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The Preparation and Characterization of Some Mixed-Ligand Complexes of Titanium(III)

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The chemistry of d^1 transition metals has been studied extensively and properties such as the optical and electron spin resonance (esr) spectra and magnetic behavior have been recorded and correlated with the ligand fields of the complexes. Relatively little work has been done with titanium(III) complexes because of the experimental difficulties in their preparation and characterization. The solid complexes of titanium(III) halides that have been studied generally have been limited to solvent adducts and complexes containing alkoxide groups.

The reactions of titanium(III) chloride with several coordinating solvents (acetonitrile, tetrahydrofuran, dioxane, 2-propanol) have been studied in order to prepare and characterize compounds in the series $TiCl_3 \cdot 3L$, $[TiCl_4 \cdot 2L]^-$, and $TiCl_3 \cdot L$, in which the chloride:nonhalide ligand ratio was varied, and compounds of the type $TiCl_3L_2L'$, which contained two different nonhalide ligands. The experimental data were examined to find correlations between changes in the properties of the complexes and the nature of the ligands. Solvent adducts have been prepared with acetonitrile,[1-3] tetrahydrofuran,[3,4] dioxane,[3-5] and 2-propanol.[6] $(C_2H_5)_4N[TiCl_4 \cdot 2CH_3CN]$ and $TiCl_3 \cdot L$ (L = acetonitrile, tetrahydrofuran) have also been prepared previously.[7-9] Since the esr spectrum has been reported only for $TiCl_3 \cdot 3CH_3CN$,[10] the esr spectra of all the compounds prepared in this investigation were recorded.

Experimental Section

Materials.—Anhydrous $TiCl_3$ was obtained from Research Organic/Inorganic Chemicals. Tetrahydrofuran, diethyl ether, and benzene were allowed to reflux at least 24 hr with lithium aluminum hydride and were distilled immediately before use. Isopropyl alcohol was refluxed with sodium isopropoxide. Dioxane was refluxed with sodium and distilled after the violet color of the disodium benzophenone complex had appeared.[11] Reagent grade acetonitrile was distilled from P_2O_5 immediately before use. Chloroform was washed with water, distilled from P_2O_5, and stored in the dark. Tetraethylammonium chloride was obtained from Eastman Organic Chemicals. Twice it was ground, boiled in dry benzene, and dried under vacuum. Matheson prepurified nitrogen was passed through a heated BTS column and an Aquasorb column to remove oxygen and water.

$TiCl_3 \cdot 3CH_3CN$.—This compound was prepared as previously reported.[1]

$TiCl_3 \cdot 3C_4H_8O$.—This compound was prepared as previously reported.[3]

$TiCl_3 \cdot 2C_4H_8O_2$.—This compound was prepared in a manner similar to that previously reported.[3,5] Longer reaction times (60, 100, and 240 hr) apparently gave the same product in contrast to the results obtained by Fowles, *et al.*[5]

$TiCl_3 \cdot 4C_3H_8O$.—This compound was also prepared as previously reported.[6]

$TiCl_3 \cdot CH_3CN$.—A portion of $TiCl_3 \cdot 3CH_3CN$ was heated at 100° under vacuum for several hours until the evolution of a gas ceased. The residue was a brown powder. *Anal.* Calcd for $TiCl_3C_2H_3N$: Ti, 24.42; Cl, 54.45; C, 12.28; H, 1.55; N, 7.17. Found: Ti, 24.54; Cl, 54.18; C, 11.98; H, 1.65; N, 6.86.

$TiCl_3 \cdot C_4H_8O$.—A sample of $TiCl_3 \cdot 3C_4H_8O$ was heated under vacuum at 75°. A gas was evolved and the sample turned light green and then gray-green. The light green substance, which may be $TiCl_3 \cdot 2C_4H_8O$, could not be isolated as the sample was never uniformly light green. The gray-green solid turns violet as it is cooled to 77°K.[12] It is presumably the compound reported by Kern.[8] *Anal.* Calcd for $TiCl_3C_4H_8O$: Ti, 21.16; Cl, 46.98; C, 21.20; H, 3.56. Found: Ti, 21.20; Cl, 46.80; C, 20.63; H, 3.61.

