A STUDY OF SELECTED NITRONIUM COMPLEXES OF NITRYL CHLORIDE

by

Richard Powell Carter Jr.

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A thesis presented to the faculty of the Department of Chemistry of Washington and Lee University in partial fulfillment of the requirements for the degree of Bachelor of Science in Chemistry.

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VITA

The author was born on February 23, 1938, in Lexington, Virginia. He now lives in Bal Harbour, Florida. His parents are Richard Powell and Thelma Mayo Carter. He attended elementary school in Miami Beach, and went to Admiral Farragut Academy to finish his high school education. At present, he is a senior chemistry major at Washington and Lee University, Lexington, Virginia, and is a candidate for the Bachelor of Science degree with special attainments in Chemistry.

Awards:

James Lewis Howe Award (1958)

Lind Prize in Chemistry (1959)

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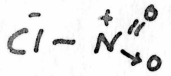
INTRODUCTION

Throughout the history of nitryl chloride there have been many nitrating and structure studies, but there have been no conclusive studies concerning the possibility of using nitryl chloride as a starting material for the production of certain nitronium complexes. In acid solution, Whitaker[1] indicated that nitryl chloride appeared to be polarized:



In neutral solutions nitryl chloride appeared to exist in two possible forms:

Thus it would seem possible to use nitryl chloride as a starting material, in "acid" solution, for the formation of various nitronium complexes. No direct statement of this possible use of nitryl chloride was found in the literature. However, Woolf[8] reported on the formation of various nitrosyl complex fluorides using bromine trifluoride. These complexes were formed by reacting bromine trifluoride with mixtures of nitrosyl chloride and substances capable of functioning as "acids" in bromine trifluoride solution. A summation scheme of his work is presented in figure 1.

Woolf and Emeléus[2] reported on the formation of certain nitronium compounds by treating mixtures of substances capable of acting as "acids" and "bases" in bromine trifluoride, with the latter. They generally used a mixture of the oxide and

Woolf

Production of Nitrosyl and Nitronium complex fluorides and fluorosulphonates with Bromine Trifluoride

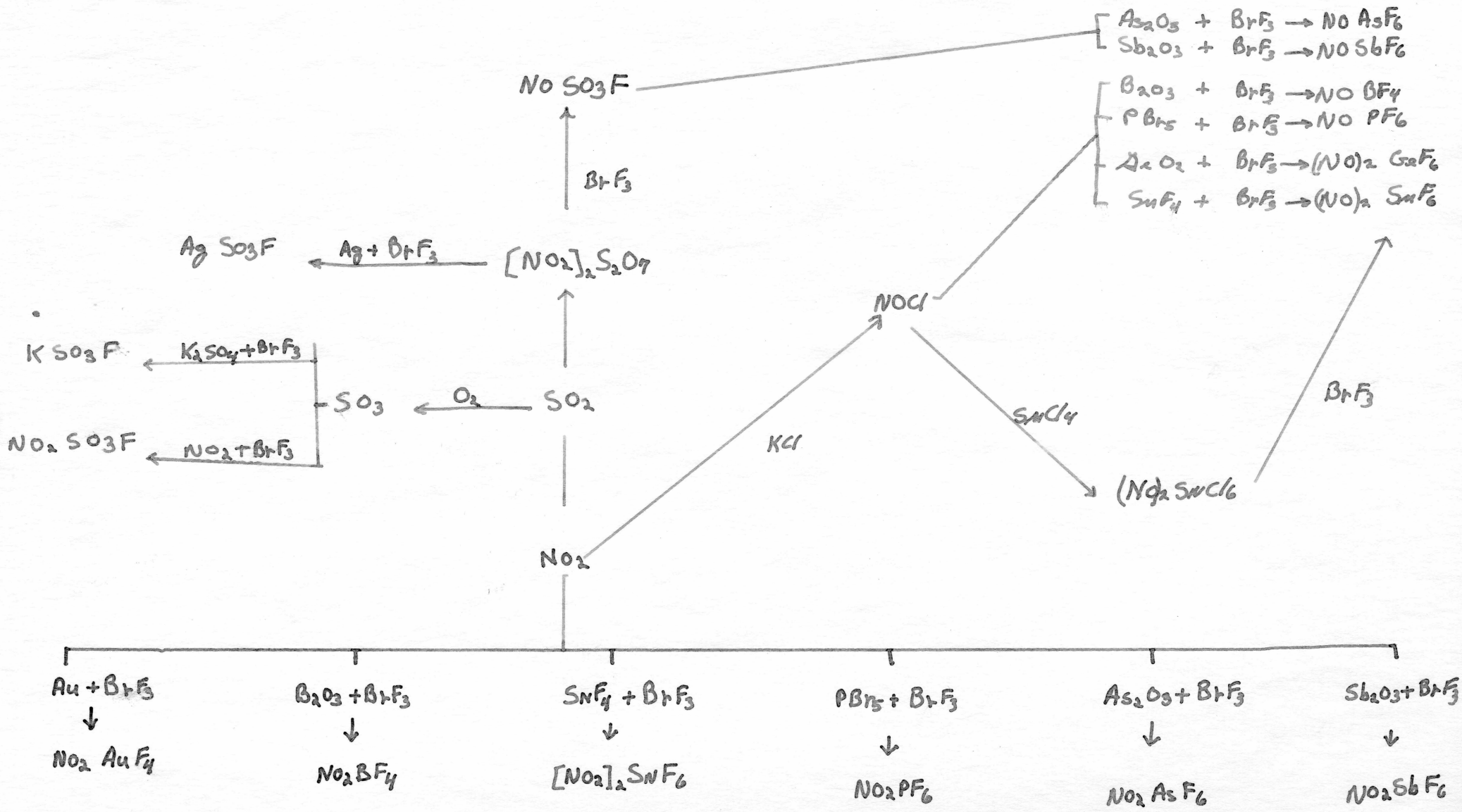


FIGURE I

and bromine trifluoride and treated this mixture with dinitrogen tetroxide. Using this method various nitronium complexes were formed, nitronium tetrafluoroborate and nitronium hexafluorophosphate, to name a few representative complexes.

There have been other preparations reported for nitronium tetrafluoroborate. Golah and Kuhn[3] reported the direct formation of the borate complex by the reaction of nitryl fluoride and boron trifluoride, and also by the reaction between nitrogen pentaoxide, hydrogen fluoride, and boron trifluoride.

Woolf,[4] in his work with cyano halides, found that mixtures of nitrosonium and nitronium fluoroborates were prepared by the reaction of bromine trifluoride, cyano halides, and Boric oxide.

Sears[5] reported the probable formation of nitronium tetrafluoroaluminate, by the reaction between nitryl chloride and aluminum trichloride.

In a very informative article, Aynsley[6] reported the reactions of nitryl fluoride with the non-metals and certain elements. Of special interest is his production of the nitronium fluoro-complexes by the reaction of nitryl fluoride with the fluorides of the respective elements. These complexes are listed in relation to the periodic table:

Gp.I	Gp.II	Gp.III	Gp.IV	Gp.V	Gp.VI	Gp.VII
		$(NO_2)BF_4$				
			$(NO_2)_2SiF_6$	$(NO_2)PF_6$		
			$(NO_2)_2GeF_6$	$(NO_2)AsF_6$	$(NO_2)SeF_5$	[$(NO_2)BrF_4$]
			$(NO_2)_2SnF_6$	$(NO_2)SbF_6$	[$(NO_2)TeF_5$]	$(NO_2)IF_6$
$(NO_2)AuF_4$						

Aynsley believes that it is highly possible that nitryl fluoride may have been involved in the reactions carried out by Woolf and Emeléus[2] in producing nitronium: tetrafluoroborate, hexafluorophosphate, hexafluoroarsenate, and hexafluoroantimonate by use of the reaction between nitrogen peroxide, bromine trifluoride, and a suitable compound of the non-metal. Of special interest is the nitronium tetrafluorobromide, first postulated by Woolf and Emeléus[2] and reported again by Aynsley[6], produced by a direct reaction between nitryl fluoride and bromine trifluoride.

It appeared rather logical that by combining certain anhydrides with nitryl chloride in bromine trifluoride solution, the respective nitronium complexes could be directly produced, avoiding the difficult conditions encountered when using dinitrogen tetroxide in the process of Woolf and Emeléus[2], and the rather unstable nitryl fluoride used by Aynsley[6]. Since these substances were capable of acting as "acids" in bromine trifluoride, the nitryl chloride would thus be a convenient source of nitronium ions.

