THE ISOTOPE EFFECT OF CARBON-14 IN THE REARRANGEMENT REACTION OF 2,2,4,4-TETRAMETHYL-3-PENTANONE-1-^{14}C

By

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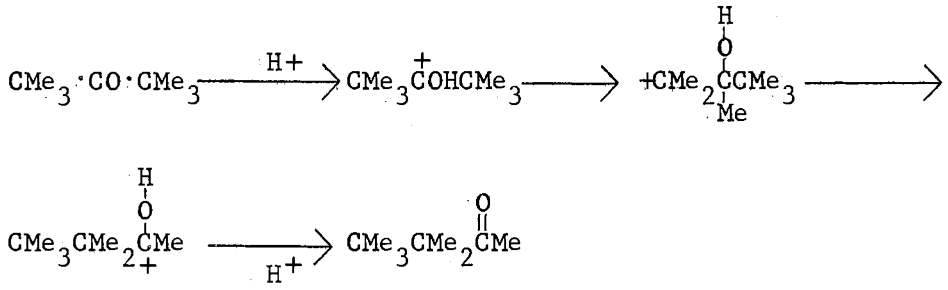
INTRODUCTION

During the past few years, the study of isotope effect in chemical reactions, has become an important tool in the determination of reaction mechanisms. For a reaction to show a measurable primary isotope effect, the bond of an isotopic atom must be broken or formed during the rate-determining step.

The following mechanism for the rearrangement of 2,2,4,4-tetramethyl-3-pentanone was proposed by Zalesskaya (17) and confirmed by Barton and Porter (1).



$$CMe_3\cdot CO\cdot CMe_3 \xrightarrow{H+} CMe_3\overset{+}{C}OHCMe_3 \longrightarrow +CMe_2\underset{\substack{|\\ Me}}{\overset{\substack{H\\ |\\ O\\ |}}{C}}CMe_3 \longrightarrow$$

$$CMe_3CMe_2\underset{+}{\overset{\substack{H\\ |\\ O\\ |}}{C}}Me \xrightarrow[H+]{} CMe_3CMe_2\overset{\substack{O\\ \|}}{C}Me$$

In our investigation carbon-14 was placed in the compound in the position where only the shift of the methyl group would involve the breaking of a carbon-14 bond. The results from this investigation will be used to determine if the shift of the methyl group in the rearrangement is the rate-determining step.

HISTORICAL

Isotope Effects

The isotope effect has been used extensively in the last few years in the determination of organic reaction mechanisms. The isotope effect arises from the difference in the masses of the isotopes which cause a difference in the vibrational frequency of the bond. The vibrational frequency of bonding is greater for a light isotope than for a heavy one. The higher the vibrational frequency the less stable the bond is; for example, the C^{12}-C^{12} bond will react faster than the C^{12}-C^{14} bond. As the reaction proceeds the concentration of the carbon-14 in the reactant will increase and the reaction will show an isotope effect. This isotope effect is apparent in changes in the equilibrium constants, rates of reaction, and bond strengths when the bond to the isotopic atom is broken or formed during the rate-determining step in a reaction.

It should be noted that not all isotope effects are easily detected. The smaller the relative difference in the masses of the isotopes, the less the isotope effect will be. For example, tritium is three times heavier than protonium so it should give a greater isotope effect than carbon-14 which is 1.167 times as heavy as carbon-12. In many of the heavier isotopes the isotope effect cannot be detected.

Isotope Effect of Carbon-14

Even though carbon-14 is a naturally occurring unstable isotope of carbon, it is produced commercially. The development of nuclear reactors has made possible large-scale production of carbon-14 of very high specific activity by the neutron bombardment of nitrogenous substances.