$TiCl_3 \cdot C_4H_8O_2$.—A portion of $TiCl_3 \cdot 2C_4H_8O_2$ heated under vacuum at 140° gave a finely divided cream powder. *Anal.* Calcd for $TiCl_3C_4H_8O_2$: Ti, 19.76; Cl, 43.89; C, 19.81; H, 3.33. Found: Ti, 19.98; Cl, 43.74; C, 19.36; H, 3.31.

$TiCl_3(C_4H_8O)_2(CH_3CN)$.—Four grams of $TiCl_3 \cdot 3C_4H_8O$ was suspended in tetrahydrofuran and 20 ml of acetonitrile was added. After the solution was stirred and heated 9 hr, the volume was reduced by vacuum evaporation to 40 ml. An equal quantity of hexane was added and the solution was stirred vigorously. The blue solid which precipitated was collected on a filter and dried under vacuum. *Anal.* Calcd for $TiCl_3C_{10}H_{19}NO_2$: Ti, 14.11; Cl, 31.33; C, 35.35; H, 5.65; N, 4.13. Found: Ti, 14.25; Cl, 31.30; C, 34.48; H, 6.02; N, 4.01.

$TiCl_3(C_4H_8O_2)_2(CH_3CN)$.—Several grams of $TiCl_3 \cdot 3CH_3CN$ was suspended in dioxane and the mixture was heated and stirred 5 hr. The very thick blue-green mixture was filtered and the solid was washed with dioxane and dried under vacuum. The blue-green powder was difficult to handle as it became charged with static electricity when it was ground. *Anal.* Calcd for $TiCl_3C_{10}H_{19}NO_4$: Ti, 12.90; Cl, 28.63; C, 32.31; H, 5.16; N, 3.77. Found: Ti, 12.98; Cl, 28.66; C, 33.40; H, 5.15; N, 3.78.

$TiCl_3(C_4H_8O_2)_2(C_4H_8O)$.—$TiCl_3 \cdot C_4H_8O$ was suspended in dioxane and the mixture was heated and stirred. After 2 hr the solid had dissolved and the solution was brown. The volume of the solution was reduced to 40 ml under vacuum and an equal quantity of diethyl ether was added. Immediate precipitation resulted and the solid was washed with dioxane and dried under vacuum. It is green-blue. *Anal.* Calcd for $TiCl_3C_{12}H_{24}O_5$: Ti, 11.90; Cl, 26.42; C, 35.79; H, 6.01. Found: Ti, 12.00; Cl, 26.38; C, 33.40; H, 5.31. The use of $TiCl_3 \cdot 3C_4H_8O$ as the starting material often did not give a homogeneous precipitate.

$TiCl_3(C_4H_8O_2)_2(C_3H_8O)$.—Ten milliliters of 2-propanol was added to 6 g of $TiCl_3 \cdot 2C_4H_8O_2$ in dioxane and the mixture was stirred and heated overnight. The volume of the solution was reduced under vacuum to 40 ml and an equal quantity of diethyl

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[1] M. W. Duckworth, G. W. A. Fowles, and R. A. Hoodless, *J. Chem. Soc.*, 5665 (1963).

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[3] R. J. H. Clark, J. Lewis, D. J. Machin, and R. S. Nyholm, *J. Chem. Soc.*, 379 (1963).

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[5] G. W. A. Fowles, R. A. Hoodless, and R. A. Walton, *ibid.*, 5873 (1963).

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[7] H. J. Seifert and F. M. Thurn, *ibid.*, **371**, 79 (1970).

[8] G. W. A. Fowles and B. J. Russ, *J. Chem. Soc. A*, 517 (1967).

[9] R. I. Kern, *J. Inorg. Nucl. Chem.*, **24**, 1105 (1962).

[10] W. Giggenbach and C. H. Brubaker, Jr., *Inorg. Chem.*, **8**, 1131 (1969).

[11] H. V. Carter, B. J. McClelland, and E. Warhurst, *Trans. Faraday Soc.*, **56**, 343 (1960).

[12] In addition to the above compound, several other nonstoichiometric substances prepared during the course of this research were thermochromic. The color change which occurred upon cooling was caused by the shifting of a charge-transfer band toward higher frequencies. In some complexes the thermochromism appeared to be related to partial oxidation of the titanium(III) materials.

ether was added while the mixture was vigorously stirred. The solution was filtered and the pale blue precipitate was dried under vacuum. *Anal.* Calcd for $TiCl_3C_{11}H_{24}O_5$: Ti, 12.26; Cl, 27.23; C, 33.84; H, 6.19. Found: Ti, 12.16; Cl, 27.28; C, 33.15; H, 6.08.

