, $^4J_{FF}$ = 1.1 Hz)[1] and $CF_3P[N(CH_3)_2]_3{}^+$ (ϕ_F 59.7 ppm, $^2J_{PF}$ = 108 Hz) in an approximate 1.3:1 (respectively) molar ratio in agreement with the stoichiometry of eq 3 and the above mass balance data. A small amount of another CF_3P containing species with similar coupling constant and chemical shift parameters (ϕ 59.8 ppm, $^2J_{PF}$ = 115 Hz) to the monotrifluoromethylphosphonium cation was also present in the product of this reaction but this species, which has not yet been identified, disappears when the phosphonium salt solution is dissolved in water. The yield of $CF_3[N(CH_3)_2]_3{}^+$, deduced from the yield of CF_3H, was approximately 35% of the phosphorane taken or about 70% of the amount of phosphorane reacted.

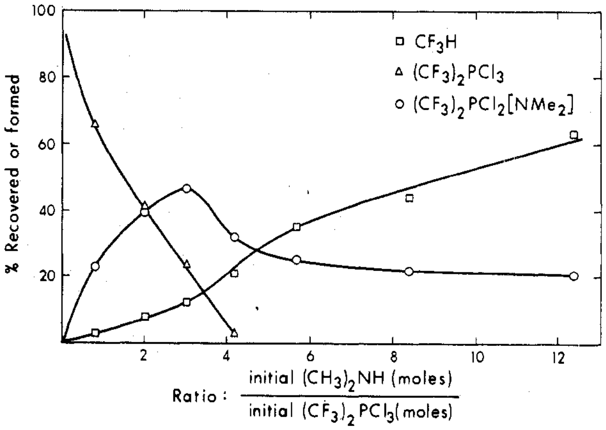

Figure 1. Product yields for different reacting ratios of dimethylamine and $(CF_3)_2PCl_3$ for reactions of short duration performed under similar conditions. The quantity of CF_3H is equal to that of $CF_3P[N(CH_3)_2]_3{}^+$ formed as indicated in the text.

Reaction of CF_3PCl_4 with $(CH_3)_2NH$. A large excess of dimethylamine (0.452 g, 10.04 mmol) (mole ratio 10:1) was added in the gas phase to CF_3PCl_4 (0.239 g, 0.99 mmol) using the apparatus described elsewhere.[1] The reaction was allowed to proceed at room temperature for 24 h. Separation of the volatile products gave unreacted $(CH_3)_2NH$ (0.182 g, 4.06 mmol; collected at −116 °C) and a minute trace of CF_3H (collected at −196 °C). The white involatile solid which remained in the reaction tube was a mixture of the $CF_3P[N(CH_3)_2]_3{}^+Cl^-$ and $(CH_3)_2NH_2{}^+Cl^-$ salts. Additional reactions between CF_3PCl_4 and $(CH_3)_2NH$ at room temperature for 24 h in the same reactor employing mole ratios of (a) 1:2 and (b) 1:6.5 of reactants gave mainly unreacted CF_3PCl_4 (in case a) or unreacted $(CH_3)_2NH$ (in case b) plus, in both cases, small amounts of unidentified volatile products. The involatile solids from both reactions, when dissolved in CD_3CN, were shown by NMR spectroscopy to consist mainly of $(CH_3)_2NH_2{}^+Cl^-$ and $CF_3P[N(CH_3)_2]_3{}^+Cl^-$ with very small amounts of several unidentified CF_3P containing compounds.

