

ADDITION OF NITROGEN TRIOXIDE

Thesis for the Degree of M. S. MICHIGAN STATE COLLEGE Earl James Robertson 1948 This is to certify that the

thesis entitled

ADDITION OF NITROGEN TRIOXIDE TO POLYBUTADIENE

presented by

Earl James Robertson

has been accepted towards fulfillment of the requirements for

M.S. degree in Chemistry

Palph I Kuile Major professor

December 10, 1948 Date

M-795

ADDITION OF NITROGEN TRIOXIDE TO POLYBUTADIENE

By

.

EARL JAMES ROBERTSON

A THESIS

Submitted to the School of Graduate Studies of Michigan State College of Agriculture and Applied Science in partial fulfillment of the requirements

for the degree of

MASTER OF SCIENCE

Department of Chemistry

1/20/49

.

.

.

ACKNOWLEDGMENT

The author wishes to express his deep appreciation for the help and encouragement of Dr. R. L. Guile during the course of this investigation.

CONTENTS

P	age
Introduction	1
Historical	2
Polybutadiene polymerization	2
Preparation of nitrogen trioxide	2
Preparation of nitrosites	2
Reduction of nitrosites	4
By catalysis	4
By tin and hydrochloric acid	4
Experimental	5
Addition of nitrogen trioxide to styrene	5
Preparation of 2-hexene	6
Addition of nitrogen trioxide to 2-hexene	6
Preparation of sodium sand catalyst	7
Preparation of polybutadiene	7
Addition of nitrogen trioxide to polybutadiene	7
Nitrogen determinations on nitrosites	8
Styrene nitrosite	8
2-hexene nitrosite	8
Polybutadiene nitrosite	8
Addition of nitrogen tetroxide to styrene and polybutadiene -	8
Reduction of nitrosites by titanium trichloride	9
Reduction of nitrosites by catalytic procedure	10
Nitrogen determinations on the reduced products	18
Titration with standard acid	18
Kjeldahl	18
Dumas	18

CONTENTS (Cont'd)

	Page
Reduction of nitrosite by tin and hydrochloric acid	19
Discussion	- 21
Summary	• 30
Bibliography	. 32

,

•

INTRODUCTION

This is the beginning work in this laboratory dealing with the addition of nitrogen oxides to unsaturated polymers. One other worker ⁽¹⁾ added nitrogen tetroxide to a maleic acid-ethylene glycol resin, but no extensive study was made of the reaction.

The present investigation deals with the addition of nitrogen trioxide to the unsaturation remaining in polybutadiene and the subsequent reduction of the compound formed by this addition. The polybutadiene was prepared by the solution polymerization of butadiene with sodium sand as a catalyst.

The addition of nitrogen trioxide to styrene and 2-hexene preceeded work on polybutadiene in order that the course of the reaction with simpler molecules might indicate the reaction to be expected with the polymer. After satisfactorily carrying out the reaction with these monomers, it was extended to the polymer.

HISTORICAL

Butadiene was first polymerized by the Russian chemist, Lebedev, in 1910. Following his lead, German workers successfully polymerized butadiene in solution using sodium sand as a catalyst and used it for making synthetic rubber. Butadiene, polymerized in this way, has just half of its unsaturation left. It is characterized by low molecular weight and a predominence of "dangling double bonds" produced by 1,2 addition ⁽²⁾.

To these double bonds halogens, halogen acids, sulphur and sulphur chloride have been added. However, very little work has been done on the addition of the oxides of nitrogen to polybutadiene or to unsaturated polymers in general with the possible exceptions of natural rubber and the terpenes.

Nitrogen trioxide has been prepared in a number of different ways. Any of the following reactions yield nitrogen trioxide in an almost pure form; the mixing of oxygen and nitric oxide in any proportions below $110^{\circ}C$. ⁽³⁾; the reduction of nitric acid by arsenious oxide ⁽⁴⁾; the action of mineral acids on sodium nitrite ⁽⁵⁾; the action of dilute nitric acid on copper ⁽⁶⁾; the action of water on nitrosyl sulphuric acid ⁽⁷⁾; and the decomposition of nitrogen tetroxide by a small quantity of water ⁽⁸⁾.

When nitrogen trioxide is added to an unsaturated linkage, a compound is formed which is known as a nitrosite. The preparation of nitrosites involves, not only on the method of making the nitrogen trioxide, but also on the method of its addition to the unsaturated compound. Nitrogen trioxide, as such, does not exist as a gas (9). Possibly because of this reason, most of the methods have been those in which the unsaturated compounds as well as the nitrogen trioxide formants are all mixed together in one reaction vessel, so that as soon as the nitrogen trioxide is formed it reacts with the double bond.

Baeyer ⁽¹⁰⁾ prepared a nitrosite in 1894 by mixing equal amounts of an olefin and sodium nitrite (dissolved in water to make a saturated solution) and adding a like amount of glacial acetic acid while cooling the reaction vessel in an ice bath.

Sidgwick ⁽¹¹⁾ prepared a nitrosite by dissolving an olefin in acetic acid and adding a saturated solution of sodium nitrite to the mixture. This reaction was also cooled by an ice bath.

Hickinbottom ⁽¹²⁾ gives a method for the preparation of the nitrosite of trimethylethylene by passing the gases from the reaction of 10 g. of arsenious acid with 80 g. of nitric acid through 20 g. of trimethylethene dissolved in 60 cc. of ether.