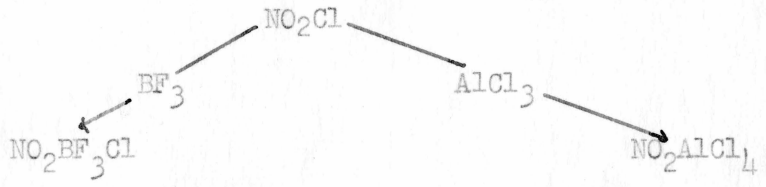
Therefore we proceeded to first form the nitronium tetrafluorobromide complex by a direct reaction between nitryl chloride and bromine trifluoride and in turn reacting this complex in bromine trifluoride solution with the respective anhydride. Both boric anhydride and phosphoric anhydride were to be used. The proposed resultant reactions were:

$$NO_2Cl + BrF_3 \longrightarrow NO_2BF_4 \xrightarrow{P_2O_5} NO_2PF_6$$

$$NO_2BF_4 \xrightarrow{B_2O_3} NO_2BF_4$$

It did not seem likely that the nitronium trifluorochloro bromide would be produced in the reaction between nitryl chloride and bromine trifluoride, due to the extremely strong fluorinating properties of bromine trifluoride.

The project was also extended to include work on the direct reaction between nitryl chloride and boron trifluoride, and also aluminum trichloride:



From the results of these reactions it was also hoped that more conclusive statements could be issued concerning the nature of nitryl chloride in the "acid" solutions, and also in the bromine trifluoride solution. My co-worker, Mr. Kotz, deals with the structure problem of nitryl chloride in his paper (7).

EXPERIMENTAL

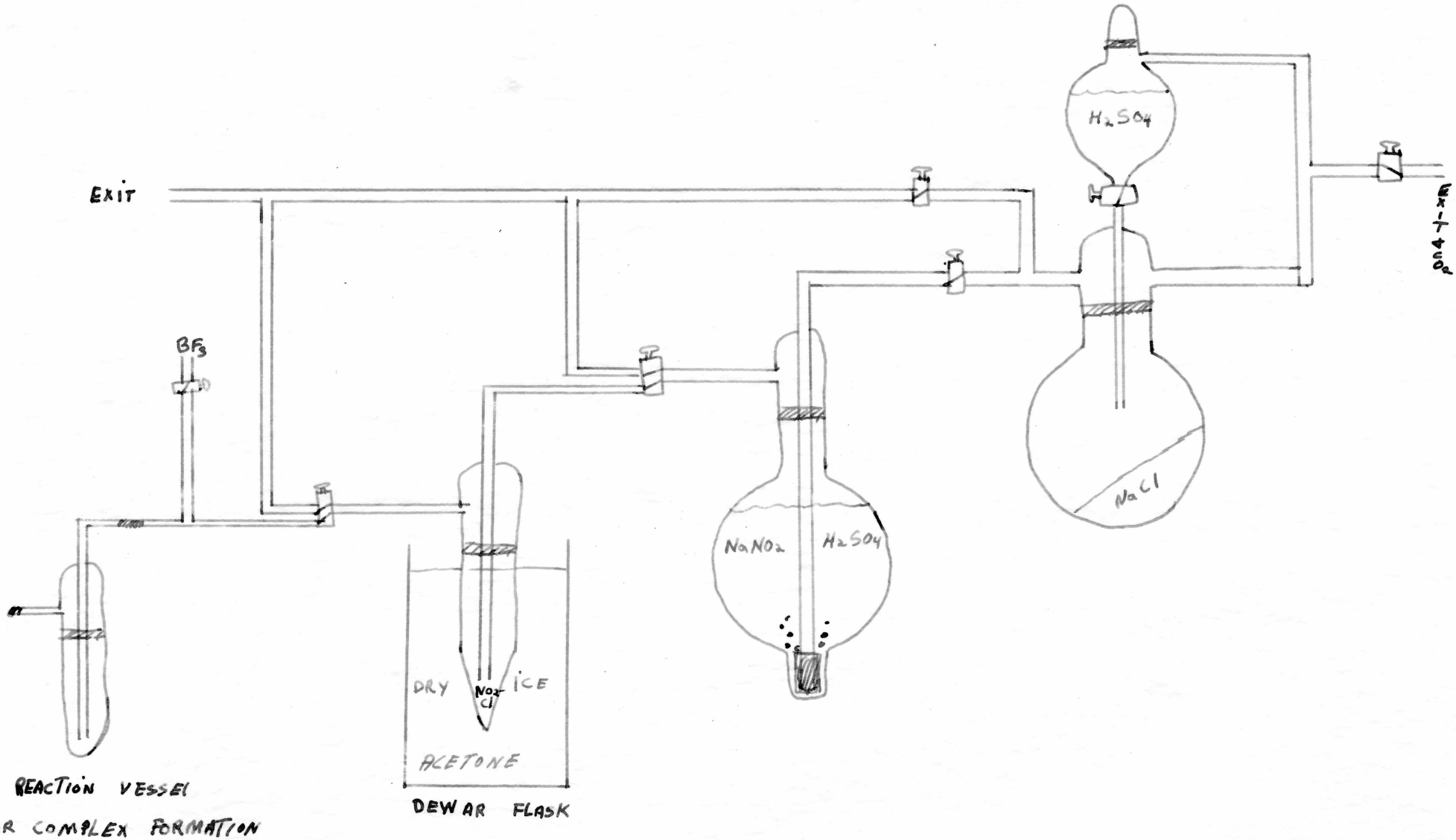
I. Preparation of nitryl chloride

Nitryl chloride was prepared by the method developed by Wise and Volpe[9] with some modifications. For an illustration of the apparatus see figure II. Gaseous hydrogen chloride, prepared by dropping concentrated sulfuric acid on sodium chloride, was bubbled through a 16 N. solution of sodium nitrate in sulfuric acid. A gas dispersion tube was used for the delivery of the hydrogen chloride. Gaseous nitryl chloride was collected in a graduated trap, cooled to dry ice-acetone temperature, or was bubbled through carbon tetrachloride to produce a saturated solution. The lines were cleared with carbon dioxide. The physical constants of nitryl chloride are: B.P. -14.3, M.P. -141 ± 2, M.W. 81.465, d = 1.32.

II. Preparation of dry solvents

A. The carbon tetrachloride, used in the spectra analyses and in the production of nitronium tetrafluoroborate, was first dried over calcium carbide, filtered, and then dried with phosphoric anhydride. The carbon tetrachloride was then filtered into a distilling flask and distilled through a Vigreaux column, the middle fraction being collected. This solvent was used immediately, or placed in a dessicator

B. The glacial acetic acid used in the spectra analyses was fortified with acetic anhydride to remove any water.



APPARATUS

FIGURE II

III. Preparation of the nitronium tetrafluorobromide

Five milliliters of bromine trifluoride(The Matheson Co. zero cylinder pressure) were placed in the collection vessel for nitryl chloride. Care was taken to avoid contact with any foreign material, as this resulted in fire. A flame was produced when bromine trifluoride came into contact with the Kel-F grease used throughout this project. Nitryl chloride was passed into the bromine trifluoride at a rate of approximately two bubbles per second. After about ten minutes a slightly yellow solid began to form in the solution. The solution became slightly more viscous in nature. During the course of the reaction the bromine trifluoride boiled very slightly and there was a reaction between excess nitryl chloride and bromine trifluoride in the waste exit-line resulting in the production of a white solid, which could not be isolated due to its high rate of sublimation. The main reaction was slightly exothermic in nature. The nitryl chloride was stopped after the formation of the yellow precipitate had ceased, taking approximately one hour per five milliliters of bromine trifluoride. Nitronium tetrafluorobromide was not isolated due to the extremely hazardous conditions faced when working with bromine trifluoride.

