THE ISOTOPE EFFECT OF TRITIUM
IN THE SYNTHESIS OF p-NITROBIPHENYL
BY THE GOMBERG COUPLING

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PREFACE

The reaction of an aromatic molecule with a diazonium salt to form a biaryl has been shown to be a free radical reaction (7). The isotope effect in such a free radical reaction has not been measured. The purpose of the research presented in this paper was to show whether or not an isotope effect exists in the reaction of a diazonium salt with benzene-t and if it exists to measure it.

HISTORICAL

The Gomberg Reaction

The synthesis of biaryls by the reaction of an aromatic hydrocarbon with a diazonium salt was developed by Gomberg. Originally he prepared dry benzenediazonium chloride and treated it with benzene (5). Since dry diazonium chlorides are explosive the reaction is conducted preferably in sodium hydroxide solution (6). Hodgen and Marsden (8) used the dry diazonium chloride but stabilized it with naphthalene-1-sulfonic acid. Increased yields were found. Elks, Haworth and Hey (3) used a water solution of the diazonium chloride with sodium acetate and obtained slightly better yields. The general equation for the reaction is:

$$\mathrm{RNNONa} + \mathrm{R'} \longrightarrow \mathrm{N_2} + \mathrm{NaOH} + \mathrm{R - R'}$$

There are three possible mechanisms for the reaction. One mechanism consists of the decomposition of the diazonium compound and its simultaneous reaction with an aromatic hydrocarbon molecule in close association with the former. There is little reason why this decomposition should take place only when a molecule of the aromatic hydrocarbon is present.

According to a second mechanism the diazonium molecule decomposes to a free radical and reacts with an aromatic hydrocarbon molecule when they come together, releasing a hydrogen atom which reacts with another free radical, as shown by the following equations:

$$\mathrm{R\cdot} + \mathrm{R'} \longrightarrow \mathrm{R - R'} + \mathrm{H\cdot}$$

$$\mathrm{R\cdot} + \mathrm{H\cdot} \longrightarrow \mathrm{RH}$$

In this case the aromatic hydrocarbon formed from the union of the free radical and the hydrogen atom would be found in the reaction products. No evidence of this compound was found in the experiments conducted.

A third possibility is that two free radicals and an aromatic hydrocarbon molecule are all in conjunction and react simultaneously to form a molecule of the biaryl and an aromatic hydrocarbon molecule.

$$R\cdot + R\cdot + R' \longrightarrow R - R' + R$$

The observation that no aromatic hydrocarbon molecule is formed from one of the free radicals tends to dispel this hypothesis.

Isotope Effect

The isotope effect has become in recent years a tool of great importance in the study of reaction mechanisms. It arises from the difference in the masses of the isotopes and is apparent in changes in equilibrium constants, rates of reactions and bond strengths. Such effects are sufficiently great to enable separation of isotopes on a large scale. Beeck, Ortvos, Stevenson and Wagner (1) found in the pyrolysis of propane that the $C^{12} - C^{12}$ bond ruptured 8% more frequently than the $C^{12} - C^{13}$ bond and obtained a higher isotope ratio in the first fraction of ethylene produced than was in the original propane. Wheeler and Pease (17) found that the relative rates of combination of protium and deuterium with ethylene to be 2.5 at 500 C., and 2 at 0 C. with a copper catalyst.

Melville (13) reports that protium and deuterium react at the same rates in the gas phase, even in reactions that have high energy of activation. If a reaction is on a surface, as in the case of the reduction of copper oxide, the greater reactivity of protium is due mainly, if not wholly, to the difference in zero-point energies of the two.

Isotope Effect of Tritium

The mass of tritium is three times that of protium, which is the largest difference of any isotopic pair. Therefore, tritium shows the largest isotope effect and can be very useful in the study of organic reactions. The usefulness is limited somewhat by the low energy of its radiations, 0.0189 Mev., and its tendency to exchange with protium atoms during a reaction. Due to these limitations, little work has been done using this isotope.