Bond ⁽¹³⁾ describes a method for the gravimetric determination of styrene by the formation of the nitrosite. He prepared the nitrosite by dissolving styrene in "skellysolve", adding this to a saturated solution of sodium nitrite and slowly adding dilute sulphuric acid. The reaction was carried out at reduced pressure to exclude as much air as possible.

These compounds, formed by adding nitrogen trioxide to the double bond, are now generally considered bis nitroso nitro compounds ⁽¹⁴⁾. The molecular weights are double those expected, in freshly prepared solutions, but after standing, the colorless solutions turn greenish yellow, characteristic of nitroso compounds, and the molecular weight is equal to that of the mono molecular nitroso nitro compound.

The molecules are joined together through the nitroso nitrogens. A number of structures have been shown to be possible (15), (16), but the most generally accepted formula is that of Hammick (17). He considered the structural formula to be a resonance hybrid of the

following: $\begin{array}{c} R & N \neq N \neq 0 \\ O \neq & R \\ R \\ R \\ equals \\ CH_3(CH_2)_x CH_2 NO_2 \end{array} \xrightarrow{R} N = N \neq 0 \\ O \neq & R \\ \end{array}$

In any case most of the nitrosites are not too stable. They decompose readily on heating to yield nitrogen, nitric oxide, and carbon dioxide. They also decompose slowly on standing with the evolution of nitric oxide (18), (19).

The nitrosites in general are soluble in polar compounds such as nitrobenzene, in compounds containing saturated rings of carbon and oxygen such as dioxan, tetrahydrofuran and tetrahydropyran, and also, to a certain extent, in esters (20).

Both nitro and nitroso groups can be easily reduced to primary amines. According to Adkins ⁽²¹⁾ these groups may be reduced to amines almost quantitatively by using high pressure hydrogenation and Raney nickel catalyst. Other workers have also successfully used Raney nickel for 'this reduction ⁽²²⁾, (23), (24).

Nitrosites have also been reduced by tin and hydrochloric acid (25).

EXPERIMENTAL

ADDITION OF NITROGEN TRIOXIDE TO STYRENE

The styrene used was first freed of inhibitor by washing with 5% sodium hydroxide solution and then distilled ($48^{\circ}-49^{\circ}C$. 20 mm, N^{2O} 1.5469).

The nitrogen trioxide was made, except where otherwise noted, by adding dilute sulphuric acid to sodium nitrite.

The method of Bond (13) was used first with slight modifications. One-half mole (52.07 g.) of styrene was dissolved in 50 cc. of "skellysolve" and placed in a 500 cc. three necked flask with fifty ccs. of a saturated solution of sodium nitrite. A dropping funnel was inserted in the center hole and a thermometer in one of the others. The third hole was fitted with a rubber stopper, with a glass tube which was connected to a saran tube leading to a safety bottle. The safety bottle in turn had three openings, one to a manometer, one to a water aspirator, and the third to the atmosphere through a needle valve. The reaction was carried out at a pressure of 100 millimeters (water aspirator) by slowly adding six normal sulphuric acid through the dropping funnel while maintaining the temperature of the reaction below 15°C. by means of an ice water bath. The flask was intermittently shaken to speed the reaction which was considered complete when brown fumes appeared above the mixture. A white precipitate settled out which was filtered by suction through a Buchner funnel and washed three times with small portions of petroleum ether $(3C-70^{\circ}C)$, once with distilled water and once with 95%ethyl alcohol. It was dried in a vacuum dessicator over concentrated sulphuric acid. The melting point after drying was 94°C., (yield 61%).

The reaction was also carried out without an ice bath at room temperature, all other conditions being as previously described. The

yield (61%) and product (m.p. 94°C.) were identical.

The procedure was next varied in that the nitrogen trioxide was generated in a separate flask and then passed into one-half mole of styrene. Forty-two grams (46.6%) of a white solid were obtained (m.p. $93^{\circ}-95^{\circ}C.$) along with a small amount of a green oil.

A still different modification was the use of acetic acid instead of dilute sulphuric. One-half mole of styrene yielded 47 g. (52%) of the nitrosite melting at $93^{\circ}-94^{\circ}$ C.

The next variation consisted of dissolving the styrene in glacial acetic acid in the same apparatus and then adding a saturated solution of sodium nitrite. From 54 g. of styrene, 40 g. of a red solid were obtained which had no definite melting point. Portions of the solid melted between 120°C. and 150°C., but a residue was left that did not melt even at 250°C. PREPARATION OF 2-HEXENE

The preparation of 2-hexene was accomplished by the dehydration of normal hexanol by a method described in "Organic Synthesis" ⁽²⁶⁾ for the preparation of 2-pentene. One hundred ccs. of normal hexanol were mixed with 100 ccs. of concentrated sulphuric acid and 100 ccs. of water, and the resulting solution was distilled into a receiver cooled with an ice bath. The crude product was then redistilled and the fraction boiling between 66° and 69° C. was collected as 2-hexene.

PREPARATION OF 2-HEXENE NITROSITE

The first of the previously described methods used on styrene was used to make the nitrosite of 2-hexene. The pressure was maintained just high enough to keep the 2-hexene from boiling at 15° C. From one-half mole of 2-hexene, 35 g. of a white solid were obtained which was 47% of the theoretical yield. There were also 21 grams of a green oil which was about 25% of the theoretical. The melting point of the 2-hexene nitrosite was $85^{\circ}-88^{\circ}C$. The compounds were soluble in 10% sodium hydroxide but insoluble in 10% hydrochloric acid.

