

THE EQUILIBRIUM ISOTOPE EFFECT IN THE  
REACTION BETWEEN BENZOPHENONE-  
CARBONYL-C<sup>14</sup> AND BENZHYDROL

By

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## INTRODUCTION

Study of the isotope effects in chemical reactions has provided much valuable information for the research chemist. Isotope effects are important in organic chemistry in the determination of reaction mechanisms. The isotope effect in reactions involving carbon and hydrogen atoms is in many cases considerable and cannot be neglected.

A great advantage to the use of this powerful tool in the study of equilibrium isotope effects is its simplicity in theoretical calculations since the mathematics involved in the treatment of a transition state are avoided.

The objectives of this work are as follows:

1. To measure the rate of the reaction between benzhydrol and benzophenone-carbonyl- $C^{14}$ .
2. To determine the equilibrium isotope effect of this reaction and to compare it with the theoretically calculated effect.

## HISTORICAL

### The Isotope Effect

The isotope effect is any difference between two molecules which contain two different isotopes, but are otherwise identical. The isotope effect arises from the difference in the masses of the isotopes. It would be expected that such properties as chemical equilibrium constants and reaction rate constants could be affected.

The isotope effect is usually small, a fact which is indicated by the almost constant isotopic composition of the elements in the earth's crust and the difficulty of isotope separation by chemical methods. However, isotopes of the lighter elements have been partially separated by chemical methods, and kinetic isotope effects have been measured for various reactions of these elements. Therefore, the isotope effect should always be considered when radioactive isotopes of the lighter elements are used as tracers.

### Exchange Reactions

Exchange reactions have played an important part in the study of reaction kinetics. Duffield and Calvin (8), Friedlander and Kennedy (9), and several other authors (15) (19) have published treatments of this problem.

In much of the early investigation, the assumption was made at first that the effect of isotopic substitution of heavier atoms (such



as carbon) on the reaction rate was negligible, and no corrections were necessary in quantitative tracer studies. This assumption, while generally justifiable for the heavy elements, introduced a few discrepancies for the lighter elements regarding both equilibrium distribution (25) and specific reaction rate (3). Beeck, Otvos, Stevenson and Wagner (2) found evidence that in the pyrolysis of propane the  $C^{12}-C^{14}$  bond ruptured 8 per cent more frequently than the  $C^{12}-C^{12}$  bond.

Exchange reactions often have a unique application to the study of reaction mechanisms and catalysis mechanisms. In addition, exchange reactions are also a convenient means for labeling compounds (22) (27).

It is evident, therefore, that among the lighter elements, tracers represent the true course of a reaction only approximately, and due regard must be given to the isotope effect in really accurate experiments.

#### Reaction Kinetics

Molecules which differ only in their isotopic composition may undergo chemical transformations at different rates. Heavier molecules usually have a lower velocity and suffer fewer collisions in the transformation. This effect is proportional to the square root of the ratio of the masses of the molecules. It is also noticed that the heavier molecules have less vibrational energy than the light molecules, and therefore require more energy for dissociation. However, for most isotopic molecules (other than those of hydrogen) both velocity and vibrational energy differences are small and therefore equilibrium distribution of isotopes (except hydrogen) among several molecular species is nearly random.

The differences in physical properties of isotopes decrease with decreasing differences in the masses of the corresponding isotopes. The

greatest effect, then should exist in the case of protium( $H^1$ ) versus tritium( $H^3$ ), where the mass of the latter is three times that of the former. On the other hand, in the case of carbon-12 versus carbon-14, a much smaller isotope effect should be expected since the mass of carbon-14 exceeds that of carbon-12 by only 16.7%.

Isotope effects have been expressed quantitatively in a variety of ways. From the standpoint of correlation of theory and experiment, the simplest, most convenient expression is  $k/k^*$ , where  $k$  and  $k^*$  refer to the specific reaction rate constants for the normal and the labeled molecules respectively. The  $k/k^*$  ratio usually has a value greater than one.

Maximum values for the ratio  $k/k^*$  have been calculated by Bigeleisen (3) for the isotopes of a number of the elements. Much lower values are actually encountered experimentally. The common ranges for isotopes of hydrogen and carbon are listed below.

Stable isotope	Tracer isotope	$k/k^*$
$H^1$	$H^3$	1 -- 15
$H^1$	$H^2$	1 -- 10
$C^{12}$	$C^{14}$	1.00 - 1.12
$C^{12}$	$C^{13}$	1.00 - 1.06

An equilibrium exchange reaction will follow first-order kinetics provided that it fulfills the following conditions: 1) there be no isotope effect, 2) there be no chemical reaction to disturb the system and 3) the exchanging atoms be chemically equivalent to each other, no matter which substance they may reside within. Harris (10), Burr (6) and Melander (17) have investigated the case in which appreciable isotope effects are involved and concluded that the exchange kinetics are approximately first order even when these conditions are not completely fulfilled, if the

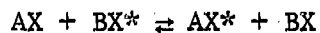
concentration of the distinguishable isotope is small.

Isotopic exchange reactions generally fall into two classes: 1) A simple isotopic exchange reaction in which chemically equivalent atoms of one molecular species are exchanged with isotopic atoms in a second molecular species, the exchanging atoms in the second species also being chemically equivalent. 2) A complex isotopic exchange reaction in which at least one reactant has two or more exchangeable atoms that are not chemically equivalent.

For the case of a complex isotopic exchange reaction, the estimation of rates of exchange as well as equilibrium constants among isotopic atoms is rather complicated (26).

H. Mckay (16) first derived an exponential exchange law for the simple case of one exchangeable atom per molecule. Other workers (4,10,17,19) have since published derivations.

Consider a simple homogeneous exchange reaction between the molecular species A and B in which atoms of a given element X, common to both species, are exchanged under a specified condition at a constant rate. Such a reaction might be represented as:



The rate,  $R$ , can be evaluated from the equation

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

where  $a = [AX + AX^*]$

$$b = [BX + BX^*]$$

$t = \text{time}$

$F = \text{activity of AX at time } t / \text{activity of AX at equilibrium.}$

$R$  is found from the slope of the line when  $\ln(1-F)$  is plotted versus  $t$ .

By using 0.5 for  $F$  and  $t_{\frac{1}{2}}$  for  $t$ , equation (1) can be rearranged to show the half-time of the reaction,

$$t_{\frac{1}{2}} = \frac{ab}{a+b} \frac{0.693}{R} \quad (2)$$

The equilibrium constant  $K$  for this reaction is given by:

$$K = \frac{Q_{2A}/Q_{1A}}{Q_{2B}/Q_{1B}} \quad (3)$$

where the  $Q$ 's represent the complete partition function of each molecule and the subscripts 1A and 2A refer to AX and AX\* respectively, and the subscripts 1B and 2B to BX and BX\* respectively. The partition function,  $Q$ , for each molecule comprises the translational energy, the vibrational energy, the rotational energy, and the energy from nuclear spin of that molecule.

If there is no interaction between the various forms of energies, so that the total energy in each state is the sum of the translational and internal, i.e., rotational, vibrational and electronic energies, the complete partition function  $Q$  is then the product of the contributions from the translational ( $Q_{tr}$ ) and internal ( $Q_{int}$ ) degrees of freedom; thus

$$Q = Q_{tr} \cdot Q_{int}.$$

Similarly,  $Q_{int}$  may be taken as the product of  $Q_{rot}$ ,  $Q_{vib}$ ,  $Q_{el}$ ,  $Q_{ns}$ , the rotational, vibrational, electronic and nuclear spin contributions. These different energy contributions are difficult to calculate individually. However, equation (3) shows that only the ratios of partition functions, not the actual values, enter into these equilibrium constants and thus make calculation of the equilibrium constant easier.

The ratios corresponding to appropriate energy contributions can be expressed in simple forms. The translational energy contribution ratio is:

$$r_{\text{tr}} = \left( \frac{M_2}{M_1} \right)^{3/2} \quad (4)$$

where  $M$  is the molecular weight. The vibrational partition function ratio becomes

$$r_{\text{vib}} = \prod \frac{1 - e^{-hc\omega_2/kT}}{1 - e^{-hc\omega_1/kT}} \quad (5)$$

where  $h$  is Planck's constant,

$c$  is the speed of light

$\omega$  is the characteristic frequency in wave numbers ( $\text{cm}^{-1}$ )

$k$  is the Boltzmann constant, and

$T$  is the absolute temperature.

