ISOTOPE EFFECT OF TRITIUM IN THE EQUILIBRIUM REACTION BETWEEN *p*-NITROPHENYLACETIC ACID AND WATER-*t*

By

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INTRODUCTION

The study of isotope effect in chemical reactions, though of recent interest, has become an important tool in the determination of reaction mechanisms as well as other pertinent data. Its effect on reactions involving the isotopes of carbon and hydrogen is in many cases considerable and cannot be ignored.

It is of considerable advantage to make use of this tool in equilibrium studies since calculations are simplified and the mathematics involved in treating the effect of a transition state are avoided.

This research was done to determine the presence of an isotope effect if present and to measure that effect in the equilibrium exchanges involving the reaction of p-nitrophenylacetic acid and tritiated water and of carbon-14 labeled benzophenone with its phenylhydrazone.

HISTORICAL

Exchange Reactions

Exchange reactions have, within the last several years, played an important part in the study of reaction kinetics. Several men have published treatments of this problem (3, 4, 6, 7, 9, 10).

In much of this early work the assumption was made that the effect of isotopic substitution on the reaction rate was negligible, i.e. the isotope effect could be ignored. This assumption, while generally justifiable for the heavy elements, introduced a few discrepancies for the lighter elements regarding both equilibrium distribution (13) and specific reaction rate (2). Studies with carbon-14 for instance showed an isotope effect of the order of 10 percent in comparison with carbon-12 in certain reactions (11, 12).

Isotope Effect

The isotope effect is an important tool in the determination of organic reaction mechanisms. It arises from the difference in the masses of the isotopes and is apparent in changes in the equilibrium constants, rates of reaction and bond strengths. Beeck *et al* (1) found in the pyrolysis of propane that the $C^{12}-C^{13}$ bond ruptured 8 percent more frequently than the $C^{12}-C^{12}$ bond and obtained a higher isotope ratio in the first fraction of ethylene produced than was present in the original propane.

Yankwich and Calvin (17) have observed that when malonic acid labeled with carbon-14 in one carboxyl group is partially decarboxylated the carbon dioxide evolved is depleted of carbon-14 while the remaining acetic acid is enriched.

Isotope Effect of Tritium

Tritium is produced in the atomic pile through the bombardment of lithium with neutrons. It has a half life of 12.5 years and disintegrates into helium-3 with the release of a beta particle.

The masses of tritium and protium have a ratio of 3 to 1, the largest ratio shown by any pair of isotopes. Tritium shows the largest known isotope effect and should be very useful in the study of organic reactions. Because of the low energy of its radiation, 0.0189 Mev., and the possibility of exchange with hydrogen atoms during a reaction, not much work has been done using tritium.

Improved methods of analysis have allowed for considerable increase in work in that field. Wilzbach, Van Dyken and Kaplan (15) have developed a method for the determination of tritium by ion-current measurement with the vibrating reed electrometer. The tritium is introduced into the ionization chamber as a gas and the disintegration rate measured by the radiation-induced ionization of the gas. Tritium in the combined state is converted into tritium gas and tritiated methane by reduction at 615° with zinc (16).

Reaction Kinetics

In an equilibrium reaction, the exchange of isotopic atoms between two substances follows first-order kinetics provided no chemical reactions disturb the system, there is no isotope effect, and the exchanging atoms are chemically equivalent within either substance.

Harris (5) and later Melander (8) have treated the case when appreciable isotope effects are involved, and concluded that the exchange kinetics approximate the first order even in this case, if the relative concentration of the distinguishable isotope is small enough. This approximation is probably justified in almost all work with radioactive tracers such as tritium or carbon-14.

In a particular system two kinds of molecules, A and B are assumed to be present in constant macroscopic amounts, and in the same homogeneous phase. Some atom or other entity will pass from A, where it is present in a molar amount a, with a constant rate measured in molar amount per unit of time, and at the same time a corresponding amount will be transferred in the opposite direction, from B where it is present in molar amount b, to A. The rate is assumed to be R for ordinary entities.

The very small fractions of tracer atoms in A and B are denoted by y and z respectively, and at the time origin, we have $y=y_0$ and $z=0$.

The isotope effect for the transfer A=B is denoted by α and that for the transfer B=A by β. The transfer rate in molar amounts of the distinguishable species will then be $y\alpha R$ and $z\beta R$, respectively. Then we have

$$ya + zb = y_0a$$

and

$$-\frac{d(ya)}{dt} = y\alpha R - z\beta R.$$

or

$$\frac{dy}{dt} = \frac{R}{ab}(\beta a y_0 - (\beta a+\alpha b)y).$$

Integration of this expression gives

$$\frac{y}{y_0} = \frac{\beta a - \alpha b e^{-\frac{(\beta a+ab)Rt}{ab}}}{\beta a - \alpha b}$$

It follows that for infinite time $z_\infty/y_\infty = \alpha/\beta$, this constant determining the isotope distribution at equilibrium. Should there be no isotope effect, the ratio α/β, would equal 1.

The fractional exchange, $(y_0 - y)/(y_0 - y_\infty) = F$, is a useful quantity, and the following simple relation holds:

$$-\ln(1 - F) = \frac{\beta a+\alpha b}{ab} Rt$$

A plot of $-\ln(1 - F)$ versus time gives a straight line with the slope equal to the quantity $\beta a+\alpha bR/ab$.

DISCUSSION OF PROCEDURE

The procedure followed in the following research work might be outlined simply as 1) performance of the reaction, 2) separation and combustion of one of the products to a gaseous state and 3) assay of the gaseous sample for radioactivity.