PREPARATION OF SODIUM CATALYST

The sodium sand catalyst used to polymerize the butadiene was prepared in the following manner. Two grams of sodium were placed in a 500 cc. magnesium citrate bottle containing 50 ccs. of dry xylene. The bottle and contents were heated in an oil bath to 135°C.; the bottle was then capped and vigorously shaken until the melted sodium was divided into very small particles.

POLYMERIZATION OF POLYBUTADIENE

To the mixture of finely divided sodium as prepared above were added 150 ccs. of dry toluene. This mixture was then cooled in an ice bath, and 75 ccs. of liquid butadiene were added. The bottle was securely capped, and the butadiene polymerized in a water bath with constant shaking at 55° C. ($\stackrel{4}{-}$ 2°C.) for three days. The sodium catalyst was removed from the polymer solution by use of a centrifuge.

The polybutadiene was then titrated with standard bromine solution. It was assumed that each unit contained one double bond and that the bromine added completely with no substitution. It was found that the solution contained .3030 grams of polymer per 10 ccs. of solution. Evaporation of the solvent gave .3120 grams of polymer per 10 ccs. of solution. ADDITION OF NITROGEN TRIOXIDE TO POLYBUTADIENE

The polybutadiene nitrosite was made by reacting 20 ccs. of the polymer solution, as prepared above, with nitrogen trioxide according to the method of Bond as used on the styrene. One and thirty-one hundredths of a gram of a greenish white solid were obtained which was 91% of the theoretical.

The solubilities of the polybutadiene nitrosite were comparable with

those of styrene and 2-hexene but it went into solution with much greater difficulty. The best solvent from all visual observations was 1,4 dioxan. Pyridine and quinoline took only a little longer to give complete solution.

A five-tenths gram sample of the polybutadiene nitrosite was dissolved in 1,4 dioxan and the resulting solution titrated with the same standard bromine solution that was used on the polybutadiene. It was found that some unsaturation remained. Assuming no substitution, the weight of bromine that added indicated that the nitrogen trioxide added to 88.9% of the double bonds present.

NITROGEN DETERMINATION OF THE NITROSITES

On each of the three nitrosites a nitrogen determination was made by the method of Kjeldahl (27). The nitrosite of styrene gave 8.1% nitrogen, that of 2-hexene 11.20% and that of polybutadiene 7.45%. The theoretical percentages are 15.47%, 13.18% and 20.40% respectively.

Because of these low values, the Kjeldahl procedure was modified. The nitrosites were allowed to stand with the salicylic and sulphuric acids for three hours instead of one-half hour. The acids were also cooled before adding so as to prevent excessive heating. The sodium thiosulphate was added and allowed to stand over night. The solution was then heated for about fifteen minutes, and the remainder of the determination was carried out according to the regular procedure. Using this method, results of 14.69%, 17.90% and 19.56% were obtained. ADDITION OF NITROGEN TETROXIDE TO STYRENE AND POLYBUTADIENE

Nitrogen tetroxide was prepared according to the following method. Anhydrous nitric acid ⁽²⁸⁾ was mixed with glacial acetic acid and cooled in an ice bath. Sulphur dioxide was passed through the cold solution to form nitrosyl sulphuric acid ⁽²⁹⁾ which was mixed with dry potassium nitrate. Upon heating this mixture, pure nitrogen tetroxide was formed.

The nitrogen tetroxide was added to one-fourth mole (26 g.) of styrene dissolved in "skellysolve" in a three necked 500 cc. flask under an atmosphere of carbon dioxide while being cooled in an ice bath. Twentyfour grams (46.15%) of a green oil were obtained which was soluble in 10% sodium hydroxide but insoluble in 10% hydrochloric acid.

Nitrogen tetroxide was also added to polybutadiene and a yellow solid was obtained. Four hundred and seventy-two thousandths of a gram yielded 1.21 g. of nitrosate which was difficultly soluble in sodium hydroxide, pyridine, nitrobenzene and 1,4 dioxan; that is, much less soluble than the nitrosite. The polymer nitrosate was completely insoluble in 10% hydrochloric acid.

REDUCTION OF NITROSITES WITH TITANIUM TRICHLORIDE

The titanium trichloride was prepared by adding in small portions, 40 g. of titanous hydride to 400 ml. of 6N. hydrochloric acid in a one liter Erlenmeyer flask. After the addition was completed, the solution was boiled on a hot plate for five minutes and then filtered into 100 ml. of 6N. hydrochloric acid in a 500 cc. glass stoppered bottle.

The reductions were carried out in a 125 ml. Erlenmeyer flask equipped with a reflux condenser and a tube for the passage of carbon dioxide. Two-tenths of a gram dissolved in 1,4 dioxan, were used. Twenty-five ccs. of titanium trichloride were added and the mixture refluxed for 3 hours, with continuous passage of carbon dioxide through the reactants. The titanium trichloride solution was titrated before and after reduction with standard ferric solution using potassium thiocyanate as an indicator.

The styrene nitrosite used 6.05 equivalents of titanium trichloride while the 2-hexene and the polybutadiene nitrosites used 6.95 and 8.42 respectively. Six equivalents would be equal to the reduction of one nitro group, while ten would be equivalent to one nitro and one nitroso group as contained in the nitrosites.

REDUCTION OF NITROSITES BY CATALYSIS

The reductions with hydrogen and Raney nickel were carried out at pressures ranging from 1200 to 2000 pounds per square inch and at temperatures ranging from 25° to 220°C. The time for the reductions was anywhere from one to six hours. The solvent used almost exclusively was 1,4 dioxan.

