# REACTIONS IN THE SYNTHESIS OF INDAZOLE

by

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## Acknowledgment

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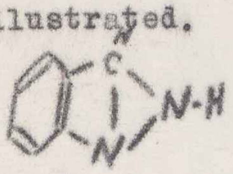
## Introduction

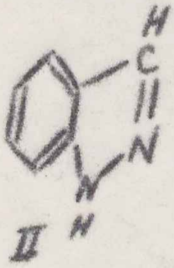
This investigation was undertaken to study the reaction mechanism involved in the formation of Indazole. A study was also made to determine the effect of a polar solvent on the yield of Indazole using Dreyfuss' method of preparation. (4).

At present, Indazole is of no practical use. Howeyer the reaction producing Indazole is of interest since it is different from the usual reaction of diazonium salts. That is, the reaction of diazonium salts with benzene to form diphenyl derivatives.

There are several proposed structures for Indazole as illustrated.



I



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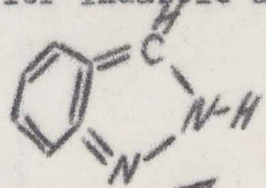

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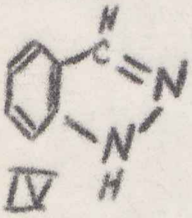
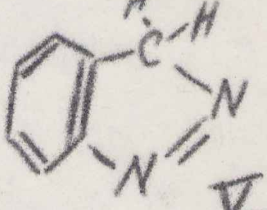


IV



V

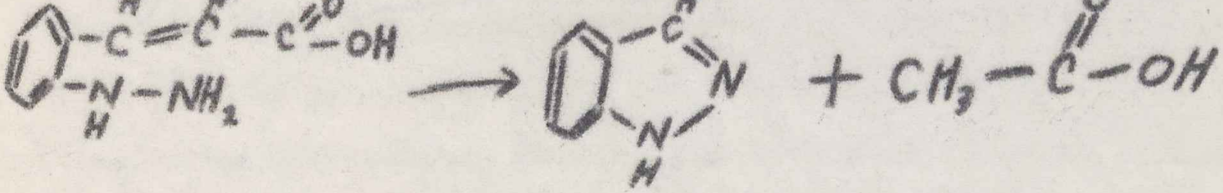
Early workers assigned the structures I to Indazole and II to Isoindazole. Auwers (1) rejects I on the basis of the difficulty in constructing a molecule with a three membered ring. Fries (7) prefers I since the 2 alkyl derivatives are colorless and show no quinoid properties. Other sources (3), (15) prefer III as Indazole, Hayes and Hunter (8) show that IV is a possible structure depending on where the substituent is attached.

Barclay (2) states that by anology with other heterocyclic compounds there is little doubt that Indazole and its derivatives are resonance hybrids, resonance mainly due to the benzene nucleus. Sigsby (19) believes that V is also a probable form if only as an intermediate.

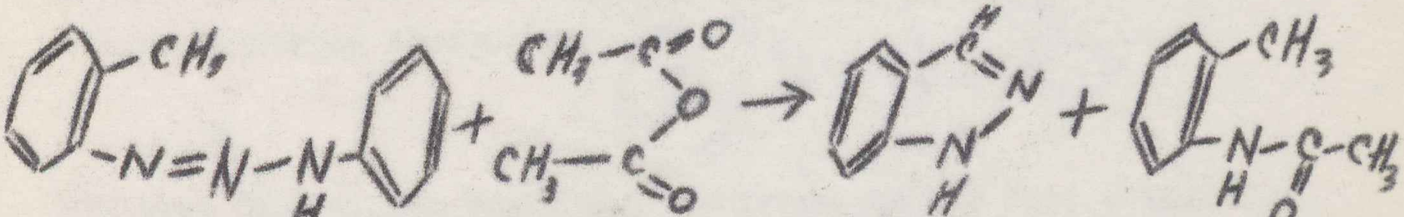
For the purpose of uniformity, the structure IV will be used throughout this paper.

## Historical

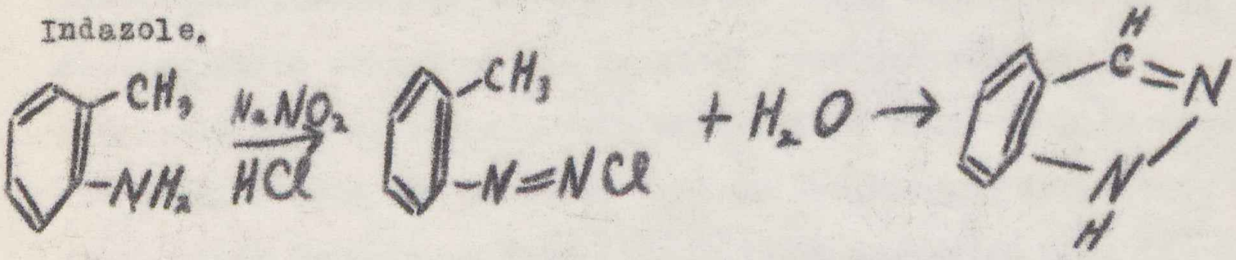
Indazole was discovered by E. Fischer and Kuzel (5). These and other workers, E. Fischer and Tafel (6) noticed that 2 Hydrozinocinnamic acid easily lost acetic acid to give Indazole.



Heusler (9) obtained a slight yield of Indazole by the reaction of tolul-diazo-toluide with acetic anhydride.

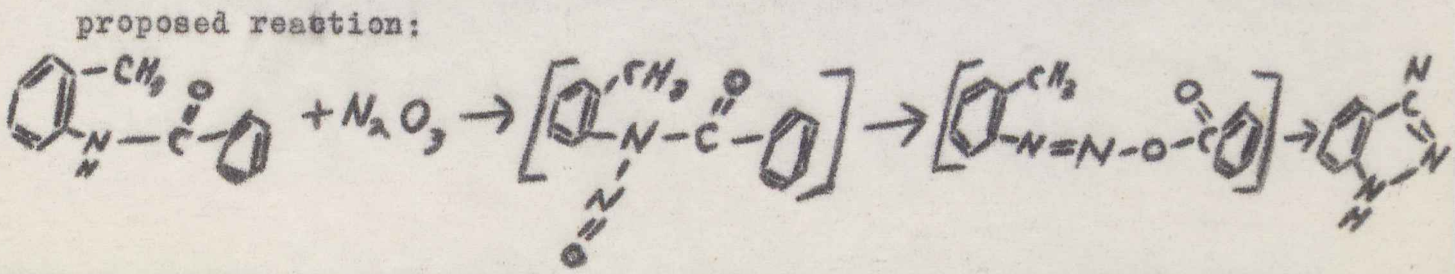


E. Noelting (16) made Indazole from O-toluidine, through the diozonium salt which was allowed to hydrolize and couple to form Indazole.



