NITRATION OF SATURATED HYDROCARBONS AND THEIR DERIVATIVES

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LII. GENERAL THEORY FOR FORMATION OF MONONITRO DERIVATIVES.

NITRATION OF TOLUENE INTO PHENYL-NITRO-METHANE.

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The present work represents the practical application of our theory for nitrating paraffins and the alkyl-benzene side chain for the purpose of developing methods for obtaining mono-nitro derivatives.

Till recently the only known way of nitrating toluene and other alkyl-benzene side chains has been the classical method of M. I. Konovalov. The latter obtained phenyl-nitro-methane by heating a mixture of hydrocarbon and nitric acid at specific gravity 1.12 in a sealed tube over a waterbath for 48 hours.

The obscure reaction mechanism has prevented Konovalov from describing the synthesis adequately. Thus, the Konovalov experiments have been performed independently by Hanch, Holleman and Van Raalte, who either did not obtain phenyl-nitro-methane at all, or at most obtained 1-2 drops of it. Neither could P. P. Shorygin (1) repeat the results obtained by Konovalov, despite the fact that his data were more favorable than the data of the others. Shorygin's attempts to account for the reasons of the failure were not successful.

Continuing our research in nitrating toluene into the side chain, we attained by now satisfactory methods for producing the reaction in open containers so as to obtain hundreds of grams of phenyl-nitro-methane. As a nitrating agent, nitrogen peroxide can be used as well as nitric acid at specific gravity 1.5; to be heated at 90 - 100 degrees /Centigrade/ for a period of 4 hours. These results, very different from the data of previous research, have been achieved from the following theoretical analysis.

According to our first reports (2,3) the mechanism of forming mononitro compounds by nitrating paraffins and their derivatives with nitrogen oxides and

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nitric acid is as follows:

(a) ~~In forming~~ the radical by ~~reacting~~ hydrocarbon with mono-

Formation of a   *the reaction of the*

meric nitrogen dioxide:

$$RH + NO_2 \rightleftharpoons R + HNO_2$$
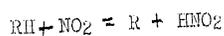
(b) Subsequently, alkyl ~~mixes~~ with the radical molecule NO_2

combines

$$RH + NO_2 \rightleftharpoons RNO_2$$
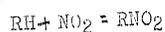
The most important reaction competing with the latter process
will be the ~~mixture~~ of alkyl with nitrogen oxide. This yields the fol-
lowing nitro-compound which subsequently is converted into phenyl-dinitro-
methane as was shown in the previous report (3). In ~~it~~ were also cleared
up the conversion conditions for nitroso-compounds into mono-nitro deriva-
tives and other products.

combination   *so-*   *this report*

A supplementary accessory reaction appears to be the interaction
of the radical with dimeric nitrogen dioxide $N_2 O_4$, giving oxidized pro-
ducts which will be explained in detail in another chapter.

From the foregoing it follows, that for accelerating the nitration
of nitric oxide in the liquid phase and guiding it into the direction of
forming mono-nitro derivatives, we should build up during the reaction
a sufficient quantity of NO_2 and reduce as far as possible the concentration
of NO and $N_2 O_4$. Working with open containers we succeeded in performing
the reaction at a temperature of about 100 degrees and by employing an ex-
cess of solvent or still better the hydrocarbon itself. The utilization
of a large quantity of hydrocarbon guarantees sufficient concentration of
NO_2 during the reaction, and the temperature rise is of minor importance
in relation to NO/NO_2 $N_2 O_4 /NO_2$ due to the sharp decrease in the solu-
bility of nitric oxide and the considerable increase in the dissociation
of $N_2 O_4$, which approaches 100 percent, under these conditions. The de-
duction about the effect of temperature and the quantity of hydrocarbon on
the yield of the mono-nitro derivative has been fully proved by experiments.