The rotational partition function ratio reduces to

$$r_{\text{rot}} = \frac{\sigma_1}{\sigma_2} \left( \frac{A_2 B_2 C_2}{A_1 B_1 C_1} \right)^{1/2} \quad (6)$$

where  $[\sigma]$  are symmetry numbers, and A's, B's, C's are the principal moments of inertia of the polyatomic isotopic molecules under discussion.

The electronic and nuclear spin partition functions may be ignored for this purpose.

These energies must be calculated relative to the hypothetical vibrationless state, i.e., with no zero-point energy or relative to the completely dissociated molecules. Since the zero-point energies can not be observed directly and since the determination of isotopic molecules relative to the completely dissociated molecules is not possible, Urey (25) assumed that the potential functions are identical for isotopic molecules and estimated the zero-point energies from the empirical formula for molecular energy levels. The ratio for zero-point energy partition function

factor becomes

$$r_{ze} = e^{\sum_i (hc\omega_i - hc\omega_i')/2kT} \quad (7)$$

When equations (4), (5), (6), and (7) are combined the ratio of the total partition functions of isotopic molecules becomes

$$\frac{Q_2}{Q_1} = \left(\frac{M_2}{M_1}\right)^{3/2} \frac{\sigma_1}{\sigma_2} \left(\frac{A_2 B_2 C_2}{A_1 B_1 C_1}\right)^{1/2} e^{\sum_i (hc\omega_i - hc\omega_i')/2kT} \prod \frac{1 - e^{-hc\omega_i/kT}}{1 - e^{-hc\omega_i'/kT}} \quad (8)$$

Urey (25) and Bigeleisen and Mayer (4) have shown that the moments of inertia of the molecules are not necessary for the calculation of isotopic exchange equilibrium constants, because all isotopic exchange equilibrium constants would be either equal to the symmetry number ratio or unity if the classical partition function for translation, rotation and vibration were valid.

Equation (8) can be simplified further by making the substitution

$$\mu_i = \frac{hc\omega_i}{kT} = \frac{h\nu_i}{kT} \quad (9)$$

and by application of a theorem of Teller and Redlich (20)

$$\left(\frac{M_2}{M_1}\right)^{3/2} \left(\frac{A_2 B_2 C_2}{A_1 B_1 C_1}\right)^{1/2} \left(\frac{m_1}{m_2}\right)^{3/2n} \prod \frac{\mu_{1i}}{\mu_{2i}} = 1 \quad (10)$$

where  $m_1$  and  $m_2$  are the atomic weights of the isotopic atoms being considered, and  $n$  is the number of isotopic atoms exchanged.

The simplified ratio of total partition functions becomes

$$\frac{Q_2}{Q_1} = \frac{\sigma_1}{\sigma_2} \prod \frac{\mu_{2i}}{\mu_{1i}} \cdot \frac{e^{-\mu_{2i}/2}}{e^{-\mu_{1i}/2}} \cdot \frac{1 - e^{-\mu_{1i}}}{1 - e^{-\mu_{2i}}} \quad (11)$$

By utilization of the relation

$$\frac{Q_2}{Q_1} = \sqrt{\frac{u_1}{u_2}} \quad (12)$$

where  $u$  is the reduced mass of corresponding isotopic species being considered,  $Q_2/Q_1$  can be calculated.

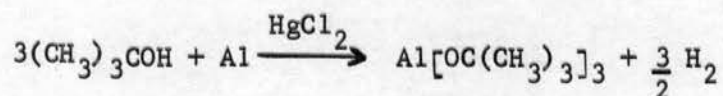
By substituting calculated values of  $Q_2/Q_1$  into equation (3), the theoretical values for the equilibrium constants of isotope exchange reactions can be obtained.

## INTRODUCTION TO EXPERIMENTAL WORK

The purpose of this section is to present an over-all picture of the experimental work involved in this project. A succinct discussion of the syntheses of the reagents and of the separation of reaction products that were carried out will be given. Details of those reactions including the equilibrium isotope effect reactions will be presented in a later section.

### Preparation of Catalyst

The catalyst used in this reaction is aluminum tert-butoxide which is not commercially available. The preparation of aluminum tert-butoxide used followed the procedure given in Organic Syntheses which was submitted by Wayne and Adkins (11). The equation for the preparation is

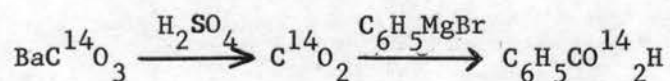


On repeating this procedure it was found that the aluminum shavings must be fine and freshly prepared. The product obtained was a slightly gray solid and the yield was good.

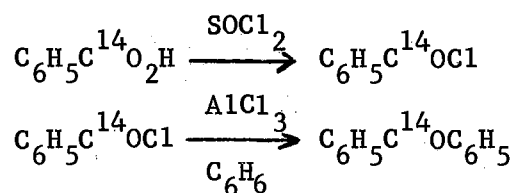
Aluminum tert-butoxide can also be prepared by refluxing dry tert-butyl alcohol with amalgamated aluminum (29). The method of preparation of amalgamated aluminum has been described by Adkins (1).

### Preparation of Benzophenone-Carbonyl-C<sup>14</sup>

The ketone was prepared by the following series of steps:







Benzoic acid was prepared by using apparatus B shown in the Appendix. Carbon-14 dioxide was liberated from barium carbonate by the use of sulfuric acid and condensed by means of liquid nitrogen in a tube containing a solution of phenylmagnesium bromide in ether. The tube was sealed and the carbonation took place upon warming to room temperature. The tip of the tube was broken off and the contents were decomposed with a small amount of water. Benzoic acid was obtained by acidification with sulfuric acid in the aqueous phase.

The benzoic acid was converted to benzoyl chloride by refluxing with excess thionyl chloride and distilling the excess reagent.

The benzoyl chloride reacted with benzene forming benzophenone in the presence of anhydrous aluminum chloride and carbon disulfide as the solvent. The yield in this Friedel-Crafts acylation was about 83% based on benzoic acid.

#### Separation of Benzophenone with 2,4-Dinitrophenylhydrazine

The measurement of the radioactivity of benzophenone at certain pre-determined times plays an important role in this exchange reaction study, therefore, a satisfactory method for the separation from the reaction mixture is required. The method usually used is to make a derivative of benzophenone and separate it from the other components of the mixture by precipitation. To be suitable for an isotope effect study, the precipitate obtained should have certain properties. It should be a solid in order to facilitate the radioactivity assays. It should be easily formed and

purified. It should be stable at room temperature. 2,4-Dinitrophenylhydrazine was chosen because it met these requirements.

The precipitation of the 2,4-dinitrophenylhydrazone was done by adding the reaction mixture to a 2,4-dinitrophenylhydrazine solution. The reaction mixture was synthesized with "dead" benzophenone, benzhydrol and aluminum tert-butoxide in benzene for the purpose of doing quantitative work.

The preparation of 2,4-dinitrophenylhydrazine solution was first carried out by dissolving 2,4-dinitrophenylhydrazine in water which was acidified with sulfuric acid. The yield from the precipitation was 66% to 77% and not consistent. A second method of preparation of 2,4-dinitrophenylhydrazine solution was tried. This consisted of dissolving 2,4-dinitrophenylhydrazine in 85% phosphoric acid and diluting with 95% alcohol. In this case, a 125% yield of precipitate was obtained. Brown and Holland (5) have reported another method. They dissolved 2,4-dinitrophenylhydrazine in a mixture of water, ethyl alcohol and sulfuric acid. In this case the precipitation was quite consistent but give a yield of 100.5% and a melting point of  $244.5^{\circ}$  which is higher than the reported value of  $237.5 - 238^{\circ}$  (12).

Ascending paper chromatography was used in order to prove the purity of this 2,4-dinitrophenylhydrazone. By using 1-butanol as the solvent and treating the paper with 10% potassium hydroxide solution, no evidence of impurities present was observed.

#### Separation of Benzhydrol from the Reaction Mixture

The radioactivity of benzhydrol at equilibrium is a key datum for this experiment; therefore the separation of benzhydrol is very important.

The method chosen here was also based on the requirements for isotope study. First of all, esterification of benzhydrol with p-nitrobenzoyl chloride was tried according to the method described by Cheronis and Entrikin (7). A yield of only 10% was obtained and the melting point of the crystals was  $110^{\circ}$ , which is much lower than the reported value  $131-2^{\circ}$  (18). With the same procedure but using 3,5-dinitrobenzoyl chloride instead of p-nitrobenzoyl chloride, a melting point of  $142^{\circ}$  was obtained, which agrees well with the reported value of  $142^{\circ}$  (24).