The reaction itself involved reacting the substances under consideration at constant temperature for a measured length of time. Weighed portions of the substances were dissolved in a suitable solvent along with a catalyst. This solution was then apportioned into several small reaction tubes, usually about 1 ml. of solution to each tube. The tubes were then immersed in a liquid nitrogen bath to freeze the contents following which, the tubes were sealed and placed in a constant temperature bath. The tubes were then withdrawn successively from the bath at some predetermined time and an assay performed on one of the reacting components to determine its activity. An idea of the amount of reaction performed per unit time could thus be obtained.

The procedure followed in preparation for assay was as follows. The reaction tube was broken open, and placed in a receptacle attached to a vacuum line distillation apparatus.

The receptacle was then immersed in a liquid nitrogen bath and the contents of the reaction tube frozen. The distillation line was then evacuated. Use of a mercury diffusion pump in series with a regular oil vacuum pump assured pressures of as low as 2 - 3 microns. When a sufficiently low pressure had been attained the distillation line was shut off from the remainder of the vacuum line, and the nitrogen bath moved to another part of the distillation apparatus equipped with a trap to collect the more volatile substances present in the solution to be distilled.

After completion of the distillation the solid left after distillation was removed from the line and washed with acid and then with distilled water. It was then dried, either in a desiccator or in a drying pistol.

If the compound to be assayed contained carbon-14, an oxidation was performed by the action of Van-Slyke solution. The oxidation was done in a closed system upon which a vacuum could be obtained. Carbon dioxide given off during the reaction was collected in a evacuated ionization chamber which was subsequently filled with dead carbon dioxide to atmospheric pressure.

Where tritium was the isotopically active constituent present, the compound was reduced in a sealed break off tube in which were also placed a small glass ampule containing 5-10 mg. water, 0.1 g. zinc and 1 g. nickelic oxide.

The tube and contents were then placed in an electric furnace for three hours at a temperature of 615°.

Following reduction the methane and hydrogen gases formed were expanded into an ionization chamber previous to assay.

Counting of the radioactivity present was done on a vibrating reed electrometer which gives results on a strip chart in millivolt readings. These millivolt readings were then converted to microcuries per millimole, a more usuable form. The equation involved in the conversion makes use of the definition of a curie, the size of the resistance used in the vibrating reed, the number of coulombs per disintegration of the carbon-14 or tritium isotope as well as the fraction of gases formed during combustion that is actually expanded into the ionization chamber. An example of the above equation is given in the experimental section.

Use was made of the equilibrium activity in determining the presence of an isotope effect. Here it was assumed that after the reaction had progressed through seven or eight half-lives, it had sufficiently approached equilibrium and that activity could be used as such. The half-life was gotten from a plot of -ln(1 - fraction reacted) versus time as well as an experimental approximation of the equilibrium activity.

EXPERIMENTAL WORK

Selection of a Reaction Solvent.

It was found that benzophenonephenylhydrazone and its homolog, the 2, 4-dinitrophenylhydrazone were only sparingly soluble in ethanol. The two were soluble in concentrated sulfuric acid as well as acetic acid, but tended to decompose particularly at temperatures above room temperature. Benzene, in which the phenylhydrazone was particularly soluble was finally selected as the solvent.

Experiment 1. Performance of an Equilibrium Reaction between Benzophenone and its Phenylhydrazone using Acetic Acid as a Catalyst.

Three milliliters of a solution of benzophenone (1.50 m moles) labeled at the carbonyl with carbon-14 and benzophenonephenylhydrazone (1.50 m moles) in benzene were apportioned into five reaction tubes. Concentrated acetic acid was present as a catalyst in the amount of five per cent by weight.

The five tubes were placed in an oil bath equipped with a stirrer, an immersion heater and a thermoregulator set so as to maintain a constant temperature of 70°. The tubes were withdrawn from the bath at 1, 2, 4, 8 and 16 hours respectively.

Separation of the constituent parts of the solution was done by distillation under vacuum. The benzene and acid were distilled off and collected in a U-tube attached to the vacuum line and immersed in a liquid-nitrogen bath (-195°). The benzophenone, being quite volatile is carried with them. Assay of the remaining phenylhydrazone was performed to determine the presence of radioactivity.

Oxidation of the phenylhydrazone and collection of the carbon dioxide gas given off are performed by wet combustion. The oxidizing mixture consisted of a solution containing 20 g. of potassium iodate and 100 g. of chromic acid to which was added 668 g. (400 ml.) of 85 per cent phosphoric acid. To this was added 1330 ml. of 20 per cent fuming sulfuric acid. The carbon dioxide given off during the oxidation reaction was swept into an evacuated ionization chamber by passing dead carbon dioxide through the system. Stannous chloride and lead peroxide traps were situated in the line to trap any water vapor and oxides of nitrogen present. The sweeping of the line by dead carbon dioxide was continued until the chamber was filled to atmospheric pressure.

Assay of the gaseous samples on a vibrating reed electrometer showed no appreciable values above the background count of the chamber and no general increasing trend from the one-hour to the sixteen-hour sample.

Experiment 2. Performance of an Equilibrium Reaction using Aluminum tert.-butoxide as a catalyst.

The previous experimental reaction was repeated reacting carbon-14 labeled benzophenone (1.5 m moles) with its phenylhydrazone (1.5 m moles), substituting aluminum tert.-butoxide (o.1300 g.) as a catalyst. Benzene was again used as the solvent. Samples were withdrawn at 2, 4, 8, 16, 32, 48, 72 and 96 hours respectively.