Parallel with the use of excess hydrocarbon, a considerable increase in the yield of mono-nitro compounds has also been brought about by introduction of oxygen during the reaction. This is explained by the following considerations. As it is shown by the stoichiometric equations of the nitrating and oxidizing reactions with nitrogen dioxide, as follows:

$$2C_6H_5CH_3 + 3NO_2 = 2C_6H_5CH_2NO_2 + H_2O + NO$$

$$C_6H_5CH_3 + 3NO_2 = C_6H_5COOH + H_2O + 3NO$$
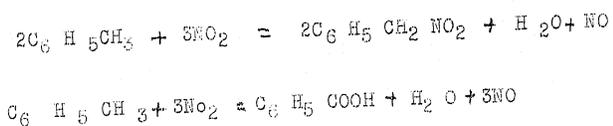
All of them form nitric oxide by the unproductive consumption of nitrogen dioxide. This circumstance involves a reduced partial pressure and consequently a concentration of NO_2 in the hydrocarbon, which decreases the rapidity of the reaction. The introduction of oxygen, transforming the nitric oxide into dioxide, ought to contribute to the more extensive and complete use of the bound nitrogen and to the acceleration of the reaction rate, a fact confirmed by experiment. The oxidizing under these conditions in the final analysis took place exclusively at the expense of the oxygen.

For effective nitration of toluene side-chains by nitric acid, according to our theory, the following should be provided:

(1) HAVE NITROGEN OXIDES PRESENT AT THE START OF THE REACTION.

(2) WITH THE HELP OF NITRIC ACID BUILD UP AND THEN HOLD THE NECESSARY CONCENTRATION OF NO_2 TO THE EXTENT DESIRED DURING THE WHOLE REACTION.

(3) CREATE CONDITIONS TO STOP THE NITRIC ACID FROM EXERTING A NITRATING EFFECT INTO THE NUCLEUS AND FROM DESTROYING THE FORMING PHENYL-NITRO-METHANE.

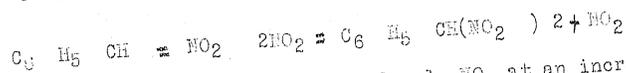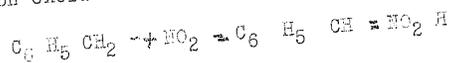(4) OBSERVE THE CYCLE OF THE REACTION DEVELOPED FOR THE NITRATION WITH NITROGEN DIOXIDE.

To fulfill the first condition it is sufficient to add initially a certain quantity of nitrogen dioxide or substances which can produce the

latter easily by reacting with nitric acid, such as trioxymethylene, to assure the required concentration of nitrogen dioxide to correspond with the equilibrium equation

$$3NO_2 + H_2O \rightleftharpoons 2 HNO_3 + NO$$
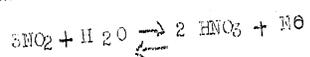
It was necessary to maintain a sufficient concentration of nitric acid in this case. This has been achieved through the gradual addition of nitric acid of specific gravity 1.5. In order to avoid nitrating toluene into the nucleus with such strong nitric acid, the latter should be converted immediately into the inorganic phase and not allowed to come into contact with the hydrocarbon. Using excess hydrocarbon gives in addition to the advantages formerly mentioned the possibility of decreasing the destructive effect of the nitric acid on the mono-nitro derivative.

It is interesting to note that in all experiments for nitrating toluene at 100 degrees centigrade with the use of oxygen, we always get a noticeable and sufficiently constant quantity of phenyl-dinitro-methane, perhaps due to the inability under these conditions of eliminating nitric oxide completely throughout the reaction. Nor is the following method of its evolution excluded

$$C_6 H_5 CH_2 + NO_2 \rightleftharpoons C_6 H_5 CH = NO_2 H$$

$$C_6 H_5 CH = NO_2 \quad 2NO_2 \rightleftharpoons C_6 H_5 CH(NO_2)_2 + NO_2$$

the reaction of alkyl with electrophylic molecule NO at an increased temperature at times split off hydrogen ion and forms the anion of the aciform, which subsequently by reacting with excess dioxide can be transformed into a dinitro derivative. The said conclusion is confirmed experimentally.

EXPERIMENTAL PART

The nitration was effected in a double-necked flask. Into the central opening was inserted a separatory funnel, the end of which reaches the bottom of the flask; the side extension of the inlet tube and the neck

- 4 -

of the funnel were connected, if necessary, with the help of a T-connection
to a source of oxygen. The offset neck of the flask was connected with a
reflux condenser, to which were consecutively attached two Tishchenko con-
densor, with nitro-benzine, surrounded by a cooling mixture. A bubble count-
ing device with a regulating tap, and, finally, a gasometer for the residu-
al gases and added to the apparatus.