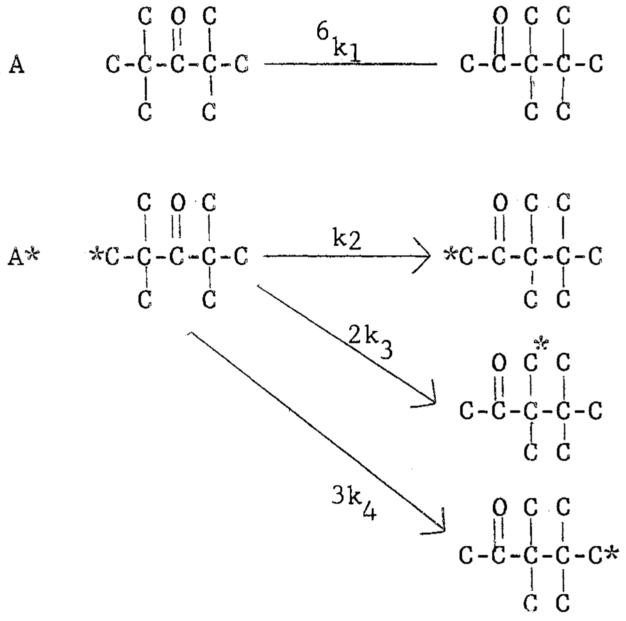
Carbon-14 decays to nitrogen-14 by the following equation (10).

$$^{14}C_6 \longrightarrow {}^{14}N_7 + {}^{o}e_{-1} + Q$$

It has a half life of 5,568 years (14) and emits β-particles with a maximum energy of 0.155 Mev.

Since carbon makes up the skeleton structure of organic compounds, there is no end to the uses of carbon-14 in determining isotope effects of organic reactions. To determine the isotope effects mathematical equations have been derived.

The equation for determining the isotope effect for this rearrangement reaction was derived in the following manner.



Consider the reaction involving A* and A, where A* represents the labeled compound and A the unlabeled one.

$$- d[A]/dt = 6k_1A \qquad \text{Eq. 1}$$

$$- d[A^*]/dt = A^*(k_2 + 2k_3 + 3k_4) \qquad \text{Eq. 2}$$

The magnitudes of k_3 and k_4 are equal to that of k_1 because none of these reactions involve the breaking of a C^{12}-C^{14} bond. If an isotope effect did occur in any of these reactions, it would be a secondary effect which could not be detected for carbon-14 in this case, therefore

$$- d[A^*]/dt = A^*(k_2 + 5k_1)$$

Rearranging and integrating Eq. 1 and Eq. 2 through the limits of A_o to A and A^*_o respectively we obtain Eq. 3 and Eq. 4.

$$- \log(A/A_o) = 6k_1t \qquad \text{Eq. 3}$$

$$- \log(A^*/A^*_o) = (k_2 + 5k_1)t \qquad \text{Eq. 4}$$

Dividing Eq. 4 by Eq. 3 gives Eq. 5.

$$\frac{\log\ (A^*/A^*_o)}{\log(A/A_o)} = \frac{k_2 + 5k_1}{6k_1} \qquad \text{Eq. 5}$$

One is subtracted from both sides and the equation is rearranged to Eq. 6.

$$\frac{\log(A^*/A)/(A^*_o/A_o)}{\log(A/A_o)} = \frac{k_2 + 5k_1}{6k_1} - 1 \qquad \text{Eq. 6}$$

The terms (A*)/(A) and $(A^*_o)/(A_o)$ represent molar radioactivities of the reactant after an extent of reaction, f, and at the start of the reaction respectively, and may be designated as N and N_o. The fraction of A reacted can be treated as the fraction of total reaction, f, that is, (1-f) is equal to A/A_o. The reaction rate of the labeled compound, k*, may be set equal to $k_2 + 5k_1$ and the reaction rate of the unlabeled compound, k, so:

$$k^*/k = 1 + \frac{\log(N/N_o)}{\log(1-f)} \qquad \text{Eq. 7}$$

This equation was used to calculate the isotope effect in the investigation.

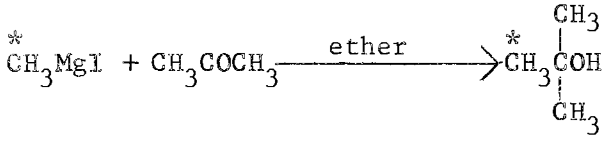
INTRODUCTION TO EXPERIMENTAL WORK

Our purpose in this investigation was to determine the isotope effect of carbon-14 in the rearrangement reaction of 2,2,4,4-tetramethyl-3-pentanone-1-^{14}C. To determine this isotope effect three experimental values were needed:

1. Activity of the starting material, N_o.
2. The degree of completion of the rearrangement, f.
3. Activity of the unreacted starting material at extent of reaction, f, N.