$(C_2H_5)_4N[TiCl_4 \cdot 2CH_3CN]$.—This compound was prepared as previously reported.[8]

$(C_2H_5)_4N[TiCl_4 \cdot 2C_4H_8O]$.—A known quantity of $TiCl_3 \cdot 3C_4H_8O$ was dissolved in tetrahydrofuran and 2.5 equiv of $(C_2H_5)_4NCl$ was added. The mixture was stirred overnight. The solution was filtered and a pale green powder was collected and dried under vacuum. *Anal.* Calcd for $TiCl_4C_{16}H_{36}NO_2$: Ti, 10.32; Cl, 30.55; C, 41.40; H, 7.82; N, 3.02. Found: Ti, 10.36; Cl, 30.52; C, 41.31; H, 8.12; N, 3.25.

When the green powder was washed with chloroform, it immediately turned orange-brown. After it had been dried under vacuum, the powder was salmon and was thermochromic. This material was also obtained from a solution of 10% tetrahydrofuran in chloroform. The material was nonstoichiometric with a titanium:chloride ratio of 1:4.5. *Anal.* Found: Ti, 11.58; Cl, 37.58.

$(C_2H_5)_4N[TiCl \cdot 2C_4H_8O_2]$.—A weighed quantity of $TiCl_3 \cdot 2C_4H_8O_2$ was suspended in dioxane and 2.5 equiv of $(C_2H_5)_4NCl$ was added. After the mixture had been stirred overnight, it was filtered and the pale green powder that was collected was dried under vacuum. *Anal.* Calcd for $TiCl_4C_{16}H_{36}NO_4$: Ti, 9.67; Cl, 28.64; C, 38.81; H, 7.31; N, 2.83. Found: Ti, 9.61; Cl, 28.70; C, 38.59; H, 7.52; Ni, 2.95.

Some Reactions of the Titanium(III) Compounds.—When the adduct of one solvent was dissolved in one of the other solvents (except dioxane), all of the nonhalide ligands were replaced by the latter solvent. When an adduct was dissolved in dioxane only two of the nonhalide ligands were replaced. This was a convenient method of preparation of complexes of the type $TiCl_3(C_4H_8O_2)_2L'$. These could also be prepared by the dissolution of complexes of the type $TiCl_3 \cdot L$ in dioxane. In coordinating solvents the ligand L was eliminated from $TiCl_3 \cdot L$ and the solvent adduct [tris, or tetrakis in the case of 2-propanol] was formed. Attempts to prepare compounds of the type $TiCl_3L_2L'$ from stoichiometric amounts of $TiCl_3 \cdot L'$ and the ligand L in a noncoordinating solvent yielded $TiCl_3 \cdot L$ or no reaction took place. When $(C_2H_5)_4NCl$ was added to compounds of the type $TiCl_3L_2L'$, the ligand L' was eliminated and $(C_2H_5)_4N[TiCl_4 \cdot 2L]$ was formed.

A sample of $TiCl_3 \cdot 4C_3H_8O$ was heated under vacuum at 75° for 10 hr. Hydrogen chloride and 2-propanol were evolved and the remaining solid turned red-brown. The compound is insoluble in water and is possibly $Ti_2Cl_3(C_3H_7O)_3$. *Anal.* Calcd for $Ti_2Cl_3C_9H_{21}O_3$: Ti, 25.52; Cl, 28.03. Found: Ti, 26.70; Cl, 29.33.

Experimental Techniques.—Since all of the titanium(III) compounds were sensitive to air and water, all reactions and manipulations were carried out in a nitrogen atmosphere or under vacuum. Schlenk-tube techniques were used throughout.[13] All compounds were stored under nitrogen or vacuum.

Analyses.—Titanium was determined by two methods that gave close agreement in most cases. Titanium(III) was determined by titration with cerium(IV) under a nitrogen atmosphere. Ferroin was used as the indicator. The total titanium content was determined spectrophotometrically as the titanium(IV) hydrogen peroxide complex in sulfuric acid.[14]

Chloride was determined by differential potentiometric titration with silver nitrate after the titanium(III) had been catalytically oxidized with oxygen in the air by use of copper sulfate in sulfuric acid.