Each sample was distilled under vacuum to separate the phenylhydrazone. It was then warmed in 50 per cent acetic acid and the recrystallized from ethanol.

Combustion and collection of the carbon dioxide gas was carried out as before. The values obtained on the vibrating reed for even the 96-hour samples showed no appreciable isotopic exchange.

Preparation and Assay of Tritiated Water.

Water-t was prepared by passing tritium (100 mc.) over hot copper oxide wire (300°). The reaction was carried on in a closed vacuum line and the tritium was continually recirculated through the system through the operation of a Toepler pump. The water formed in the reaction was frozen in a trap immersed in a liquid nitrogen bath. When most of the hydrogen in the system was used up, the Toepler pump was again filled with hydrogen and this was introduced into the system as before. When this hydrogen had reacted, the furnace was allowed to cool, and the stopcock on the container of water was opened. When the system had been flushed with dead water, the trap was removed, and inactive water added to the prepared water to dilute it.

A 5-mg. sample of the tritiated water was weighed into an ampoule, sealed, and enclosed in an evacuated reaction tube containing 1 g. of zinc and 100 mg. of nickelic oxide. The ampoule of water was then broken inside the reaction tube, and the tube heated to 625° for three hours. After the tube had cooled, the gas in the tube was 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 was evacuated and filled with methane to obtain a background reading.

For calculation of the activity, certain volumes were needed. These were obtained by using a bulb of known volume and applying Boyle's law. Correction was made for the varying volume of the manometer by calculating its volume per unit length.

<u>Summary of Volume Determinations</u>

Standard Bulb 210 ml.
Line Volume 60.3 ml.
Bulb Stem 6.7 ml.
Break-off Tube 104.5 ml.
No. 1 chamber 256.7 ml.
No. 2 Chamber 256 ml.
Manometer Correction 0.28 ml./cm.

Calculation of Activity

$1 \text{ curie} = 3.7 \times 10^{10}$ disintegrations/sec.

1 disintegration of tritium in methane $= 3.09 \times 10^{-17}$ coulombs

$1 \text{ c.} = 3.7 \times 10^{10} \times 3.09 \times 10^{-17}$ coulombs/sec.

$= 11.37 \times 10^{-17}$ amperes

Resistor No. 2 $= 0.96 \times 10^{10}$ ohms

$1 \text{ c.} = 11.37 \times 10^{-7} \times 0.96 \times 10^{10}$ ampere ohms

$= 10.98 \times 10^{3}$ volts

1 uc. = 10.98 mv.

1 mv. = 0.0912 uc.

The portion of the total activity of the sample which is transferred to the ionization chamber is

$$\frac{\text{Volume of chamber}}{\text{Volume of chamber} + \text{break-off tube-reaction tube}} = F$$

Therefore to find the specific activity of a sample the following expression is used:

$$\text{mv.} \times 0.0911 \times \frac{1}{F} \times \frac{1}{\text{weight (in mg.)}} = \text{uc./mg.}$$

Three determinations of the activity of the water gave an average of 7.13 mc./g.

Experiment 3. Equilibrium Reaction between p-Nitrophenylacetic acid and water-t.

Five hundred milligrams of tritiated water was added by a micropipette to a solution of p-nitrophenylacetic acid (1.88 m moles) in 1,4-dioxan and this resultant solution was diluted to 5 ml. with additional dioxan. The dioxan was originally purified by a method described by Weissberger and Proskauer (17). One milliliter of the solution was placed in each of five small reaction tubes which were subsequently sealed and then placed in an oil bath equipped with stirrer, immersion heater and thermoregulator set so as to maintain a constant terperature of 50°. The tubes were withdrawn successively over a period of twelve and one-half days.

In each case, the tube, upon removal was broken open and the water and dioxane distilled off under vacuum. A few drops of concentrated hydrochloric acid were added to the p-nitrophenylacetic acid, following which, the acid was suspended in water and then dried in a drying pistol under vacuum.

Five to ten milligrams of the acid was weighed into a small porcelain boat which was then sealed in an evacuated combustion tube along with an ampoule containing approximately 5 mg. of water, 1 g. of zinc and 0.1 g. of nickelic oxide. This tube which was equipped with a break-off point was then heated to 625° in a furnace for three hours to effect complete reduction to the tritiated hydrogen and methane.

When the combustion tube was placed in a swivel tube attached to the vacuum line, the gases were allowed to expand into an ionization chamber, which was in turn attached on a vibrating reed electrometer and the gases assayed.

The results of the assay indicated that even at the end of 302 hours, exchange was negligible so as to be almost indistinguishable from the chamber background. The results were indeed erratic and no attempt was made to evaluate them.

Experiment 4. Equilibrium Reaction between p-Nitrophenylacetic acid and water-t.

In this experiment the procedure was the same as in the previous run. However, in an attempt to speed up the reaction, the concentrations of the p-nitrophenylacetic acid and the water were increased. Five hundred milligrams of the water-t along with 1.2489 g. of acid were dissolved in 1,4-dioxan so as to give a final solution 3 ml. in volume. This solution was apportioned into five reaction tubes. The tubes were withdrawn from a bath set at 50° at intervals of 1, 2, 3, 6 and 8 days respectively.

Assay of 5-mg. samples still showed the reaction to be extremely slow proving to be less than 3 per cent of the way towards equilibrium at the end of eight days. Again, the values were hardly distinguishable from background counts.

Experiment 5. Equilibrium Reaction between p-Nitrophenylacetic acid and water-t at an elevated temperature.