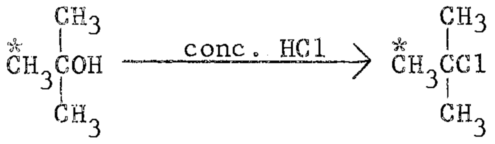
The labeled ketone was prepared according to the following procedure.

$$\overset{*}{C}H_3I + Mg \xrightarrow{\text{ether}} \overset{*}{C}H_3MgI \qquad (1)$$



$$\overset{*}{C}H_3MgI + CH_3COCH_3 \xrightarrow{\text{ether}} \overset{*}{C}H_3\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}OH$$

(2)



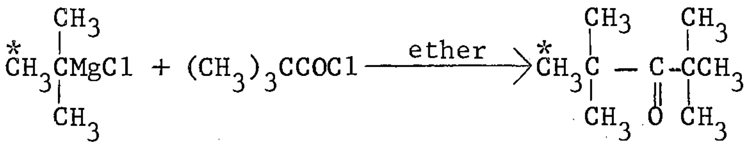
$$\overset{*}{C}H_3\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}OH \xrightarrow{\text{conc. HCl}} \overset{*}{C}H_3\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}Cl$$

(3)

$$\overset{*}{C}H_3\ \underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}Cl + Mg \xrightarrow{\text{ether}} \overset{*}{C}H_3\ \underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}MgCl$$

(4)

$$(CH_3)_3CCOOH + C_6H_5COCl \xrightarrow{\text{heat}} (CH_3)_3CCOCl + C_6H_5COOH \qquad (5)$$



$$\overset{*}{\mathrm{C}}\mathrm{H_3}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{MgCl} + \mathrm{(CH_3)_3CCOCl} \xrightarrow{\mathrm{ether}} \overset{*}{\mathrm{C}}\mathrm{H_3}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}} - \underset{\mathrm{O}}{\overset{}{\mathrm{C}}}\text{-}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{CH_3} \qquad (6)$$

The ketone was purified by preparative-scale gas chromatography, and a pure sample was assayed by wet oxidation with Van Slyke-Folch solution prepared by the method given by Glascock. (9) The apparatus in Figure 1 was used.

A weighed sample was placed in tube C and an evacuated ionization chamber was opened to the assay system. The oxidizing solution was added to C by using stopcock I and the sample was heated to effect complete oxidation. The carbon dioxide produced passed through the U-tube E, which contained stannous chloride to remove halogens. From E it passed through the tube E', which contains lead peroxide to remove nitrogen oxides, and into the ionization chamber. Tube C is flushed with "dead" carbon dioxide which carries the active carbon dioxide through the passage into the ionization chamber. The "dead" carbon dioxide is also used to complete the filling of the ionization chamber to one atmosphere of pressure.

The instrument used to measure the ion current was an Applied Physics Corporation Model 30 vibrating reed electrometer. The ionization chamber is attached to the electrometer, and the drift rate is measured. In order to convert the drift rate to activity in terms of μc./mmole, it is necessary to calibrate the chamber by determining the drift rate of a sample of carbon dioxide of known activity. A standard sample of sodium bicarbonate containing 0.0338 μc./g. gave a drift of 15.29 mv./sec. g. This factor was used to determine the molar activity of the labeled ketone which was 0.382 ± 0.003 μc./mmole. Although the