In order to prevent the formation of a derivative of tert-butyl alcohol which might be produced from the hydrolysis of aluminum tert-butoxide, the crude reaction mixture was subjected to steam distillation before derivatization of the benzhydrol. However, no derivative was obtained with such a method. After investigation, it was found that most of the benzhydrol was distilled along with the water vapor. The yield of the derivative was always low (12-16%) even with improved steam distillation. It was then assumed that tert-butyl alcohol does not react easily with 3,5-dinitrobenzoyl chloride. Therefore, the derivative of benzhydrol was prepared directly from the reaction mixture without prior distillation. The reaction between 3,5-dinitrobenzoyl chloride and benzhydrol took place in the presence of isopropyl ether and pyridine. A yield of 65% was obtained after purification.

#### Isotope Exchange Reaction

The equilibrium reaction under consideration took place at constant temperature for a measured length of time. Weighed portions of benzophenone-carbonyl- $C^{14}$  and benzhydrol were dissolved in dry benzene along with the aluminum tert-butoxide. This solution was then apportioned into

several small reaction tubes, usually about 1 ml. of solution in each tube. These tubes as well as the remainder of the solution in the flask were then immersed in a constant temperature bath. The tubes were withdrawn successively from the bath at predetermined time. The benzophenone was precipitated as the 2,4-dinitrophenylhydrazone, and the latter was purified and then assayed for radioactivity.

At equilibrium, a portion of the solution was withdrawn and the benzhydrol was derivatized with 3,5-dinitrobenzoyl chloride. The derivative was purified and assayed to determine its radioactivity.

From the activities of both components at equilibrium, the experimental value of equilibrium constant was determined.

## EXPERIMENTAL PROCEDURE

Preparation of Aluminum tert-Butoxide: This was essentially the method by Adkins (11) with certain modifications.

In a three-neck 1-l round-bottom flask bearing a reflux condenser protected by a calcium chloride tube, and two dropping funnels with pressure stabilizers, were placed 32 g. (1.185 gram atoms) of fine, freshly prepared aluminum shavings, 0.4 g. of mercuric chloride, and 50 g. of dry tert-butyl alcohol. The mixture was shaken vigorously until the mercuric chloride was homogeneously distributed and then heated slowly until the reaction started. The heating was interrupted when the reaction began. Another 50-g. portion of tert-butyl alcohol was added gradually through the dropping funnel and then 50 ml. of dry benzene was added at one time. The reaction started again upon gentle heating and continued vigorously without further heating. An additional 120 ml. of tert-butyl alcohol and 100 ml. of dry benzene were added alternatively. After about two hours the reaction subsided and the reaction mixture was refluxed for twenty-eight hours. The benzene and unreacted tert-butyl alcohol were removed by distillation from the steam bath, the final traces being removed with the aid of a vacuum pump. Five hundred milliliters of dry ether was added, and the solid aluminum tert-butoxide was dissolved by refluxing for a short period. After the mixture cooled, 25 ml. of moist ether was added, and the mixture was shaken vigorously. After standing two hours the solution was spun in a Lourdes refrigerated centrifuge for sixty minutes at a speed of 12,000 r.p.m. at 0° to remove

unused aluminum, aluminum hydroxide, and mercury. The resulting light tan solution was transferred to a 1-l. round-bottom flask. The solvent was removed by distillation on the steam bath, and the final traces under vacuum. The flask was allowed to cool with a calcium chloride tube. The yield was high and the product was a slightly gray solid.

Preparation of Benzoic Acid-carboxyl-C<sup>14</sup>: A modification of the method used by Rowton (21) was applied.

A solution of phenylmagnesium bromide was prepared from 3.925 g. (25 mmole) of bromobenzene in 25 ml. of ether and 0.61 g. (26 mmole) of magnesium turnings, using magnetic stirring. A very small iodine crystal was added as the catalyst. The reaction started with slight heating; the reaction mixture was refluxed about two hours. In the meantime, apparatus B shown in the Appendix was assembled and evacuated.

The Grignard solution was placed in the reaction tube of apparatus B. The 50-ml. pear-shape generating flask held 0.5319 g. (2.7 mole) of barium carbonate, which contained 3.59 mc. of activity due to carbon-14, on top of which was a layer of sand and a wad of glass wood to prevent spattering. The dropping funnel contained 50 ml. of concentrated sulfuric acid. After re-assembly, the reaction tube was cooled in liquid nitrogen and the apparatus was again evacuated. Sulfuric acid was introduced over a period of one hour. The carbonation tube was then sealed off, and left in the bath for sixteen hours while the liquid nitrogen evaporated. The reaction tube was shaken with the protection of an iron tube, and stood at room temperature for one day to complete the carbonation.

The tip of the reaction tube was broken off and the contents were acidified with 5 ml. of concentrated hydrochloric acid in 10 ml. of water; 0.5 g. of "dead" benzoic acid was added to the water layer as scavenger and the mixture was extracted with ether. Two 5-ml. portions of 1.5 N sodium hydroxide solution were successively used to extract the combined ether layer, and the basic solution was retained. Another 0.3 g. of "dead" benzoic acid was added to the ether layer, and another 5-ml. portion of 1.5 N sodium hydroxide solution was used to extract the ether layer. The combined basic solution was acidified with 10 ml. of concentrated hydrochloric acid in 15 ml. of water and the benzoic acid was extracted with ether. The ether layer was evaporated and boiled gently with 25 ml. of water for half an hour. After the solution was cooled the crystals of benzoic acid were filtered off, washed and dried. The benzoic acid had a melting point of 122-123° and an activity of 8  $\mu$ c./mmole.

Preparation of "Dead" Benzophenone: The method used involved treatment of benzoic acid with thionyl chloride and Friedel-Crafts reaction of benzoyl chloride and benzene.

In a 50-ml. round-bottom flask fitted with a water-cooled condenser were placed 3 g. (24.56 mmole) of benzoic acid and 11.68 g. (98 mmole, 300% molar excess) of thionyl chloride. The reaction with the thionyl chloride was effected by warming the reaction mixture on the steam bath for half an hour. The excess of thionyl chloride was then evaporated. After the benzoyl chloride had cooled to room temperature, 3 g. (38.4 mmole) of dry benzene, 13 g. (0.17 mole) of dry carbon disulfide and 3 g. (22.5 mmole) of finely powdered aluminum chloride were

added quickly. The reaction started promptly without heat and the evolved hydrogen chloride gas was detected with ammonium hydroxide. When the reaction slowed, the reaction mixture was refluxed for eight hours by external heating. The carbon disulfide was then distilled on a water bath and the still-warm residue was carefully poured into a 125-ml. beaker containing 30 ml. of ice water and 1 ml. of concentrated hydrochloric acid. The contents of the reaction flask were washed into the beaker of ice water with ether. The reaction mixture in the beaker was boiled gently on a hot plate for 15 minutes. The cold residue was extracted with ether and the ethereal solution was washed three times with water (using 25 ml. each time) and then with 30 ml. of 2% sodium hydroxide solution. It was dried over calcium chloride overnight, filtered and distilled. The fraction boiling at 200-300° was retained. The yield was about 83%, but its melting point had a range of 35°-40°.

This material was then dissolved in denatured alcohol and recrystallized by cooling with dry ice. A melting point of 46° was obtained. The reported melting point of benzophenone is 47.8° (13).

Preparation of Benzophenone-carboxyl-C<sup>14</sup>: The procedure used was essentially the same as for preparation of "dead" benzophenone.

In a 50-ml. round-bottom flask fitted with a water-cooled condenser were placed 3.0716 g. (25.15 mmoles) of benzoic acid, 0.4616 g. of which was benzoic acid-carboxyl-C<sup>14</sup> from the above preparation, and 6 g. (50.4 mmole) of thionyl chloride. The acid was dissolved by heating and a few milliliters of carbon tetrachloride were introduced and evaporated to remove traces of thionyl chloride. After the flask cooled, 2 g.



(21.3 mmole) of "dead" benzoyl chloride, 6 g. (76.7 mmole) of dry benzene, 26 g. (34.2 mmole) of carbon disulfide, and 6 g (45 mmole) of aluminum chloride were added. The reaction mixture was refluxed at 50° for three hours. The carbon disulfide was distilled and the reaction mixture was poured carefully on 50 ml. of ice and water containing 4 ml. of concentrated hydrochloric acid. The cold mixture was extracted with ether; the latter was washed with water and dilute potassium carbonate solution and then dried. The ether was removed by distillation, and the residue was distilled off under a vacuum. Three portions of 3 g. of "dead" benzophenone were used to remove all the radioactivity. The distillate was recrystallized from petroleum ether by use of dry ice. The yield was 71%. The activity was 0.586  $\mu\text{c./mmole}$ .