Ten m moles of the p-nitrophenylacetic acid along with 500 mg. of tritiated water were reacted as before in five reaction tubes immersed in an oil bath. The reaction temperature, however, was increased to 98°. The tubes were withdrawn from the bath at 1, 2, 3, 4 and 6 days respectively.

While this reaction did approach equilibrium much more so than previous runs, the activity at 144 hours represented only a little over one half-life, not sufficient in itself to be conclusive.

Experiment 6. Determination of the Presence of Ring Substitution by Tritium on p-Nitrophenylacetic acid.

It was suggested that some substitution might be occurring on the ring which would alter the final equilibrium value.

In a reaction involving the oxidation of tritium active p-nitrophenylacetic acid by potassium permanganate, the alpha carbon and its hydrogen atoms are removed leaving p-nitrobenzoic acid. One hundred milligrams of p-nitrophenylacetic acid was dissolved in 1 -2 ml. of 1N NaOH. This was heated under reflux and potassium permanganate in 1-2 ml. of sodium hydroxide solution were added until a slight purple color remained. The solution was then filtered and the purple color discharged by the addition of sodium bisulfite. This solution was made strongly acid by the addition of concentrated hydrochloric acid. The crystals which were precipitated were then washed and dried.

The benzoic acid was reduced by the method previously explained for the phenylacetic acid. Assay of 5-10 mg. samples of the p-nitrobenzoic acid showed no activity, indicating that ring substitution had not taken place.

Experiment 7. Repeat of the Exchange Reaction using a Sodium Hydroxide Buffer.

A weighed portion of p-nitrophenylacetic acid (0.4609 g.)

was dissolved in 1,4 dioxan (2.9512 g.). To this was added water-t (0.4965 g.) and 0.25 ml. of 5N sodium hydroxide solution. This solution was apportioned into five tubes which as in previous cases were sealed and immersed in a bath set at 98°. The tubes were withdrawn at the end of 0.5, 1, 2, 4 and 24 hours respectively. Considerable decomposition had occurred in the latter tube and it was not assayed with the others.

A plot of the activities versus time showed that in contrast to previous work, the reaction had occurred at so fast a rate, that by the time the first sample had been removed from the bath at the end of 30 mins, the reaction had nearly approached equilibrium. Little or no conclusions could be drawn from the evidence.

Experiment 8. Repeat of the Exchange Reaction decreasing the Concentration of Sodium Hydroxide Buffer.

Water-*t* (2.75 m moles) and *p*-nitrophenylacetic acid (2.6 m moles) in 5 ml. of solution with 1,4-dioxan and 0.85 N sodium hydroxide (1 ml.) were reacted as before at a temperature of 98°. Samples were removed at the end of 0.5, 1, 2, 4 and 8 hours. Combustions and assays were performed on 5-10 mg. samples from each as well as on the water-dioxan distillate collected during distillation of the 8-hour sample. Again the reaction was considerably advanced before the first sample was removed from the bath.

Experiment 9. Repeat of the Exchange Reaction decreasing the Reaction Temperature.

A reaction mixture containing water-t (2.75 m moles), p-nitrophenylacetic acid (2.6 m moles) and 0.53 m mole of sodium hydroxide in 1,4-dioxan was split between five reaction tubes and immersed in a constant temperature bath set at 49°. The tubes were removed from the bath at 1, 2, 4, 8 and 20 hours respectively. Distillation, reduction and assay were performed as in all previous cases. The results were quite satisfactory, lacking only additional time to allow the reaction to proceed through several half lifes.

Experiment 10. Repeat of Experiment 9, increasing the Length of Reaction Time.

The reaction mixture of p-nitrophenylacetic acid (5.1 m moles) and water-t (5.53 m moles) was dissolved in dioxan and buffered by the addition of two milliliters of dilute sodium hydroxide (1.10 m moles) giving a total volume of 10 milliliters. The resultant solution was then apportioned into 10 different tubes which were then sealed and immersed in a constant temperature bath set at 49°. These tubes were withdrawn at various times so as to give as nearly as possible a mathematically progressive series. The times were as follows: 6, 12, 24, 48, 72, 120 and 160 hours respectively. Two tubes were withdrawn at each of the last two times mentioned.

Following the usual procedure, the solvent was distilled under vacuum, any salt separated from its acid by the addition of hydrochloric acid and the solid acid dried in a drying pistol. The samples of the acid were then weighed, reduced to methane and hydrogen and assayed for activity on the vibrating reed electrometer. An assay was also performed on the water-dioxan mixture collected during the distillation of the 160-hour samples.

RESULTS

Exchange Reaction Between *p*-Nitrophenylacetic Acid and Water-*t*.