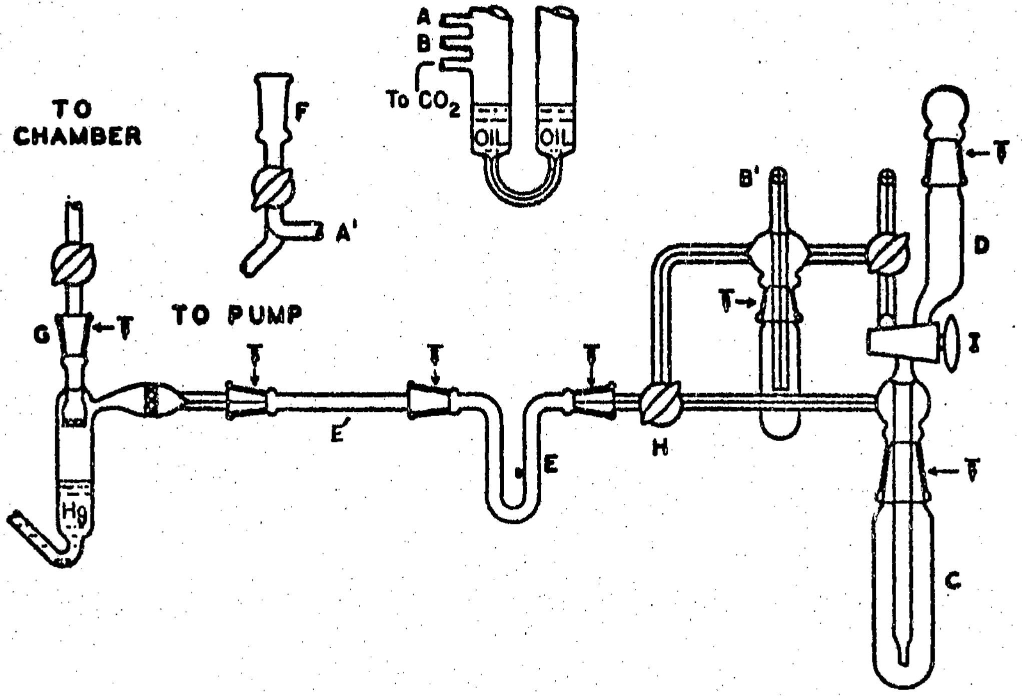


Fig. 1. Carbon-14 Assay Apparatus

molar activity of the ketone was found, the isotope effect was calculated using the relative rates of drift.

The starting material was then shaken for 12 hours in 81.3% sulfuric-acid to obtain approximately 80% rearrangement. After the reaction mixture was worked up the unreacted ketone was isolated with gas chromatography and assayed with the same procedure as above.

Equation 7 was used to determine the intermolecular isotope effect which is the ratio of reactivities of a normal molecule and an isotopically labeled molecule for a particular reaction.

$$\frac{k^*}{k} = \frac{\log(N/N_o)}{\log(1-f)} + 1$$

f = fraction reacted.

k^* = rate of reaction of the labeled compound.

k = rate of reaction of the normal compound.

N = activity of the isotopic mixture of reactant after fraction of reaction f.

N_o = activity of initial reactant.

From the values of N_o (activity of the starting material), N (activity of starting material at extent of reaction f), and f (the degree of completion), the k^*/k ratio (isotope effect) can be calculated.

EXPERIMENTAL

Preparation of 2-chloro-2-methylpropane-1-^{14}C

In a 300-ml. three-neck flask were placed 5.35 g. (0.22 moles) of magnesium turnings, 50 ml. of anhydrous ether and a magnetic stirring bar. Connected to the three-neck flask was a condenser with a calcium chloride drying tube, a 250-ml pressure-equalizing dropping funnel, and an inlet tube for nitrogen. Nitrogen was passed through the system until the reaction was started. In the dropping funnel were placed 31.23 g. (0.22 moles) of ^{14}C-methyl iodide containing 1 mc. of activity and 65 ml. of anhydrous ether. This methyl iodide-ether solution was added to the magnesium turnings over a period of 1.5 hours with vigorous stirring. During this time ether was added as needed to replenish the ether which escaped from the reaction mixture. After formation of the Grignard reagent was complete, 13.3 g.(0.23 moles) of acetone and 65 ml. of anhydrous ether were added through a dropping funnel to the solution of the Grignard reagent over a period of 1.5 hours with vigorous stirring. The Grignard complex was decomposed on an acidic ice mixture and the layers were separated. The aqueous layer was washed three times with 250-ml. portions of ether which were added to the separated layer and dried with anhydrous magnesium sulfate. The ether was distilled at a reflux ratio of 15 to 1 (one drop removed for every 15 refluxing back) until the temperature in the distillation flask reached 56°. After cooling, the solution was transferred to separatory funnel which contained concentrated hydrochloric acid in the ratio of 5 volumes of hydrochloric acid to 1 volume of reaction solution (6). It was shaken vigorously for 10 minutes, the layers were allowed to separate and the tert-butyl chloride was collected. The tert-butyl chloride solution was neutralized with 5% sodium bicarbonate and washed with 20 ml. of 5% sodium thiosulfate solution. After drying overnight with calcium chloride, 9.92 g. of tert-butyl chloride and ether were collected at 48-52°.