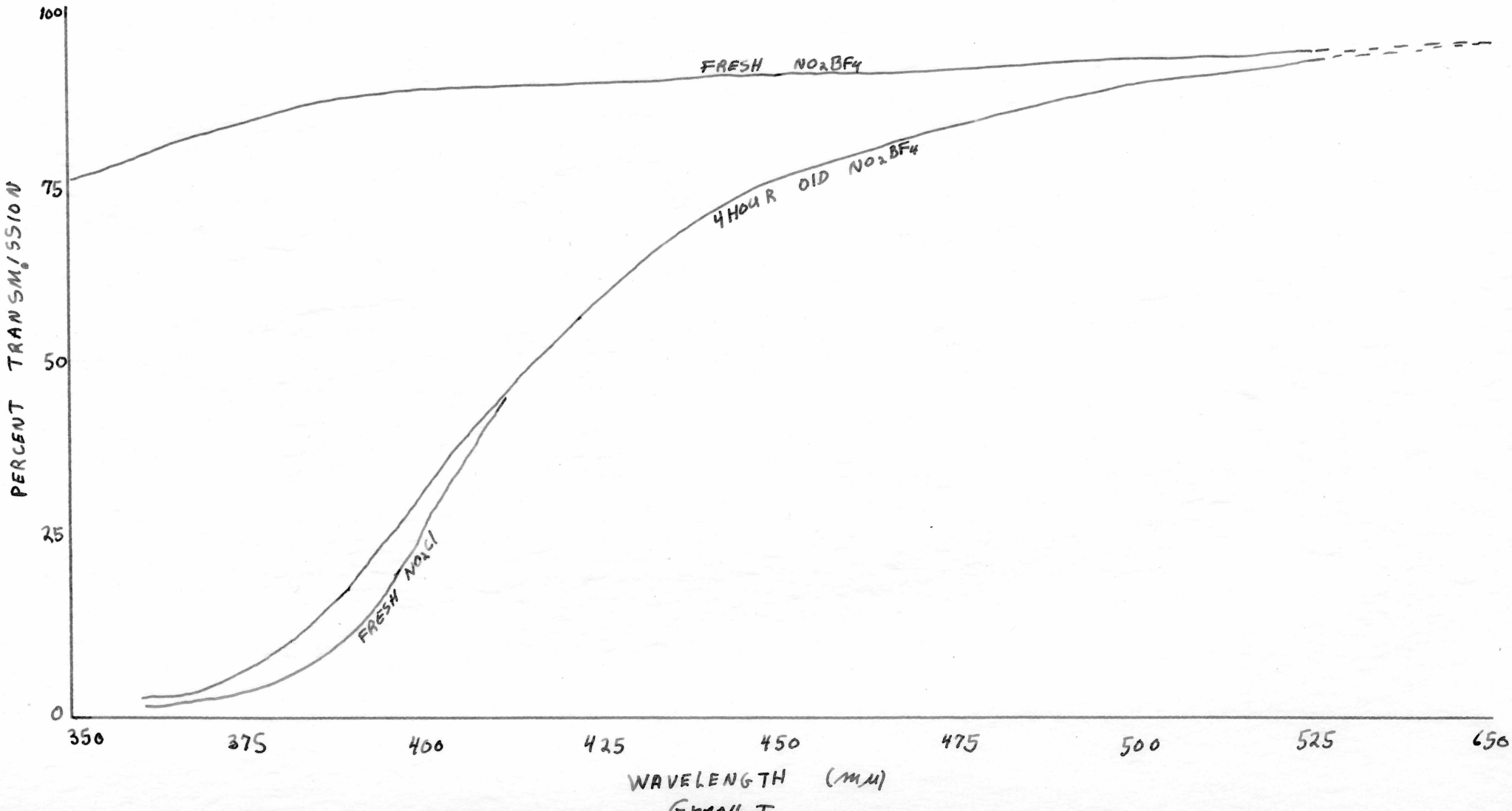
IV. Preparation of the nitronium tetrafluoroborate

The bromide complex in bromine trifluoride was placed in a strong hood. Boric anhydride was added, and a very exothermic reaction took place. Heavy fumes were produced (boron trifluoride)

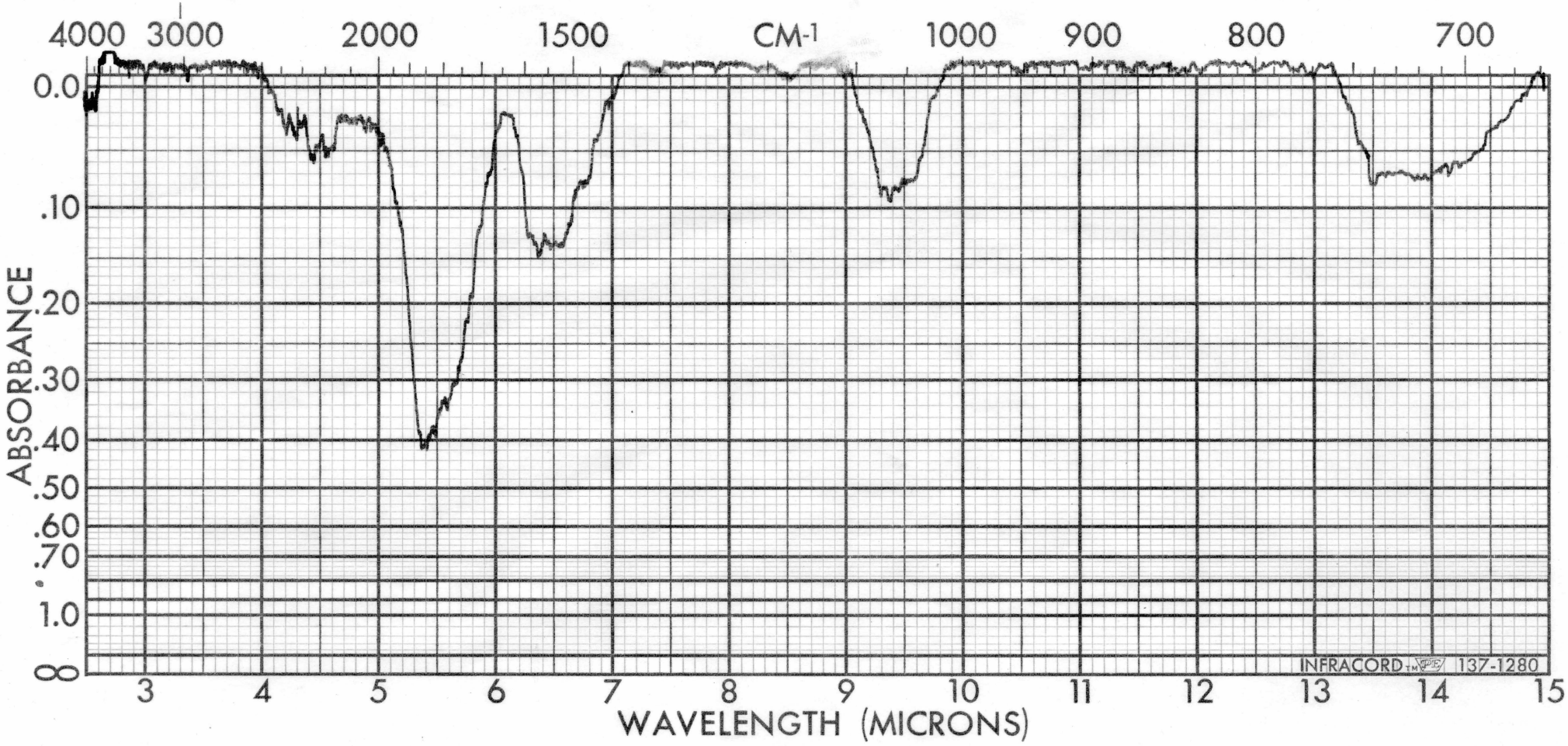
and the addition of boric anhydride was stopped after continued addition failed to produce any reaction. At this time the bromine trifluoride had boiled away, and there was only a white mass left in the reaction vessel. This mass was placed on a paper towel. The excess boric anhydride had conveniently fused into a solid mass, and this was easily separated from the product. Besides the fused mass there was also produced a white powdery solid which was hydroscopic in nature and sublimed rather heavily at room temperature. Visible and infrared spectra were run at varying time intervals in acetic acid solvent (see graphs I, IR). This compound reacted vigorously with water producing a very acid solution, which gave no precipitate with silver nitrate.