Tritium has the advantage of having a long half life, 12.5 years, disintegrating into helium-3 with the release of a beta particle. It is relatively inexpensive, being produced in the atomic pile by bombarding lithium with neutrons.

In a study of the hydrogen displacement in aromatic compounds (10), the reaction rate constant ratio of tritium to protium was unity for nitration. In sulfonation the tritium substitution was slower and the ratio was found to be 0.55 (12).

In the reduction of o- and m-nitrobenzenediazonium chloride by methanol and ethanol carrying tracer amounts of tritium, it was found that protium reacts seven times as fast as tritium (11).

Work in the field has been increasing since Wilzbach, Van Dyken and Kaplan (16) developed a method for determining tritium by ion-current measurement with a vibrating reed electrometer. Tritium is introduced into the ionization chamber as a gas and the disintegration rate measured by the radioisotope-induced ionization of the gas. Tritium in the combined state is converted into tritium gas and tritiated methane by reduction at 600°C. with zinc (15).

INTRODUCTION TO EXPERIMENTAL WORK

The object of this investigation was to measure the intramolecular and intermolecular isotope effects in the reaction of p-nitrobenzenediazonium chloride and benzene-t according to the equations given below. The intramolecular isotope effect is the ratio of reativities of a normal atom and an isotopic atom in the same molecule in a particular reaction, in this case, k_3/k_2. The intermolecular isotope effect is the ratio of reactivities of a normal molecule and an isotopically labled molecule for a particular reaction, represented in this case by $6k_1/(5k_3+k_2)$.

The reactions involved are:

$$\text{p-}NO_2C_6H_4NNCl + C_6H_6 + NaOOCCH_3 \xrightarrow{6k_1} \text{p-}NO_2C_6H_4C_6H_5 + N_2 + HOOCCH_3 + NaCl$$

$$\text{p-}NO_2C_6H_4NNCl + C_6H_5T + NaOOCCH_3 \xrightarrow{k_2} \text{p-}NO_2C_6H_4C_6H_5 + N_2 + NaCl + TOOCCH_3$$

$$\text{p-}NO_2C_6H_4NNCl + C_6H_5T + NaOOCCH_3 \xrightarrow{5k_3} \text{p-}NO_2C_6H_4C_6H_4T + N_2 + NaCl + HOOCCH_3$$

The equations which relate the rate constants to the radioactivity are:

(1) $$\frac{5k_3 + k_2}{6k_1} = 1 + \frac{\log \frac{N_1}{N_0}}{\log (1-F)}$$ (See Appendix I for derivation)

(2) $$\frac{5k_3}{6k_1} = \frac{N_2}{N_0} \quad (F \longrightarrow 0)$$ (See Appendix II for derivation)

F = fraction reacted

N_0 = molar activity of initial reactant

N_1 = molar activity of reactant at time corresponding to F

N_2 = molar activity of product

The molar activity was measured in microcuries per millimole.

It may be seen from the above equations that it is necessary to measure the extent of reaction and to isolate, purify and measure the activity of the product at one or more low extents of reaction and that of the remaining reactant at several higher extents of reaction.

The first step was to prepare p-nitrobiphenyl to study the reaction and to find suitable separation techniques. This was done by reacting p-nitroaniline with hydrochloric acid and a solution of sodium nitrite at 0°C., reacting the p-nitrobenzenediazonium chloride so formed with benzene in a sodium acetate media at 10°C. for one hour, and allowing the temperature to come to room temperature. The product was separated and purified by recrystallizing from ethyl alcohol.

Tritiated benzene was made by the Grignard method by treating phenylmagnesium bromide with tritiated water. The product was dried and distilled over sodium.