The processing of the reaction mass and the recovery of its com-
ponents was accomplished by a method similar to the one described earlier.
/4/ A substantial improvement was introduced for the extraction of phenyl-
nitro-methane. To accelerate and expedite the maximum recovery of phenyl-
nitro-methane, which was exceptionally difficult in the presence of excess
toluene, several grams of diethylamine were added. The latter, as shown
by special experiments, reacts rapidly with phenyl-nitro-methane, even in
the toluene solution, with the formation of crystalline diethylammonium
salts of "aciform". Due to the low solubility of diethylamine in 10 per-
cent NaOH, which was used for the recovery, the amine was almost entirely
found in the hydrocarbon layer, where it reacted with phenyl-nitro-methane,
as was shown directly above:

$$C_6 H_5 CH_2 NO_2 + NH(C_2 H_5)_2 + (C_6 H_5 CH = NO_2) (NH_2 (C_2 H_5)_2)$$
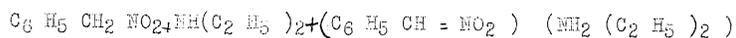
The formed salt, passing, as an ionic compound, into the alkaline
solution, was transformed there into a sodium derivative with simultan-
eous regeneration of diethylamine, which again entered the cycle. The
addition of diethylamine has, in a number of experiments, permitted short-
tening the time necessary for obtaining phenyl-nitro-methane to one hour,
instead of the 20 to 30 hours which were necessary while working in the
usual way. A still greater effect was observed in the recovery of diphenyl
nitro-methane and methyl-phenyl-nitro-methane.

Let us check some instances of the isolation and identification of
phenyl-nitro-methane. Thus, for example, it is revealed that before the
acidification of the solution of phenyl-nitro-methane salts, which always
contain a large quantity of nitrate, we add a small quantity of potassium
bicarbonate and carbamide with the hope of diminishing the harmful action

- 5 -

of the liberated nitric oxides and the strong acidity of the acinitro compound.

The success of the distillation of phenyl-nitro-methane in vacuum depends on accidental, still not altogether explained circumstances. In the majority of cases it is performed successfully even when we use more than one hundred grams of the substance, and signs of the dissolution were observed only towards the end of the process. Never has a sudden strong dissolution of the substances taken place even during the experiments when the used product had been successfully distilled earlier. Later, we found out that analogous phenomena has been observed by Konovalov and Coim. /5/

In order to separate at once the phenyl-nitro-methane in a pure and reactive aciform, we proceeded as follows: The alkaline extract was boiled in a water bath to the point of crystallization, which subsequently was allowed to complete itself in the cold. The released colorless sodium salt of aci-phenyl-nitro-methane is drawn off in a glass filter, and is washed with a 20 percent solution of sodium chloride. In repeating the process with the mother solution we can obtain a certain quantity of the product. Thus more than 80 percent of the formed phenyl-nitro-methane could be freed.

The obtained phenyl-nitro-methane was distilled at 10 mm pressure and 105 - 107 degrees Centigrade into a light yellowish oil with a specific gravity of 1.5341. Its exact identification has been achieved by reduction with zinc dust in an alkaline solution with a quantitative discharge into amine, and then in the absence of a depressed temperature for the fusion of the oxalate and picrate of the latter, in the mixture of the product with the respective salts of benzylamine obtained from benzyl chloride, as per Kanitzaro. For the identification of phenyl-nitro-dibromomethane, it is converted into phenyl-nitro-methane, according to Ter-Meer by heating it with alcoholic alkaline solution and pottassium nitrite.

The surplus toluene, is distilled from the reaction mass, after the extraction of phenyl-nitro-methane, at the remaining pressure of 40 - 50 mm and a temperature of the water bath not more than 50 degrees Centigrade.

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TABLE I

	No. of Experiment	
	1	2
		10 liters

	1	2
Used O_2		
Obtained:	6.1 grams	10.6 grams
N_2 O_4 (regenerated)	34.2 grams	56.1 grams
Phenyl-nitro-methane	51.0 %	52.5 %
Phenyl-nitro-methane	2.7 grams	3.8 grams
	2.7 %	2.7 %
	7.1 %	11.2 %
Benzoic Acids	26.2 grams	35.8 grams
Residue Oils	39.2 %	33.6 %

(c) THE EFFECT OF THE QUANTITY OF HYDROCARBON. The results of the studies on the effect of the factor of dilution at regular temperature have been reported earlier. We will report on an experiment at 100 degrees Centigrade. Duration of adding 43 grams of nitrogen peroxide -- 2 hours; oxygen consumed -- 8 liters: the rest of the data as shown in Table below.