The Raney nickel was prepared according to a method of Adkins and (31) Pavelac

The reductions were carried out in a Parr hydrogenation apparatus #40Cl model HC-11, high pressure type. The apparatus consisted of a reaction bomb, a bomb heater, an oscillating mechanism for rocking the bomb, and suitable gas connections, pressure gage and valves for the controlled release or introduction of gas while the bomb was in motion. The material was placed in a glass liner which was fitted with a clip to allow easy insertion and removal from the bomb. The capacity was 150 ml. with the glass liner, 250 ml. without.

Reductions of the styrene nitrosite were carried out at temperatures ranging from 25° to 170°C. Two gram samples were used with one-half gram of Raney nickel as catalyst. After reduction, the contents of the glass liner was titrated with standard acid to a methyl orange end point. Table I includes a summary of the results of these reductions.

The weight of actual amine present was calculated from the following formula.

wt. of amine present = ccs. of acid used x normality x M.E. wt. of amine This weight divided by the weight of theoretical amine that would be produced if all the nitro and nitroso groups present were reduced to primary amines would give the percent reduction. It was taken into account that the polymer was only 89.8% saturated with nitrogen trioxide in the calculations by multiplying the atomic weight of nitrogen by .898 to find the molecular weight of the amine.

TABLE ||

REDUCTIONS OF STYRENE NITROSITE AT VARIOUS TIMES & TEMPERATURES

Temp.	Pressure	Wt. Sample	Cat. Wt.	Time	% Red.
24°C.	1500 <i>4</i>	2.0120	ž 5.	3 hrs.	C%
110	1600	2.1400	28.	6	28.0
130	1600	2.0005	2 8.	3 4	22.2
170	1400	4.4400	1 3.	4 z	33.6

The product of the reduction was a dark red oil in each case. An attempt was made to isolate some of the diamine by distillation at lmm. pressure but no product distilled over at the boiling point of phenylethylene diamine, (104°C. at lmm.). However, the compound decomposed into a dense white gas at 200°C. This oil was insoluble in 10% sodium hydroxide and difficultly soluble in 10% hydrochloric acid.

The 2-hexene nitrosite (solid material) was reduced at 130° C. and 1500 pounds pressure for six hours. The percent reduction was calculated to be 69.3. The product was similar in appearance and in solubility to that of the styrene nitrosite. It was also insoluble in 10%sodium hydroxide and only slightly soluble in 10% hydrochloric acid. The polybutadiene nitrosite was reduced in the same manner. The results are tabulated in table II. Immediately following the removal of the hydrogen from the bomb the contents were placed in a beaker and titrated with standard acid using a Cenco Titration-Ph meter. Complete titration curves were run on three samples but since the pH at the middle of the curve was the same in each case the rest of the titrations were carried only up to the end point of 4.9.

Table II contains the results as calculated from the standard acid titrations, 100% reduced being considered as the point at which every nitro and nitroso group was reduced to the primary amine.

TABLE III

REDUCTIONS OF POLYBUTADIENE NITROSITE USING HYDROGEN AND RANEY NICKEL AT VARIOUS TEMPERATURES AND TIMES

1	emp.	Time	Sample	Wt.	Catalyst	Wt. %Re	duction
1.	108°C.	2 hrs.	.475	g.	1 4 6.		0%
2.	145	'2	.475		1 4		2.22
3.	160	2	.475		$\frac{1}{4}$		6.72
4.	175	2	.475		<u>1</u> 4	4	.8.50
5.	220	2	.475		- 4	·2	20.00
6.	175	l	.475		<u>1</u> 4	·2	8.80
7.	175	,2	.475		<u>1</u> 4	4	5.05
8.	175	3	.475		<u>1</u> 4	e	32.25
9.	175	6	• • 475		4	7	2.00
10.	160	5	2.001		1.2	4	8.40
11.	178	6	1.827		12	e	5.62

Table III, IV, V show the results of the titrations of the reduction products with standard acid. The results of these titrations are also

TABLE ||||

TITRATION VALUES OF THE REDUCTION PRODUCTS OF POLYBUTADIENE NITROSITE WITH HYDROGEN USING RANEY NICKEL CATALYST FOR 2 HOURS AT 145°C.

CCS.	рH	CCS.	pH
.5	8.2	·3. 0	5.6
.7	8.2	3.2	5.3
1.0	8.0	3.5	4.8
1.2	7.7	3.7	4.5
1.5	7.4	4.0	4.1
1.7	7.2	4.2	3.7
2.0	7.0	4.5	3.4
2.2	6.65	4.7	3.3
2.5	6.'20	5.0	3.1
2.7	6.0	7.0	2.3

TABLE IV

TITRATION VALUES OF THE REDUCTION PRODUCTS OF POLYBUTADIENE NITROSITE WITH HYDROGEN USING RANEY NICKEL CATALYST FOR TWO HOURS AT 168C.

pH	CCS.	pH	CCS.
6.1	3.4	8.2	.2
5.6	4.0	8.0	•5
5.5	4.2	7.8	•7
5.0	5.0	7.4	1.0
4.3	5.5	7.2	1.5
3.4	6.0	6.9	2.0
2.4	7.0	6.5	2.5
2.0	9.0	6.0	-3.0
		6.1	3.2

TITRATION VALUES OF THE REDUCTION PRODUCTS OF POLYBUTADIENE NITROSITE WITH HYDROGEN USING RANEY NICKEL CATALYST FOR TWO HOURS AT 220°C.

.