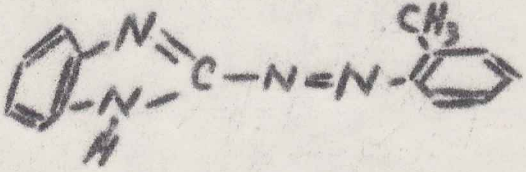
This synthesis was attempted by Rzesotarski (17), but no Indazole was obtained.

Dreyfuss (4) was able to prepare Indazole, in relatively high yield, from N-benzoyl-o-toluidine using acetic acid and acetic anhydride as solvents for the nitrosation and pyridine as a catalyst. The nitrosated starting material coupled intramolecularly to yield Indazole and benzoic acid according to the proposed reaction:



At present this is the easiest preparation of Indazole.

The mechanism of the decomposition of the Nitroso compound invokes considerable interest. Previous workers speak of coupling, with the elimination of nitrogen as $N_2$ (18) (20) (12) (11). Dreyfuss (4) suggested cyclic mechanism for reactions of diazonium salts, formed from O-toluidine. Mention has been made of other products formed by side reactions (20). A possible product formed would be the resulting product from the reaction of Indazol with the undecomposed nitroso derivative.



Diphenyl derivatives could also be formed. De Tar (13) obtained Indazole from the decomposition of As-2-stilbenediazonium fluoborate and postulated the reaction as being ionic, involving an electrophilic attack of the terminal nitrogen atom at the ethylenic bond followed by the addition of water to give Indazole and benzaldehyde. In the work done on the nitroso derivative of acetanilide by Huisgen (11) (12), it was suggested that the decomposition involved the formation of the diazonium ester as the rate determining step. Huisgen (11) also showed this reaction to be free radical in nature and of first order.

It has been determined that the decomposition rate is unaffected by the presence of a coupling compound such as B-napthol. This fact was utilized by Huisgen and Sigsby (19) in studying the reaction rate. Sigsby showed that the color produced by the coupling with B-napthol was directly proportional to the concentration of the nitroso compound. This was the method used for studying the reaction rate. Sigsby(19) found that the decomposition rate of the nitroso derivative of N-benzoyl-o-toluidine in the presence of benzene was first order.

## Apparatus

The nitrosations were carried out in two Milligan bottles connected in series to the gas generator. The gas generator consisted of a one liter three necked grignard flask fitted with a dropping funnel and an outlet in the smaller necks. The large neck was stoppered. Rubber stoppers were used to minimize the corrosive action of the gas. A 250 ml. Erlenmeyer flask was fitted with a two hole rubber stopper and connected in series between the gas generator and the Milligan bottles as a safety trap.

The only apparatus necessary to work up the yield of Indazole was a simple distillation apparatus.

The rate determination by coupling with B-napthol required special equipment. The apparatus used to store the B-napthol solution in an atmosphere of nitrogen was the same as that used by Sigsby (19) with one modification. The 500 ml. separatory funnel was replaced with a 1000 ml. separatory funnel to permit the preparation of a larger volume of solution. The 1000 ml. funnel was calibrated at the one liter level. It was found to be accurate to 5cc.

The apparatus for storing and drying the nitroso derivative consisted of a large Dewar flask for insulation, and a long cylindrical tube, closed at one end, which fit inside the Dewar flask and was held in place with a three prong clamp. The Dewar flask was fitted with a loose fitting fiber top with a hole in the center to accommodate the tube. The tube was fitted with a one hole rubber stopper and connected to a drying tube. The drying tube contained calcium chloride and phosphorous pentoxide, in series. The drying materials were placed in the tube so that the phosphorous pentoxide was between the calcium chloride to protect it from the air.

The decomposition of the nitroso derivative was carried out in a constant temperature bath with a mercury thermo regulator.

The concentration analyses were made with a Fisher A.C. Electrophotometer.

About twenty-five separatory funnels and twenty-five 100 ml. volumetric flasks were necessary to hold the samples. A pipetter was used to pipette toxic liquids.

## Storing and drying the Nitroso Derivatives

The rate determinations would be more convenient if the nitroso derivative could be stored and dried. For this reason experiments to store and dry the nitroso derivative were undertaken. The apparatus used has been described under the section entitled "Apparatus". The nitroso derivative was prepared and isolated according to the method outlined by Sigsby (19). The gas generator was charged with a solution of 250 gm. sodium nitrate in 300 gm. water and dilute sulphuric acid was added to liberate the gas. The Milligan bottle was charged with 20 gm. N-Benzoyl-o-toluidine, 60 ml. acetic acid, 40 ml. acetic anhydride and 8 ml. pyridine. The nitrosation was carried on until the solution was clear green. The nitroso derivative was isolated by pouring the green solution into ice water. It was found that a volume of water of 200-300 ml. brought about most complete precipitation. The precipitate was superficially dried with paper towels. two grams of the derivative were then removed and dissolved in 30 ml. of benzene at 25° C. a ten ml. portion of this sample was removed immediately and coupled with ten ml. of 0.2N B-Napthol solution (0.2N B-Napthol in 10% sodium hydroxide solution). The remainder of the nitroso derivative was placed inside the tube and the Dewar flask filled with ice. The drying tube was attached and the system evacuated to increase the rate of evaporation of the water. The complete storage apparatus was placed in a refrigerator.

After three days another two gm. sample was removed and given the same treatment as the first sample. The same procedure was followed on the fourth day. The samples were then extracted with benzene and diluted 1000 times. The absorbancy was measured in the photometer. The following chart shows the results.

| Weight Sample | Time in Storage | Absorbancy |
|---|---|---|
| 2 gm. | 0 | 26.75 |
| 2 gm. | 3 days | 33.6 |
| 2 gm. | 4 days | 34 |

Since the absorbancy is directly proportional to the concentration the results show that no measurable amount of decomposition had occured after four days. The difference between the first sample and the second and third is believed to be due to the greater purity of the second and third samples, since they were stored long enough for the drying tube to be effective.