TABLE II

	No. of Experiment	
	1	2
	175 milli-liters	1750 milli-liters

	1	2
Input Input of toluene	175 milli-liters	1750 milli-liters
Recovered:		
Phenyl-nitro-methane	15.3 grams	41.7 grams
	49.8 %	49.8 %
Phenyl-dinitro-methane	1.5 grams	4.7 grams
	3.6 %	4.2 %
Benzaldehyde	2.5 grams	2.4 grams
	6.2 %	3.6 %
Benzoic Acid	7.5 grams	3.6 grams
	26.6 %	4.7 %
Residue Oils	4.4 grams	32.3 grams
	13.8 %	38.2 %

- 7 -

The degrees of transforming toluene into phenyl-nitro-methane are practically the same in both experiments, but the absolute yield of the mono-nitro compound in this case, sue to the great quantity of hydro-carbon used, is almost three times higher than in the first experiment.

2. NITRATION WITH NITRIC ACID

The apparatus described earlier is filled with toluene and a buffer solution of 8 grams of nitric acid at specific gravity 1.38, 40 grams 50 percent sulfuric acid and 0.5 grams trioxymethylene. To this while heating in a water bath for 3.5 hours, is added from the drop funnel 50 milliliters of nitric acid at specific gravity 1.5. The admission of oxygen, if the test called for it, was slow at first, then accelerated with the development of the reaction, and guided, as described above.

In the most favorable case, the output of raw phenyl-nitro-methane by nitric acid on toluene, represents more than 50 percent of the theoretical quantity and the total utilization of the bound nitrogen is about 90 percent

- 8 -

TABLE III

| No. of Experiment	Reaction Conditions	Yield of Reaction Products			
		illegible	illegible	illegible	illegible
1	200 milliliters toluene without O_1	23.6 g. 44.6 %	2.0 g. 2.6 %	16.2 g. 35.9 %	
2	500 ml. toluene without O_2	35.3 g. 50.1 %	3.2 g. 3.5 %	14.7 g. 23.5 %	16.2 g.
3	1750 ml. toluene without O_2	53.9 g. 54.6 %	5.0 g. 3.8 %	9.4 g. 10.1 %	31.1 g. 31.5 %
4	500 ml. toluene 8 liters O_2	48.4 g. 48.7 %	3.6 g. 2.8 %	24.5 g. 27.5 %	20.9 g. 21 %
5	17 ml. toluene 8 liters O_2	6.7 g. 3.7 %	14.3 g. 11.9 %	39.7 g.	

The rate of the transformation of toluene into phenyl-nitro-methane is fairly constant; it fluctuates within the limits of 45 - 55 percent; it decreases with the decrease in the quantity of toluene, most probably due to the acceleration in the process of decomposition of the nitro compound in the acidic layer.

With certain simplifications, the described method for nitration is very good for producing phenyl-nitro-methane.

CONCLUSIONS

1. The lack of correct concepts on the mechanism of this reaction has not permitted the earlier scientific investigators to reproduce the described nitration of the paraffin chain, and produce sufficient outputs of monomitro-compounds.

2. Basically, the formation of mononitro derivatives in the paraffin chain passes thru the following stages:

- 9 -

$$R \longrightarrow H + NO_2 \qquad R \longrightarrow + NO_2 \qquad R \longrightarrow NO_2$$

$$\longrightarrow HNO_2$$
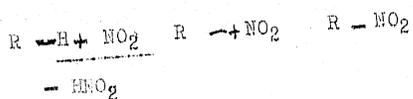
The inter action of the intermediately generated radicals with the nitric oxide and the dimeric nitrogen peroxide $N_2 O_4$ as a rule, leads to the production of homodinitro compounds and oxidation products.

3. The indicated process for nitration of the paraffin chain, is further confirmed by the experiments for producing phenyl-nitro-methane, thru nitration of toluene with nitrogen peroxide and nitric acid at specific gravity 1.5 in open vessels -- an output of more than 50 percent than stoichiometrically possible, was obtained.

4. A method for the acceleration of the conversion of pseudo-acids into aciform salts by the addition of mines was proposed, and its applicability for the extraction of primary and secondary mononitro compounds, was established.

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