CCS.	рH	CCS.	рH
.1	8.6	8.0	7.5
.5	8.4	10.0	7.1
1.0	8.25	10.5	6.9
1.3	8.20	11.0	6.7
1.6	8.05	12.0	6.5
2.0	8.00	13.0	6.2
2.5	8.00	14.0	5.6
3.0	7.90	14.5	4.9
3.5	7.90	15.0	4.35
4.5	7.90	16.0	3.6
6.0	7.75	20.0	2.3
7.0	7.60		

.

TITRATION OF THE REDUCTION PRODUCTS OF POLYBUTADIENE NITROSITE USING HYDROGEN AND RANEY NICKEL FOR TWO HOURS AT 145°C.



GRAPH IIII



CCS. OF HCL



CCS. OF HCL

DETERMINATIONS OF NITROGEN CONTENT ON REDUCED PRODUCT

The product of the reductions were large brown particles insoluble in the reducing media. The Raney nickel was washed free from the solid by placing the substances on a fine screen and washing freely with water. The fine nickel particles were readily washed through the screen while the large polymer particles remained behind.

The longer the reaction and the higher the temperature, the darker the color of the product and the greater its insolubility in 10% hydrochloric acid. In no case was any solubility in sodium hudroxide observed except in sample numbers 1 and 2 in Table II. Sample number three gave a small amount of swelling but no definite solubility.

TITRATION OF REDUCED NITROSITE

The products of the reductions of runs number 6,7,8 and 9 (Table II) were ground in a mortar and dried in a vacuum dessicator over concentrated sulphuric acid. Two-tenths of a gram samples were placed in 20 ccs. of one-tenth normal hydrochloric acid and left to stand with intermittent stirring for one hour. The hydrochloric acid was then titrated with standard base to a brom-thymol blue end point and the percent of theoretical amine present on the polymer itself was calculated. The results are tabulated in Table VI.

KJELDAHLS ON REDUCED NITROSITES

Also on runs number 6,7,8 and 9 Kjeldahl determinations for nitrogen were carried out in the same modified manner as with the nitrosites. Five-tenth gram samples were used in the determinations, the results of which also are tabulated in Table VI.

DUMAS ON REDUCED NITROSITES

A micro Dumas ⁽³²⁾, ⁽³³⁾ nitrogen determination was next run on each of the same products. Five milligram samples were used and the results

likewise tabulated in Table VI.

TABLE VI

PERCENT OF INITIAL NITROSITE NITROGEN FOUND IN THE PRODUCTS OF REDUCTION of Polybutadiene nitrosite at 175°C. With Hydrogen and Raney Nickel

Time	Basic Nitrogen by Titration of Reaction Mixture	Basic Nitrogen Titration of Polymer	Nitrogen by Kjeldahl	Nitrogen by Dumas	Unaccounted for Nitrogen
l hr.	28.80%	25.01%	81.00%	81.35%	14.68%
2	45.05	30.10	60.11	68.10	16.95
3	62.25	36.47	48.91	60.37	13.85
6	72.00	2.10	2.56	18.13	11.97

REDUCTION USING TIN AND HYDROCHLORIC ACID

A third type of reduction was tried using tin and hydrochloric acid. One gram of polybutadiene nitrosite and 10 g. of mossy tin were placed in a 200 cc. round bottom flask fitted with a reflux condenser. Fourteen ccs. of concentrated hydrochloric acid were slowly added through the reflux condenser. After the reaction subsided it was heated at a slow reflux temperature for one-half hour. The product, a light brown solid, was separated physically from the tin mass. It was irsoluble in 10% sodium hydroxide as well as 10% hydrochloric acid.

A similar reaction was carried out with the same amount of materials, but the reaction was not heated, but allowed to stand for three days instead. The appearance of the product was the same and although it was insoluble in 10% hydrochloric acid it exhibited pronounced swelling on standing in sodium hydroxide solution.

On each of the products of these two reductions, titrations, Kjeldahls and micro Dumas were run, the results of which are tabulated in Table VII.

TABLE VII

PERCENT OF INITIAL NITROSITE NITROGEN FOUND IN THE PRODUCTS OF REDUCTION OF POLYBUTADIENE NITROSITE BY TIN AND HYDROCHLORIC ACID

		Basic Nitrogen Titration of Polymer	Nitrogen by Kjeldahl	Nitrogen by Dumas
Heated	-	9.36%	16.73%	26.21%
Room Temp.	-	0.10%	61.05%	61.64%

-

DISCUSSION

Of the methods tried for making nitrosites that of Bond appeared to be the best since, using styrene as a control, better yields and purer products, as evidenced by melting point and color, were obtained by this method. Bond obtained quantitative yields in his work, but he was dealing with 10% samples whereas in this investigation 50% samples were used and yields of only 61% were obtained. The precipitate was very fine and large amounts ran through the filter paper. For this reason, a sintered glass funnel should be used to minimize loss of material.

This method gave almost a pure white solid with a definite melting point of 94°C. The other methods gave either slightly red, yellow, or greenish colored compounds. There are a number of possible explanations. (a) The nitrogen trioxide is not the only gas formed; (b) once formed, some of the nitrogen trioxide is oxidized to nitrogen tetroxide or nitrogen pentoxide; (c) the nitrosite after forming oxidized to the nitrosate; (d) the styrene polymerized to dimers or trimers before the addition takes place.

In the reaction carried out by generating the nitrogen trioxide in a separate flask some formation of a green oil was noted along with the white precipitate of styrene nitrosite. Since the passing of nitrogen tetroxide through styrene gives only the green oil it is possible that the product formed was the nitrosate. However, the mono molecular nitrosite would also be a green oil, but since none was formed in the first method it is more than probable that this was not the case. Also, there is a greater possibility of oxidation of the nitrogen trioxide using this method since the gas has a longer distance to traverse before it comes in contact with the unsaturated compound. In the method in which the styrene was dissolved in glacial acetic acid and sodium nitrite was added, it is possible that the styrene was partially polymerized to dimers or trimers before the addition of the gas was complete. The high and indefinite melting point of the product is an indication of this.