### Effect of increasing the solvent to solute ratio on rate of nitrosation.

An attempt to increase the rate of nitrosation by doubling the ratio of solvent to solute. The Milligan bottle was charged with 20 grams N. Benzoyl-o-toluidine, 18 ml. pyridine, 120 ml. acetic acid and 80 ml. acetic ambydride. The nitrosation was started at 2:00 P.M. and at 8:00 P.M. the nitrosation was not yet complete. Since the nitrosation normally takes from two to three hours this showed that increasing the solvent to solute ratio had an adverse effect on the nitrosation rate.

In all nitrosations the Milligan bottles were placed in two liter beakers and surrounded with ice water.

## The Decomposition Rate of the Nitroso Derivatives

The first run was made to confirm the results of Sigsby (19). The conditions of the decomposition were identical with those of Sigsby's experiment.

The nitrosation was carried out as described using two Milligan bottles in series. The Milligan bottles were each charged with 20 grams of N-Benzoyl-o-toluidine, 60 ml. acetic acid, 40 ml. acetic anhydride and 9 ml. pyridine. The nitrosation was carried out until the solutions in both Milligan bottles were clear green. After drying the nitroso compound, 20.3 grams were placed in 300 ml. of benzene and theromostated at 30.1° C. Ten milliliter samples were withdrawn every five minutes and coupled with 10 milliliters of B-napthol. Samples were withdrawn for approximately three hours. Another sample was taken the following day to obtain an infinity reading. The samples were allowed to stand overnight to couple. The colored azo dye, formed by the coupling reaction, was extracted from the aqueous layer with benzene. Benzene was then added to bring the dilution up to 100 times. The absorbancy of the samples was measured in the photometer. A plot was made of Log absorbancy vs. time. See "Discussion" for further treatment.

## Decomposition rate of Nitrosated Acetanilide

The second run was made under the same conditions as the first with the substitution of 20 grams of acetanilide for the N-benzoyl-o-toluidine in the nitrosation. It was noticed that the acetanilide was nitrosated faster due to its greater solubility in the acetic-anhydride solvent. When the contents of the Milligan bottle, fartherest from the gas generator, were poured into ice water, unnitrosated acetanilide was precipitated. For this reason the amount of the nitroso derivative available for rate study was only 4.5 gm. The temperature and volume of benzene were kept the same as in the first run so that the results would be comparable. Since the decomposition resulted in the formation of a colored by-product it was decided to try to follow the formation of the by-product as well as the decomposition of the nitroso derivative. The decomposition of the nitroso compound was followed by the same procedure as in the first run. Ten Milliliter samples were removed at ten minute intervals and coupled with ten milliliters of B-napthol. The samples were allowed some time to complete the coupling and then extracted, diluted and measured as before. The formation of the colored by-product was studied by withdrawing a ten milliliter sample, diluting 100 times and measuring the color in the photometer. The rate of decomposition of the nitroso compound and the rate of formation of the colored by-product were ploted on the same graph. See data sheets and graphs which follow.

## Decomposition rate of the Nitroso Derivative of N-Benzoyl-o-toluidine and the rate of Formation of Colored By-product

The third run was a duplicate of the first run with the modification of following the formation of the colored by-product, as described in the second run. Forty grams of N-benzoyl-o-toluidine were nitrosated as before. A portion of the dried nitroso intermediate (20.3 grams) was allowed to react in 300 ml. of benzene at 30.2° C. Samples were taken every ten minutes and coupled with B-napthol and extracted as before. In addition, ten milliliter samples were withdrawn, diluted and the absorbance read immediately. For results see charts and graphs which follow.

## Effect of Polar Solvent on the formation of Indazole from N-benzoyl-o-toluidine

An attempt was made to increase the yield of Indazole by using a polar solvent instead of benzene. The procedure was that outlined by Dreyfuss (4) with the substitution of Nitromethane for benzene as solvent. The N-benzoyl-o-toluidine was nitrosated as before. Twenty grams of the dry nitroso compound were dissolved in 150 ml. of nitro methane and allowed to stand at room temperature for one week (overnight is probably sufficient). The solution became dark red and homogeneous. The solution was refluxed for ten minutes and then 100 mls. of nitro methane were distilled off. The remaining solution was washed with 50 mls. of a saturated sodium carbonate solution. On washing a brown precipitate was formed. The precipitate partially dissolved in 6 N hydrochloric acid to give a clear red homogeneous lower layer and an upper layer of brown floculent precipitate. The lower layer was drawn off and neutralized with 10% sodium Hydroxide solution. The solution turned cloudy but the precipitate (supposedly Indazole) was so fine and in such small quantity that it couldn't be recovered.

## Effect of Polar Solvent on the rate of Decomposition of the Nitroso Derivative of N-Benzoyl-o-Toluidine and on the rate of formation of Colored By-Product

The fourth run was carried out in the same manner as the third run with the exception of replacing the reacting solvent of pure benzene with a mixed solvent of 150 mls. nitromethane and 150mls. benzene. Samples were taken in the same manner. However, the intensity of colored by-products was much greater than in previous runs and it was necessary to dilute 1000 times to obtain a reading. The extraction of the colored compounds was made difficult due to the intensity of color and the fact that benzene-nitro methane solvent formed a stable emulsion with the aqueous B- napthol solution. In order to make the coupled compound relative to the colored by-products, the former was diluted 1000 times also. The color was measured as before and the absorbancy vs. time was ploted for both the coupled compound and the colored by-products. (See following graphs).