The rest of the benzoic acid-carboxyl- $\text{C}^{14}$  (0.5005 g.) was treated by the same procedure. By using the benzophenone-carbonyl- $\text{C}^{14}$  prepared above as the scavenger, 3.66 g. of a product of about 2  $\mu\text{c./mmole}$  was obtained.

By dissolving all the benzophenone-carbonyl- $\text{C}^{14}$  in 35 ml. of petroleum ether and recrystallizing, 13.2155 g. of final product with an activity of about 1  $\mu\text{c./mmole}$  was obtained. This benzophenone-carbonyl- $\text{C}^{14}$  was used in the isotope exchange reaction.

#### Separation of Benzophenone from the Reaction Mixture

Since the separation of benzophenone is an important step for this isotope exchange reaction study, it was necessary to develop a satisfactory method for this separation. Since benzophenone forms insoluble 2,4-dinitrophenylhydrazone, this method was tried. However, its success depends primarily upon the preparation of the

2,4-dinitrophenylhydrazine solution. Three ways of preparation were tried as follows:

A) In a 1-l. volumetric flask were placed 200 ml. of water, 25 ml. of concentrated sulfuric acid, and 2 g. of 2,4-dinitrophenylhydrazine. Solution of the 2,4-dinitrophenylhydrazine was effected by adding another 25 ml. of concentrated sulfuric acid with vigorous shaking. Addition of water was continued until exactly one liter of solution was attained; shaking was continued for one hour. The solution was allowed to stand for one day and was then filtered.

B) In a 50-ml. volumetric flask, 2.5 g. of 2,4-dinitrophenylhydrazine was dissolved in 30 ml. of 85% phosphoric acid on a steam bath. The solution was diluted to exactly 50 ml. with 95% alcohol and clarified by suction filtration through a medium-porosity filtering crucible. This phosphoric acid-ethanol solution of 2,4-dinitrophenylhydrazine was first prepared by Johnson (14) and found to be very useful.

C) This solution was prepared according to the method of Brown and Holland (5). The solution was prepared by dissolving 2,4-dinitrophenylhydrazine in 15 ml. of water, 10 ml. of concentrated sulfuric acid, and 75 ml. of ethyl alcohol and then filtered through a medium-porosity filtering crucible.

One milliliter of a synthetic reaction mixture of known concentration was added to an aliquot of each of these three solutions containing a 100% molar excess of 2,4-dinitrophenylhydrazine. The precipitated 2,4-dinitrophenylhydrazone was separated and weighed. Of the three solutions only the third gave results satisfactory for this study;

therefore, only the procedure for the third solution was used; it is given in more detail as follows:

Exactly one milliliter of the reaction mixture was withdrawn with a pipet and added immediately to a 15 ml. beaker containing 10 ml. of 2,4-dinitrophenylhydrazine solution. The mixture was stirred with a glass rod for two minutes. The beaker was then covered and allowed to stand overnight. The precipitate was filtered with suction in a medium-porosity filtering crucible. The suction was continued for 10 minutes to ensure that all the solution was gone, and the precipitate was washed successively with 25 ml. of ethyl alcohol and 25 ml. of water. The precipitate was dried in a vacuum desiccator and recrystallized from 40 ml. of denatured alcohol. The final precipitate had a melting point of  $244.5^{\circ}$ . The reported value is  $237.5-238^{\circ}$  (12).

When other samples were treated by exactly the same procedure, the results were consistent. The actual yield was 100.5% of the theoretical, and the average deviation was 0.2%.

The use of ascending paper chromatography provided a further proof of the purity of the 2,4-dinitrophenylhydrazone derivative.

A pencil line was drawn about one centimeter from one end of each of three strips of filter paper. 2,4-Dinitrophenylhydrazine solution was applied to a spot at the pencil line of each strip. The paper strips were placed in three test tubes so that the end with the pencil line was down. One test tube contained about 1 ml. of 1-butanol, another 1 ml. of hexane, and another 1 ml. of 50%-50% acetone-hexane. These tubes were stoppered and allowed to stand overnight. The spots on all three strips of paper moved to the upper end, and their colors changed to brown when washed with 10% potassium hydroxide. The same treatment was applied

with a solution of the 2,4-dinitrophenylhydrazone in ethyl acetate. No movement, as well as no change of color, of the spot on the paper sheet in 1-butanol was observed. When the filtrate from the preparation of 2,4-dinitrophenylhydrazone was treated in the same way using 1-butanol as solvent, the 2,4-dinitrophenylhydrazine spot moved up as before and also a spot remained at the original point. After washing the spots with 10% potassium hydroxide solution, the color of the migrated compound changed. This experiment thus indicated that the 2,4-dinitrophenylhydrazone was quite pure.

#### Separation of Benzhydrol from the Reaction Mixture

The procedure which was used for this purpose was found to be the best after investigation of many of the methods that have been reported in the literature for making derivatives of alcohols.

In a 35-ml. pear-shape flask fitted with a condenser protected by a calcium chloride tube and a magnetic stirrer, 14 ml. of isopropyl ether, 12 ml. of pyridine, 3 ml. of reaction mixture (containing 1.5 mmole of benzohydrol), and 0.5 g. (2.8 mmole) of 3,5-dinitrobenzoyl chloride were placed. The mixture was refluxed for two hours. The cooled mixture was acidified with dilute sulfuric acid solution to react with the pyridine and was extracted with 50 ml. of ethyl ether. The ether layer was dried over Drierite overnight and filtered. The ether, benzene, and alcohol were evaporated in a hood. The yellow residue was crystallized from 40 ml. of denatured alcohol and filtered in a medium-porosity filtering crucible. The crystals were washed once with 10 ml. of alcohol and twice with 10 ml. of water and dried in a vacuum desiccator. The melting point was 139°. The product was recrystallized from 40 ml. of denatured alcohol

with a yield of 65% and had a melting point of 141°.

Equilibrium Isotope Exchange Reaction Between Benzophenone-Carbonyl-C<sup>14</sup>  
and Benzhydrol

In a 25 ml. volumetric flask were placed 2.2753 g. (12.5 mmole) of benzophenone-carbonyl-C<sup>14</sup>, 2.3003 g. (12.5 mmole) of benzhydrol, and 3 g. (12.5 mmole) of aluminum tert-butoxide; dry benzene was added to transfer completely all reactants to the flask. The addition of aluminum tert-butoxide was conducted under nitrogen gas in a plastic bag. The mixture was vigorously shaken until all reactants had dissolved and was made up to exactly 25 ml. of solution at room temperature.

About one milliliter of reaction mixture was placed in each of thirteen reaction tubes. Ten of them were sealed and put into an oil bath at 40° along with the remainder of the reaction mixture. The contents of the other three reaction tubes were treated immediately by the procedure described previously. The 2,4-dinitrophenylhydrazone was assayed to determine the specific radioactivity of the benzophenone.

Five to ten milligrams of the phenylhydrazone was weighed accurately into a small platinum boat which was then placed in a combustion tube. The tube was connected to Apparatus A of the Appendix. Oxidation of the phenylhydrazone was effected by wet combustion. The oxidizing mixture consisted of a solution of 5 g. of potassium iodate and 25 g. of chromic acid in 100 ml. of 85% phosphoric acid to which 332 ml. of 20% fuming sulfuric acid. The carbon dioxide given off during the oxidation reaction was swept into an evacuated ionization chamber by passing "dead" carbon dioxide gas through the system. The line was swept with "dead" carbon dioxide until the chamber was filled to atmospheric pressure. The ionization chamber was attached to a vibrating reed electrometer and the ion current was measured.

ion current was measured.

Two reaction tubes were removed every day at the same hour and precipitated and assayed as mentioned.

The result showed that the reaction required 84 days to reach equilibrium at 40°.

The temperature of the oil bath was then raised to 81° in order to increase the rate of this exchange reaction.

The remainder of the reaction mixture from the first run was divided into 10 reaction tubes. Eight of them were put into the oil bath. The other two were precipitate immediately. The tubes were withdrawn at predetermined times, and the benzophenone was precipitated as the 2,4-dinitrophenylhydrazone, which was assayed for radioactivity.

Two more runs were conducted. Only one tube instead of two was examined each day. At equilibrium, 3 ml. of the reaction mixture was used for making a derivative of the benzhydrol by the procedure already described.

