

ACID SOLUTIONS OF NITRYL CHLORIDE

NITRATIONS OF BENZENE

A THESIS

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Washington and Lee University as a completion of work  
for a Bachelor of Science degree in Chemistry.

By

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## VITA

The author was born in Newport News, Virginia on December 7, 1932, the son of Vesta Taylor and William Douglas Goode. He attended both elementary and high school in Newport News. He graduated from Newport News High School in June of 1951. He entered Washington and Lee University in the fall of that year, and is a candidate for a Bachelor of Science degree in Chemistry.

### Awards

Cary T. Grayson Memorial Scholarship (1951 to 1955)

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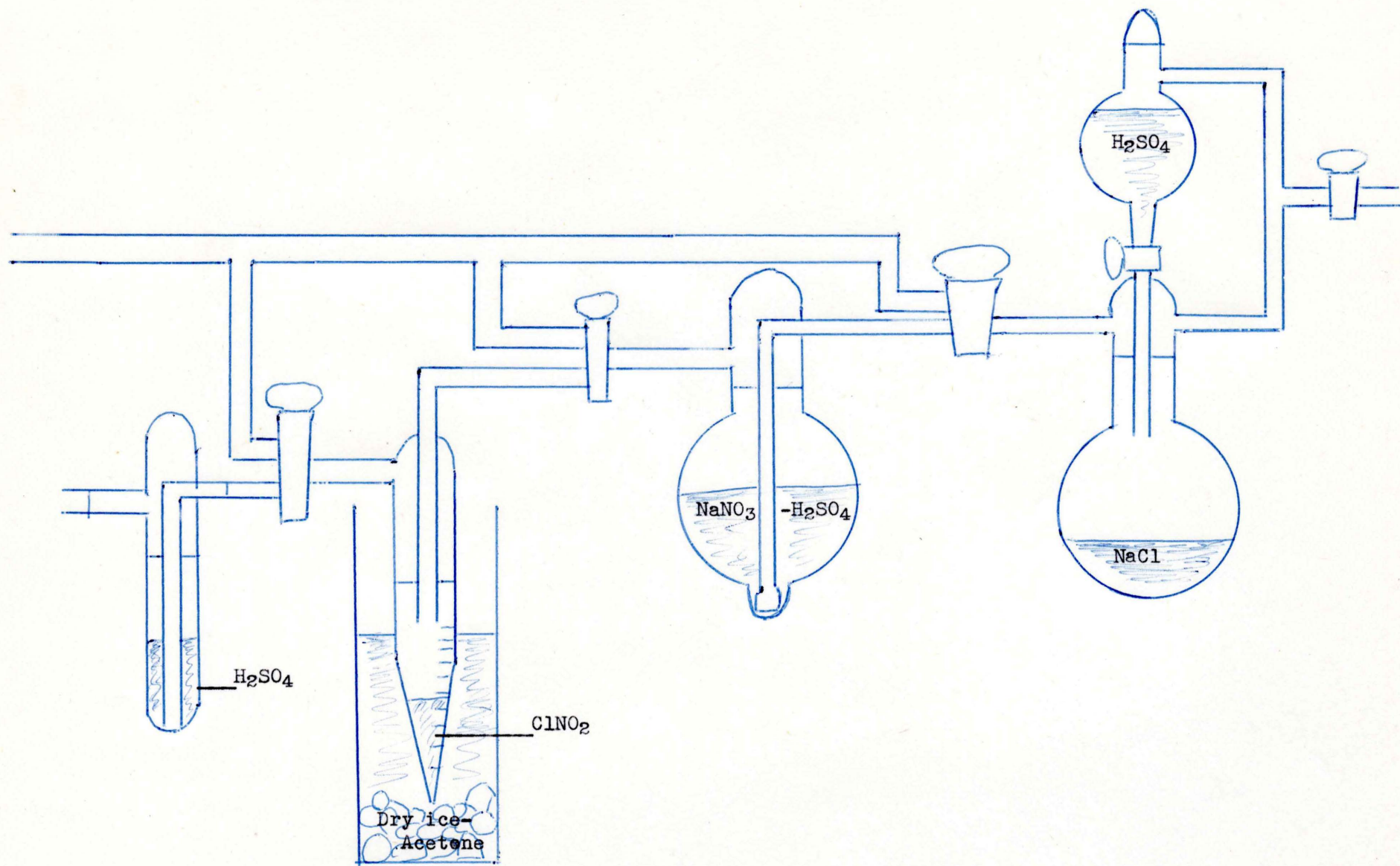
## I. Introduction