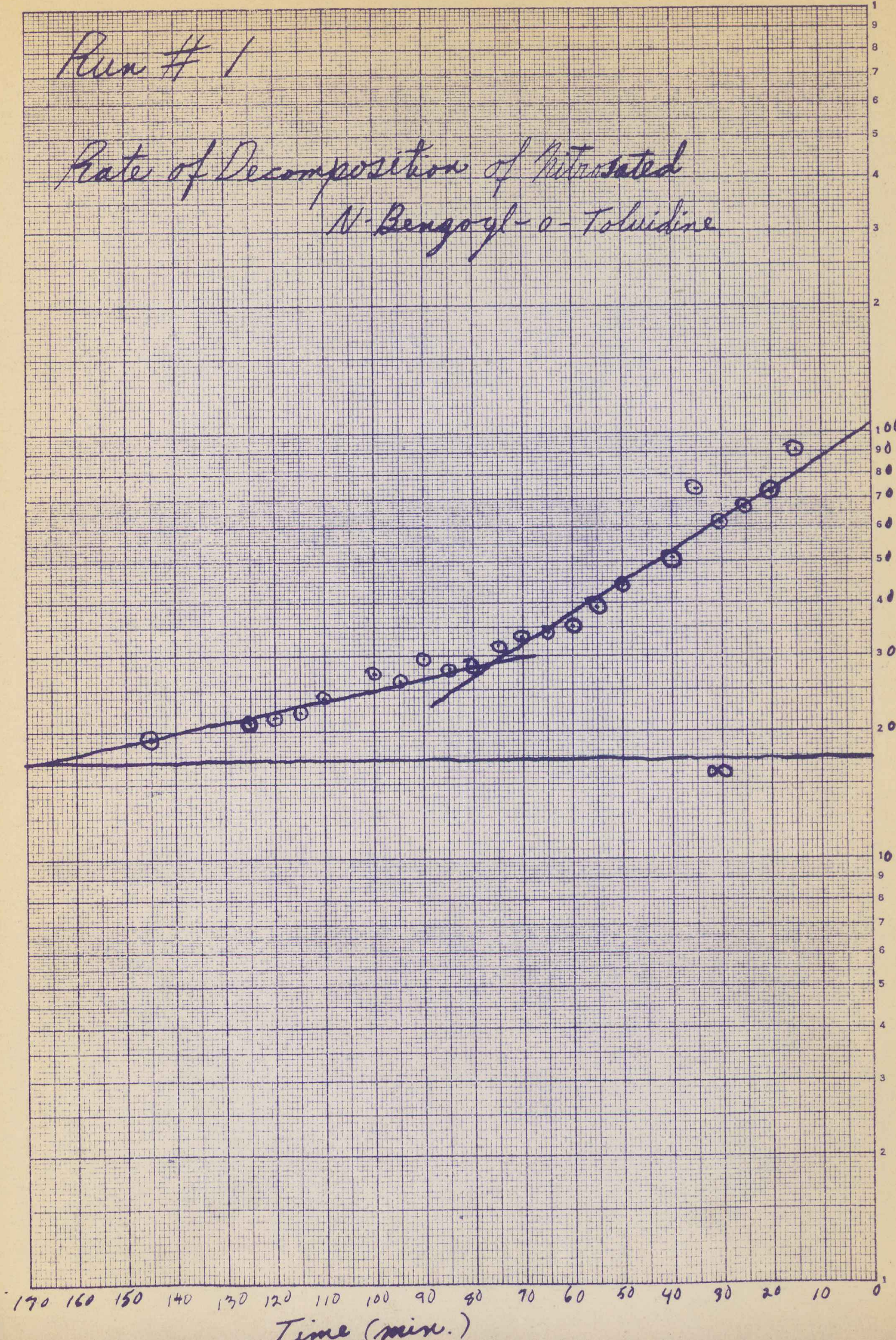
The large amount of colored products formed made measurements very difficult. Therefore, the results are not expected to be very accurate or reproducible. It is recommended that the same procedure be followed with the substitution of nitro benzene for nitro Methane - benzene mixture or nitrobenzene for nitro methane.

Run # 1

**Decomposition rate of Nitroso Derivative of N-Benzoyl-o-Toluidine**

| Sample Number - | Time Minutes | A | %T |
|---|---|---|---|
| 1 | 10 | above 100 | - |
| 2 | 15 | 91 | 12.3 |
| 3 | 20 | 73.4 | 18.6 |
| 4 | 25 | 66.8 | 21.6 |
| 5 | 30 | 62 | 24 |
| 6 | 35 | 74.5 | 18 |
| 7 | 40 | 51 | 30.9 |
| 8 | 45 | 48.5 | 32.7 |
| 9 | 50 | 44.8 | 35.6 |
| 10 | 55 | 39.6 | 40.4 |
| 11 | 60 | 35.7 | 44.1 |
| 12 | 65 | 34.7 | 45 |
| 13 | 70 | 33.3 | 46.3 |
| 14 | 75 | 31.7 | 48.3 |
| 15 | 80 | 28.6 | 51.6 |
| 16 | 85 | 28 | 52.4 |
| 17 | 90 | 29.2 | 51.1 |
| 18 | 95 | 26.2 | 55 |
| 19 | 100 | 27.1 | 53.5 |
| 20 | 105 | 24.4 | 57 |
| 21 | 110 | 24.1 | 58.7 |
| 22 | 115 | 22.2 | 60 |
| 23 | 120 | 21.7 | 60.7 |
| 24 | 125 | 21.4 | 61.2 |
| 25 | 145 | 19.4 | 64 |
| 26 | 175 | 19.2 | 64.3 |
| 27 | ∞ | 17 | 67.5 |