C, H, and N analyses were performed by the microanalytical laboratory of the Institute of Water Research, Michigan State University, which reported that the samples were very difficult to handle and analyze.

Magnetic Moments.—The magnetic susceptibilities were determined by the Gouy method at 77, 196, and 297°K. If the sample exhibited normal paramagnetism, the susceptibilities were also measured at several intermediate temperatures so that a graph of μ_{eff} *vs.* kT/λ' could be obtained. $Hg[Co(SCN)_4]$ was used as the calibration standard.[15] Pascal's constants were used for the correction for the diamagnetism of the cations and the ligands.[16]

Spectroscopic Measurements.—The infrared spectra of the compounds were determined by means of Nujol mulls in sodium chloride plates on a Unicam Model SP-200 spectrophotometer. The visible and ultraviolet spectra were obtained by use of a Unicam Model SP-800 and a Cary Model 14 spectrophotometer. The solid samples were mulled with Nujol and enclosed in quartz plates. Since most of the compounds react with solvents, no solution spectra of the complexes were obtained. A Beckman Model DU spectrophotometer was used for the spectrophotometric analysis of titanium. The X-band electron spin resonance spectra were recorded at 297 and 77°K by means of a Varian Model E-4 spectrometer system and a Varian Model 4501-04 spectrometer. A Model E-257 variable-temperature unit, which employs liquid nitrogen as the coolant, was used in the variable-temperature studies.

Results and Discussion

The infrared spectrum of each of the compounds described in the Experimental Section was obtained. In general, the spectra show the shifts in absorption bands associated with coordination of the solvents. In addition, the spectra of complexes of the type $TiCl_3L_2L'$ show some shifts of absorption bands from their positions in the parent complexes $TiCl_3 \cdot nL$ and $TiCl_3 \cdot nL'$. Considerable changes in the spectra take place when the chloride:nonhalide ligand ratio is increased. These changes may be caused by changes in both the symmetries and ligand field strengths of the complexes. The far-infrared spectra are too broad to provide useful information about the symmetries or ligand bond strengths.

The visible spectrum of each of the compounds is reported in Table I. Although the symmetries of the complexes varied widely, all the spectra have two d–d absorption bands. Since no amount of trigonal distortion of the basic octahedral symmetry will remove the degeneracy of the upper (^2E) d orbital level, all of the complexes contain some elements of tetragonal or lower symmetry. The locations of the absorption bands of the complexes $TiCl_3L_2L'$ are about 100 cm⁻¹ higher than the values predicted from Jorgensen's rule of

TABLE I
ELECTRONIC ABSORPTION SPECTRA[a,b]

Compd	Absorption bands,[c] cm⁻¹	
	$^2B_2 \rightarrow {}^2B_1$	$^2B_2 \rightarrow {}^2A_1$
$TiCl_3 \cdot 3CH_3CN$	17,100	14,700
$TiCl_3 \cdot 3C_4H_8O$	14,700	13,500
$TiCl_3 \cdot 2C_4H_8O_2$	14,800	12,800
$TiCl_3 \cdot 4C_3H_8O$	16,700	14,300
$TiCl_3(C_4H_8O)_2(CH_3CN)$	15,600 (15,550)	14,000 (13,900)
$TiCl_3(C_4H_8O_2)_2(CH_3CN)$	15,680 (15,570)	13,325 (13,433)
$TiCl_2(C_4H_8O_2)_2(C_4H_8O)$	14,780 (14,770)	13,100 (13,034)
$TiCl_3(C_4H_8)_2(C_3H_8O)$	15,400 (15,140)	13,220 (13,110)
$TiCl_3 \cdot CH_3CN$	16,000 (15,832)	11,900 (12,900)
$TiCl_3 \cdot C_4H_8O$	17,300 (14,032)	13,000 (12,500)
$TiCl_3 \cdot C_4H_8O_2$	17,900 (14,055)	14,600 (12,270)
$Ti_2Cl_3(C_3H_7O)_3$	18,950	17,450
$(C_2H_5)_4N[TiCl_4 \cdot 2CH_3CN]$	15,150 (15,800)	14,150 (13,800)
$(C_2H_5)_4N[TiCl_4 \cdot 2C_4H_8O]$	14,900 (14,200)	14,150 (13,000)
$(C_2H_5)_4N[TiCl_4 \cdot 2C_4H_8O_2]$	15,000 (14,270)	14,100 (12,730)

[a] All spectra were determined in Nujol mulls. [b] Values in parentheses are those expected from Jorgensen's rule of average environment and the average *Dq* values of the ligands. [c] Assignments assume tetragonal or lower symmetry.