The suggestion has been made by Wise and Volpe<sup>(1)</sup> that solutions made from nitryl chloride and concentrated sulfuric acid may contain the nitronium ion. This was based upon the fact that these solutions contain no chlorine. It was also found that nitryl chloride could be regenerated from the solutions by passing hydrogen chloride through them. The latter reaction was similar to that of the production of nitryl chloride using a solution of sodium nitrate in concentrated sulfuric acid. The presence of the nitronium ion in such solutions is well established.

The possibility of nitrating benzene with solutions of nitryl chloride in sulfuric acid was suggested by an experiment of Shirley's.<sup>(2)</sup> A product of m-dinitrobenzene was isolated when an attempt was made to nitrate n-hexane containing benzene impurities with such a solution.

In this set of experiments, we have studied the solubility of nitryl chloride in concentrated sulfuric acid and the nature of such solutions as indicated by their nitrating power. All studies were made on the basis of yields of m-dinitrobenzene, although under certain conditions nitrobenzene is the principle product. An attempt was made to obtain a maximum yield of m-dinitrobenzene from nitryl chloride by varying the conditions of nitration.

Whitaker<sup>(3)</sup> gives a summary of the literature pertaining to the use of nitryl chloride as a nitrating agent and its reactions in acidic, basic and neutral media. He has also performed some experiments on the reactions of nitryl chloride with aromatic hydrocarbons under neutral conditions.



APPARATUS



## II. Experimental

### A. The preparation of nitryl chloride.(1)

HCl was generated by slowly dropping concentrated  $\text{H}_2\text{SO}_4$  onto pure NaCl (or KCl in some cases). The HCl was bubbled through a solution of  $\text{NaNO}_3$  in concentrated  $\text{H}_2\text{SO}_4$  ranging in concentration from 120 gms/liter to 135 gms/liter. The gaseous product was condensed in a graduated vessel immersed in a dry ice-acetone bath at  $-60$  to  $-70^\circ\text{C}$ . At first, the vapors were allowed to escape.

After the  $\text{NaNO}_3\text{-H}_2\text{SO}_4$  solution had turned slightly greenish-yellow, the rate of HCl generation was increased by dropping the  $\text{H}_2\text{SO}_4$  on the NaCl at a faster rate. Shortly after this point, the outlet on the collection vessel could be closed as no further gases escaped, and a partial vacuum was established in the vessel.

The condensed product was a light yellow liquid at low temperatures. It could be evaporated by allowing it to slowly attain room temperature. During this process, the gases turned brown due to the presence of decomposition products believed to be  $\text{NO}_2$ .

### B. Preparation of a solution of nitryl chloride in concentrated $\text{H}_2\text{SO}_4$ .

After generating the  $\text{ClNO}_2$ , as above, the product was allowed to vaporize slowly and the vapors were led into a vessel containing concentrated  $\text{H}_2\text{SO}_4$ . The  $\text{ClNO}_2$  was allowed to bubble through the acid, and the escaping vapors were led out the exhaust. This vessel was so constructed that it might be removed from the apparatus and weighed accurately to 10 mg. The contents of the vessel could be weighed before and after bubbling in the  $\text{ClNO}_2$ .

The gases given off above the  $\text{H}_2\text{SO}_4$  were visibly discolored. The solution turned slightly green and increased in both weight and volume.

C. Nitration of benzene by  $\text{ClNO}_2\text{-H}_2\text{SO}_4$  solution.

Ten ml. of the solution of  $\text{ClNO}_2$  in concentrated  $\text{H}_2\text{SO}_4$  were prepared as above. Benzene was added dropwise with stirring to the solution at room temperature. With each drop of benzene, a localized red-brown color appeared. But this disappeared with stirring, the solution turning greenish-yellow. Heat was generated in this reaction.