Half life = 54 minutes



Run # 1

Rate of Decomposition of Nitrosated N-Benzoyl-o-Toluidine

A

Run # 2

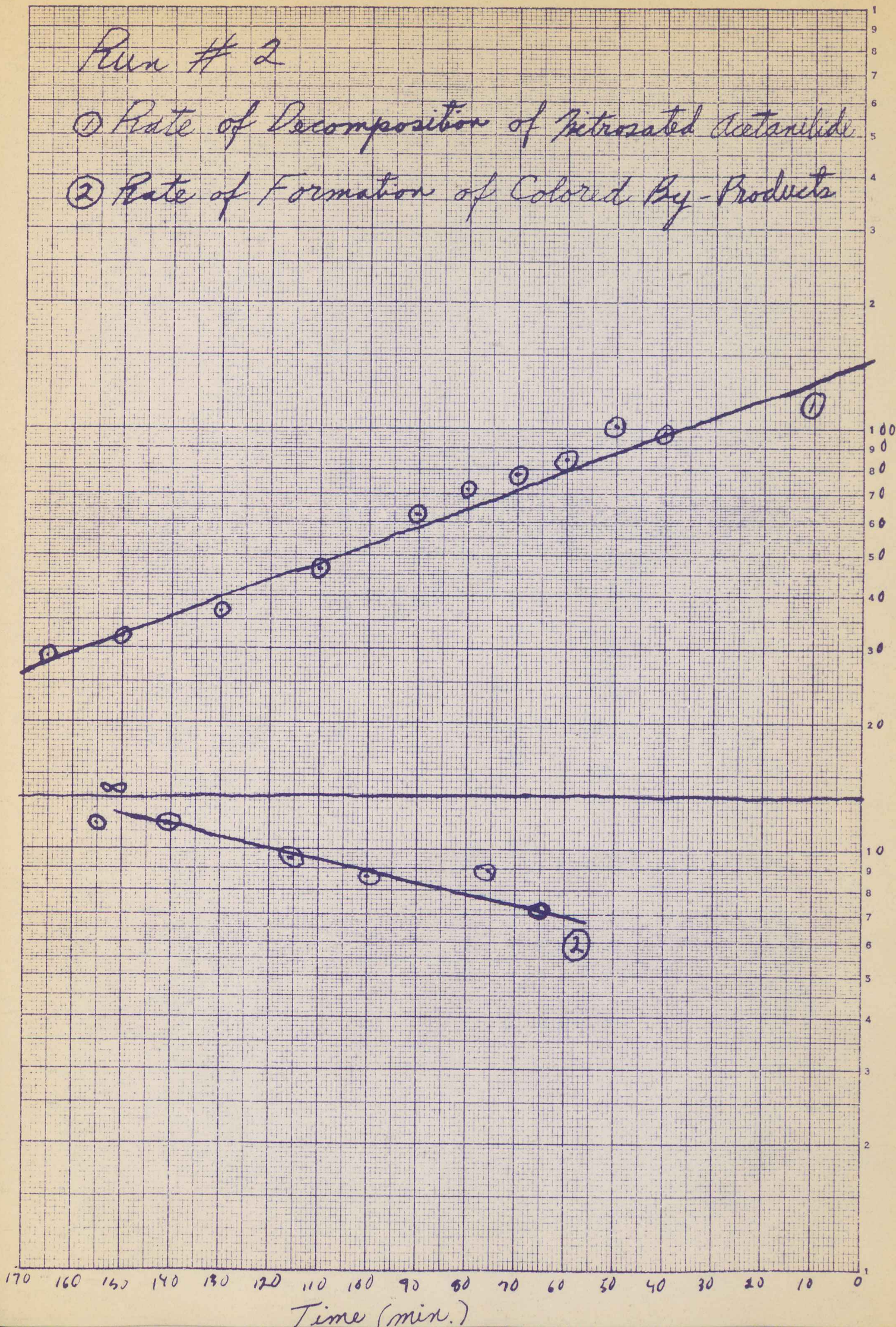
## Rate of Decomposition of Nitrose derivative of Acetanilide

| Sample Number | Time Minutes | A | % T |
|---|---|---|---|
| 1 | 10 | above 100 | - |
| 2 | 20 | above 100 | - |
| 3 | 30 | above 100 | - |
| 4 | 40 | 97.5 | 10.6 |
| 5 | 50 | 100 | 10 |
| 6 | 60 | 84 | 14.2 |
| 7 | 70 | 78 | 16.5 |
| 8 | 80 | 71 | 19.6 |
| 9 | 90 | 61.9 | 24.2 |
| 10 | 110 | 46 | 33.2 |
| 11 | 130 | 36 | 43.6 |
| 12 | 150 | 30.6 | 49.4 |
| 13 | 165 | 29.2 | 51.1 |
| 14 | ∞ | 13.1 | 73.9 |

Half Life = 84 minutes

## Rate of Formation of Colored By-Product

| | | |
|---|---|---|
| 1 | 65 | 7.2 |
| 2 | 75 | 8.8 |
| 3 | 100 | 8.5 |
| 4 | 115 | 9.4 |
| 5 | 140 | 11.4 |
| 6 | 155 | 11.4 |


Run # 2
① Rate of Decomposition of Nitrosated Acetanilide
② Rate of Formation of Colored By-Products
①
②
∞
100
90
80
70
60
50
40
30
20
10
9
8
7
6
5
4
3
2
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Time (min.)

A

Run # 3

**Rate of Decomposition of Nitroso derivative of N-benzoyl -o-toluidine**

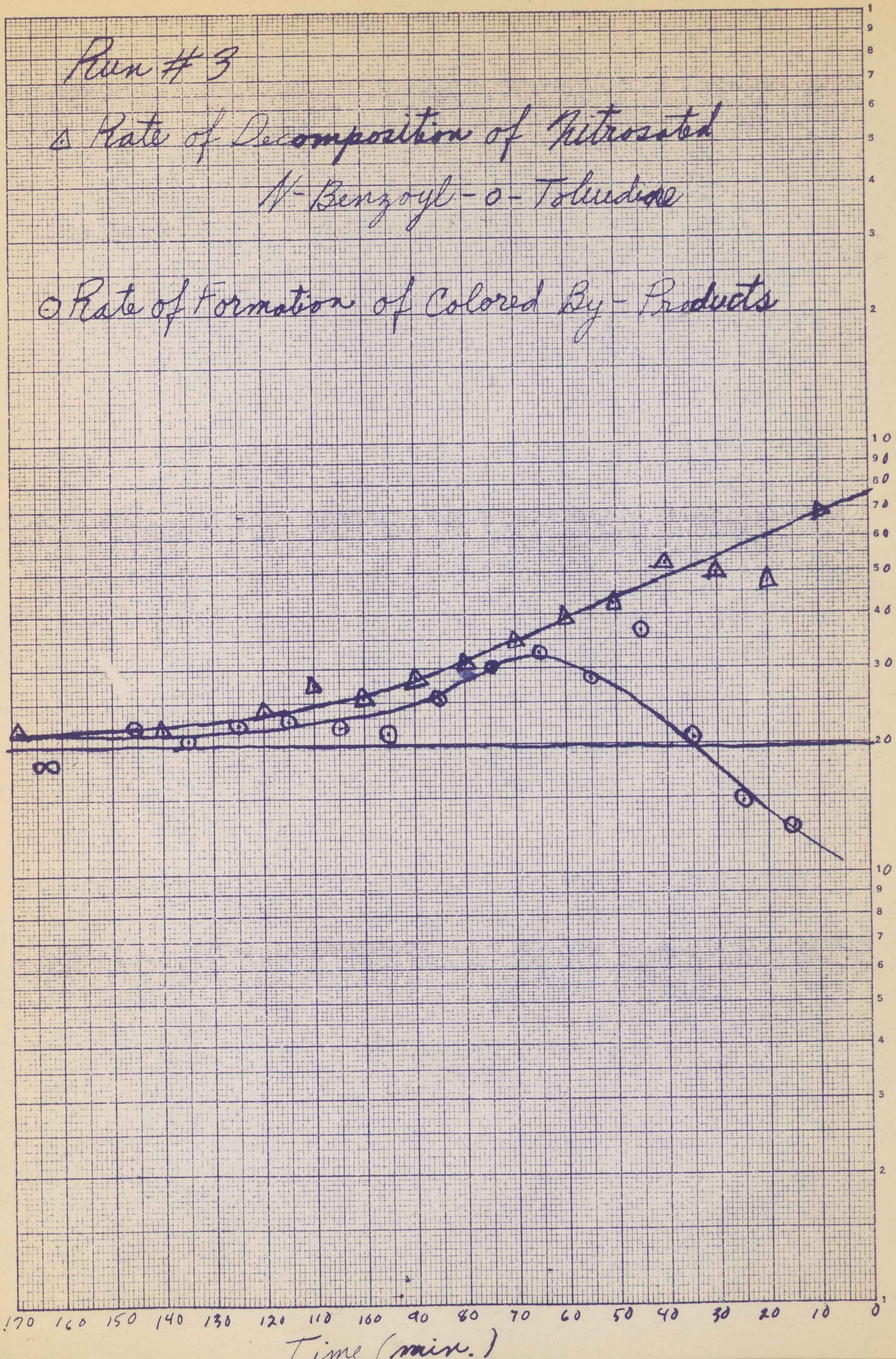
| Sample Number | Time minutes | A | % T |
|---|---|---|---|
| 1 | 10 | 68.5 | 20.7 |
| 2 | 20 | 47.9 | 33.3 |
| 3 | 30 | 49.8 | 31.7 |
| 4 | 40 | 52.6 | 29.8 |
| 5 | 50 | 42.5 | 33.4 |
| 6 | 60 | 39.6 | 40/2 |
| 7 | 70 | 34.5 | 45.1 |
| 8 | 80 | 30.5 | 49.6 |
| 9 | 90 | 28.6 | 51.8 |
| 10 | 100 | 25.8 | 55.3 |
| 11 | 110 | 27.6 | 53 |
| 12 | 120 | 23.7 | 57.9 |
| 13 | 140 | 21.9 | 60.4 |
| 14 | 170 | 21.2 | 61.4 |
| 15 | $\infty$ | 19.7 | 63.5 |