The 2-hexene nitrosite was made because it was thought that it might be more similar to polybutadiene nitrosite in its reactions than styrene nitrosite. The main drawback in using it was the fact that there is very little in the literature on the nitrosites of hexene or its 1,2 diamines. However, the results as obtained agree with the little data that is in the literature. The green oil obtained in this reaction is probably the mono molecular form of the nitrosite and the white solid is the dimolecular form, since Ivanoff ⁽²⁵⁾ studied a similar reaction with dimethylbutadiene and obtained similar products.

The Kjeldahls that were run on the nitrosites were particularly interesting. The first results were consistently low; i.e. the styrene nitrosite contained just about half the theoretical nitrogen, the 2hexene just a little above half and the polybutadiene about one third. This seemed to indicate that at least one of the nitrogen groups was not being reduced. The theory behind this type of Kjeldahl determination is that the nitrogen groups are first transferred to the salicylic acid and then reduced by the sodium thiosulphate. Since the nitrosites decompose on heating it is probable that some of the nitrogen was lost in this way, because of the high heat of reaction upon the addition of the sulphuric and salicylic acids. For this reason the acids were cooled before adding to the nitrosites. This slowed down the reaction considerably and no noticeable amounts of heat were formed. Furthermore, since the styrene and 2-hexene nitrosites are bimolecular addition

complexes and polybutadiene nitrosite is a complex polymer the reaction should be considerably slower than for ordinary nitro compounds. For this reason the nitrosites were allowed to remain in contact with the salicylic acid for three hours instead of the customary one-half hour. They were also left in contact with the sodium thiosulphate for a longer time before heating. These modifications gave results very close to the theoretical nitrogen percentages; 14.69% as compared to 15.47% for the styrene nitrosite, 17.90% as compared to 18.18% for the 2-hexene nitrosite and 19.56% as compared 20.40% for the polybutadiene nitrosite.

From the titrations with bromine, from the Kjeldahls and from the fact that the nitrosite of polybutadiene is a greenish color instead of the white as are the styrene and 2-hexene nitrosites, it is probable that the polybutadiene has a structure somewhat similar to the following, rather than having a bimolecular structure due to association between nitroso groups.

Η н н Н Η Η ΗН Η НН НН Η Η H H NO NO2^H H H HC NO H H NO NO₂ H H **‡** Η H $^{N}Q_{\mathcal{S}}$ NO HC-NO HC NQ. L HC-NO2 Η

TITANIUM TRICHLORIDE REDUCTION OF THE NITROSITES

To reduce completely one nitrosite grouping it would take ten equivalents of titanium trichloride, six for the nitro group and four for the nitroso group. However, the nitrosite of styrene used only six, that of 2-hexene seven and that of polybutadiene eight and one-half equivalents. This further substantiates the idea previously expressed that one of the nitrogen groups is not too stable. One explanation is that the compounds decomposed liberating nitrogen which would not be reduced by the titanium trichloride. This seems to indicate that the

2-hexene nitrosite is more stable than styrene nitrosite and that the polybutadiene nitrosite is more stable than either. REDUCTION OF THE INITROSITES WITH RANEY NICKEL

The reductions of the styrene nitroaite with Raney nickel and high pressure hydrogen were very inconclusive. The temperature for reduction was much higher and the time much longer than expected from reduction of other nitro compounds. The catalyst used was supposed to be very active for hydrogenations under 100° C. It reduced styrene to ethyl benzene quantitatively at room temperature in fifteen minutes and mesitylene to trimethyl cyclohexane at 250° in six hours. No tests were made on its activity other than to let it dry out on a filter paper. A considerable number of sparks were discharged and the paper ignited. However, it is possible that the Raney nickel was not as active as it should have been. Further research might be directed toward the use of more recent Raney nickel catalysts or entirely different catalysts.

In any case, no phenylethylene diamine could be isolated. A dark red oil was the product of the reduction and it did not boil at the temperature of the diamine (104°C. 1 mm.) but decomposed at 200°C. (1 mm.). Furthermore, neither acetyl picrate or benzil derivatives could be isolated. Also 33% was the maximum amount of nitrogen reduced. It is possible that as soon as any groups were reduced they reacted with other groups with the liberation of ammonia forming a polymer or a heterocyclic ring compound. Both types of reactions are common to amine groups especially at these temperatures. The high boiling oil would be an indication of some type of polymerization. As in the titanium trichloride reductions, it is possible that the nitrosite decomposed to some extent liberating nitrogen which could not be reduced.

It was thought that the nitrosite of 2-hexene might be more stable

to heat and could be reduced more easily with this method. However, as in the case of styrene no diamines could be isolated. Likewise no derivatives could be made. An oil similar to that formed from the styrene nitrosite reduction was the product, which decomposed at 230°C. (1 mm.). The same conclusions about polymerization are probably true for this compound as was for the styrene nitrosite.

Even though no amines were isolated reduction to some extent did take place so the method was tried with the polybutadiene nitrosite. Since polymer reactions are slower, it was thought that the reaction might be easier to stop before the amines reacted with each other if this were the case.

Reductions of polybutadiene nitrosite were carried out for two hours at various temperatures to determine the optimum temperature for reduction. From the titrations immediately following the reductions the best temperature seemed to be 175°C. For this reason samples were reduced at this temperature for various lengths of time and a number of determinations run on the products.