Experiments were conducted to perfect a method of measuring the extent of reaction. It was found that determination of the amount of unreacted benzene was suitable for this purpose. The water layer was partially separated from the benzene layer, and the benzene was distilled on the vacuum line. Then runs were made with normal benzene to find the extent of reaction at various times.

Runs were made with benzene-t at 10°C. to the extent of 5, 10, 60, 80, and 90% completion. In the 5% and 10% runs 50 mg. of the p-nitrobiphenyl were isolated to be assayed. In the remaining runs at least 50 mg. of benzene was recovered for assay. In each case the extent of reaction was measured by the amount of unreacted benzene. The data were then used to calculate the isotope effects in the reation.

EXPERIMENTAL WORK

Preparation of p-Nitrobiphenyl

One quarter mole of p-nitroaniline, with 80 ml. of hydrochloric acid (d. 1.16) and 90 ml. of water, was diazotized at 0°C. by the dropwise addition of one quarter mole of sodium nitrite in water solution. The mixture was continually stirred.

The diazonium compound was filtered through a cotton plug into a round-bottom flask containing 25 ml. of benzene and 25 g. of sodium acetate in 115 ml. of water. The mixture was stirred vigorously. A temperature of 10°C. was maintained the first three hours and then it was allowed to rise slowly to room temperature and stay there for forty-eight hours.

The benzene layer was separated and the benzene distilled off. The distillation was carried up to 250°C. with nothing coming off above 85°C., indicating that no nitrobenzene (b.p. 210.9°) was formed during the reaction. The p-nitrobiphenyl remaining was then recrystallized three times from ethanol.

Thirty grams of the product was recovered which gave a theoretical yield of 60%. The colorless needles melted at 112-113°C., lit. (9) 113-114°C.

The presence of 4, 4'-dinitrobiphenyl could not be detected. Since it is not soluble in water, only slightly soluble in benzene and soluble in hot ethanol, the insoluble residue from the reaction was treated with hot alcohol. Nothing crystallized out.

Preparation of Benzene-t

Two grams of magnesium turnings, 15 ml. of anhydrous ether, and a small crystal of iodine were placed in a three-neck flask, fitted with a sealed stirrer, a separatory funnel, and reflux condenser which was fitted with a calcium chloride trap. About 4 ml. of bromobenzene were added and the mixture was heated to boiling. The reaction started and the external heating was stopped. Seventy milliliters of anhydrous ether was added. The remaining bromobenzene to a total of 25 ml. was added dropwise through the funnel.

After the reaction had ceased, one milliliter of water-t (7.12/μc/mg.) prepared by Flynn (4), 10 ml. of hydrochloric acid (d. 1.17), 5 ml. of water and finally 20 ml. additional of hydrochloric acid was added.

The ether layer was separated, washed with water, sodium hydroxide, and again with water, and dried with anhydrous calcium sulfate. Each vessel used was washed with a small quantity of benzene which was added to the ether layer. The ether was distilled away and the benzene was twice distilled from sodium. In the first fractionation a 79-80° C. cut was made and in the second all the liquid came over at 80°C.: 13.2 g. of benzene boiling at this point was obtained.

A 5-mg. sample of the benzene was weighed into an ampoule and sealed. The same was done for 5 mg. of water. The two ampoules were enclosed in an evacuated reaction tube along with 100 mg. of nickelic oxide and 1 g. of zinc. The ampoules were then broken inside the reaction tube. The tube was placed in a furnace at 625° C. for three hours for reduction of the benzene which formed hydrogen gas and methane. After cooling, the gasses were transferred to an ionization chamber by means of the vacuum line. The chamber was then filled to atmospheric pressure with methane and attached to the vibrating reed electrometer for measurement of the activity. The chamber had previously been evacuated and filled with methane and the background read.

CALCULATION OF ACTIVITY

1 curie = 3.7×10^{10} disintergrations/second

1 disintegration of tritium in methane = 3.09×10^{-17} coulombs

1 curie = 11.37×10^{-7} amperes

Resistor No. 3 = 10^{12} ohms

1 curie = 1.133×10^{6} volts

1 μc. = 1.133×10^{3} mv.