Half life = 41 Minutes

Run # 3

Rate of formation of colored by-product

| Sample Number | Time minutes | A | % T |
|---|---|---|---|
| 1 | 15 | 12.8 | 74.5 |
| 2 | 25 | 14.9 | 71 |
| 3 | 35 | 20.9 | 61.9 |
| 4 | 45 | 36.7 | 43 |
| 5 | 55 | 28.8 | 51.6 |
| 6 | 65 | 32.1 | 57.7 |
| 7 | 75 | 30 | 50 |
| 8 | 85 | 25.6 | 55.5 |
| 9 | 95 | 21.1 | 61.5 |
| 10 | 105 | 21.7 | 60.6 |
| 11 | 115 | 22.8 | 59.1 |
| 12 | 125 | 22.1 | 60.1 |
| 13 | 135 | 20.6 | 62.2 |
| 14 | 145 | 22.0 | 60.4 |
| 15 | ∞ | 20.9 | 61.8 |



Run # 3

△ Rate of Decomposition of Nitrosated N-Benzoyl-o-Toluedine

○ Rate of Formation of Colored By-Products

A

Run # 4

Rate of decomposition of Nitroso derivative of N-Benzoyl - o - toluidine

| Sample number | Time minutes | A | % T |
|---|---|---|---|
| 1 | 10 | 69.1 | 20.4 |
| 2 | 20 | 41 | 39 |
| 3 | 30 | 39.4 | 49.6 |
| 4 | 40 | 27.6 | 52.9 |
| 5 | 50 | 26 | 55 |
| 6 | 60 | 24.6 | 56.6 |
| 7 | 70 | - | - |
| 8 | 80 | - | - |
| 9 | 90 | 22.5 | 59.6 |
| 10 | 100 | 25.1 | 56.1 |
| 11 | 110 | 21.8 | 60.5 |
| 12 | 120 | 23.7 | 57.9 |
| 13 | 160 | 23.7 | 57.9 |
| 14 | ∞ | 8.4 | 82.5 |

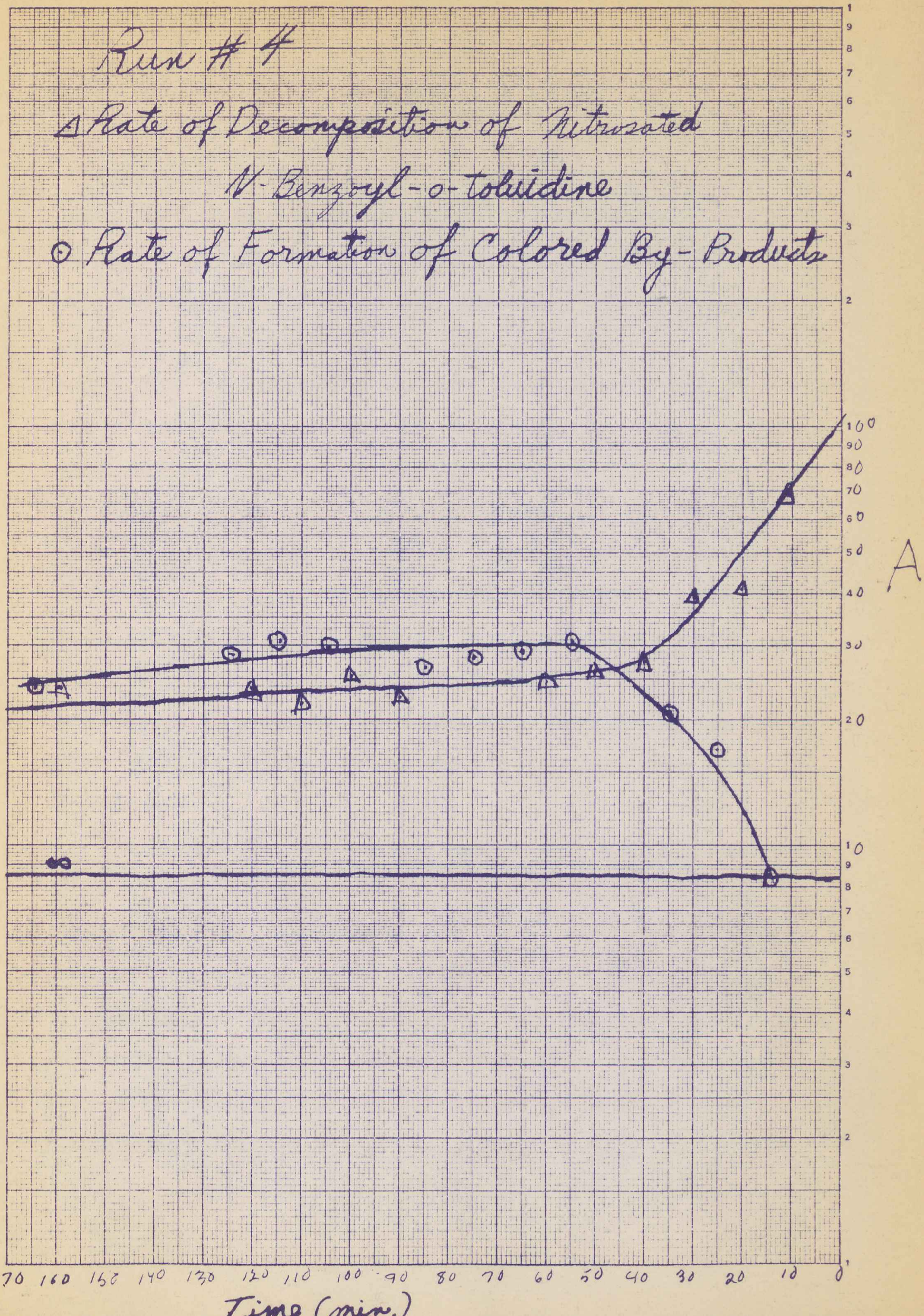
Samples 7 and 8 couldn't be extracted due to formation of emulsions.