Experiment	Time, Hrs.	Activity *p*-Nitrophenylacetic acid (uc/m mole)	1 - Fraction Reacted
5	24	6.80	0.869
	48	11.80	0.772
	72	21.98	0.576
	92	27.47	0.470
	144	39.13	0.245
7	0.5	13.52	0.333
	1	15.60	0.230
	2	15.98	0.212
	4	16.26	0.198
8	0.5	7.14	0.326
	1	8.24	0.222
	2	10.42	0.016
	4	10.45	0.014
	8	10.44	0.014
9	1	0.657	0.962
	2	1.59	0.908
	4	2.97	0.828
	8	5.46	0.684
	20	10.62	0.385
10	6	4.01	0.743
	12	5.98	0.616
	24	9.94	0.362
	48	14.02	0.110
	72	15.11	0.030
	96	15.32	0.017
	120	15.55	0.002
	120'	15.53	0.003
	160	15.56	0.001
	160'	15.57	0.001

Activity of water-*t* at equilibrium: 17.36 uc/m mole

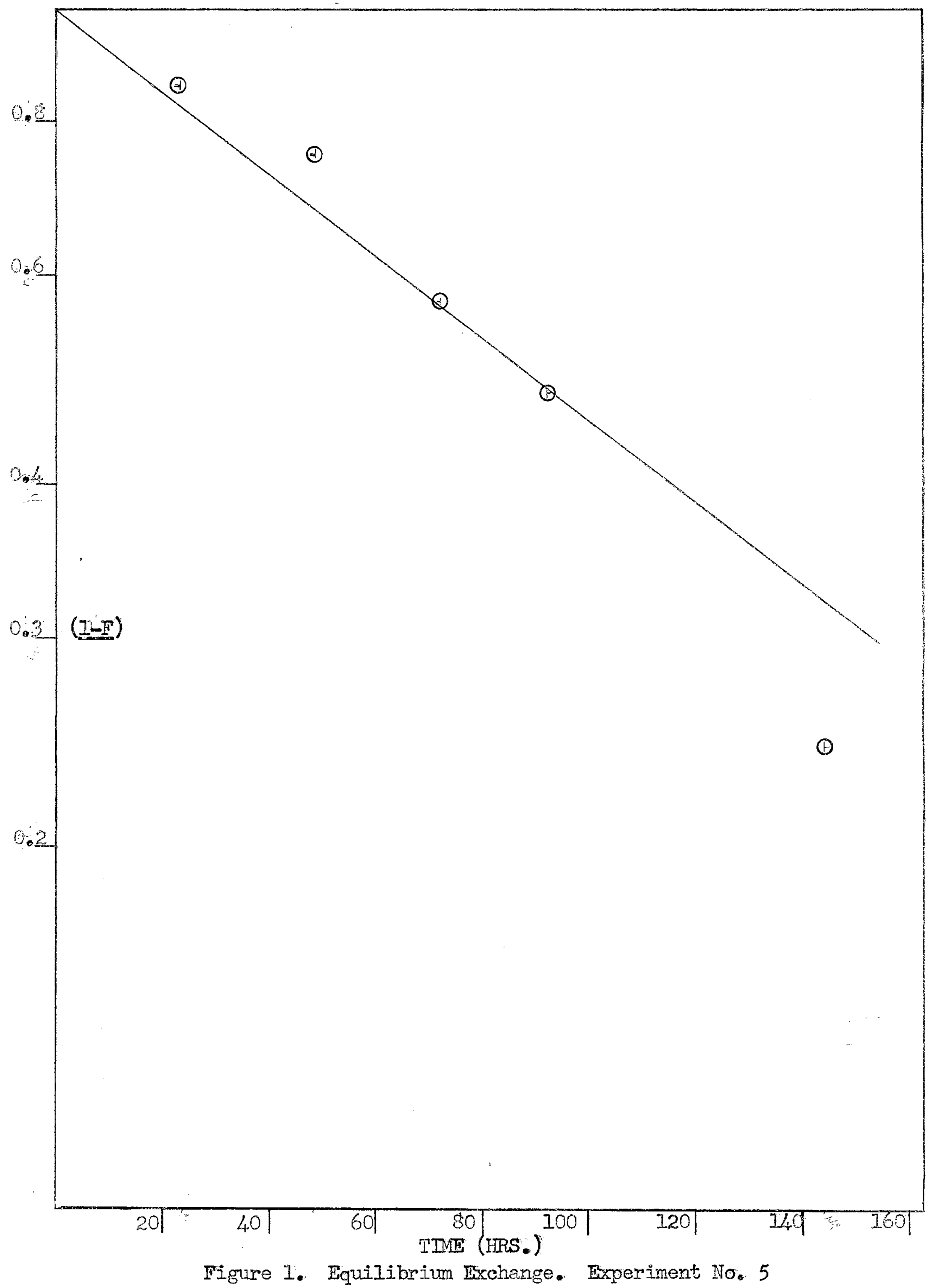

Figure 1. Equilibrium Exchange. Experiment No. 5

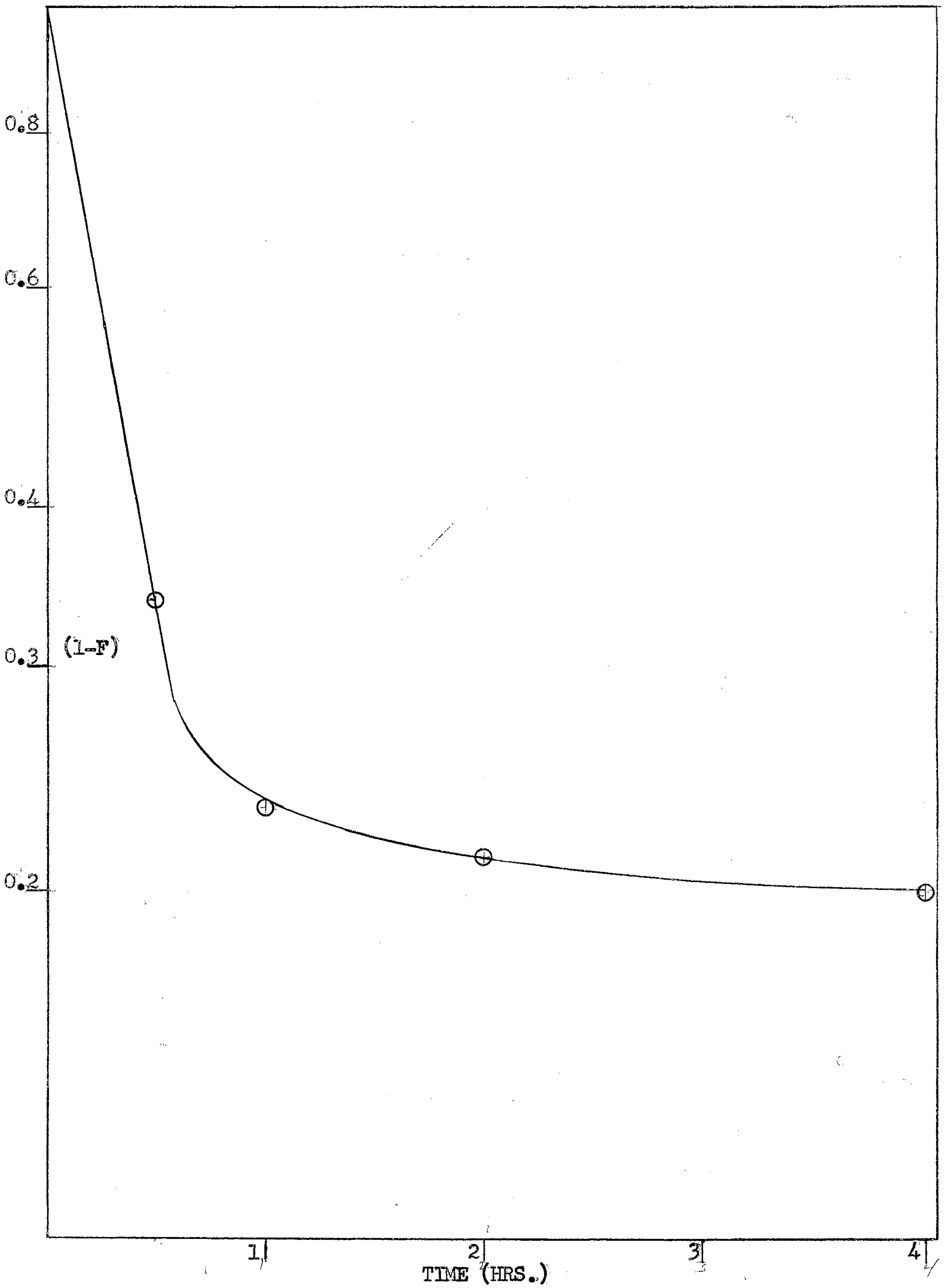