V. Preparation of the nitronium hexafluorophosphate

To the same bromide complex in bromine trifluoride was added phosphoric anhydride. An extremely exothermic reaction took place, as expected, with the production of a small flame. The addition of the anhydride was stopped after continued addition failed to produce a reaction. Heavy fumes were also produced in this reaction, and after the excess bromine trifluoride had boiled away the reaction mass was placed on a paper towel. Most of the excess phosphoric anhydride had conveniently fused into a solid mass. There was also produced a solid covered with a heavy yellow oil, and when pressed into the paper towel the oil burned with a small flame, leaving a white hydroscopic solid, which sublimed heavily at room temperature. Visible and infrared spectra were run in


100
75
50
25
0
PERCENT TRANSMISSION
FRESH NO2BF4
4 HOUR OLD NO2BF4
FRESH NO2Cl
350
375
400
425
450
475
500
525
550
WAVELENGTH (mμ)

GRAPH I

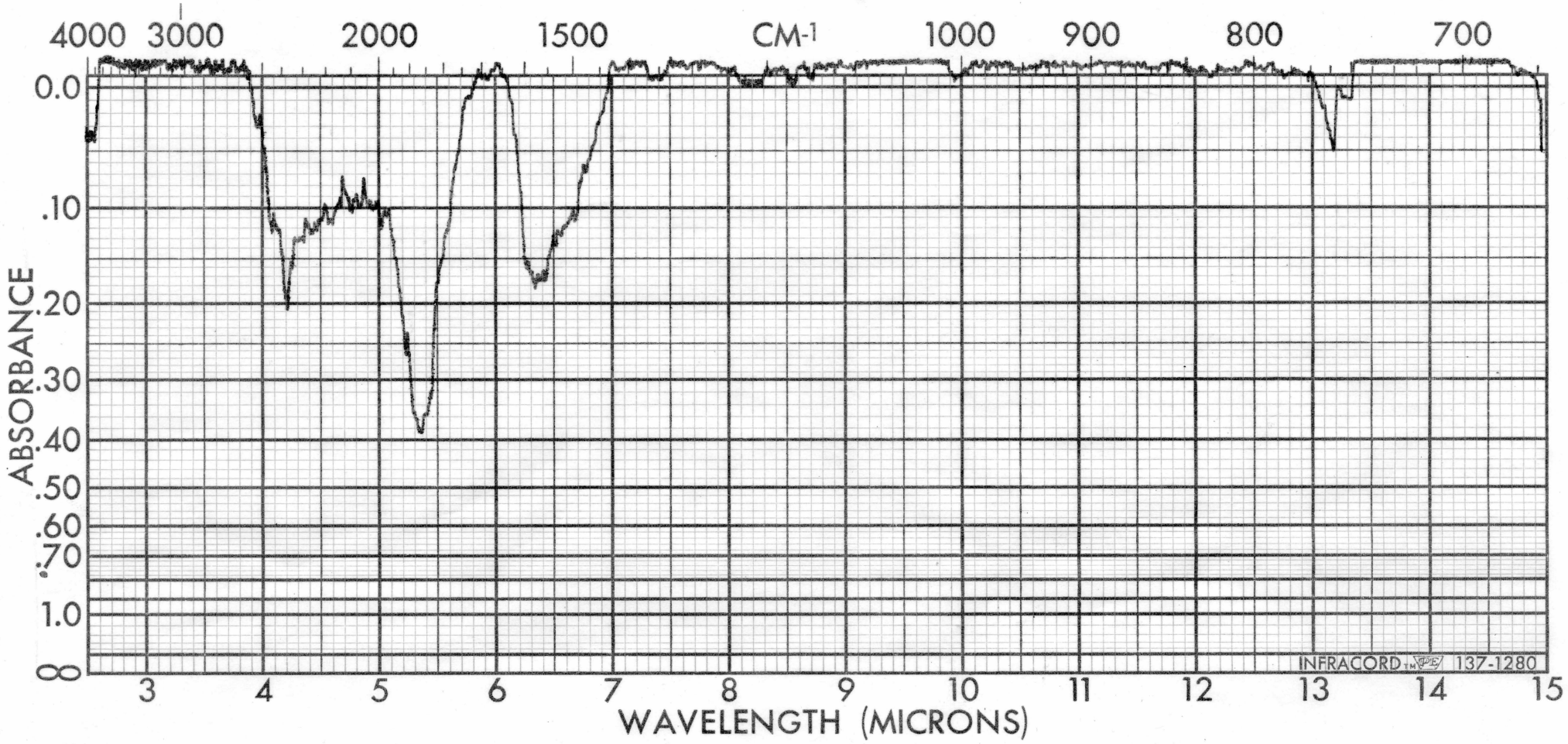


SPECTRUM NO.	ORIGIN	LEGEND	REMARKS
SAMPLE ①		1.	fairly dilute
NO_2BF_4 / HOAc & AcOAc	PURITY	2.	
	PHASE	DATE	soln yellow in 15 min
	THICKNESS	OPERATOR	

SPECTRUM NO. _____
SAMPLE _____

GRAPH I-R

THE PERKIN-ELMER CORPORATION, NORWALK, CONN.



SPECTRUM NO.	ORIGIN	LEGEND	REMARKS
SAMPLE NO_2BF_4 #2		1.	
same as #1	PURITY	2.	
1 hour later	PHASE	DATE	
	THICKNESS	OPERATOR	

SPECTRUM NO.
SAMPLE

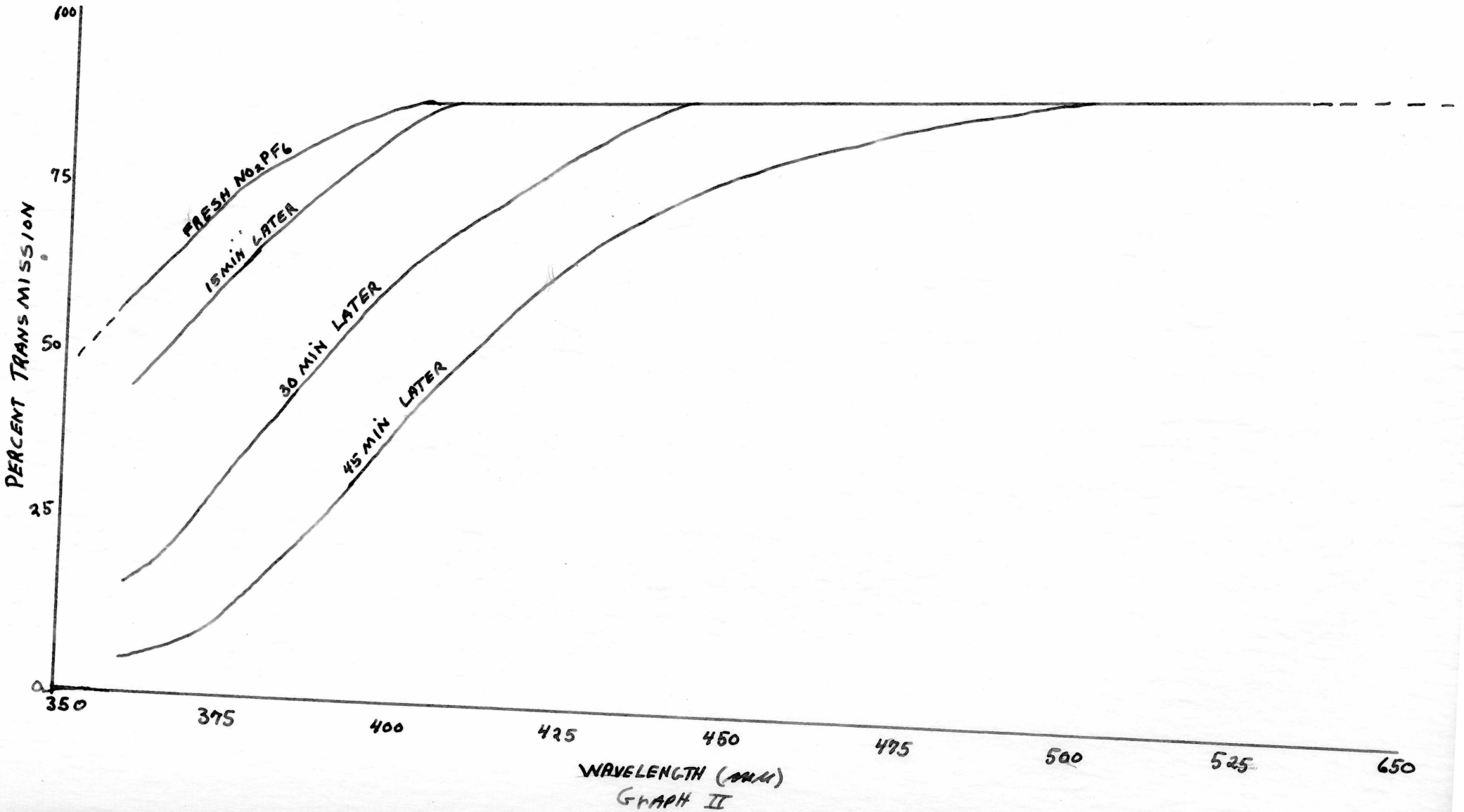
GRAPH I-R

THE PERKIN-ELMER CORPORATION, NORWALK, CONN.