Half life = 18 Minutes

Run # 4

## Rate of formation of Colored By-products

| Sample number | Time minutes | A | % T |
|---|---|---|---|
| 1 | 15 | 8.5 | 82 |
| 2 | 25 | 17 | 67.5 |
| 3 | 35 | 20.3 | 58 |
| 4 | 55 | 30.9 | 49.1 |
| 5 | 65 | 29.2 | 51.1 |
| 6 | 75 | 28.3 | 52.1 |
| 7 | 85 | 26.3 | 54.6 |
| 8 | 95 | 28.2 | 52.3 |
| 9 | 105 | 29.2 | 51.1 |
| 10 | 115 | 30.3 | 50.4 |
| 11 | 125 | 28.5 | 51.8 |
| 12 | 165 | 23.5 | 68.2 |
| 13 | $\infty$ | 8.7 | 81.9 |


Run # 4
△ Rate of Decomposition of Nitrosated N-Benzoyl-o-toluidine
⊙ Rate of Formation of Colored By-Products
100
90
80
70
60
50
40
30
20
10
9
8
A
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Time (min.)

## Discussion

The first run was made to confirm the results obtained by Sigsby (19). The results were found to be comparable to Sigsby's. The curve was of the same general shape as Sigsby's with a slight translation of the curve in the direction of increased concentration of undecomposed nitroso compound ( i.e. - greater absorbancy). This was believed to be due to the greater purity of the author's nitroso derivative due to the drying process. Sigsby's graph consisted of two intersecting straight lines ( see graph for run # 1). However it is believed that the points after about 65 minutes actually fall on a curve. This curvature is believed to be caused by the formation of colored by-products which interfered in the analysis for the colored coupled compound. The half life for the decomposition of the nitroso derivative of N-benzoyl - o - toluidine at 30.1° C. was determined by Sigsby as 26 minutes while the author found it to be 54 minutes.

The second run was made to follow the rate of formation of these colored by-products as well as the decomposition of the nitroso compound. The results ( see graph for run # 2) showed that the color produced by the formation of by-products, built up linearly and follows first order kinetics. However the color of the by-product of the decomposition of the nitroso derivative of acetanilide were not as intense as those of the derivative of N-benzoyl - o - toluidine. Thus the deviation from the linearity was not very great. The half life of the nitroso derivative of acetanilide as determined at 30.1° C. was 84 minutes. Huisgen (11) determined the half life at 32° C. to be 32 minutes.

The third run was made using the nitroso derivative of N-benzoyl-o-toluidine. The decomposition curve ( see graph run # 3) followed the same pattern as the previous runs. The curve of formation of colored by-products increased linearly and reached a peak at about 70 minutes, then decreased until the two curves coincided. The reason for the decrease is explained in the discussion of run # 4. From the shape of the curve, it appears that, at 30° C. the reaction is virtually complete after 150 minutes.

A graph to correct for the interference of the colored by-products was made from the graph of run # 3. This was done by subtracting the absorbancy values for the colored by-products from the values of the coupled compound. The new value for absorbance was plotted against time as before (see graph # 5). This graph seems to be as distorted as the others after about 70 minutes.

The synthesis of Indazol using a polar solvent ( nitromethane) was undertaken to try and increase the yield. However the experimental results show that the presence of the polar solvent markedly decreases the yield of Indazol.

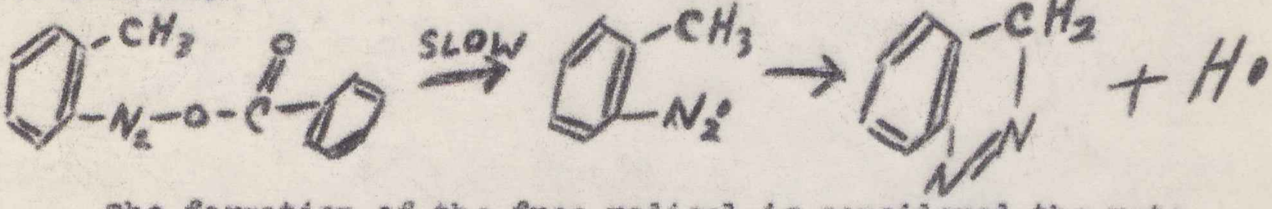
The fourth run was undertaken to study the effect of a polar solvent on the reaction rate of the nitroso derivative. A half and half mixture of nitromethane and benzene was used to keep the conditions similar to the other runs ( i. e. have benzene present as a possible reactant). The curves have the same general shape as the others. (See graph for run # 4) The curves show a greater amount of color produced by the formation of colored by-products than the color produced by the coupled compound plus the colored by-products. Since this is impossible, it is felt that difficulty encountered in extracting the coupled compound prevented complete extraction. It seems quite feasible that the curves would coincide if a more accurate method were used. For future study, it is suggested that the rate of decomposition be followed by measuring the amount of nitrogen evolved.