Figure 2. Equilibrium Exchange. Experiment No. 7

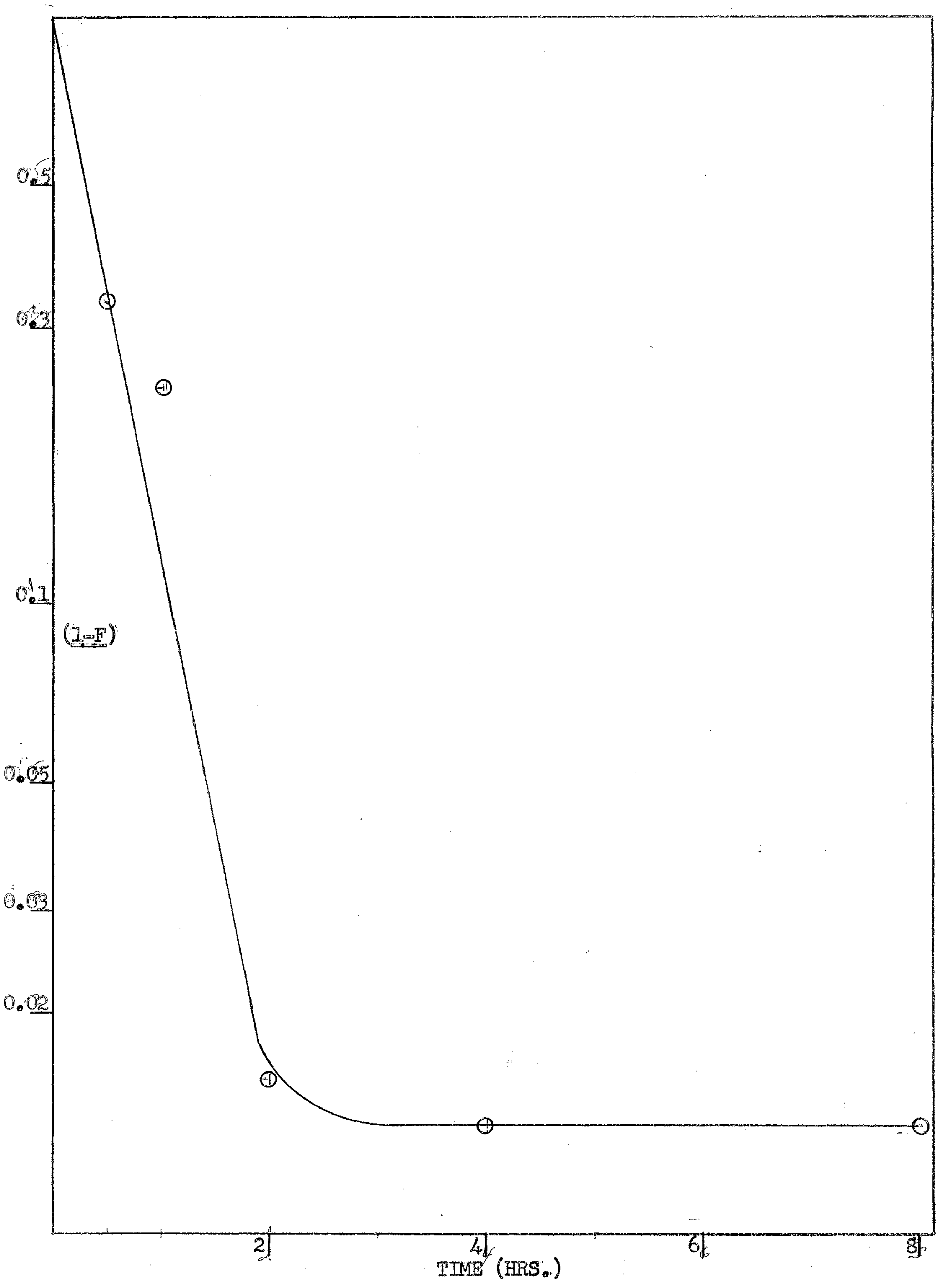

Figure 3. Equilibrium Exchange. Experiment No. 8

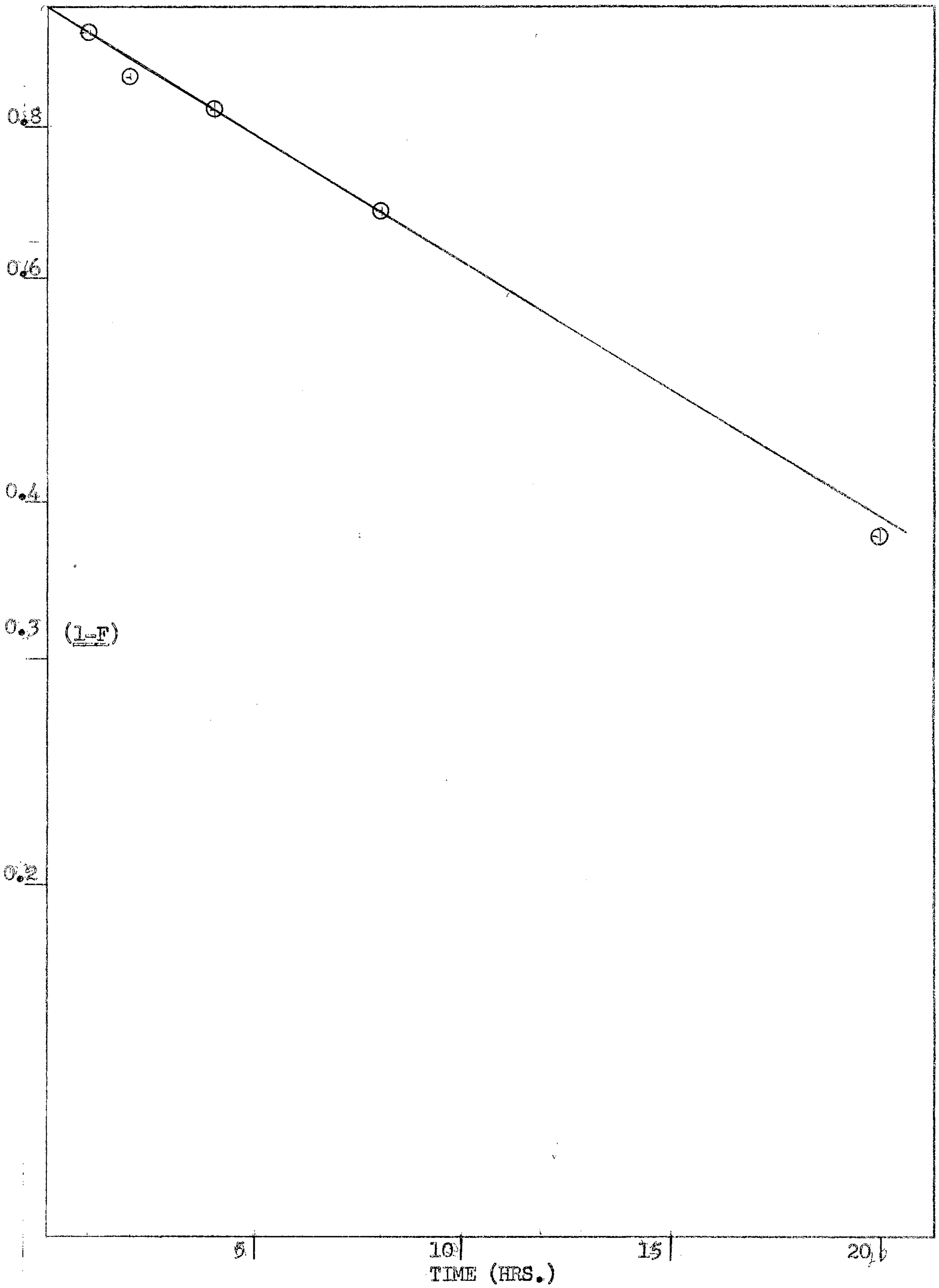

Figure 4. Equilibrium Exchange. Experiment No. 9

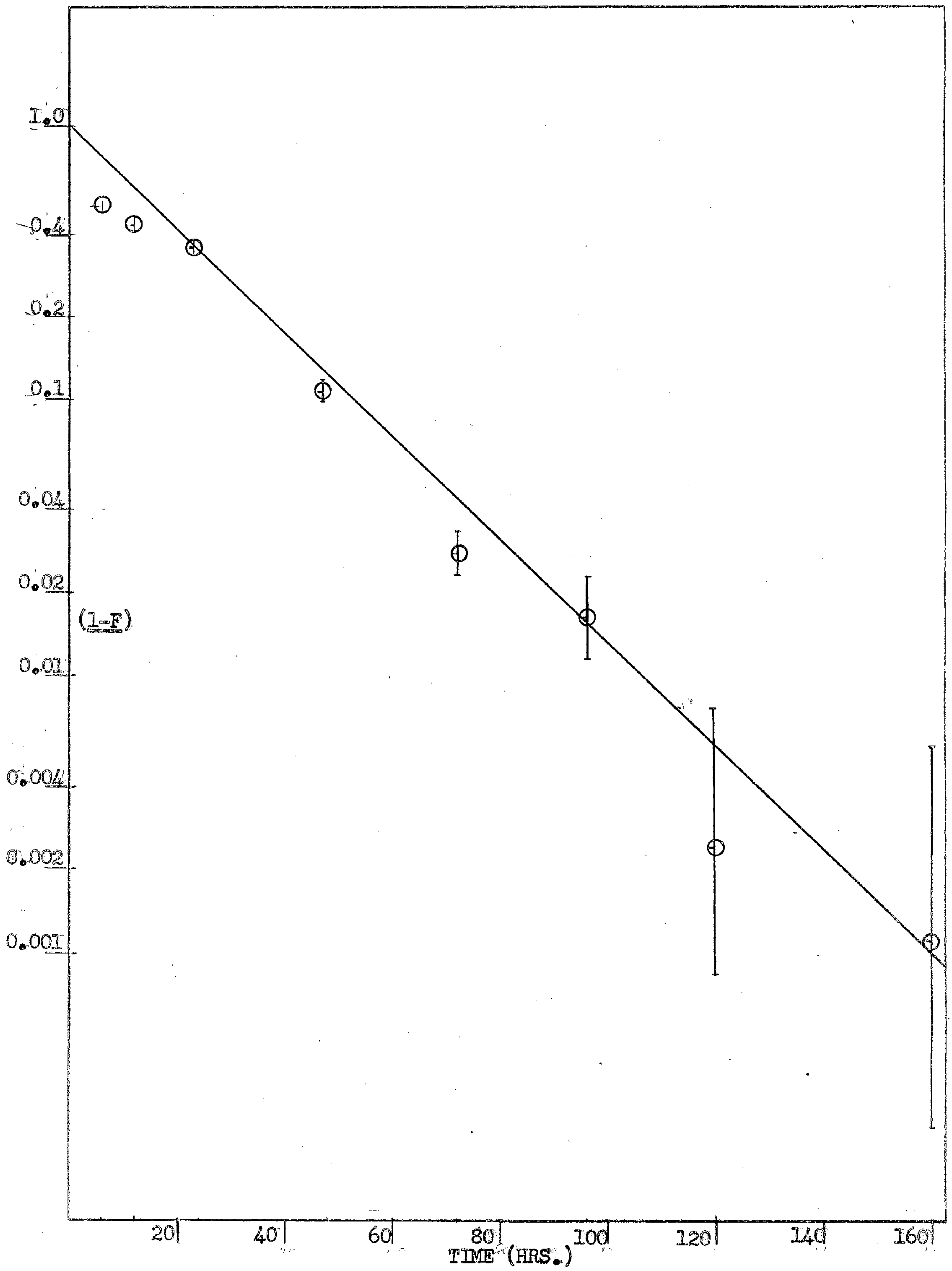

Figure 5. Equilibrium Exchange. Experiment No. 10

DISCUSSION OF RESULTS

The ratio α/β representing the equilibrium isotope distribution is shown experimentally as that ratio of the activities of the p-nitrophenylacetic acid to water-t obtained after completion of 160 hours of reaction. From the data obtained, it has a value of 0.897. This variation from $\alpha/\beta = 1$, indicates the presence of an isotope effect.