After a certain amount of benzene had been added, the whole solution turned brown. The amount of benzene depended on the concentration of  $\text{ClNO}_2$  in the solution. The addition of more benzene after this point was reached showed no sign of further reaction (no additional coloration or generation of heat). The solution had an odor of nitrobenzene.

After the addition of benzene, the solution was pipeted slowly into water. The water became cloudy and the products separated out on standing. The product was predominately a solid. It was filtered off and recrystallized from alcohol and water.

To accurately determine the composition of the product, tests were run upon the solid product formed from freshly distilled benzene and the  $\text{ClNO}_2\text{-H}_2\text{SO}_4$  solution. The solid was recrystallized twice and melting points taken after each recrystallization. A mixed melting point was run with m-dinitrobenzene having a melting point of 89 to 90.5°C. The product was analyzed for nitrogen, sulfur, and chlorine.

D. Nitration of benzene by adding solutions of benzene and nitryl chloride to concentrated  $\text{H}_2\text{SO}_4$ .

The  $\text{ClNO}_2$  was generated as in procedure A above. It was collected in a vessel having a delivery tube for the direct

addition of benzene. Two or three ml. of  $\text{ClNO}_2$  was collected at  $-60$  to  $-70^\circ\text{C}$  and benzene was added through the delivery tube. The benzene froze on contact with the  $\text{ClNO}_2$ . The mixture was allowed to gradually heat up to room temperature.

At room temperature, the solution was dark red, giving off a brown gas. If heated, the brown gas was evolved rapidly, leaving the solution yellow.

When the dark red solution was added dropwise to about 30 ml. of concentrated  $\text{H}_2\text{SO}_4$ , colored droplets formed at first. Later, the  $\text{H}_2\text{SO}_4$  turned dark red and a light brown layer formed on top. When this mixture was added to water, an oil separated. The oil was yellow and smelled like nitrobenzene.

E. Nitration of benzene by bubbling nitryl chloride through concentrated  $\text{H}_2\text{SO}_4$  with a layer of benzene on top.

The procedure is approximately the same as in procedure B except that on top of 10 ml. of  $\text{H}_2\text{SO}_4$  was a layer of benzene. As the  $\text{ClNO}_2$  was bubbled through the system at room temperature, the benzene layer became orange and a red coloration formed in the  $\text{H}_2\text{SO}_4$  adjacent to the benzene. This coloration spread as the reaction proceeded and the benzene layer disappeared. Finally, the color of the  $\text{H}_2\text{SO}_4$  solution became gradually light brown and the benzene layer completely disappeared. When the reaction was complete, the vessel was weighed and the increase in weight was found as in procedure B.

The solution was then pipeted into water, a solid separated, and the product was recrystallized.



F. Nitration of benzene by  $\text{NaNO}_3\text{-H}_2\text{SO}_4$  solution.

A solution of  $\text{NaNO}_3$  in concentrated  $\text{H}_2\text{SO}_4$  was made up, and 10 ml. of it was used in the reactions. The benzene was added dropwise with stirring to the solution at room temperature. At first the solution turned light yellow with some heating. After about 0.5 ml. of benzene had been added, a localized brown coloring developed and disappeared on stirring. After about 0.6 ml. of benzene had been added, the brown color dispersed and the heating ceased with the addition of more benzene.

The solution was pipeted into water. A precipitate formed and was isolated as was the solid product in procedure C.

### III. Results and Discussion

#### A. Preparation of nitryl chloride.

The yields of  $\text{ClNO}_2$  from procedure A using approximately 120 gms. of  $\text{NaNO}_3$  to a liter of  $\text{H}_2\text{SO}_4$ , were around 80%, ranging from 76.5% to 89.8%. These results checked pretty well with those of Shirley.<sup>(2)</sup> Lower yields were obtained when the reaction was run too fast.

#### B. Solutions of nitryl chloride in $\text{H}_2\text{SO}_4$ .

The concentrations of the solutions of  $\text{ClNO}_2$  in concentrated  $\text{H}_2\text{SO}_4$  were measured by the gain in weight of the solution. The concentrations seemed to depend upon the amount of  $\text{ClNO}_2$  used. Higher concentrations were found at room temperature than at  $0^\circ\text{C}$ .<sup>(3)</sup> Using 11 to 12 ml. of  $\text{ClNO}_2$  at room temperature, a concentration of 0.093 moles of  $\text{ClNO}_2$  per mole of  $\text{H}_2\text{SO}_4$  was obtained. However, note that in runs 2 and 3 (Table IV) approximately the same concentrations were obtained from differing amounts of  $\text{ClNO}_2$  under the same conditions.