The gas chromatography analysis showed that 94.9% by weight of the 9.92 g. was tert-butyl chloride. This was a 46.2% yield from methyl iodide to tert-butyl chloride.

During the addition of acetone to the Grignard reagent, it was found that the lower concentration of the reactants gave less base-catalyzed side products.

Preparation of 2,2,4,4-tetramethyl-3-pentanone-1-^{14}C

The Grignard reagent of tert-butyl chloride was prepared using the procedure of Whitmore and Badertscher (15). In a 300-ml. three-neck flask were placed 5 g. (0.206 moles) of magnesium turnings, a magnetic stirring bar and enough ether to cover the turnings. Connected to the three-neck flask was a condenser with a calcium-chloride drying tube, a 250-ml. pressure-equalizing dropping funnel, and an inlet connected to a nitrogen source. Again nitrogen was passed through the system until the reaction was started.

To start the reaction 1.5 ml. of the tert-butyl chloride-ether solution and 2 drops of methyl iodide were added to the reaction flask. The remainder of the ether solution was added at the rate of one drop each 1-1.5 sec. It was important to continue vigorous stirring at all times and to replenish the ether lost by evaporation. After addition of the ether solution, the Grignard reagent was stirred for one hour. It was allowed to settle overnight, then filtered under a nitrogen atmosphere through glass wool into a dropping funnel. The dropping funnel was connected to a 300-ml. three-neck flask containing 24.1 g. (0.2 moles) of pivalic chloride, 10 g. of cuprous chloride catalyst and 200 ml. of anhydrous ether (11). A condenser with a calcium-chloride drying tube and an inlet to maintain a nitrogen atmosphere until the reaction was started were connected to the three-neck flask. The Grignard solution was added to the acid chloride over a period of 1 hour with vigorous stirring; the complex was decomposed on ice and the layers were separated. The aqueous layer was washed with a 200-ml. portion of ether, which was added to the ether layer already separated. This ether solution was neutralized with 5% sodium bicarbonate solution and washed with 25 ml. of sodium thiosulfate solution. The ether solution was dried with anhydrous magnesium sulfate and the ether was distilled at a reflux ratio of 8 to 1. When the fraction following the ether was distilled, 12.3 g. of the labeled ketone was collected at 148-154^{o}. After purification of the labeled compound by preparative gas chromatography, it was assayed, with the results shown in Table I. The radioactive yield from methyl iodide was 3.3%.

In 1949 Cook and Percival (7) reported that cuprous chloride increases the yield of hexamethylactone from 32% to 70-80% in the reaction of <u>tert</u>-butylmagnesium chloride and trimethylacetyl chloride. In 1953 Percival, Wagner and Cook (11) reported further that with the use of anhydrous ferric chloride as the catalyst the yield of hexamethylacetone was increased to 84%. In the present investigation the use of ferric chloride caused reduction, where the cuprous chloride gave a normal yield of hexamethylacetone. In trying to minimize the loss of labeled Grignard reagent, it was not completely filtered of excess magnesium, whereas in the investigation of Percival, Wagner and Cook, the filtered Grignard reagent was used. In 1941 it was shown by Whitmore et al. (16) that the excess of magnesium did not cause the reduction. We believe that the excess magnesium reduced the ferric chloride in our reaction and the reaction proceeded without catalyst. Even in a large excess of ferric chloride the side product was still formed. In the case of the cuprous chloride, it was already in its lower valence state and was not effected.

Preparation of trimethylacetyl chloride

The compound was prepared according to the procedure of Brown (4). In a 500-ml. round-bottom flask connected to the fractionating column was placed 1 mole of the acid and 2 moles of benzoyl chloride. The mixture was heated strongly until it began to boil, and the acid chloride was distilled out of the reaction mixture as rapidly as was consistent with good separation from the other constituents in the flask. This was accomplished by distilling at a rate such that the temperature at the top of the column did not exceed the boiling point of the acid chloride. Usually the temperature registered will be several degrees below the true boiling point, due to the fact that the acid chloride is partially carried over by the hydrogen chloride given off from the reaction mixture. If the preparation has been carried out correctly, the distillate is practically pure acid chloride containing a small amount of dissolved hydrogen chloride. However, to insure purity the acid chloride was distilled again.