Characterization of the Phosphonium Salt. Attempted separation of the components of the white solid mixture of dimethylammonium chloride and $CF_3PCl[N(CH_3)_2]_3$ obtained from completed reactions of either chlorophosphorane by means of their solubility properties in CCl_4, ether, $CHCl_3$, and n-pentane were unsuccessful. Addition of an aqueous KPF_6 solution to an aqueous solution of the above mixture resulted in the formation of a white precipitate identified as $CF_3P[N(CH_3)_2]_3{}^+PF_6{}^-$. Anal. Calcd for $C_7H_{18}F_9N_3P_2$: C, 22.29; H, 4.82; F, 45.33; N, 11.12; P, 16.42. Found: C, 22.31; H, 4.97;, F, 45.46; N, 10.95; P, 15.67. Of the several solvents tested, CH_2Cl_2 and CH_3CN dissolved this fluorophosphate salt and the ^{19}F NMR spectra of the resultant solution showed the following NMR signals (in CD_3CN): ϕ_F 59.8 ppm $^2J_{PF}$ = 108 Hz, doublet of multiplets of total intensity ratio of 1; ϕ_F 72.0 ppm, $^1J_{PF}$ = 707 Hz, doublet of total intensity ratio 2. The former is due to a CF_3P group and the latter the PF_6^- ion.[7] The ^1H NMR spectrum showed a doublet of quartets (τ_H 7.24, $^3J_{PH}$ = 10.5 Hz, $^5J_{FH}$ = 0.75 Hz) due to the $N(CH_3)_2$ group. All of these signals except that due to the PF_6^- ion were present in the CD_3CN solution spectra obtained on the original salt mixture, which also possessed NMR signals typical of the $(CH_3)_2NH_2^+$ ion. The hydrogen to fluorine ratio in the cation was determined by NMR to be 6:1 using a measured quantity of fluorobenzene as an internal standard. The ^{31}P spectrum of $CF_3P[N(CH_3)_2]_3^+PF_6^-$ in CD_3CN solution showed a quartet of multiplets which counted to 19 lines in each with the parameters $\delta(^{31}P$ vs. $P_4O_6)^8$ = +69 ppm; $^2J_{PF}$ = 107.5 Hz and $^3J_{PH}$ = 10.3 Hz in agreement with the values obtained from ^1H and ^{19}F spectra.

The infrared spectrum of the fluorophosphate salt corresponded to a composite of the spectra of KPF_6 and the original solid, after subtraction of the $(CH_3)_2NH_2^+$ peaks.

Alkaline Hydrolysis of $(CF_3)P[N(CH_3)_2]_3^+PF_6^-$. Alkaline hydrolysis of $CF_3P[N(CH_3)_2]_3^+PF_6^-$ (0.099 g, 0.26 mmol) with 0.8 ml of degassed 10% NaOH solution at room temperature for 2 h gave CF_3H (0.019 g, 0.27 mmol). Proton and ^{19}F NMR spectrum of the remaining aqueous solution indicated the presence of the PF_6^- ion[7] and $OP[N(CH_3)_2]_3$.[10] The latter parameters were further confirmed by ^1H and ^{19}F NMR measurements on an authentic sample of $OP[N(CH_3)_2]_3$ dissolved in H_2O and in a 10% NaOH solution.

Results and Discussion

Dimethylamine reacted with $(CF_3)_2PCl_3$ to form both $(CF_3)_2PCl_2[N(CH_3)_2]$ and $CF_3P[N(CH_3)_2]_3^+Cl^-$ at all of ratios of reactants investigated. Since the major CF_3P-containing species observed were those listed above, we suggest that CF_3H is formed uniquely by a displacement of one CF_3 group on phosphorus by dimethylamine; therefore the CF_3H yield is equivalent to the yield of trifluoromethylphosphonium salt. The overall stoichiometry for complete reaction (eq 1)

$$(CF_3)_2PCl_3 + 5(CH_3)_2NH \rightarrow CF_3H + CF_3P[N(CH_3)_2]_3^+ + 2(CH_3)_2NH_2^+ + 3Cl^- \quad (1)$$

was clearly demonstrated by a reaction performed at room temperature for 4 days. Significant yields of the major intermediate, $(CF_3)_2PCl_2[N(CH_3)_2]$,[1] were obtained with short reaction times, suggesting that the reaction proceeds in a stepwise fashion with the initial fast displacement of one Cl substituent by dimethylamine (eq 2) to form $(CF_3)_2PCl_2[N(CH_3)_2]$ being followed by slower replacement of Cl and one CF_3 by dimethylamine (eq 3) in a more complex process.

$$(CF_3)_2PCl_3 + 2(CH_3)_2NH \rightarrow (CF_3)_2PCl_2[N(CH_3)_2] + (CH_3)_2NH_2^+Cl^- \quad (2)$$

$$(CF_3)_2PCl_2[N(CH_3)_2] + 3(CH_3)_2NH \rightarrow CF_3H + CF_3P[N(CH_3)_2]_3^+ + 2Cl^- + (CH_3)_2NH_2^+ \quad (3)$$