The solutions, upon standing, showed no trace of chloride ions when analyzed.<sup>(3)</sup> The assumption is that the chloride was liberated in the form of  $\text{HCl}$  gas. Therefore, the increase in weight was due to  $\text{NO}_2$  in some form. For reasons to be stated later, we believe this to be the  $\text{NO}_2^+$  ion in some form of association with the  $\text{H}_2\text{SO}_4$ . Therefore, we will say the concentration given above was 0.165 moles of  $\text{NO}_2^+$  per mole of  $\text{H}_2\text{SO}_4$ , or 1.42 gms. of  $\text{NO}_2^+$  in 10 ml. of  $\text{H}_2\text{SO}_4$ .

Since we wished to nitrate benzene, using as little  $\text{ClNO}_2$  as possible, to give the best yields of m-dinitrobenzene, less concentrated solutions were used predominately. The values of  $\text{NO}_2^+$

given in Table IV are in grams per 10 ml. of  $\text{H}_2\text{SO}_4$ . In runs 1, 2, and 3, they refer to the solutions of  $\text{ClNO}_2$  in  $\text{H}_2\text{SO}_4$ . Run 1 refers to a solution that had stood for a sufficient time for the chlorine to escape, while runs 2 and 3 refer to solutions in which there is still some chlorine of undetermined quantity. The weight given is believed to be predominately that of  $\text{NO}_2^+$ .

In runs 4, 5, and 6, the values are given in  $\text{NO}_2^+$  per 10 ml. of acid. However, this value includes any  $\text{NO}_2^-$  combined with the benzene and any  $\text{ClNO}_2$  that may remain as such in the final solution.

C. The nitration of benzene with  $\text{ClNO}_2\text{-H}_2\text{SO}_4$  solutions.

The solid product prepared in procedure C, using freshly distilled benzene, was established to be m-dinitrobenzene. See Tables I, II, and III.

Table I

## Melting Point of Solid

Sample	M.P. °C	M.P. °C	Ave. M.P. °C
1st recrystallization	87-89	89.5-90.5	88.25-89.75
2nd recrystallization	88.5-89.5	87-90.5	87.75-90.0

Table II

Mixed Melting Point With m-Dinitrobenzene

Sample	M.P. °C	Mixed M.P. °C
Product	87.8-90.0	89.5-90.5
<u>m</u> -dinitrobenzene	89-90.5	

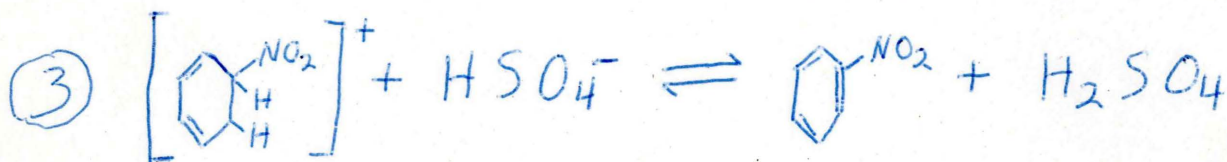
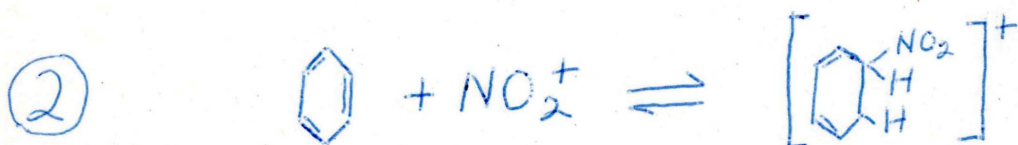
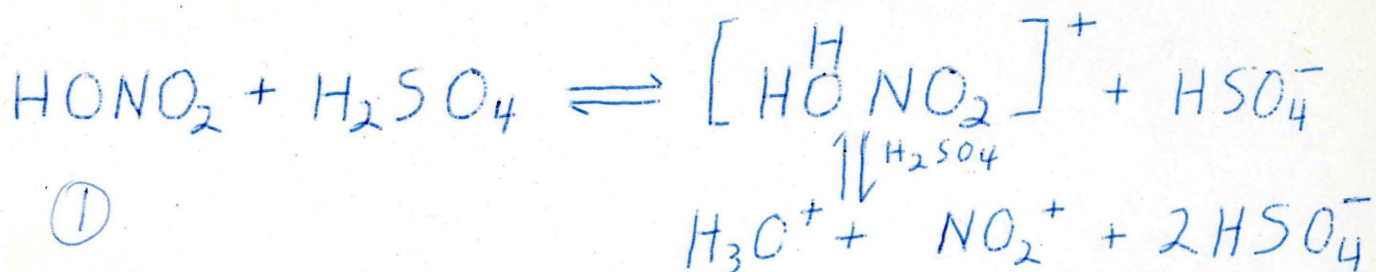
Table III