The graphs of the titrations of the reduction products immediately following the reductions with Raney nickel, if the nitrosites were completely reduced to primary amines, would be curves with two definite equivalence points at two different pHs. However, since the reduction products are a complex mixture of at least two different and possibly more basic substances the curve turns out as one would expect with no clear definite end point. With careful scrutiny it is possible to detect a slight break in the curve at a pH of 7, with a definite though gradual break between the pHs of 6 and 3. This latter break is probably enhanced by any ammonia present in the solution, since its equivalence point is just about 5. The main **va**lue of these titrations and graphs was for the approximate determination of the end point which was very close to the same pH in each of the three graphs.

More extensive studies were made on the reduction products of the polybutadiene nitrosites. Titrations were run on each of the samples immediately after reduction to indicate the total amount of base present including any ammonia, formed by decomposition or cross linking, any amines of low molecular weight hydrocarbons that might have split off from the polymer under the influence of heat, as well as any polymer amines that might be present. The reduction Kjeldahls were run to indicate any amine groups on the polymer as well as any unreduced nitro or nitroso groups left. The titration of the powdered polymer with standard acid was used to indicate the amine groups present on the polymer. The Dumas was used to indicate any nitrogen present in the polymer in any form including any that might have formed cross linkages between polymer chains.

It was assumed from the bromine titrations that the nitrogen trioxide added to 88.9% of the double bonds. If $- \begin{array}{c} H \\ C \\ H \end{array}$, $- \begin{array}{c} H \\ C \\ C \\ M \end{array}$, $\begin{array}{c} H \\ C \\ M \end{array}$, were taken as the basic unit the compound would be 21.5% nitrogen. This would have a molecular weight in round numbers of 130. Instead of taking atomic weights of nitrogen and oxygen, as 14 and 16 respectively, the values were multiplied by .889 and the molecular weight of 121.5 used instead of 130.

This would give .204 grams of nitrogen in each gram of sample. If this nitrogen was completely changed to amine groups or ammonia, it would be 100% reduced. The percent nitrogens as determined by titrations, Kjeldahl determinations and Dumas determinations were divided by this number to give the % reduction.

The sample that was reduced for one hour at 175°C, gave a total titration of 28.8% of the nitrogen present in either amine form or as ammonia and a polymer titration of 25.0% of the theoretical amine groups present on the polymer. Therefore, 3.8% must be in the form of free ammonia or low molecular weight amines. The second sample that ran for two hours had a difference of 15.00%, after three hours 36.5% and after four hours 69.9%. The possible explanations are that nitro or nitroso groups are split off and reduced to ammonia, that some type of cross linking takes place with the liberation of amonia, that amine groups. once formed, split off from the polymer and form ammonia or that the long chain polymer splits certain linkages to form a few low molecular weight amines. It is possible that all these reactions take place to some extent. The fact that the six hour sample contained very few amine groups is an indication of any of the last three possibilities. It is also known that nitrosites liberate nitric oxide on heating which could also easily be reduced to ammonia.

The Kjeldahls indicate that 56.0% of the nitrogen still remained unreduced after one hour, 30.0% after two hours, 12.4% after three hours and .5% after six hours. Seventy percent of the reduction, therefore, takes place during the first two hours. This seems like a long time under the conditions of the reaction, but the fact that we are dealing with large molecules which are hard to reach even in solution might account for the unusual length of time.

The difference between the Kjeldahl determinations and the Dumas determinations should indicate the amount of cross linkage present. Because Dumas determinations are usually a little high, it is probable that during the first hour of the reductions run at 175°C. no cross linking takes place; after the second hour about 10.0% of the nitrogen

was in the form of cross linkages; after 3 hours 11.5%; and after six hours 15.7%.

From all indications the polymer loses nitrogen by decomposition in the form of amine groups which form ammonia. The basis for this statement is the fact that whereas the three hour sample contained 60% of the nitrogen, 11.46% as cross linkages the six hour sample contained only 18.1% nitrogen, 15.7% being cross linked. The decrease in nitrogen in amine groups over the same period was from 36.47% down to 2.1%, a loss of 34.4%.

The cross linking would account for a loss of 4.23%. Therefore, 34.14% of nitrogen was lost through removal of amine groups. Since the total nitrogen difference between the two samples was 52.2%, the rest of the nitrogen must have been lost by the splitting off of nitro or nitroso groups either before or after reduction.

The Dumas determination accounts for all the nitrogen in the polymer, and the difference between the titration of the solution and of the polymer material would be the amount of ammonia or soluble amines present. The sum of the Dumas determination and this difference subtracted from one hundred would be what might be termed the unaccounted for nitrogen. This is a fairly constant number of about 15%. The probable reason is that about 15% of the nitrogen is liberated from the nitrosite as nitrogen gas and could not be reduced. Other workers have reported nitrogen gas as one of the decomposition products but no one has given any specific values.

The reductions with tin and hydrochloric acid were carried out more or less as a curiosity. No systematic study was made of the reaction. The principle disadvantage in using tin and hydrochloric acid lies in the fact that whereas ordinary amines can be separated from the tin mass

after reduction by steam distillation polymer amines cannot. This is the principle reason why catalytic methods were used.

In this reduction the polymer was not dissolved in solvent, but was mixed with the tin and then the acid. The solid material was then hand picked from the tin mass after reduction. This would not be conducive to the greatest amount of reduction since the nitro and nitroso groups would be difficult to reach. It was felt, however, that if the nitrosite were first dissolved and then reduced it would come out of solution as an inseparable mass with the tin.