This second step (eq 3) was readily verified as a reasonable overall process by a separate experiment. No additional intermediates were isolable in this reaction suggesting that the component steps occur at competitive rates and it seems reasonable to suggest that the overall reaction (eq 3) is facilitated by the increased crowding around phosphorus which accompanies the introduction of relatively bulky dimethylamino groups and by the fact that Cl^- is a good leaving group. It is notable that the yield of $(CF_3)_2PCl_2[N(CH_3)_2]$ intermediate (which reaches a maximum at an amine:$(CF_3)_2PCl_3$ reacting ratio of 3:1) did not decrease to zero in the set of short reactions even at high amine concentrations indicating that the aminolysis of this intermediate is relatively slow. The overall behavior is qualitatively illustrated in Figure 1 wherein some of the data given in Table I are plotted. In general, the total accounting of the various CF_3P species was reasonable considering the difficulties inherent in the separation of compounds of low volatility especially where the quantities of some products are small, as at intermediate reaction ratios. It is notable that the accountability is poorest in this intermediate region even when the unidentified species (which is presumably another intermediate in either phosphonium salt or phosphorane form) is included in the recovery data, suggesting that additional unobserved unstable or reactive CF_3P-containing intermediates may be important at these reacting ratios, but since these products are likely to be solids and are either insoluble in or destroyed by the solvents employed, it is not likely that they can be observed by NMR spectroscopic techniques such as that (i.e., ^{19}F NMR) used here. Considerably more elaborate investigations of the solid reaction products would be required to evaluate this possibility.

Table II. Infrared Spectra of Phosphonium Salts[a,b]

$CF_3P[N(CH_3)_2]_3^+PF_6^-$	$CF_3P[N(CH_3)_2]_3^+Cl^- + (CH_3)_2NH_2^+Cl^-$	
3010 vw		ν(C–H)$[(CH_3)_2NH_2^+]$
2935 w	3000 s, br	ν(C–H)$[(CH_3)_2N]$
2877 w, sh	2700 s, br	
2840 w		
	2420 vs	ν(C–H)
1640 w	1635 w	
	1585 w	$(CH_3)_2NH_2^+$
1493 m	1490 w	$\delta(CH_3)$
1470 m	1469 m	
1459 m	1455 w	$\nu_s(C_2N)$
1319 s	1316 vw	
	1255 vw	
1199 s	1199 s	ν(C–F)
1174 s	1172 s	
1155 s, sh		
1147 vs	1146 vs	
1070 s	1066 m	
	1020 s	$(CH_3)_2NH_2^+$
1010 vs	1010 vs	$\nu_{as}(C_2N)$
	883 vs	$(CH_3)_2NH_2^+$
874 vs, sh		PF_6^-
	864 vs	$(CH_3)_2NH_2^+$
767 m	769 w	$\delta_s(CF_3)$
652 m	653 m	$\nu_{as}(N_2P)$
575 s		PF_6^-

[a] All values in cm^{-1}. [b] Abbreviations: ν, stretching; δ, deformation; s, stron; m, medium; w, weak; v, very; sh, shoulder; subscript as, asymmetric; subscript s, symmetric; br, broad.

The new, water-stable phosphonium ion $CF_3P[N(CH_3)_2]_3^+$ is the first trifluoromethylphosphonium species to be definitely characterized although $(CF_3)_3PCl^+$ ions were postulated to explain electrical conductivity of liquid $(CF_3)_3PCl_2$.[11] Recently halodifluorophosphonium salts have been obtained[12] and used as difluorocarbene sources. Anionic trifluoromethylfluorophosphates are also known.[13-15] Good yields of the new phosphonium salt are easily obtained by treatment of CF_3PCl_4 with a large excess of dimethylamine

$$CF_3PCl_4 + 6(CH_3)_2NH \rightarrow CF_3P[N(CH_3)_2]_3^+Cl^- + 3(CH_3)_2NH_2^+Cl^- \quad (4)$$

The identification of the phosphonium ion $CF_3P[N(CH_3)_2]_3^+$ is supported by the infrared spectral data (Table II) and especially by the NMR data for the ion in solution. The doublet of quartets appearing in the ^1H NMR (τ 7.24) spectrum is readily assigned to coupling of the protons to phosphorus ($^3J_{PH}$ = 10.2 Hz) and to three equivalent fluorine atoms ($^5J_{FH}$ = 0.75 Hz), confirming the presence of the CF_3P structural unit. The doublet of broad multiplets which appeared in the ^{19}F spectrum (ϕ 60.8 ppm) arises from coupling of the CF_3 group to phosphorus ($^2J_{PF}$ = 108 Hz) and from unresolved coupling to 18 equivalent protons of the three $N(CH_3)_2$ groups yielding an overall peak width consonant with the value of $^5J_{FH}$ obtained from the ^1H spectrum. The ^{31}P NMR spectrum is a quartet of multiplets of 19 lines due to coupling of the phosphorus to three equivalent fluorine atoms ($^2J_{PF}$ = 107.5 Hz) and the 18 equivalent protons of threee $N(CH_3)_2$ groups ($^3J_{PH}$ = 10.3 Hz). The ^{31}P chemical shift (δ vs. P_4O_6: +69 ppm) is in the correct range for a phosphonium salt[16] and is comparable to the ^{31}P chemical shifts of $CH_3P[N(CH_3)_2]_2F^+$ (+40.6 ppm) and $C_6H_5P(F)[N(CH_3)_2]_2^+$ (+56.0 ppm).[17] All of the ^{31}P chemical shifts are much smaller than those expected[16,18] for analogous phosphoranes.