Rearrangement of 2,2,4,4-tetramethyl-3-pentanone-1-^{14}C

The ketone was rearranged following the procedure of Zook, Smith and Greene (19). A 3-g. sample was dissolved in 150 ml. of 81.3% sulfuric acid in a 250-ml. Erlenmeyer flask. The mixture was shaken for 12 hours at 23° then poured on 250 ml. of ice. The organic compounds were extracted with carbon tetrachloride in 60-ml., 60-ml. and 30-ml. portions. The first 120 ml. of extract was washed with 60 ml. of distilled water and the last 30 ml. used to wash the water layer. The three extracts were dried with Drierite, and the carbon tetrachloride was distilled at a 10 to 1 reflux ratio. After most of the carbon tetrachloride had been removed, the residue was vacuum distilled to get a 100% transfer of the reaction mixture. Gas chromatography was used to determine the per cent of rearrangement and to collect the pure unreacted starting material. Three runs were made using the same procedure. Samples from each run were assayed and the isotope effect was determined for each run. The assay analyses are in Tables II, III, and IV.

RESULTS

TABLE I

ASSAY OF STARTING MATERIAL: 2,2,4,4-TETRAMETHYL-3-PENTANONE-1-^{14}C

Sample Number	Activity of the ketone, mv./sec.mg.	Deviation	Fraction unreacted (1-f)
1	1.204	0.009	
2	1.216	0.003	
3	1.229	0.016	
4	1.198	0.015	
5	1.219	0.006	
	Ave. 1.213	0.010	1.00

TABLE II

ASSAY OF UNREACTED 2,2,4,4-TETRAMETHYL-3-PENTANONE-1-^{14}C

RUN 1

Sample Number	Activity of the ketone, mv./sec.mg.	Deviation	Fraction unreacted (1-f)
1	1.242	0.033	
2	1.205	0.004	
3	1.200	0.009	
4	1.187	0.022	
	Ave. 1.209	0.017	0.174

Isotope effect

$(1-f)_{ave.}$ = 0.174

$N_{ave.}$ = 1.209

$N_{o_{ave.}}$ = 1.213

k^*/k = 1.002

TABLE III

ASSAY OF UNREACTED 2,2,4,4-TETRAMETHYL-3-PENTANONE-1-^{14}C

RUN 2

Sample Number	Activity of the ketone, mv./sec.mg.	Deviation	Fraction unreacted (1-f)
1	1.232	0.014	
2	1.217	0.001	
3	1.214	0.004	
4	1.208	0.010	
	Ave. 1.218	0.007	0.139

Isotope effect

$(1-f)_{ave.}$ = 0.139

$N_{ave.}$ = 1.218

$N_{o_{ave.}}$ = 1.213

k^*/k = 0.998

TABLE IV

ASSAY OF UNREACTED 2,2,4,4-TETRAMETHYL-3-PENTANONE-1-^{14}C

RUN 3

Sample Number	Activity of the ketone, mv./sec.mg.	Deviation	Fraction unreacted (1-f)
1	1.209	0.007	
2	1.216	0.000	
3	1.229	0.013	
4	1.210	0.006	
	Ave. 1.216	0.006	0.209