## Element Qualitative Analysis

Nitrogen	Sulfur	Chlorine
present	absent	absent



The accepted mechanism for the nitration of benzene using mixed nitric and sulfuric acids is as follows:<sup>(4)</sup>



Thus, if  $\text{NO}_2^+$  was the attacking agent in the mixed acid, it seems logical that it was the agent in solutions of  $\text{ClNO}_2$  in  $\text{H}_2\text{SO}_4$  which was responsible for the nitration of benzene. This is supported by the fact that these solutions, upon standing, gave no test for  $\text{Cl}^-$ .<sup>(1,3)</sup> Thus the reaction of  $\text{ClNO}_2$  and concentrated  $\text{H}_2\text{SO}_4$  might be represented as suggested by Wise and Volpe:<sup>(1)</sup>



The formation of the actual compound,  $\text{NO}_2\text{HSO}_4$ , did not seem to be indicated<sup>(3)</sup>, but, by some arrangement, the  $\text{NO}_2^+$  ion was available for nitrations.



D. Comparisons of  $\text{ClNO}_2\text{-H}_2\text{SO}_4$  and  $\text{NaNO}_3\text{-H}_2\text{SO}_4$  solutions as nitrating agents.

Table IV

run	1	2	3	4	5	6	7	8
procedure*	C	C	C	E	E	E	F	F
Reactants								
gms. $\text{NaNO}_3$ **							1.17	0.80
" $\text{ClNO}_2$	>.35	7.8	4.68	6.4	4.37	3.28		
" $\text{NO}_2^+$ ***	1.42	0.85	0.84	1.32	1.44	1.10	0.58	0.43
" benzene	1.76	0.56	0.68	1.12	0.78	0.72	1.76	0.923
Yields								
gms.	0.46	0.29	0.32	0.27	0.80	0.43	0.42	0.47
on benzene	12.2%	24 %	21.9 %	11.2 %	47.6 %	36.1 %	11.1 %	23.6 %
on $\text{NaNO}_3$							36.4 %	59.5 %
on $\text{ClNO}_2$		3.6 %	6.6 %	4.1 %	17.8 %	12.7%		
on $\text{NO}_2^+$	17 %	19 %	20.9 %	11.2 %	30.2 %	21.2 %		

\*Procedure C: Nitration of benzene by  $\text{ClNO}_2\text{-H}_2\text{SO}_4$  solution.

Procedure E: Nitration of benzene by bubbling  $\text{ClNO}_2$  through  $\text{H}_2\text{SO}_4$  with a layer of benzene on top.

Procedure F: Nitration of benzene by  $\text{NaNO}_3\text{-H}_2\text{SO}_4$  solution.

\*\*Grams of reagent per 10 ml. of  $\text{H}_2\text{SO}_4$ .

\*\*\*See Section III, B.

The nitrating power of  $\text{ClNO}_2$  in concentrated solutions as compared to  $\text{NaNO}_3$  in concentrated solutions is shown by comparing run 1 with run 7 in Table IV. In these runs, the  $\text{ClNO}_2$  solution was approximately 3.1 molar; the  $\text{NaNO}_3$  solution was approximately 1.38 molar. The amount of benzene used and the conditions of reaction were the same. The amount of m-dinitrobenzene recovered was approximately the same in



both runs. The yields on the basis of the nitrogen used (as  $\text{NaNO}_3$  or  $\text{ClNO}_2$ ) were quite in favor of the  $\text{NaNO}_3$  solution.