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TABLE II

MAGNETIC PROPERTIES OF TITANIUM(III) COMPLEXES

Compd	Temp, °K	$10^6\chi_m'$, cgsu	μ_{eff}, BM
$TiCl_3 \cdot 4C_3H_8O$	297	1270	1.74
	250.3	1416	1.69
	209.7	1616	1.65
	196	1692	1.64
	175.5	1859	1.62
	148	2120	1.59
	77	3738	1.52
$TiCl_3(C_4H_8O)_2(CH_3CN)$	297	1381	1.77
	250.3	1491	1.73
	209.7	1708	1.70
	196	1796	1.69
	175.5	1988	1.68
	148	2311	1.66
	77	4122	1.60
$TiCl_3(C_4H_8O_2)_2(CH_3CN)$	297	1230	1.72
	250.3	1370	1.66
	209.7	1575	1.63
	196	1621	1.60
	175.5	1745	1.57
	148	1957	1.53
	77	3302	1.43
$TiCl_3(C_4H_8O_2)_2(C_4H_8O)$	297	1243	1.72
	250.3	1401	1.68
	209.7	1587	1.64
	196	1686	1.63
	175.5	1815	1.60
	148	2060	1.57
	77	3533	1.48
$TiCl_3(C_4H_8O_2)_2(C_3H_8O)$	297	1255	1.73
	250.3	1428	1.70
	209.7	1670	1.68
	196	1748	1.66
	175.5	1926	1.65
	148	2231	1.63
	77	3928	1.56
$TiCl_3 \cdot CH_3CN$	297	789	1.37
	196	971	1.24
	77	1928	1.09
$TiCl_3 \cdot C_4H_8O$	297	431	1.02
	196	356	0.75
	77	305	0.43
$TiCl_3 \cdot C_4H_8O_2$	297	1357	1.80
	250.3	1477	1.73
	209.7	1625	1.66
	196	1624	1.60
	175.5	1776	1.59
	148	1990	1.54
	77	2269	1.19
$(C_2H_5)_4N[TiCl_4 \cdot 2C_4H_8O]$	297	1318	1.78
	250.3	1461	1.72
	209.7	1664	1.68
	196	1758	1.67
	175.5	1870	1.63
	148	2165	1.61
	77	3668	1.51
$(C_2H_5)_4N[TiCl_4 \cdot 2C_4H_8O_2]$	297	1265	1.74
	250.3	1394	0.68
	209.7	1600	0.64
	196	1638	1.61
	175.5	1765	1.58
	148	2008	1.55
	77	3242	1.42

average environment and the average *Dq* values of the ligands. In the $[TiCl_4 \cdot 2L]^-$ complexes the locations of the absorption bands are almost identical although Jorgensen's rule predicts that the band of the acetonitrile complex should be at a higher frequency. The absorption bands in compounds of the type $TiCl_3 \cdot L$ are considerably higher than would be predicted. It would be expected from Jorgensen's rule that the location of the absorption bands would shift to lower frequencies as the chloride:nonhalide ligand ratio increased. However, it is found that the frequencies of the absorption bands increase with increasing chloride content of the titanium(III) complexes.

The magnetic properties of the compounds which are given in Table II have not been published earlier.

The electron spin resonance spectra, which were measured at 297 and 77°K, are reported in Table III.