The apparent peak and then decrease in the formation of colored by-products, as shown by the graphs of runs # 3 and #4 is probably due to the use of a filter photometer in the analysis. During the reaction, the color of the solution changes so that the filter is not adequate for the color range of the entire solution. The filter apparently filters out some color produced in the later stages of the reaction. The use of a photometer with a more accurate control of wavelength would probably eliminate this trouble.

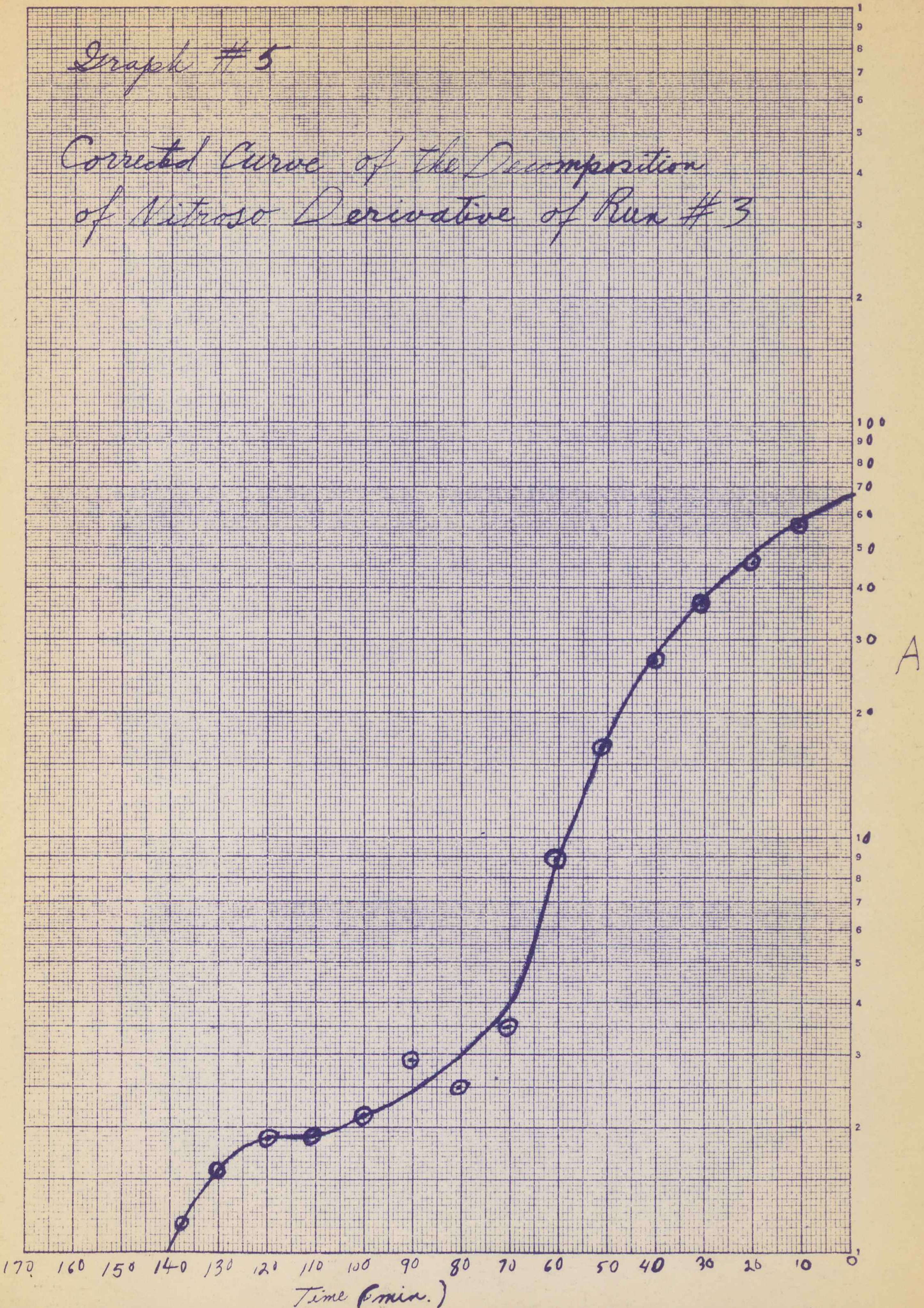
The results of runs # 3 and # 4 are significant evidence in favor of the decomposition of the nitroso derivative of N - benzoyl - o - toluidine by a free radical reaction.

Ziegler (13) and others have shown that the rate of free radical reactions are unaffected by the solvent. Hey and Waters (10) showed the decomposition of nitroacetanilide to be only slightly effected by the solvent. Hey and Waters concluded the reaction to be free radical. In run # 3 a non-polar solvent, benzene, was used while in run # 4 a very polar solvent, mixture of benzene and nitromethane, was used. The half lives were 41 minutes in benzene and 18 minutes in nitromethane - benzene, showing conclusively that the rate of reaction was uneffected. Further evidence for the hypothesis of a free radical reaction can be seen in the corrected values for run # 3. (See graph) This curve shows a slight lag at the start of the reaction. This phenomenon has been noticed with other free radical reaction.

On the basis of the preceding evidence, the following equation might be presented as the mechanism of the formation of Indazole.



The formation of the free radical is considered the rate determining step. The shape of the curves ( before the concentration of the colored by-products is sufficient to cause interference) shows the reaction follows first order kenetics and adds further support to the above hypothesis. The high reactivity of the free radical explains the formation of the multitude of by-products since the free radical can react with the solvent, unnitrosated starting material or the products formed.



Graph #5

Corrected Curve of the Decomposition of Nitroso Derivative of Run #3

## Summary

1. Increasing the solvent to solute ratio inhibits the nitrosation of N-benzoyl-o-toluidine.

2. The nitroso derivative of N-benzoyl-o-toluidine decomposes very slowly at 0° C. making storage and drying possible.

3. A polar solvent decreases the yield of Indazole.

4. The mechanism of the decomposition of the nitroso compound is believed to be free radical on the basis of:
   a - No appreciable change of rate by change of solvents.
   b - A slight induction period at the start of the reaction.

5. The decomposition of the nitroso derivative of N-benzoyl-o-toluidine decomposes according to first order kinetics.

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