#### Calculation of Activity

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

$$1 \text{ disintegration of carbon-14 in CO}_2 = 1.39 \times 10^{-16} \text{ coulombs. (28)}$$

$$\text{Resistor} = 1 \times 10^{12} \text{ ohms}$$

$$1 \text{ c.} = 3.7 \times 10^{10} \times 1.39 \times 10^{-16} \text{ coulombs/sec.}$$

$$= 5.143 \times 10^{-6} \text{ amperes}$$

$$= 5.143 \times 10^{-6} \times 10^{12} \text{ ampere ohms}$$

$$= 5.143 \times 10^6 \text{ volts}$$

$$1 \text{ } \mu\text{c.} = 5.143 \times 10^3 \text{ mv.}$$

$$1 \text{ mv.} = 1.944 \times 10^{-4} \text{ } \mu\text{c.}$$

The specific activity of a sample can be expressed as following:

$$\text{mv.} \times 1.944 \times 10^{-4} \frac{\text{molecular weight (in mg.)}}{\text{weight of sample (in mg.)}} = \mu\text{c./mmole.}$$

### Experimental Results

Results of four runs of this equilibrium isotope exchange reaction have been summarized in the form of four charts shown as Figures 1 to 4. Figures 1 and 2 represent data obtained with the same reaction mixture at two different reaction temperatures. All reactions took place at 81° except the first run, which was at 40°. The individual radioactivity measurements are averages of ten converted millivolt readings as obtained from the strip chart of the recorder attached to the electrometer. The specific activities were averaged for each sample.

### Data

Data for the various runs are given in Tables 1 to 4.

When these data for Run 1 are plotted as in Figure 1 (time vs. log 1-F) the half-life of the reaction appears to be about 12 days. Assuming that seven half-lives were required to reach equilibrium, 84 days of reaction would be needed at a temperature of 40°. In order to shorten the time of reaching equilibrium to about one week, the temperature of the oil bath was raised to 81°.

TABLE I

Data for Run 1

Time, days	Activity of Benzophenone, $\mu\text{c.}/\text{mmole}$	Standard Deviation	Fraction Unreacted, 1 - F
0	0.966	0.009	1.000
	0.966		
	0.980		
	0.974		
	0.971		
	0.977		
	0.985		
	0.985		
	Ave. 0.976		
1	0.944	0.010	0.957
	0.965		
	0.046		
	0.952		
	0.964		
2	0.914	0.019	0.890
	0.942		
	0.901		
	0.942		
4	0.859	0.010	0.735
	0.854		
	0.856		
	0.839		
	0.837		
	0.832		
6	0.811	0.006	0.686
	0.821		
	0.825		
	0.828		
	0.825		
	0.825		



8

0.771  
0.770  
0.788  
0.804  
0.811  
0.803

Ave. 0.791

0.017

0.622

TABLE II

Data for Run 2

Time, days	Activity of Benzophenone, $\mu\text{c.}/\text{mmole}$	Standard Deviation	Fraction Unreacted, 1 - F
0	0.701		
	0.705		
	0.703		
	0.730		
	0.716		
	Ave. 0.711	0.012	1.000
2/3	0.603		
	0.601		
	0.624		
	Ave. 0.609	0.013	0.559
1	0.572		
	0.573		
	0.574		
	Ave. 0.573	0.001	0.391
2	0.531		
	0.525		
	0.527		
	Ave. 0.528	0.003	0.178
3	0.504		
	0.512		
	0.511		
	Ave. 0.509	0.004	0.079
4	0.488*		
	0.494		
	0.492		
	Ave. 0.493	0.001	0.030
6	0.490		
	0.491		
	0.486		
	Ave. 0.489		

\* Discarded Value

TABLE III

Data for Run 3

Time, days	Activity of Benzophenone, $\mu\text{c.}/\text{mmole}$	Standard Deviation	Fraction Unreacted, 1 - F
0	0.944		
	0.951		
	0.942		
	0.950		
	0.944		
	0.948		
	0.944		
	Ave. 0.946	0.004	1.000
1	0.685		
	0.684		
	0.676*		
	Ave. 0.685	0.001	0.446
2	0.570		
	0.554		
	0.565		
	Ave. 0.563	0.008	0.190
3	0.523		
	0.526		
	0.512*		
	Ave. 0.525	0.002	0.109
4	0.496		
	0.495		
	0.504		
	Ave. 0.498	0.005	0.054
5	0.588		
	0.467*		
	0.482		
	Ave. 0.485	0.004	0.025
6	0.479		
	0.477		
	0.480		
	Ave. 0.479	0.002	0.012

\* Discarded Value

TABLE IV  
Data for Run 4

Time, days	Activity of Benzophenone, $\mu\text{c.}/\text{mmole}$	Standard Deviation	Fraction Unreacted (95% confidence level)
0	0.919	0.005	$1.000 \pm 0.038$
	0.914		
	0.921		
	0.930		
	0.912		
	0.914		
	0.934		
	0.920		
	Ave. 0.919		
1	0.711	0.008	$0.530 \pm 0.040$
	0.699		
	0.621*		
	Ave. 0.705		
2	0.568	0.004	$0.223 \pm 0.027$
	0.552		
	0.562		
	Ave. 0.566		
3	0.516	0.004	$0.113 \pm 0.026$
	0.520		
	0.512		
	Ave. 0.516		
4	0.487	0.003	$0.053 \pm 0.022$
	0.487		
	0.492		
	Ave. 0.489		
5	0.473	0.004	$0.022 \pm 0.026$
	0.468*		
	0.478		
	Ave. 0.475		
6	0.461	0.004	$0.000 \pm 0.026$
	0.468		
	0.465		
	Ave. 0.465		

6	0.457 <sup>#</sup>	
	0.459	
	0.453	
	Ave. 0.456	0.003

\* Discarded Value

<sup>#</sup> Activity of Benzhydrol,  $\mu\text{c.}/\text{mmole}$ .

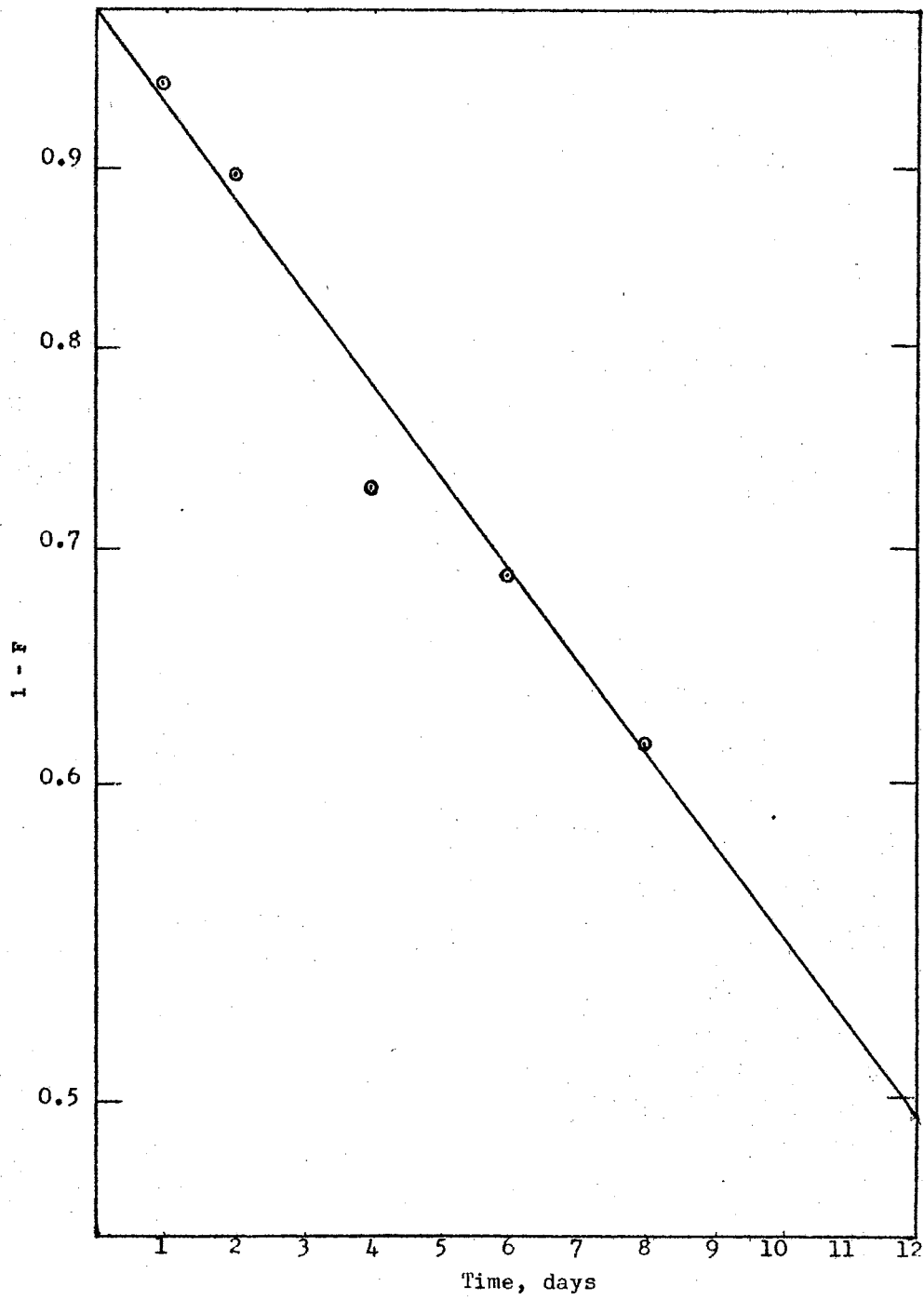


Figure I (Run 1)