Alkaline hydrolysis of $CF_3P[N(CH_3)_2]_3^+PF_6^-$ yields (eq 5) 1 molar equiv of CF_3H and transforms the cation to

$$(CF_3)P[N(CH_3)_2]_3^+ + H_2O \rightarrow CF_3H + OP[N(CH_3)_2]_3 + H^+ \qquad (5)$$

$OP[N(CH_3)_2]_3$. The PF_6^- ion resists hydrolysis in alkaline solution.[16] Similar resistance of the P–N linkage to hydrolysis under similar conditions has been observed in some (trifluoromethyl)dimethylaminophosphoranes.[18]

Formation of the aminophosphonium salts from CF_3PCl_4 and $(CF_3)_2PCl_3$ rather than the phosphoranes may be due to the prohibitive steric requirements of the $(CH_3)_2N$ group as well as the tendency of the system to form Cl^-. The successful synthesis of six-coordinate catechol phosphates[19] suggests that steric restrictions are probably unimportant relative to electronic factors. Further study of the system would likely be rewarding.

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Registry No. $CF_3P[N(CH_3)_2]_3Cl$, 60439-31-8; $(CH_3)_2NH_2Cl$, 506-59-2; CF_3H, 75-46-7; $(CF_3)_2PCl_2[N(CH_3)_2]$, 60478-97-9; $CF_3P[N(CH_3)_2]_3^+PF_6^-$, 60439-33-0; $(CF_3)_2PCl_3$, 353-77-5; $(CH_3)_2NH$, 124-40-3; CF_3PCl_4, 1066-48-4; ^{31}P, 7723-14-0; $CF_3P[N(CH_3)_2]_3^+Cl^-$, 60439-34-1.

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Trends in the Charge Distribution in Sulfanes, Sulfanesulfonic Acids, Sulfanedisulfonic Acids, and Sulfurous Acid

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Trends in the charge distribution of sulfur chains belonging to the families H_2S_x, HS_xSO_3H, $S_x(SO_3H)_2$, and H_2SO_3 were calculated with an extended Hückel model based on spectral atomic parameters. The results were correlated to the acidity constants of sulfanes, data on the reaction mechanism of sulfur degradation by sulfite, and the formation of elemental sulfur from thiosulfate. Furthermore, the relative stability of various sulfite species was considered. The charge trends in sulfanes parallel the trend of the experimentally determined acid constants. The charge distribution in the SO_3^- family correlated well to the observed stability of these species, and the charge distribution in sulfanemonosulfonic acids supports a model based on experimental study of the degradation of labeled sulfur by sulfite.

Introduction

The main purpose of the present work was to determine the qualitative trends of the charge distribution in families of unsubstituted and substituted catenated sulfur species and to test whether the charge distributions calculated for the free molecules could be correlated to the experimentally established behavior of the aqueous species. These species are all related to Wackenroder's liquid, which is obtained by the reaction of H_2S with SO_2. The reactions in this system are important intermediates in many SO_2-abatement reactions which are still very poorly understood.

Several semiempirical models have been successfully used to compute the properties of various inorganic sulfur molecules. Miller and Cusachs[2,3] calculated the electronic energy levels of S_4, S_6, and S_8 rings and H_2S, H_2S_2, and S_6^{2-} chains in order to determine the role of the sulfur 3d orbitals and to explain the stability of various molecules and their mixture in liquid sulfur. Buttet[4] used the Wolfsberg–Helmholtz method[5] to predict the diradical properties of S_4, S_6, S_8, and S_{10} chains. Müller and Heegn[6] used a three-dimensional free-electron model to predict the relative stability of elemental sulfur chains and rings. The properties of sulfanes and substituted sulfanes were computed and discussed by Feher,[7] who used Kuhn's electron gas model, McGlynn,[8] Boyd,[9] Seel,[10] Colton,[11] and Leibovici.[12] The electronic structure of S_8 has recently been reexamined by Palma[13] and Kortela.[14] Carlson and Pederson[15] conducted an ab initio calculation. Cotton[16] used the SCF–SW–X$_2$ method to study S_2^-, S_3^-, and S_3^{2-}. All calculations, including our own,[17] agree with Miller and Cusachs' finding[2,3] that the sulfur 3d orbitals have little effect