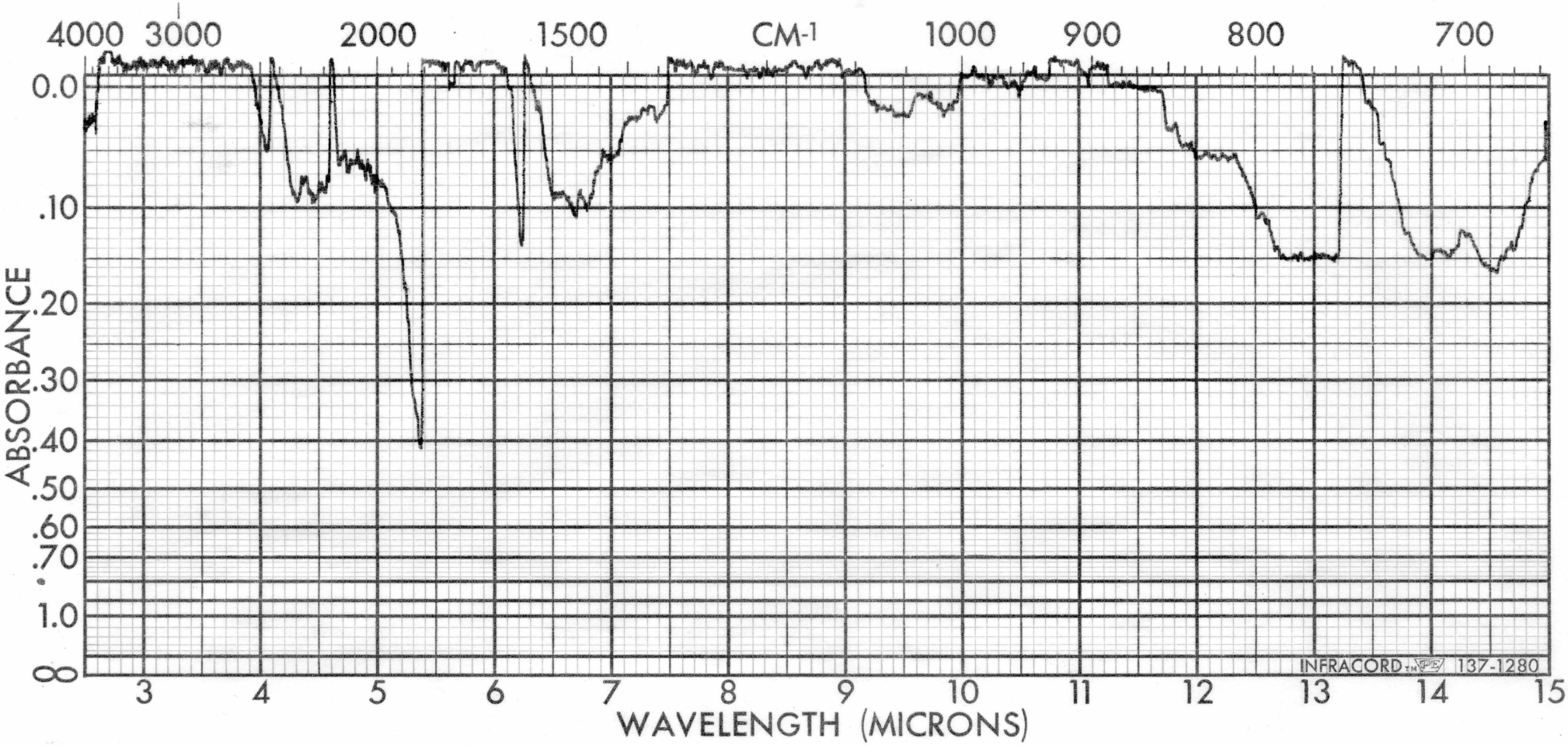
acetic acid solution (see graphs II, IIR). The compound reacted vigorously with water and the resultant water solution was very acid in nature and gave no precipitate with silver nitrate.

VI. Preparation of the nitronium trifluorochloroborate

A. Gas phase reaction: Five milliliters of nitryl chloride was collected in a reaction vessel at dry ice-acetone temperature. While still at this temperature, boron trifluoride (The Matheson Co. 1600 psi cylinder pressure)was bubbled through the nitryl chloride at a rate of two bubbles per second. A reaction started to take place at this temperature, and a yellow precipitate was formed. The addition of the boron trifluoride was continued until the reaction ceased, taking approximately fourty minutes. The color of the nitryl chloride solution had changed to a deeper yellow. Then the solution was allowed to come to room temperature and also boron trifluoride was added at the previous rate. The yellow precipitate dissolved at the increased temperature, and after five minutes a white precipitate began to form. At this time the nitryl chloride began to boil and a direct reaction between the nitryl chloride and the boron trifluoride was also taking place in the gas phase. It took about fourty-five minutes to complete this reaction. A great loss of product was encountered as the gas phase reaction took place mainly in the waste exit-line. Also a large amount of nitryl chloride boiled away at this temperature. The reaction was slightly exothermic in nature. If pure (colorless) nitryl chloride was used the reaction did not take


100
75
50
25
0
PERCENT TRANSMISSION
FRESH NO2PF6
15 MIN LATER
30 MIN LATER
45 MIN LATER
350
375
400
425
450
475
500
525
650
WAVELENGTH (mμ)

GRAPH II



SPECTRUM NO.	ORIGIN	LEGEND	REMARKS
SAMPLE NO_2PF_6		1.	more concentrated
	PURITY	2.	than NO_2BF_4 - but
	PHASE	DATE	not much
	THICKNESS	OPERATOR	v.v. yellow 15 min