This difference in the effectiveness of  $\text{ClNO}_2$  and  $\text{NaNO}_3$  in concentrated  $\text{H}_2\text{SO}_4$  solutions indicates that the  $\text{NO}_2^+$  ion was less available in the solutions of  $\text{ClNO}_2$  than in those of  $\text{NaNO}_3$ .

A factor which entered into these determinations was the question of what happened to the unused benzene. Some of it was evidently converted into nitrobenzene. In run 7, there was evidence of a considerable amount of unreacted benzene which separated as a layer on the acid solution of the product. No such layer formed in run 1. This may indicate that a greater amount of nitrobenzene was produced in reaction 1. When the acid solution was pipeted into water, some drops of oil formed with the solid product. Considering that this oil was nitrobenzene, there is the possibility that some m-dinitrobenzene was dissolved in it. This would have led to a low yield of the product, but this lowering would not be important in relation to the difference in percentage yields.

When a large excess of benzene was used in procedure D and E, the product was an oil, presumably nitrobenzene. Since the nitrating powers of the reagents in the different methods was based on the amounts of m-dinitrobenzene produced, these amounts of nitrobenzene were not recorded.

#### E. Comparisons of the nitrating power of $\text{ClNO}_2$ by different methods.

In attempting to enhance the yield of m-dinitrobenzene using  $\text{ClNO}_2$  as a nitrating agent, procedures D and E were attempted. Only oily products were obtained by procedure D. Procedure E gave good yields with certain proportions of  $\text{ClNO}_2$  and benzene



(see runs 5 and 6, Table IV). The best yield on the basis of the  $\text{ClNO}_2$  used was obtained in run 5. A comparison of run 3 with run 5, which used approximately the proportions of  $\text{ClNO}_2$  to benzene, shows that procedure E gave better yields than procedure C.

However, comparing run 5 with run 8, we see that  $\text{NaNO}_3$  was still a more effective nitrating agent in respect to the amount of nitrogen taken.

#### F. $\text{ClNO}_2$ in acetic acid solution.

A nitration of benzene was attempted using procedure E, with the proportions of  $\text{ClNO}_2$  to benzene the same as in run 5 and replacing the  $\text{H}_2\text{SO}_4$  with 10 ml. of acetic acid. No nitration occurred. The  $\text{ClNO}_2$  and/or its decomposition products were quite soluble in the solution of acetic acid and benzene as shown by visible discoloring of the solution and a considerable gain in weight.

✓+ This indicates that the  $\text{NO}_2^+$  ion was not formed in solutions of  $\text{ClNO}_2$  in acetic acid.

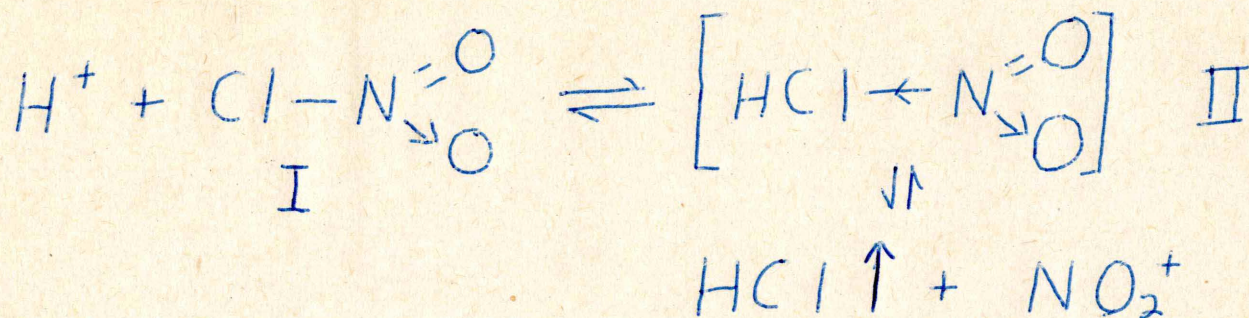
#### IV. Summary

The optimum yields of m-dinitrobenzene using  $\text{ClNO}_2$  as a nitrating agent were obtained by bubbling the vapours from 3 ml. of  $\text{ClNO}_2$  at  $-60$  to  $-70^\circ\text{C}$  through 10 ml. of concentrated  $\text{H}_2\text{SO}_4$  with a layer of 0.8 gms. of benzene on top. The reaction is run at room temperature. This method did not compare favorably with one using a solution of  $\text{NaNO}_3$  in concentrated  $\text{H}_2\text{SO}_4$  at room temperature.