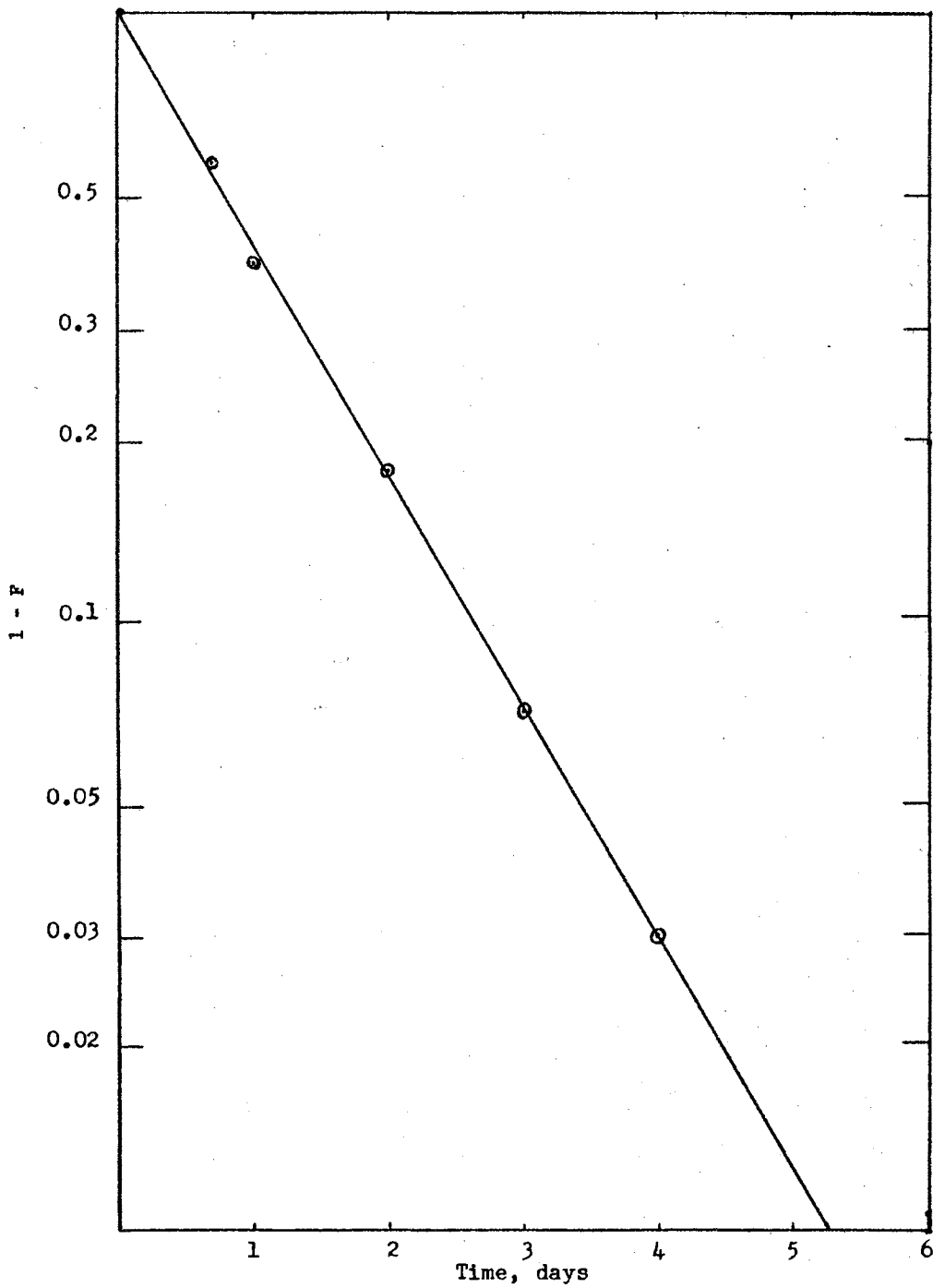
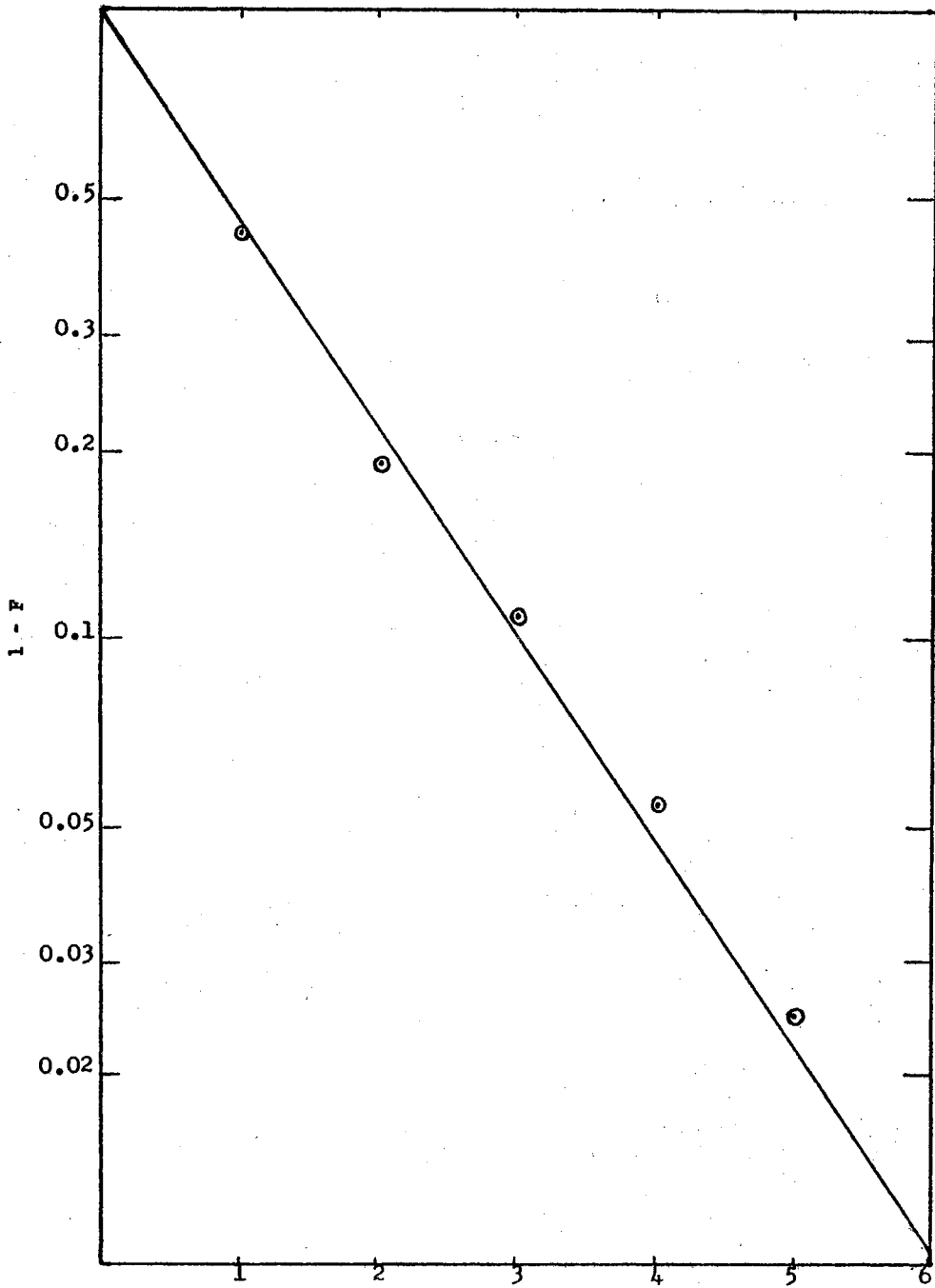