SPECTRUM NO. _____
SAMPLE _____

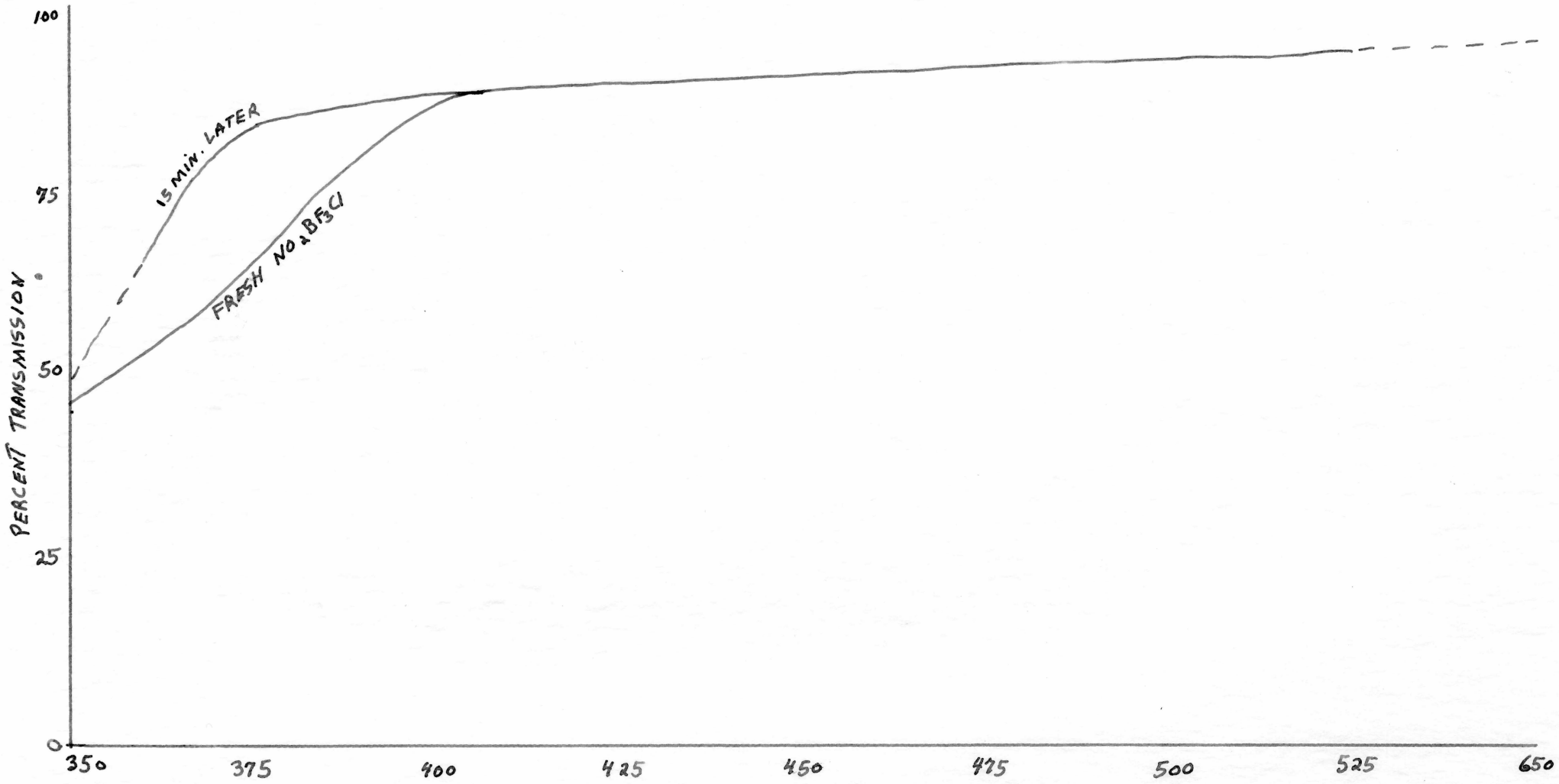
GRAPH II-R THE PERKIN-ELMER CORPORATION, NORWALK, CONN.

place. The product was a white powdery solid which was extremely hydroscopic in nature, and sublimed heavily at room temperature. Visible and infrared spectra were run in acetic acid solution (see graphs III,IIIR). The compound reacted vigorously with water, and the resultant water solution was very acid and did not give a precipitate with silver nitrate, even after boiling.

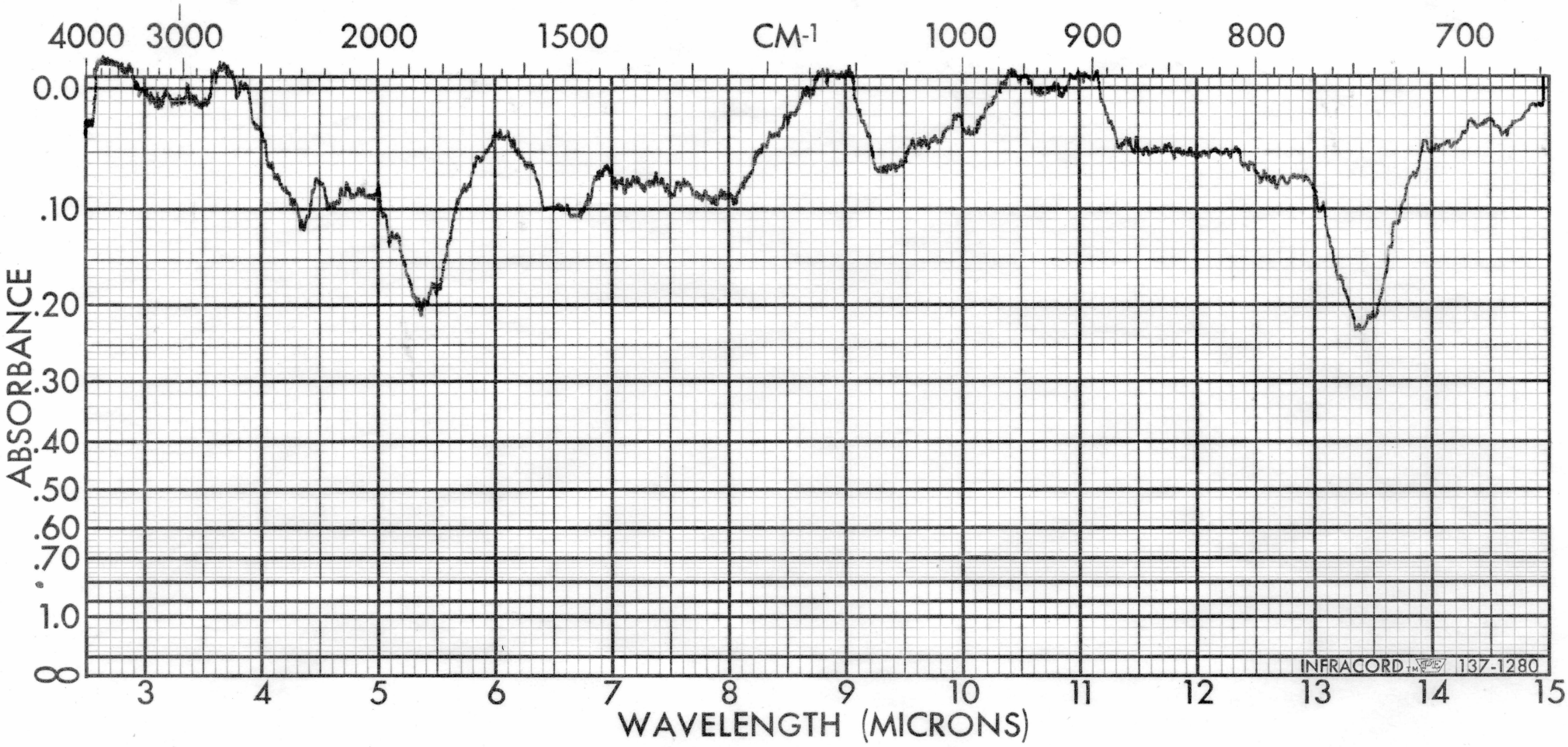
B. Preparation carried out in carbon tetrachloride: A saturated solution of nitryl chloride in carbon tetrachloride was prepared and boron trifluoride was passed in at a rate of two bubbles per second until the formation of the precipitate ceased. The reaction took approximately fourty-five minutes to complete, per 100 milliliters of saturated carbon tetrachloride. The product had the same characteristics as that prepared by the direct reaction, but it was very hard to isolate due to its heavy sublimation, and very hydroscopic nature. A visible spectrum was run on the carbon tetrachloride solution (see graph IV).

VII. Preparation of the nitronium tetrachloroaluminate

Two grams of aluminum trichloride were placed in the nitryl chloride reaction vessel. The nitryl chloride was collected in the vessel at dry ice-acetone temperature. The aluminum trichloride turned a deeper yellow color, but most of the nitryl chloride did not react. The mixture was also stirred and then allowed to come to room temperature. The excess nitryl chloride boiled away. The remaining mass was found to be slightly hydroscopic in nature and sublimed slightly at room temperature. There was a slight nitryl chloride odor, and the mass continued to crackle for three days. The new product was tried in the aro-


100
75
50
25
0
PERCENT TRANSMISSION
15 MIN. LATER
FRESH NO2BF3Cl
350
375
400
425
450
475
500
525
650
WAVE LENGTH (mμ)