Isotope effect

$(1-f)_{ave.}$ = 0.209

$N_{ave.}$ = 1.216

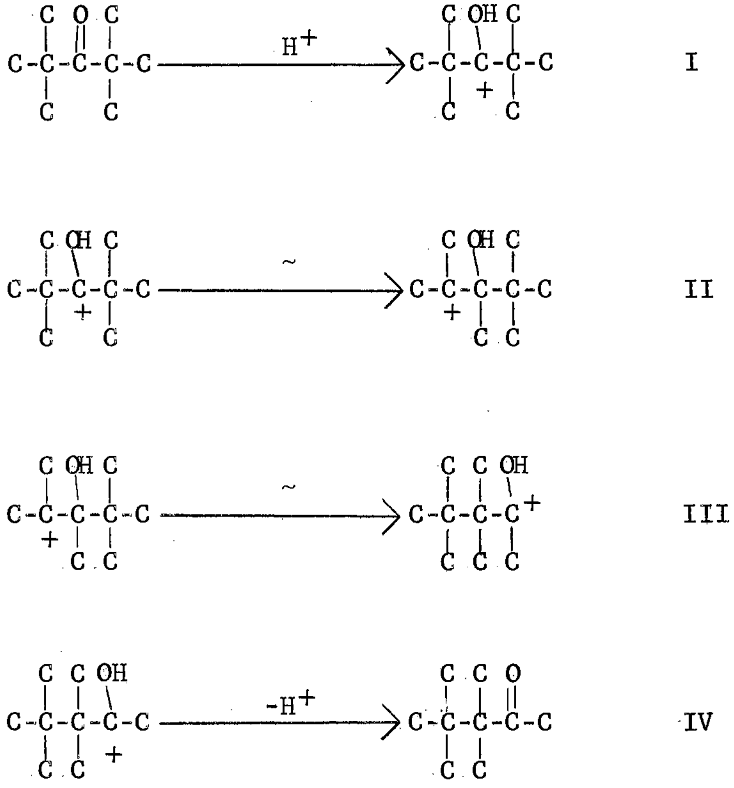
$N_{o_{ave.}}$ = 1.213

k^*/k = 0.998

DISCUSSION OF RESULTS

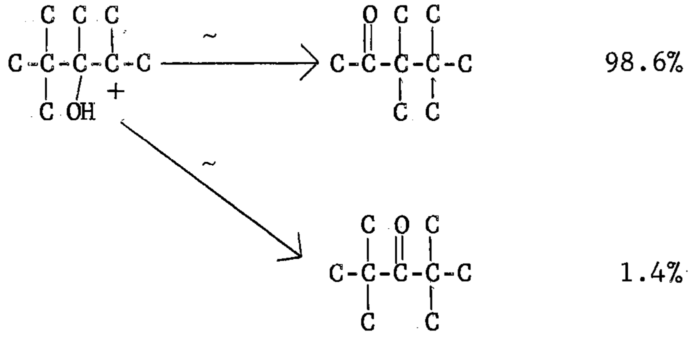
The purpose of this investigation was to determine the isotope effect of carbon-14 in the rearrangement of 2,2,4,4-tetramethyl-3-pentanone-1-^{14}C. From the results of this investigation and previous works, it is hoped to draw some conclusions about the rate-determining step of this rearrangement.

Several mechanisms have been proposed for this type of rearrangement. Barton, Morton, and Porter (2) and Zook and Paviak (18) proposed mechanisms involving the migration of the oxygen atom. Zalesskaya (17) proposed a mechanism in which the oxygen atom remains attached to its carbon atom. This mechanism is given below.

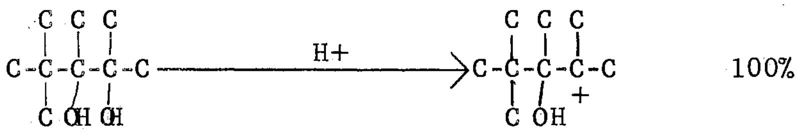


In 1956 Barton and Porter (1) found by tracer studies of the rearrangement of 2,2,4,4-tetramethyl-3-pentanone-3-^{14}C that most of the oxygen remains attached to its carbon as proposed by Zalesskaya. This fact tends to support a mechanism that involves a methyl and *tert*-butyl rearrangement rather than a shift of the oxygen atom.

In 1959 Stiles and Mayer (13) found with a tracer study of a pinacol rearrangement that the *tert*-butyl group migrates more readily than a methyl group.