The equilibrium activity of water in the absence of an isotope effect can be calculated by considering all the activity equally divided between the hydrogen atoms of the water, that on the carboxyl group and those on the carbon adjacent to the carboxyl group. Since there are two replaceable hydrogen atoms at the alpha carbon of p-nitrophenylacetic acid, the following quantities hold for the last experiment:

Total m moles of active hydrogen	353.05
Activity of water	3036.7 uc/g
Weight of HOH-t present	0.9989 g

$$\frac{(3036.7 \times 0.9989)\,2}{353.05} = 17.18 \text{ uc/ m mole.}$$

Experimentally, the reaction tended to approach an equilibrium value of 15.58 uc/m mole. This represents the fraction of tracer atoms present in the acid at infinite time and the fraction of tracer atoms present in water at infinite time is represented by the value obtained from assay of the water distilled off the 160-hour sample. We then have:

$$\frac{z_\infty}{y_\infty} = \frac{\alpha}{\beta} = \frac{15.58}{17.36} = 0.897$$

This, then, is the isotopic equilibrium distribution.

A study of the plot of -ln(1 - Fraction reacted) versus time gives a half life of 14.5 hours.

SUMMARY

The rate of exchange of tritium atoms between tritiated water and the alpha hydrogen atoms of p-nitrophenylacetic acid in dioxane solution has been measured. The exchange rate is greater when part of the acid is neutralized with base. Water-t (17.36 uc./m mole) is in equilibrium at 49° with p-nitrophenylacetic acid (15.58 uc./m mole); the equilibrium isotope effect is 0.897.

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