GRAPH III

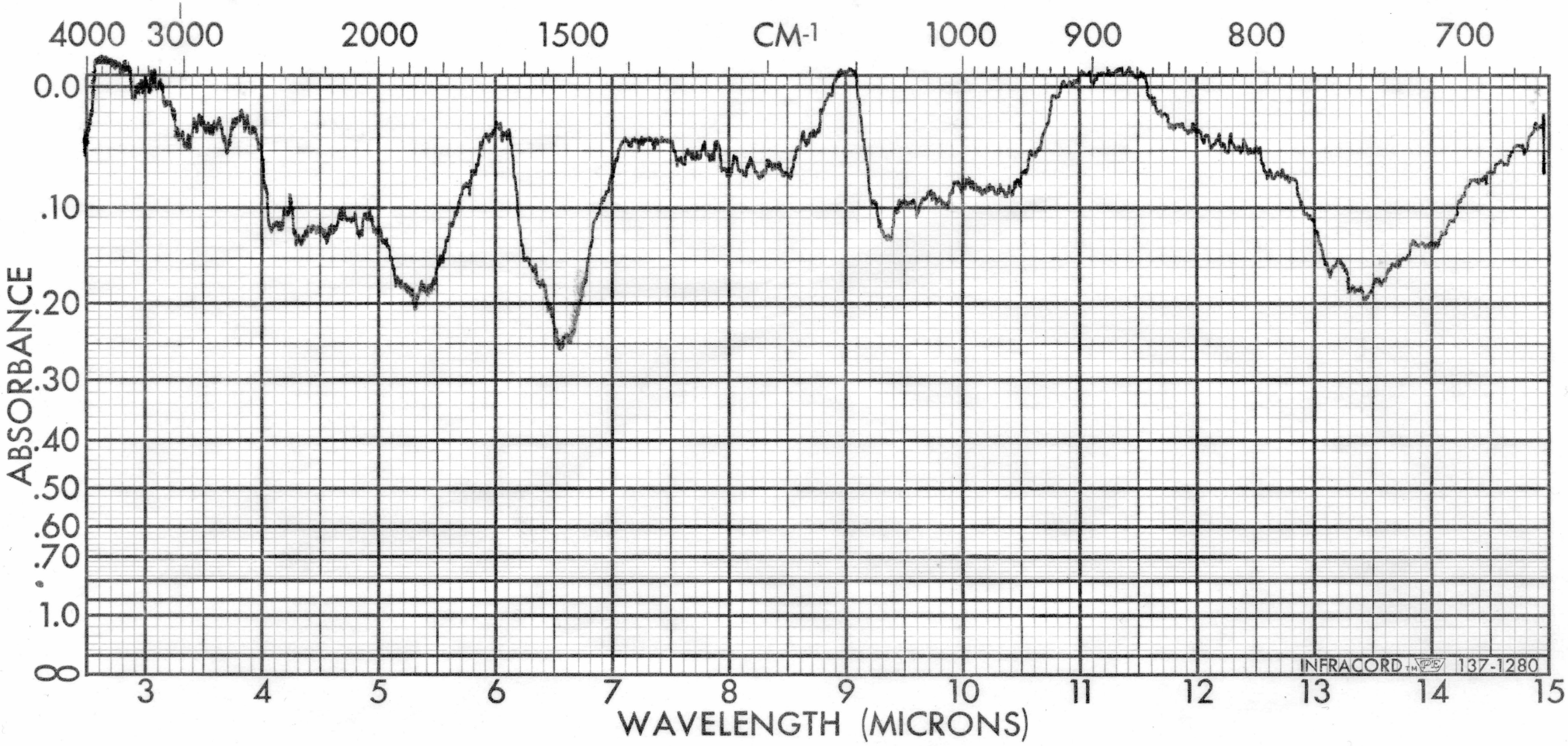


SPECTRUM NO.	ORIGIN	LEGEND	REMARKS
SAMPLE NO_2BF_3 CO		1.	abnormal
Fresh (1.)	PURITY	2.	NO_2BF_4
	PHASE	DATE	
	THICKNESS	OPERATOR	

SPECTRUM NO. SAMPLE

GRAPH III-R

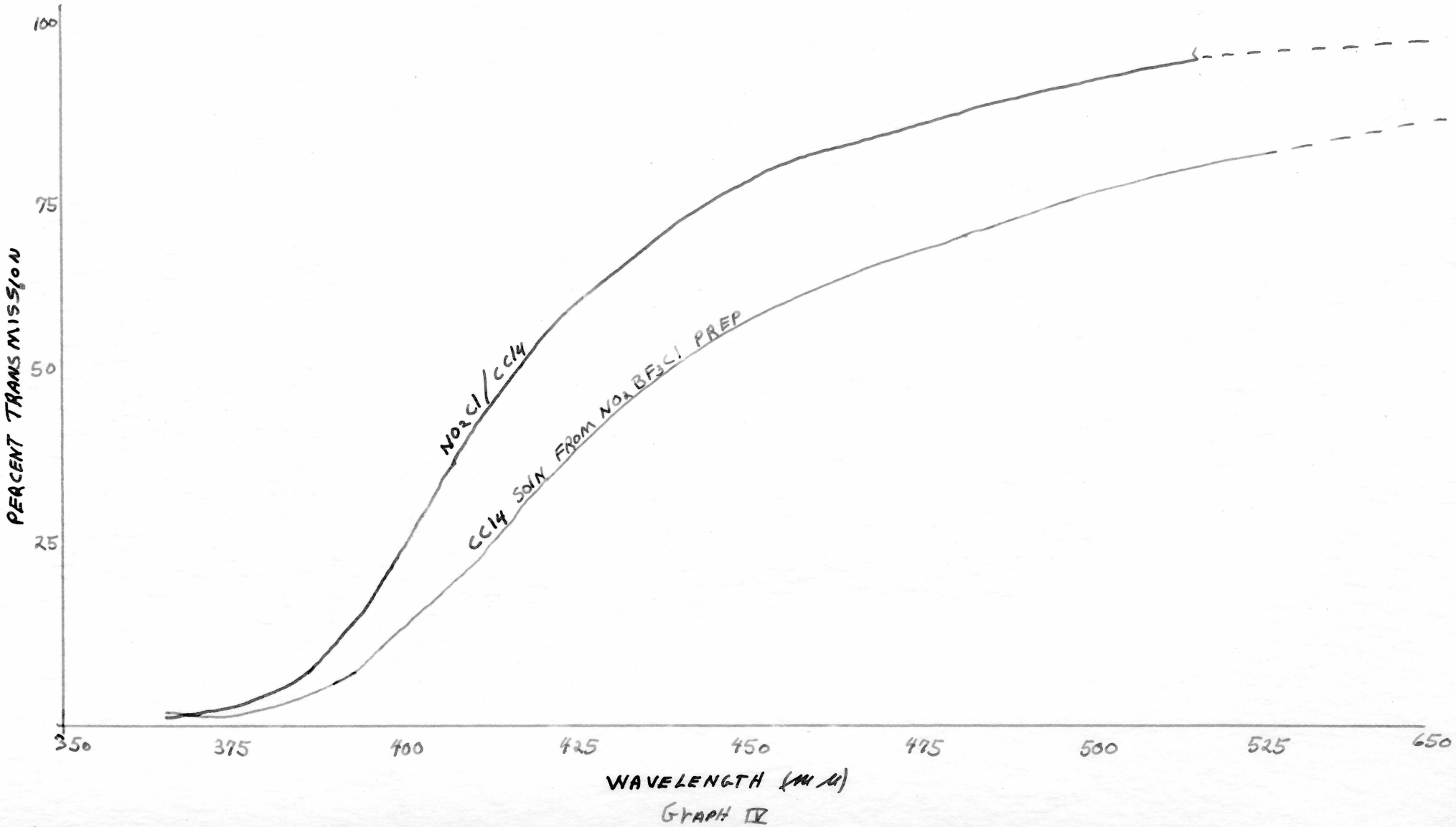
THE PERKIN-ELMER CORPORATION, NORWALK, CONN.



SPECTRUM NO.	ORIGIN	LEGEND	REMARKS
SAMPLE NO_2BF_3Cl #2 30 min later	PURITY	1.	SPECTRUM NO.
	PHASE	2.	SAMPLE
	THICKNESS	DATE	
		OPERATOR	

GRAPH III-R

THE PERKIN-ELMER CORPORATION, NORWALK, CONN.


100
75
50
25
PERCENT TRANSMISSION
NO2Cl/CCl4
CCl4 SOLN FROM NO2BF3Cl PREP
350
375
400
425
450
475
500
525
650
WAVELENGTH (mμ)

GRAPH IV

maticity test and did not give the characteristic colors produced by pure aluminum trichloride. No spectrum was run on this complex due to lack of proper solvents.