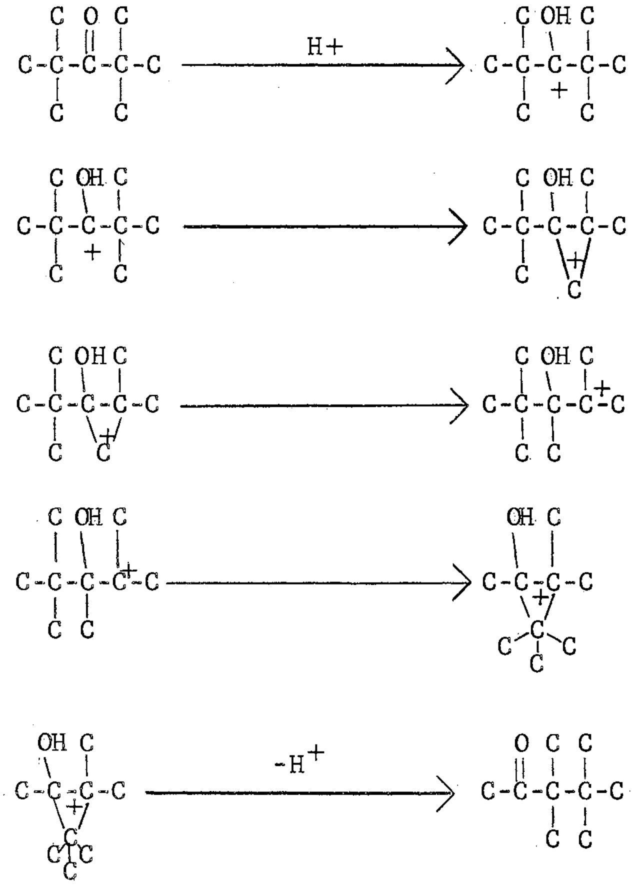
They also found that the oxygen atom which was lost came from the carbon atom not holding the *tert*-butyl group.



In view of these results it seems reasonable to assume that the rearrangement of ion II to ion III would be faster than the rearrangement of ion I to ion II. Therefore, the rearrangement of I to II would be the rate-determining step of the reaction. Consequently, the latter should show an isotope effect if the methyl group is labeled with carbon-14. In 1949 Bigeleisen (3) stated: "The largest ratio in the [reaction] rates occurs when the isotopic atoms are essentially free in the activated complex".

However, the results of this investigation show no isotope effect in the rearrangement of 2,2,4,4-tetramethyl-3-pentanone-1-^{14}C. It is believed that this lack of an isotope effect in the reaction is due to the transfer of the methyl group by an intramolecular shift rather than by formation of classical carbonium ion.

Consequently, the shift of the methyl group in the rearrangement of 2,2,4,4-tetramethyl-3-pentanone-1-^{14}C could be the rate-determining step and yet show no isotope effect if it is an intramolecular shift. We, therefore, propose the following mechanism for this reaction.



To complete this investigation and verify the mechanism, 2,2,4,4-tetramethyl-3-pentanone-2-^{14}C and 2,2,4,4-tetramethyl-3-pentanone-3-^{14}C should be rearranged and their isotope effects determined. If the shift of the methyl group is the rate-determining step in the rearrangement of 2,2,4,4-tetramethyl-3-pentanone-2-^{14}C an isotope effect should be found, since the shift of a methyl group would break a carbon-14 bond in one-half of the cases. On the other hand if the shift of the *tert*-butyl group is the rate-determining step, no isotope effect should be detected in the rearrangement of this compound because the shift of the *tert*-butyl group involves both the breaking and the formation of a carbon-14 bond.

When 2,2,4,4-tetramethyl-3-pentanone-3-^{14}C is rearranged, a reverse isotope effect is expected with the shift of the methyl group if it is the rate-determining step. In this case a carbon-14 bond would be formed in the rate-determining step. If the shift of the *tert*-butyl group is the rate-determining step, a normal isotope effect could be expected since a bond to the carbon-14 atom would be broken.

After the completion of the investigation of 2,2,4,4-tetramethyl-3-pentanone-2-^{14}C and 2,2,4,4-tetramethyl-3-pentanone-3-^{14}C, the rate-determining step and the mechanism of the rearrangement can be proposed with more certainty.

SUMMARY

The isotope effect in the rearrangement of 2,2,4,4-tetramethyl-3-pentanone-1-^{14}C has been determined. The average value for three runs was 0.999 ± 0.002. This value is within experimental error of 1 which indicates no difference in reactivities of the labeled and the unlabeled compound and no isotope effect. Since no isotope effect was detected, it was concluded that the shift of the methyl group was through a bridged ion instead of classical carbonium ion. The next step in this investigation should be to determine the isotope effects of 2,2,4,4-tetramethyl-3-pentanone-2-^{14}C and 2,2,4,4-tetramethyl-3-pentanone-3-^{14}C.

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