1 mv. = 0.000883 μc.

As only a portion of the gas (1/F) is transferred to the chamber a correction must be made. It is:

$$F = \frac{291.1 - \frac{\text{weight of tube}}{2.5}}{256.1}$$

Therefore:

$$\text{μc./mg.} = \frac{\text{mv.} \times 0.000883 \times F}{\text{weight of sample (in mg.)}}$$

Three determinations of the activity of the benzene-t were made. The average was 1.134 μc./m mole. Since 13.2 g. of benzene was produced, the activity yield was 494 μc., being 6.9% of the starting activity.

Reaction Kinetics

Runs were made synthesizing normal *p*-nitrobiphenyl, both to gain some idea of the kinetics of the reaction and to determine the time needed to reach the extents wanted. The following method was used in each case.

In a 50-ml. beaker 0.69 g. of p-nitroanaline with 0.16 ml. of hydrochloric acid (d. 1.16) was diazotized with an excess of sodium nitrite at approximately 0°C. About 1 ml. of benzene was placed in a previously weighed reaction vessel (a lengthened 19/22 standard-taper joint with a test tube bottom). The vessel with the benzene in it was then weighed. A solution of 0.5 ml. of sodium acetate in 2.3 ml. of water was added to the benzene and the vessel was placed in a constant temperature bath maintained at 10°C.

The diazonium solution was poured into the vessel and a stirrer was started. The reaction was allowed to go for various lengths of time. The stirrer was removed and the vessel was connected to an apparatus consisting of an outer 19/22 standard taper joint, a stopcock and an inner 19/38 standard taper joint. Most of the water layer was drained off through the stopcock and then the apparatus was connected to the vacuum manifold.

The benzene was distilled through anhydrous calcium sulfate into a previously weighed vessel. This vessel with the benzene was then weighed. The difference in the amount of benzene recovered and of that originally present divided by the latter gave the extent of the reaction.

Table I gives the results of the runs made with normal benzene. In one run the above procedure was carried out except that the sodium nitrite was omitted so as not to allow the reaction to proceed. Of 0.9786 g. of original benzene, 0.9781 g. was recovered after running for 4 hours, thereby demonstrating that the method of measuring the extent of reaction was valid.

The data in Table I were analyzed in order to determine the order of the reaction and the magnitude of the reaction rate constant. As

TABLE I

Reaction of p-Nitrobenzenediazonium Chloride with Benzene

Run	Time (Hours)	Extent of Reaction (%)	Ratio of Benzene to Diazonium Chloride
		Benzene	
1.	40.17	97.6	1:1
2.	26.00	90.7	1:2
3.	15.00	87.7	1:0.5
4.	13.00	86.6	1:1
5.	2.50	55.6	1:1
6.	2.42	55.0	1:1
7.	1.50	45.9	1:1
		Benzene-t	
I.	17.00	87.8	1:1
II.	8.75	79.9	1:1
III.	4.25	65.7	1:1
IV.	4.00	60.4	1:1
V.	0.58	12.8	2:1
VI.	0.25	5.6	2:1

Zero order to about 45% with a rate constant of 4.62×10^{-5} moles/minute, intermediate to about 87.5%, first order after 87.5% with a rate constant of 7.25×10^{-5} /minute.

would be expected in a reaction between two immiscible liquid phases the reaction was of zero order in the early stages and became first order with respect to the benzene later. The transition between orders began at about 45% of reaction and became definitely first order about 85%. The zero order is due to the constant surface area between the two phases; as more of the benzene is lost in reaction, it is probable that the stirring begins to force more and more of it in droplet form through the water phase and at high extents of reaction all of the benzene is in this droplet form which is proportional to the concentration of the benzene remaining, thereby causing the reaction to be first order with respect to benzene. The concerntration of the water phase does not decrease during the reaction since it is not a reactant.