VIII. Spot test for the nitronium ion

A modified spot test for the nitronium ion was also developed. A drop of glacial acetic acid, a microspatula of THYODENE, and a small crystal of KI are placed on a spot plate. The nitronium containing compound or a solution of the compound in glacial acetic acid is added to the mixture on the spot plate. If the nitronium ion is present the mixture will have a purple-brown coloration. All the nitronium complexes produced in this project gave the characteristic coloration.

IX. Conductivity measurements

The conductivity measurements were carried out using a model RC Conductivity Bridge (Industrial Instruments Inc.) The cell constant was found to be .360.

Conductivity, K = cell constant, K_c/ resistance of solution, R

Equivalent conductance, Λ = K / concentration of the solution, c

For a .1 N solution of nitronium tetrafluoroborate in acetic acid:

Λ = .360 / 21,040 x 1 / .1 x 1000

Λ = . 16

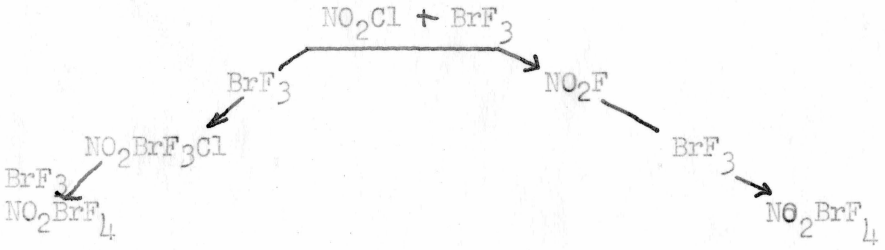
For a .1 N solution of sodium acetate in acetic acid:

Λ = .360 / 13,040 x 1 / .1 x 1000

Λ = . 28

DISCUSSION

I. The nitronium tetrafluorobromide is still a very controversial complex. As the conditions encountered while working with it are so bad, we did not attempt to isolate the complex. Our reaction product seems to be somewhat in agreement with Aynsley's work, using nitryl fluoride[6]. He experienced the same increase in viscosity of the bromine trifluoride solution and the same yellow coloration, which he attributed to the nitronium ion. The solid formed on the walls of the reaction vessel could have been the unstable complex. The question may be raised concerning the possible formation of nitronium trifluorochlorobromide, but this seems very unlikely. If this complex was formed it would not be stable in the strong fluorinating solution. It is highly possible that the nitryl chloride was first converted to the nitryl fluoride and this in turn reacted with bromine trifluoride to produce the complex:



If nitryl fluoride was produced the our method is not the most direct, but it is the safest, although Aynsley reported that there were no adverse conditions encountered when working with nitryl fluoride.

II. In the production of nitronium tetrafluoroborate and nitronium hexafluorophosphate we followed a different course than that reported in the literature. Aynsley[6] reacted nitryl fluoride directly with the element's fluoride. This appears to be a more direct method of production and somewhat easier. Our reactions are convenient, especially with the excess anhydride fusing into a solid mass. However, the heat produced could cause some serious trouble. In any case, our method is far superior to that of Woolf and Emeléus[2]. Our complexes have the same appearance as those described in the literature. We did not calculate yields due to the nature of the reactions.

After looking at the spectra it appears that nothing very conclusive can be established. The most interesting case is that of the nitronium tetrafluoroborate. After standing in acetic acid solvent four hours there was a shift to a higher absorption, to the same area as reported for nitryl chloride (360 mu-400mu)[10]. It is proposed that the cause of this shift is a disproportionation of the complex:

$$NO_2BF_4 \longrightarrow NO_2F + BF_3$$

As the absorption peak is that reported for the nitronium group. The phosphate complex experienced the same shift in a period of one hour. The infrared spectra offer no conclusive results and are included only for future reference. The peaks in the four to seven micron area are in the same relative position as those reported for the nitronium group.

III. The nitronium trifluorochloroborate has never been reported

in the literature and this seems to be our main claim to fame at the present time. The trifluorochloroborate ion in water solution is very stable, giving no precipitate with silver nitrate. The acidity of the water solutions of these complexes can be accounted for by hydrolysis:[2]

$$(NO_2)_xAF_y + HOH \longrightarrow xHNO_3 + H_xAF_y$$

$$(NO_2)_xAF_yCl + HOH \longrightarrow xHNO_3 + H_xAF_yCl$$

Due to the fact that no yield was obtained in the direct reaction between pure (colorless) nitryl chloride and boron trifluoride it can be assumed that some nitryl chloride impurity catalyzes the reaction. The visible spectrum of the decanted carbon tetrachloride shows a heavy absorption in the region for the nitronium ion, due to nitryl chloride and nitronium trifluorochloroborate in solution.

IV. The tetrachloroaluminate offers one of the most interesting areas of research. It was impossible to determine if the reaction did occur, but due to Sears[5] comments it seems highly probable that it did. There is no doubt that some reaction did take place. There would seem to be a good future in this compound as a nitrating and chlorinating agent.

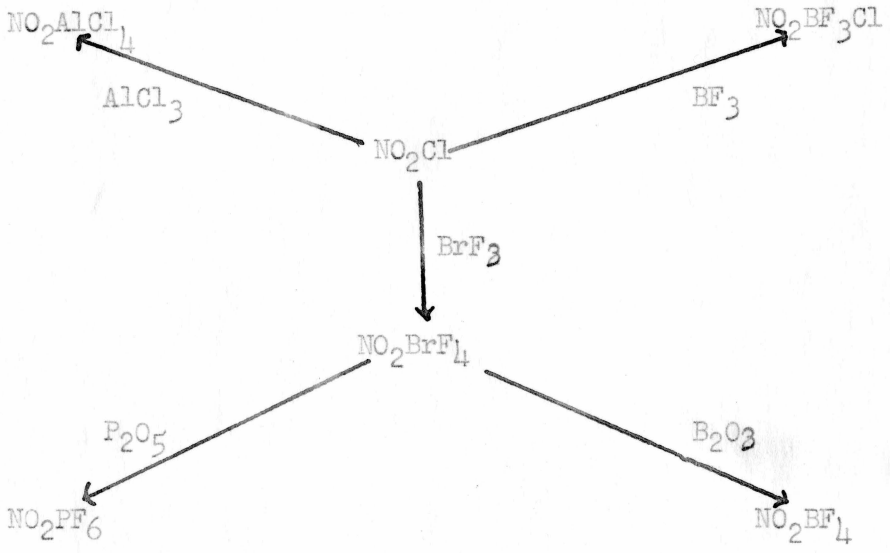
V. It was impossible to obtain any physical constants of these complexes. However, the conductivity measurement gives a very good idea as to the ionicity of these nitronium complexes. They are on the same order of magnitude as sodium acetate.

VI. As far as determining the behavior of nitryl chloride in bromine trifluoride solution, the complexes offered little help. If the nitryl chloride was not converted to nitryl fluoride then it appears that the nitronium group is sufficiently positive to enter into this reaction(complex formation). However, if the chloride was converted into the fluoride, which the author favors, then the nitronium group would be positive enough to enter into complex formation. There is not much doubt that this nitronium bromide complex could be used as a base for the production of numerous nitronium fluoro-complexes. The only other necessary starting material would be the respective anhydride. It also appears that nitryl chloride has sufficient nitronium content to form the borate complex by a direct reaction, catalyzed by the nitryl chloride impurities.

SUMMARY

Due to Aynsley's work (6) it appears rather useless to propose that our nitronium bromide complex be used to prepare the respective nitronium fluoro complexes, although this would be an interesting project. There is little doubt that these complexes can be prepared in this manner. However, there is a big area for conclusive spectra work on these complexes, and this work will be carried out in the very near future.

Summary schematic of this project



There are three definite areas of useful research that should be investigated.

1. Nitryl chloride should be reacted with the elements under varying conditions. The reactions should be classified and the products identified. Much care should be taken to insure anhydrous conditions.

2. Nitryl chloride should be reacted with the various chlorides of the elements in another systematic study.

3. Nitryl chloride should be reacted with the various fluorides of the elements in another systematic study.

Of course the nitrating properties of these complexes should be investigated, especially with nitryl chloride used as a catalysis.

There is little doubt that nitryl chloride has great potentials if only more research can be carried out. The method of producing nitryl chloride which was used in this project is very inexpensive and easy to handle. The chemistry of nitryl chloride is slowly clearing up, and it appears that in the near future the full benefits of this compound will be recognized.

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