In the sample carried out with no heating, there was very little, if any, reduction. With heating there was reduction as well as a small amount of cross linking. With various conditions, it might be possible to reduce the entire nitrosite to a primary diamine. However, as was said before, there is much more research left on this phase of the problem.

'SUMMARY

1. Various methods for making nitrosites were tried but the method of Bond was found to be the most satisfactory. This consisted of making nitrogen trioxide by the action of dilute sulphuric acid on sodium nitrite and adding it to the unsaturated compound.

2. Styrene and 2-hexene nitrosites were made and conformed to the compounds as reported in the literature.

3. Styrene and 2-hexene nitrosites were reduced by Raney nickel and high pressure hydrogen but at the high temperatures needed decomposition and some type of polymerization readily took place.

4. Butadiene was successfully polymerized by sodium sand catalyst.
5. Nitrogen trioxide added to 88.9% of the double bonds of the polybutadiene to give a greenish-white, rubbery solid which was soluble in 10% sodium hydroxide and in certain organic solvents particularly 1,4 dioxan.

6. Nitrogen determinations indicate the addition product to be a nitrosite.

7. Reductions with titanium trichloride indicate that polybutadiene nitrosite is more stable than 2-hexene nitrosite which in turn is more stable than styrene nitrosite.

8. Reductions of the polybutadiene nitrosite were also carried out with Raney nickel and high pressure hydrogen. The temperature and lengths of time as with the styrene and 2-hexene nitrosites were much higher than expected. Three hours at 175°C. gave the best product with 36% of the possible amines present. Indications were that a large amount of decomposition to ammonia and low molecular weight amines as well as cross linking took place.

9. Reductions of the polybutadiene nitrosite were also carried out

with tin and hydrochloric acid, but only 9.36% of the possible amine groups were obtained.

.

.

BIBUIOGRAPHY

- Burton, C.D., "Derivatives of an Unsaturated Polyester", Thesis for Master's Degree Michigan State College, 1948, p. 16.
- 2. D'Janni, J.D., Ind. Eng. Chem., 402, 253 (1948).
- 3. Francesconi and Sciacca, Gazetta, 34, 447 (1904).
- 4. Lunge, Ber., <u>11</u>, 1229 (1878).
- 5. Friend, "A Textbook of Inorganic Chemistry", Charles Griffin and Co., London, 1928, vol. VI, p. 164.
- 6. Bagster, Trans. Chem. Soc., <u>82</u>, 119 (1921).
- 7. Rammelsberg, Ber., <u>5</u>, 310 (1872).
- Friend, "A Textbook of Inorganic Chemistry", Charles Griffin and Co., London, 1928, vol. VI, p. 164.
- 9. Mellor, J.W., "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", Longmans Green and Co., New York, 1928, vol. VIII, p. 449.
- 10. Baeyer, "Annalen", 278, 108 (1894).
- 11. Taylor and Baker, "Sidgwick's Organic Chemistry of Nitrogen", Oxford Press, London, 1945, p. 225.
- 12. Hickinbottom, W.J., "Reactions of Organic Compounds", Longmans, Green and Co., London, 1938, p. 22.
- 13. Bond, G.R., "Anal. Chem.", 19, 390-392 (1947).
- 14. Levy, N. Scaife, C.W., J. Chem. Soc., 1093-1104 (1946).
- 15. Ingold and Piggott, J. Chem. Soc., <u>125</u>, 168 (1924).
- 16. Proc. Roy. Soc., <u>133</u>, 668 (1931).
- 17. Hammick, J. Chem. Soc., <u>131</u>, 3105 (1931).
- 18. Monti, L., Gazz. Chim. Ital., <u>60</u>, 787-97 (1930).
- 19. Monti, L. and Bucci, F., Gazz. Chim. Ital., <u>63</u>, 708-12 (1933).
- 20. Chem. Abstracts, <u>41</u>, 2068 (1947).

- 21. Adkins, H. and Winans, J. Am. Chem. Soc., <u>55</u>, 2051 (1933).
- 22. Stevinson and Hamilton, J. Am. Chem. Soc., <u>57</u>, 1298 (1935).
- 23. Covert, Connor and Adkins, J. Am. Chem. Soc., <u>54</u>, 1651 (1932).
- 24. Covert and Adkins, J. Am. Chem. Soc., <u>54</u>, 4116 (1932).
- 25. Ivanov, A.A., J. Gen. Chem. (U.S.S.R.) <u>16</u>, 647-56 (1946).
- 26. Gilman and Blatt, "Organic Syntheses", John Wiley and Son, New York, 1941, coll. vol. I, p. 430.
- 27. Treadwell and Hall, "Analytical Chemistry", John Wiley and Sons, New York, 1942, vol. II, p. 493.
- 28. Biltz, H. and Biltz, W., "Lab Methods of Inorganic Chemistry", John Wiley and Sons, New York, 1928, p. 69.
- 29. Ibid, p. 206-7.
- 30. Partington, J.R., "A Textbook of Inorganic Chemistry", Macmillan and Co., London, 1939, p. 587.
- 31. Pavlic, A.A., and Adkins, H., J. Am. Chem. Soc., <u>68</u>, 1471 (1946).
- 32. Pregl, F., "Die Quantitative Organische Mikroanalyse", Julius Springer, Berlin, 1935, p. 85-104.
- 33. Niederl and Niederl, "Micromethods of Quantitative Organic Analysis", John Wiley and Sons, New York, 1942, p. 79-99.



T547.2	
R649	Robertson

.