The zero order rate constant was found to be 4.62×10^{-5} moles/minute and the first order rate constant was 7.25×10^{-5} /minute.

Reaction of Benzene-t with p-Nitrobenzenediazonium Chloride at 10°C.

The reactions with benzene-t were run in the same manner as those described above with benzene. The long runs were made to 87.8%, 79.9%, 65.7% and 60.4% completion. Five-milligram samples of the recovered benzene from each run were placed in ampoules and the specific activities were measured and recorded in Table II. These activities were used in the formula:

$$\frac{k_2 + 5k_3}{6k_1} = 1 + \frac{\log \frac{N_1}{N_0}}{\log (1-F)}$$

and the ratio was calculated. The results were listed in Table III.

TABLE II

Reaction of p-Nitrobenzenediazonium Chloride with Benzene-t

Run	Extent of Reaction (%)	Activity of Benzene-t (μc/mmole)	Activity of p-Nitrobiphenyl (μc/mmole)
I.	84.8	1.69	
II.	79.9	1.62	
III.	65.7	1.45	
IV.	60.4	1.36	
V.	12.8		0.873
VI.	5.6		0.852
Original		1.13	

TABLE III

Ratios of Reaction Rate Constants

Run	Extent of Reaction (%)	$\frac{k_2 + 5k_3}{6k_1}$	$\frac{5k_3}{6k_1}$
I.	87.8	0.808	
II.	79.9	0.766	
III.	65.7	0.771	
IV.	60.4	0.812	
V.	12.8		0.772
VI.	5.6		0.745
Extrapolation	0.0		0.724

Reactions were run to 12.80% and 5.61% of completion. The reaction vessel was washed with benzene to dissolve the p-nitrobiphenyl. The benzene was evaporated on a water bath. The product was recrystallized from hot ethanol in ten-millimeter centrifuge tubes. The crystals formed on cooling were separated by centrifuging. Recrystallization continued until the crystals melted at exactly 113° C. Five-milligram samples of the product were placed in preweighed boats and the activities were measured by the same method used for benzene-t. The specific activities were listed in Table II. These activities were used in the formula:

$$\frac{5k_3}{6k_1} = \frac{N_2}{N_0} \qquad (\text{as } F \longrightarrow 0)$$

The ratios were calculated and extrapolated to 0% reaction. The results were recorded in Table III.

Limits of error at the 95% confidence level were calculated for the values of $(k_2 + 5k_3)/6k_1$ as outlined by Snedecor (14). These results are found in Table IV. The limits for the value of $5k_3/6k_1$ extrapolated to 0% reaction, also recorded in Table IV, were found by combining the high and low values of the activities of the p-nitrobiphenyl at the low extents of reaction in the most imfavorable way.

TABLE IV

Calculation of Limits of Ratio of Reaction Rate Constants at 95% Confidence Level

$\frac{k_2 + 5k_3}{6k_1}$	$X-\bar{X}$	$(X-\bar{X})^2$
0.808	0.019	0.00036
0.766	-0.023	0.00053
0.771	-0.018	0.00032
0.812	0.023	0.00053
3.157	0.000	0.00174