TABLE III

THE *g* VALUES FROM ESR SPECTRA OF THE COMPLEXES

Compd	Temp, °K	g_1	g_2	g_3
$TiCl_3 \cdot 3CH_3CN$	297	1.907		
	77	1.921	1.883	
$TiCl_3 \cdot 3C_4H_8O$	297	1.884		
	77	1.894	1.849	
$TiCl_3 \cdot 2C_4H_8O_2$	297	1.972	1.880	
	77	1.982	1.880	1.826
$TiCl_3 \cdot 4C_3H_8O$	297	1.901		
	77	1.977	1.899	1.828
$TiCl_3(C_4H_8O)_2(CH_3CN)$	297	1.909		
	77	1.909		
$TiCl_3(C_4H_8O_2)_2(CH_3CN)$	297	1.963	1.890	1.836
	77	1.987	1.903	1.837
$TiCl_3(C_4H_8O_2)_2(C_4H_8O)$	297	1.885		
	77	1.939	1.898	1.827
$TiCl_3(C_4H_8O_2)_2(C_3H_8O)$	297	1.887		
	77	1.911	1.855	
$TiCl_3 \cdot CH_3CN$	297	1.911		
	77	1.907		
$TiCl_3 \cdot C_4H_8O$	297	1.898		
	77	1.898		
$TiCl_3 \cdot C_4H_8O_2$	297	1.879		
	77	1.881		
$(C_2H_5)_4N[TiCl_4 \cdot 2CH_3CN]$	297	1.941	1.869	1.807
	77	1.940	1.869	1.806
$(C_2H_5)_4N[TiCl_4 \cdot 2C_4H_8O]$	297	1.977	1.885	1.796
	77	1.978	1.886	1.796
$(C_2H_5)_4N[TiCl_4 \cdot 2C_4H_8O_2]$	297	1.983	1.886	1.815
	77	1.983	1.885	1.813

No hyperfine structure is observed for any of the compounds. The spectra show that the solvent adducts $TiCl_3 \cdot 3CH_3CN$ and $TiCl_3 \cdot 3C_4H_8O$ had axial symmetry. The compounds $TiCl_3 \cdot 4C_3H_8O$, which has only two coordinated chloride ions, and $TiCl_3 \cdot 2C_4H_8O_2$, which has bridging chloride ions, both have a three-line esr spectrum which indicates that the compounds have cis configurations. A three-line esr spectrum was expected for compounds of the type $TiCl_3L_2L'$ which have no axial symmetry. However, this type of spectrum was observed only for $TiCl_3(C_4H_8O_2)_2(CH_3CN)$ and $TiCl_3(C_4H_8O_2)_2(C_4H_8O)$. The unsymmetrical spectrum of $TiCl_3(C_4H_8O_2)_2(C_3H_8O)$ may be an unresolved three-line spectrum. The spectrum of $TiCl_3(C_4H_8O)_2(CH_3CN)$ remains a single absorption peak even at 77°K because of the large splitting of the ground-state orbitals which quenches the orbital angular momentum and causes the *g* value to be isotropic. The complexes of the type $TiCl_3 \cdot L$ have axial symmetry but only a single absorption peak is observed in their esr spectra. In the case of $TiCl_3 \cdot C_4H_8O_2$ the spectrum is a very broad peak due to the small separation of the t_{2g} sublevels. The amount of separation could not be evaluated from the magnetic data of the other complexes of the type $TiCl_3 \cdot L$. The spectra show that complexes of the type $(C_2H_5)_4N[TiCl_4 \cdot 2L]$ have cis configurations.

As the symmetries of the complex become more distorted from octahedral symmetry, the orbital angular momenta are quenched and the average *g* values approach 2.00. Since most of the complexes have average *g* values close to 1.89, it is difficult to establish the existence of any definite correlations of the *g* values with ligand field parameters. However, the distortion of the complexes and the approach of the average *g* values to 2.00 appear to be in the same order as the ligand field strengths of the complexes with the ligands in the order $CH_3CN > C_3H_8O > C_4H_8O_2 \approx C_4H_8O > Cl$, but clearly this order does not hold for all of the types of compounds.

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CONTRIBUTION FROM THE SCHOOL OF CHEMICAL ENGINEERING,
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Nitrodifluoramine and the Mass Spectral and Energetic Characterization of All Known Nitrogen-Oxygen-Flourine Compounds at Cryogenic Temperatures[1]

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In recent years there has been a great interest in nitrogen-oxygen-fluorine compounds because of their possible use as high-energy oxidizer ingredients. Four of the five heretofore known compounds, nitrosyl fluoride (ONF), nitryl fluoride (NO_2F), fluorine nitrate (NO_3F), and trifluoramine oxide (ONF_3), have been well reviewed.[2] The fifth member of this group, nitrosodifluoramine ($ONNF_2$), a dark purple substance which decomposes even below −70°, has been reported by only one laboratory.[3]

The mass spectral and energetic characterization of each of these compounds was undertaken, but those for $ONNF_2$ and a new compound reported herein, O_2NNF_2, were impossible without rather elaborate cryogenic inlet techniques[4] due to the instability of these two compounds.