Figure II (Run 2)



Time, days  
Figure III (Run 3)



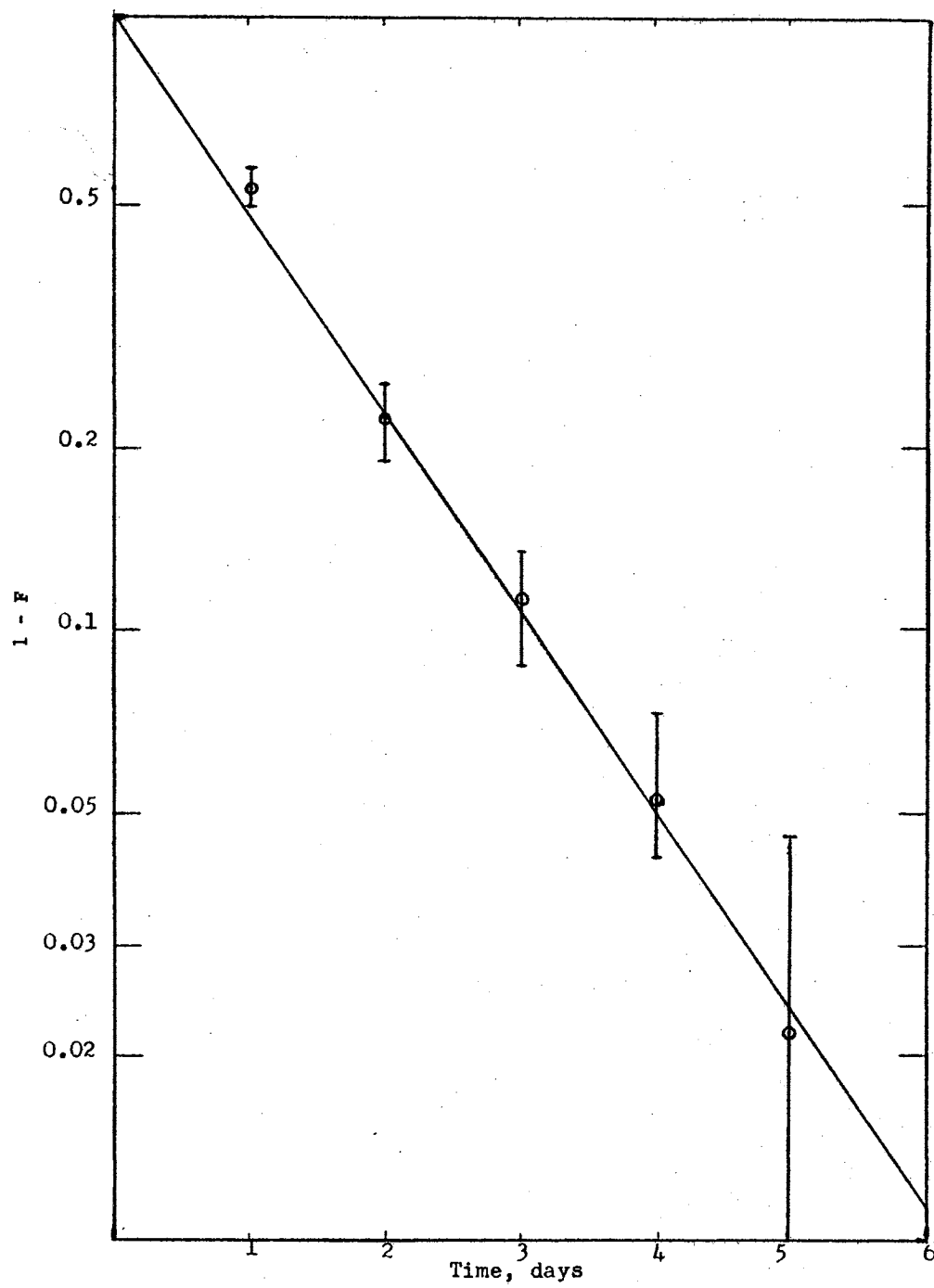


Figure IV (Run 4)

## THEORETICAL EVALUATION OF THE EQUILIBRIUM CONSTANT

An attempt has been made to evaluate theoretically the isotope effect for the exchange reaction. For an accurate calculation one would need the fundamental vibrational frequencies of the molecule for both isotopic species. Since the fundamental vibrational frequencies involving carbon-14 bonds have not been determined, they are approximated from the frequencies of the corresponding carbon-12 bonds by application of the equation  $\omega_2/\omega_1 = \sqrt{u_1/u_2}$ .

The stretching frequencies are considered the most important in bond breakage and have been used exclusively in the calculation. The stretching frequencies for the bonds C=O, C-O, and C-H are taken as  $1650 \text{ cm}^{-1}$ ,  $1200 \text{ cm}^{-1}$ , and  $3000 \text{ cm}^{-1}$  respectively (23). By substituting each of these values into the expression  $\omega_2/\omega_1 = \sqrt{u_1/u_2}$ , the corresponding frequencies for C<sup>14</sup>=O, C<sup>14</sup>-O and C<sup>14</sup>-H become  $1581 \text{ cm}^{-1}$ ,  $1150 \text{ cm}^{-1}$  and  $2980 \text{ cm}^{-1}$ . The partition function for C-H is neglected in the actual calculation since its ratio is almost equal to 1. The calculation of the ratio of partition functions for benzophenone and benzhydrol are outlined as follows.

Calculation of  $\mu$  by substituting

$$h = 6.62577 \times 10^{-27} \text{ erg sec/molecule}$$

$$c = 2.99790 \times 10^{10} \text{ cm/sec}$$

$$k = 1.38026 \times 10^{-16} \text{ erg/deg.molecule}$$

$$T = 273 + 81 = 354^\circ$$

$\omega$  = corresponding frequencies into  $\mu = hc\omega/kT$ , one gets

Bonds	$\omega(\text{cm}^{-1})$	$\mu$
C=O	1650	6.7073
C <sup>14</sup> =O	1581	6.4268
C-O	1200	4.8780
C <sup>14</sup> -O	1150	4.6748
C-H	3000	12.1950
C <sup>14</sup> -H	2980	12.1137

Calculation of  $e^{-\mu/2}$

$$\log e = 0.43429$$

Bonds	$\mu/2$	$\log e^{-\mu/2}$	$e^{-\mu/2}$
C=O	3.3536	-1.4564	0.0350
C <sup>14</sup> =O	3.2134	-1.3955	0.0402
C-O	2.4390	-1.0592	0.0873
C <sup>14</sup> -O	2.3374	-1.0151	0.0966
C-H	6.0975	-2.6481	0.0022
C <sup>14</sup> -H	6.0568	-2.6304	0.0023

Calculation of  $1 - e^{-\mu}$

Bonds	$\log e^{-\mu}$	$e^{-\mu}$	$1 - e^{-\mu}$
C=O	-2.9129	0.0012	0.9988
C <sup>14</sup> =O	-2.7911	0.0016	0.9984
C-O	-2.1185	0.0076	0.9924
C <sup>14</sup> -O	-2.0302	0.0093	0.9907
C-H	-5.2962	0.0000	1.0000
C <sup>14</sup> -H	-5.2609	0.0000	1.0000

Calculation of  $Q_{2B}/Q_{1B}$  for benzophenone

$$\begin{aligned} \frac{Q_{2B}}{Q_{1B}} &= \frac{\sigma_1}{\sigma_2} \frac{\mu_2}{\mu_1} \left( \frac{e^{-\mu_2/2}}{e^{-\mu_1/2}} \right) \left( \frac{1 - e^{-\mu_1}}{1 - e^{-\mu_2}} \right) \\ &= \frac{6.4268}{6.7073} \left( \frac{0.0402}{0.0350} \right) \left( \frac{0.9988}{0.9984} \right) \\ &= 1.1031 \end{aligned}$$

Calculation of  $Q_2/Q_1$  for benzhydrol.