$\bar{X} = 0.789$

$S^2 = 0.00174/3 = 0.00058$

$S = 0.0243$

$S_{\bar{X}}^2 = 0.00058/4 = 0.00015$

$S_{\bar{X}} = 0.0122$

For d.f. = 3 and t at 95% confidence

The limit is: 3.182 x 0.0122 = 0.0388

$$\frac{k_2 + 5k_3}{6k_1} = 0.789 \pm 0.039$$

$$\frac{5k_3}{6k_1} = 0.724 \pm 0.011$$

RESULTS

TABLE V

Ratios of Reaction Rate Constants at 95% Confidence Level

$$\frac{k_2 + 5k_3}{6k_1} = 0.789 \pm 0.039$$

$$6k_1/(k_2 + 5k_3) = 1.265 \pm 0.053$$

$$\frac{k_3}{k_1} = 0.870 \pm 0.013$$

$$\frac{k_1}{k_3} = 1.15 \pm 0.02$$

$$\frac{k_3}{k_2} = 2.23 \pm 1.55$$

$$\frac{k_1}{k_2} = 2.56 \pm 1.77$$

DISCUSSION OF RESULTS

The lack of any nitrobenzene and 4, 4'-dinitrobiphenyl produced during the reaction aids in establishing the credibility of the mechanism of the simultaneous formation of a free radical and coupling. The orders of the reaction found shed no light on this question as they seem to be dependent on the surface area only.

The increase in activity of the benzene as the reaction shows the presence of an isotope effect. The value of k_3/k_1 was obtained by extrapolation from the 5.6% and 12.8% reactions, this value was 0.870 ± 0.013. The ratio k_1/k_3 becomes 1.15 ± 0.02, which indicates a 15% secondary isotope effect which is in agreement with other known values of the secondary isotope effect of tritium, for example, 15% in the decomposition of 2-p-nitrophenylethyl-2-t-trimethylammonium iodine (4) and 16% in the acid chromate oxidation of benzyl-α-t alcohol (9a).

Using the value of 0.789 ± 0.038 for $(k_2 + 5k_3)/6k_1$, the value of the intermolecular isotope effect is 1.265 ± 0.053. Using this value and the value for k_3/k_1, the value of the ratio k_1/k_2 was found to be 2.56 ± 1.77, and the intramolecular isotope effect, k_3/k_2, was found to be 2.23 ± 1.55, all at the 95% confidence level.

These ratios indicate that the rate of reaction of benzene-t with p-nitrobenzenediazonium chloride in sodium acetate at 10°C. is different from the normal compound. The accepted theory of the isotope effect is that these differences are caused by the bond of the hydrogen atom being broken in the rate-determining step. This shows that if in the mechanism for this reaction a free radical is formed by decomposition of the diazonium compound as a separate step, it is not the rate-determining step.

SUMMARY

The tritium isotope effect in the reaction of p-nitrobenzenediazonium chloride with benzene-t in a sodium acetate solution at 10°C. has been measured. The normal molecule reacts 1.265 times as fast as the labeled molecule. A protium atom on a tritiated benzene molecule reacts 2.23 times as fast as a tritium atom on the same ring. A protium atom on an unlabeled benzene molecule reacts 1.15 times as fast as one on a labeled molecule.

These differences in the rate of reaction establish that the rate-determining step is the breaking of a bond between a hydrogen atom and a carbon atom in the benzene ring.

APPENDIX I

Derivation of First Rate Equation

A = conc. of benzene at time t
A_0 = initial conc. of benzene
B = conc. of benzene-t at time t
B_0 = initial conc. of benzene-t

$$-\frac{dA}{dt} = 6k_1 A$$

$$-\frac{dB}{dt} = k_2 B + 5k_3 B$$

$$\frac{dA}{dB} = \frac{6k_1 A}{(k_2 + 5k_3)B}$$

$$(k_2 + 5k_3) \log A/A_0 = 6k_1 \log B/B_0$$

$$\frac{k_2 + 5k_3}{6k_1} = 1 + \frac{\log B/B_0}{\log A/A_0} - 1$$

$$\frac{k_2 + 5k_3}{6k_1} = 1 + \frac{\log B/B_0 - \log A/A_0}{\log A/A_0}$$

$$\frac{k_2 + 5k_3}{6k_1} = 1 + \frac{\log (B/A)(B_0/A_0)}{\log A/A_0}$$

$B/A = N_1$
$B_0/A_0 = N_0$
$A/A_0 = (1 - F)$

$$\frac{k_2 + 5k_3}{6k_1} = 1 + \frac{\log N_1/N_0}{\log(1 - F)}$$

APPENDIX II

Derivation of Second Rate Equation (2)