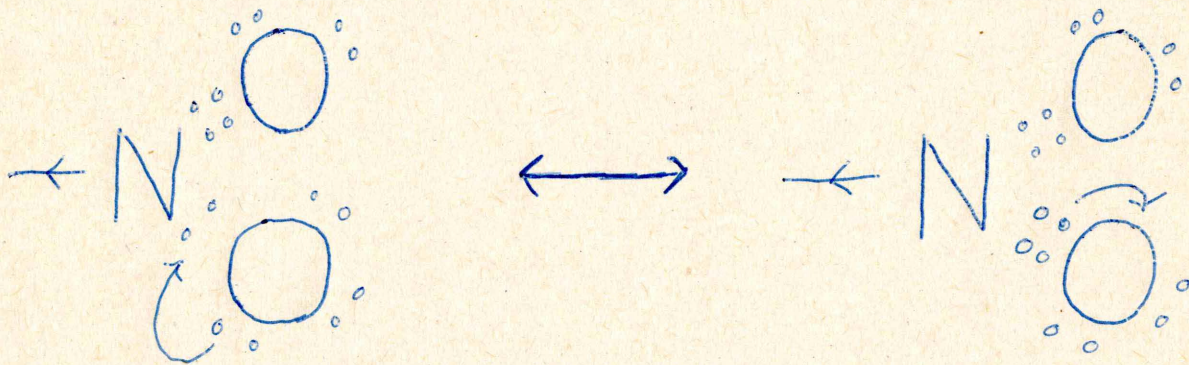
✓ When gaseous  $\text{ClNO}_2$  is bubbled through concentrated  $\text{H}_2\text{SO}_4$ , the molecule is effectively split into  $\text{Cl}^-$  and  $\text{NO}_2^+$  ions. A suggested



mechanism is by the attack of the acid on the chloride group:



This is, of course, based on the structure of  $\text{ClNO}_2$  as that shown in I. This structure has not been accepted, but we offer the possibility of the mechanism above as supporting evidence for such a structure. Considering the intermediate II, there should be a shift of electrons toward the chloride group. This shift can be compensated for by the electrons in the nitrogen to oxygen bonds:



Such a mechanism is similar to that given by Alexander<sup>(4)</sup> for the formation of the  $\text{NO}_2^+$  ion from nitric acid.



✓+ Little can be said of the fate of the  $\text{NO}_2^+$  ion coming from  $\text{ClNO}_2$ . It is definitely less effective than that coming from  $\text{NaNO}_3$ , and yet the solution contains no chlorine to tie it up.

✓+ Comparisons of solutions of  $\text{NO}_2^+$  from  $\text{ClNO}_2$  and mixed acid solutions should be made with respect to ultra violet and Raman spectra, vapor pressure, freezing points and electrolysis experiments (see references given by Alexander<sup>(4)</sup> on page 250). These should give further evidence of the presence of  $\text{NO}_2^+$  in the former. ✓+ They may also give some indication of the association of the ion with  $\text{H}_2\text{SO}_4$ .

✓+ The fact that nitration of benzene failed in acetic acid solutions indicates that a very strong acid is necessary in order to get effective production of  $\text{NO}_2^+$  ions. ✓+ In order to measure the concentration of the strong acid needed to yield  $\text{NO}_2^+$  ions, it is suggested that solutions of  $\text{H}_2\text{SO}_4$  and  $\text{ClNO}_2$  diluted with acetic acid be studied with respect to ability to nitrate benzene.

✓+ Work on  $\text{ClNO}_2$  in neutral and basic media is considered by Whitaker<sup>(3)</sup> Briefly, it is found that the  $\text{ClNO}_2$  seems to split into  $\text{Cl}^+$  and  $\text{NO}_2^-$  ions in basic media. In neutral media, it seems to have intermediate behavior.



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