$$\begin{aligned} \left( \frac{Q_2}{Q_1} \right)_{\text{C-O}} &= \frac{\sigma_1}{\sigma_2} \frac{\mu_2}{\mu_1} \left( \frac{e^{-\mu_2/2}}{e^{-\mu_1/2}} \right) \left( \frac{1 - e^{-\mu_1}}{1 - e^{-\mu_2}} \right) \\ &= \frac{4.6748}{4.8780} \left( \frac{0.0966}{0.0873} \right) \left( \frac{0.9924}{0.9907} \right) \\ &= 1.0627 \end{aligned}$$

$$\begin{aligned} \left( \frac{Q_2}{Q_1} \right)_{\text{C-H}} &= \frac{\sigma_1}{\sigma_2} \frac{\mu_2}{\mu_1} \left( \frac{e^{-\mu_2/2}}{e^{-\mu_1/2}} \right) \left( \frac{1 - e^{-\mu_1}}{1 - e^{-\mu_2}} \right) \\ &= \frac{12.1137}{12.1950} \left( \frac{0.0023}{0.0022} \right) \left( \frac{1}{1} \right) \\ &= 1.0348 \end{aligned}$$

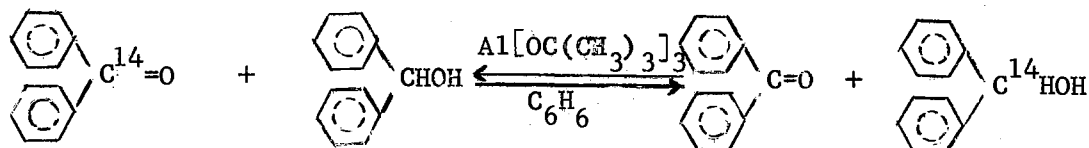
$$\begin{aligned} \frac{Q_{2A}}{Q_{1A}} &= \left( \frac{Q_2}{Q_1} \right)_{\text{C-O}} \left( \frac{Q_2}{Q_1} \right)_{\text{C-H}} = 1.0627 \times 1.0348 \\ &= 1.0997 \end{aligned}$$

Calculation of equilibrium constant by substituting  $Q_{2A}/Q_{1A}$  and  $Q_{2B}/Q_{1B}$  into equation (3),

$$\begin{aligned} K &= \frac{Q_{2A}}{Q_{1A}} \bigg/ \frac{Q_{2B}}{Q_{1B}} \\ &= \frac{1.0997}{1.1031} = 0.997 \end{aligned}$$

## DISCUSSION OF RESULTS

The main object of this study was to determine the equilibrium constant of the following isotope exchange reaction:



The reaction is reversible and the equilibrium constant  $K$  may be expressed as

$$K = \frac{[(\text{C}_6\text{H}_5)_2\text{C}^{14}\text{HOH}][(\text{C}_6\text{H}_5)_2\text{C}=\text{O}]}{[(\text{C}_6\text{H}_5)_2\text{C}^{14}=\text{O}][(\text{C}_6\text{H}_5)_2\text{CHOH}]} \quad (9)$$

$$= \frac{S_A}{S_B}$$

where  $S_A$  = specific activity of benzhydrol at equilibrium.

$S_B$  = specific activity of benzophenone at equilibrium.

If there is no isotope effect,  $K = S_A/S_B = 1$ , and any deviation of the value of  $K$  from 1 means there is an isotope effect. The data obtained from Run IV were

$$S_A = 0.456 \pm 0.003 \text{ } \mu\text{c./mmole}$$

$$S_B = 0.465 \pm 0.004 \text{ } \mu\text{c./mmole}$$

therefore, at  $81^\circ$

$$K = S_A/S_B = 0.456 \pm 0.003 / 0.465 \pm 0.004 = 0.981 \pm 0.022$$

The slight deviation of this value of  $K$  from 1 shows that the isotope effect is small for this exchange reaction.

Calculation of the theoretical isotope effect is done in the previous

section. The theoretical value for this exchange is  $K = 0.997$ .

It is apparent that the experimentally determined values do not quite match the theoretically determined value. However, the theoretically determined value was calculated from data and assumptions that are not exact.

Though only the fourth run gave complete data experimentally, it agreed well with the results obtained by calculating the activity of the benzhydrol from that of the benzophenone at the beginning and at the end of the reaction. According to the law of conservation of radioactivity, the total activity of the benzhydrol should equal the difference between the initial activity of benzophenone and the final activity of benzophenone. By substituting the calculated values of the final activities of benzhydrol into equation (9), the isotope effects obtained are;

at 81°	Run 2	$K = 0.991$
	Run 3	$K = 0.982$
	Run 4	$K = 0.982$

A study of the plot of  $\ln(1 - \text{Fraction Reacted})$  versus time gives a half-life of 11.9 days, 0.8 day, 0.92 day and 0.95 day for run 1, 2, 3 and 4 respectively. From the half-lives of these exchanges, it is apparent that the reaction was very slow at low temperature and increased rapidly with increasing temperature.

Though the experimental value of the equilibrium constant shows there is about 2% isotope effect, from Run 4, we found that there is about 2% experimental error. In summary, we might say that the isotope effect of this reaction is very small.

## SUMMARY

The position of equilibrium in the reaction between benzophenone-carbonyl- $C^{14}$  and benzhydrol in benzene solution has been measured in the presence of the catalyst aluminum tert-butoxide at certain specified conditions. The rate of the reaction varied from run to run because of the differences of catalyst concentration present in each run. The equilibrium isotope effect of this reaction is 0.98.

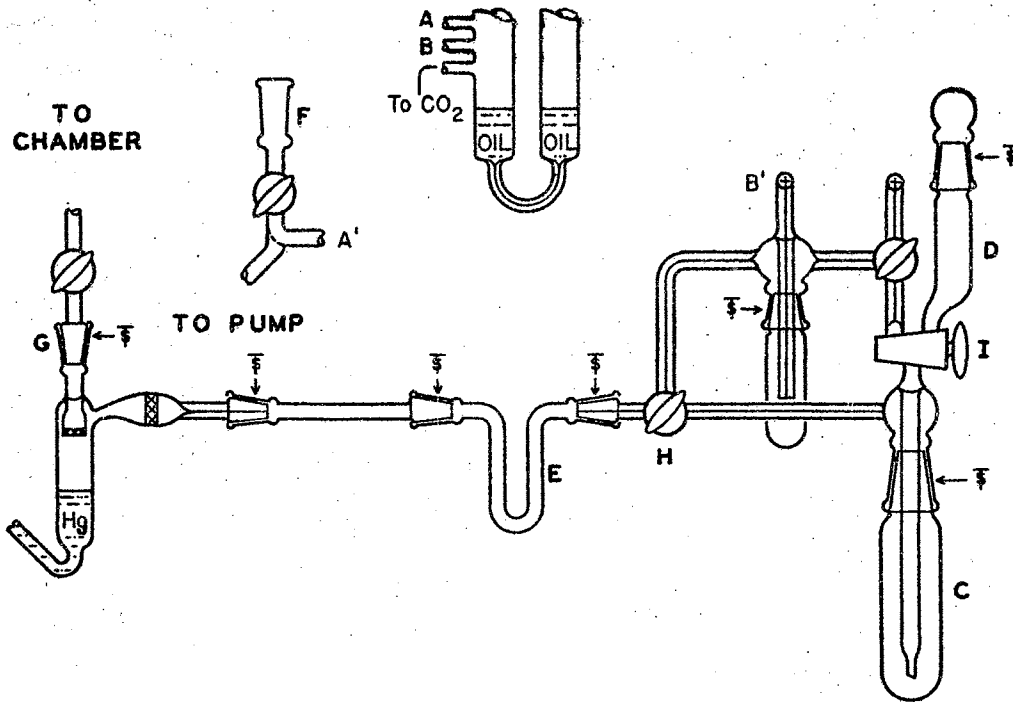
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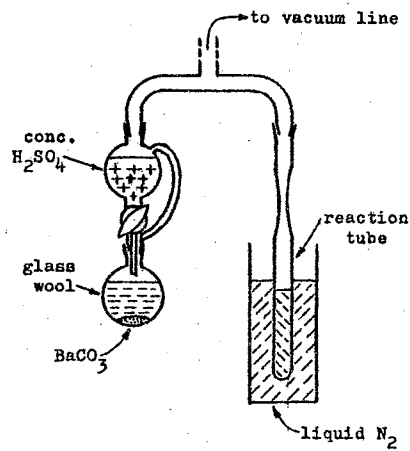
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APPENDIX



Apparatus A

Wet Combustion Apparatus for the Oxidation of Radiocarbon Compounds for C<sup>14</sup>O<sub>2</sub> Counting



Apparatus B

VITA

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Candidate for the Degree of

Master of Science

Thesis: THE EQUILIBRIUM ISOTOPE EFFECT IN THE REACTION BETWEEN BENZOPHENONE-CARBONYL-C<sup>14</sup> AND BENZHYDROL

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