X = conc. of p-nitrobiphenyl at time t, formed from benzene
Y = conc. of p-nitrobiphenyl at time t, formed from benzene-t
Z = conc. of p-nitrobiphenyl-t at time t
A_0 = initial conc. of benzene
B_0 = initial conc. of benzene-t

$$\frac{dX}{dt} = k_1(A_0 - X)C$$

$$\frac{dY}{dt} = k_2(B_0 - Y - Z)C$$

$$\frac{dZ}{dt} = k_3(B_0 - Y - Z)C$$

$$\frac{dY}{dZ} = \frac{k_2}{k_3}$$

$$Y = (k_2/k_3)Z$$

$$\int_0^X \frac{dX}{k_1(A_0 - X)} = \int_0^X \frac{dZ}{k_3\left[B_0 - (k_2/k_3)Z\right]}$$

$$(k_3/k_1)\log(A_0 - X)/A_0 = -\left[1/(1 + k_2/k_3)\right]\log\left[B_0 - (1 + k_2/k_3)Z\right]/B_0$$

$$Z/B_0 = 1 - \left[(1 - X/A_0)^{k_3(1+k_2/k_3)/k_1}\right] /(1 + k_2/k_3)$$

$$N_2 = Z/X$$

$$N_0 = A_0/B_0$$

$$N_2/N_0 = 1 - \left[(1 - X/A_0)^{k_3(1+k_2/k_3)/k_1}\right] /(1 + k_2/k_3)X/A_0$$

If X/A_0 is very much smaller than one, then the first two terms of an expansion should be accurate.

$$N_2/N_0 = k_3/k_1$$

BIBLIOGRAPHY

1. Beeck, O., Ortovos, J.W., Stevenson, D.P., and Wagner, C.D., J. Chem. Phys., 16, 255 (1948).

2. Bigeleisen, J., Science, 110, 14 (1949).

3. Elks, J., Haworth, J.W., and Hey, D.H., J. Chem. Soc., 1940, 1285.

4. Flynn, J.J., Master of Science Thesis, 1955, Stillwater, Oklahoma Agricultural and Mechanical College.

5. Gomberg, M., and Bachmann, W., J. Am. Chem. Soc., 46, 2339, (1924).

6. Gomberg, M., and Parnert, S., J. Am. Chem. Soc., 48, 1372, (1926).

7. Hey, D.H. and Walters, W.A., Chem. Rev., 21, 178 (1937).

8. Hodgson, H. and Marsden, E. E., J. Chem. Soc., 1940, 208.

9. Hodgman, C.D., "Handbook of Chemistry and Physics," 33rd ed., 1951, Cleveland, Chemical Rubber Pub. Co.

9a. Hodnett, E.M., Private Communication.

10. Melander, L., Arkiv Kemi, 2, 213-92 (1950).

11. Melander, L., Arkiv Kemi, 3, 525-538 (1951).

12. Melander, L., Arkiv Kemi, 6, 219-299 (1953).

13. Melville, H.W., Nature, 133, 947 (1934).

14. Snedecor, G.W., "Statistical Methods," 4th ed., 1950, Ames, Iowa State College Press.

15. Wilzbach, K.E., Kaplan, L., and Brown, W.G., Argonne National Laboratory Report 5056 (1953), Science, 118, 522 (1953).

16. Wilzbach, K.E., Van Dyken, A.R., and Kaplan, L., Anal. Chem., 26, 880 (1954).

17. Wheeler, A. and Pease, R.N., J. Am. Chem. Soc., 58, 1665 (1936).

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THESIS TITLE: THE ISOTOPE EFFECT IN THE SYNTHESIS OF
p-NITROBIPHENYL BY THE GOMBERG COUPLING

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