Experimental Section

Equipment.—Syntheses employed a passivated copper vacuum rack assembly and either Pyrex or Monel reactors. Analyses employed a Bendix Model 14-107 time-of-flight mass spectrometer adapted to include a cryogenic analytical facility which permitted the reaction products to be analyzed without prior warm-up.[4]

N-O-F Compounds.—The known N-O-F compounds were prepared using previously published methods: ONF by the gas phase reaction of F_2 and NO;[5] NO_2F and NO_3F by passing F_2 over solid $NaNO_2$ and KNO_3, respectively;[6,7] $ONNF_2$ in 90–95% yield by passing a 10:1 mixture of NO–N_2F_4 through a glass capillary at 310° followed by a quench at −196°;[3] and ONF_3 in 20–40% yields by electric discharge of NF_3–OF_2–Ar mixtures (1:1:2) at −183° which is similar to earlier techniques[8] but gives much higher yields.

Analytical Procedure.—After the reaction products were condensed at either −196 or −183° and the volatile gases were pumped away, the sample was continuously pumped and slowly warmed whereupon the vaporized fractions were sequentially distilled into the mass spectrometer. All mass spectra and ionization efficiency curves were determined at temperatures which corresponded to a total reactor pressure of 0.1–0.2 Torr. Excess amounts of all components were pumped away before raising the temperature to volatilize the next fraction.

Appearance Potentials.—Appearance potentials were determined from the ionization efficiency curves using the extrapolated voltage difference method[9] with standard argon, $I(\mathrm{Ar}) = 15.76$ eV.

Reactions of N_2F_4.—N_2F_4 and NO_2 react immediately at room temperature yielding complete conversion to NF_3 and other stable products. However, the highly unstable white solid compound, nitrodifluoramine, O_2NNF_2, was formed in 50–75% yield by passing N_2F_4 alone through the capillary furnace at 310°, mixing with NO_2 at the exit of the capillary, and immediately quenching to −196°. Typical conditions were a total flow rate of 0.15 mmol/min and an NO_2:N_2F_4 mole ratio of about 2:1. During the warm-up procedure, small amounts of unreacted N_2F_4 and $ONNF_2$ were pumped away at −160 and −140°, respectively. Mass spectra between −135 and −130, above −105, and above −75° were attributed to O_2NNF_2, N_2O_3, and NO, respectively.

The reaction of N_2F_4 with O_3 was studied by passing N_2F_4 through the glass capillary furnace at 310° and immediately quenching the effluent onto a thin layer of liquid O_3 at −196°. All six N-O-F compounds were produced, but in repeating this experiment to obtain a more detailed characterization of the reaction products, a violent explosion occurred when the pyrolyzed N_2F_4 was initially added to the condensed ozone. The reaction of N_2F_4 with O_3 therefore looks promising, but this has not yet been pursued further due to the dangers of explosions. Similar gas-phase experiments followed by an immediate quench to −196° indicated essentially no reaction.

Results

Mass Spectra.—The data are summarized in Table I wherein small corrections for O_2NNF_2 have been made to account for the presence of varying amounts of N_2F_4 (based upon the mass peak at *m/e* 85, *i.e.*,

TABLE I

POSITIVE ION MASS SPECTRA OF N-O-F COMPOUNDS

		Rel intens at 70 eV, %					
m/e	Ion	ONF	NO_2F	NO_3F	$ONNF_2$	ONF_3	O_2NNF_2
14	N^+	6.0	4.5	2.0	8.0	3.0	6.0
16	O^+	4.0	11.0	10.0	2.5	2.5	8.0
19	F^+	5.0	3.5	2.0	3.0	7.0	2.0
28	N_2^+				3.0		4.0
30	NO^+	100.0	75.0	43.0	100.0	100.0	80.0
33	NF^+	3.5	1.5		28.0	5.5	20.0
35	OF^+			4.0			
44	N_2O^+				<0.2[a]		0.5
46	NO_2^+		100.0	100.0			100.0
47	N_2F^+				<0.1[a]		<0.3[a]
52	NF_2^+				18.0	1.5	15.0
65	NO_2F^+		1.5				
68	ONF_2^+					75.0	
87	ONF_3^+					0.1	
Temp,[b] °C		−140 to −145	−150 to −155	−140 to −145	−148 to −153	−165	−130 to −135

[a] Possibly due to impurities. [b] Temperatures at which spectra were observed correspond to vapor pressures of 0.1–0.2 Torr.

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