

A STUDY OF THE ISOTOPE EFFECTS IN THE POLYMERIZATIONS
OF CARBON-14 LABELED STYRENES

by

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INTRODUCTION

This work was undertaken to obtain more information about the mechanism of the propagation step in the polymerization of styrene.

More specifically, the aim has been to prepare styrene- β - C^{14} and styrene- α - C^{14} in tracer quantities, to determine the magnitude of the kinetic isotope effect for the polymerization of these tagged monomers in various reaction conditions, and to use these isotope effects to elucidate the mechanism of the propagation step in free-radical and cationic polymerizations. By comparing the observed isotope effects with various values which have been calculated from theoretical considerations, it is possible to obtain a better insight into the transition states for the reactions under consideration.

HISTORICAL

The Kinetic Isotope Effect

It is known that isotopic molecules do not react at identical rates, particularly if a bond to the isotopic atom is broken during the reaction. This difference in reaction rates is called the isotope effect, and in the case of carbon-14 versus carbon-12 its magnitude is often in the range of 4-10%. It is generally agreed that the isotope effect is shown only when a bond to the isotopic atom is broken or formed in the rate-determining step of a reaction. Summaries of work done on carbon isotopes have been given by Ropp (27) and Yankwich (34). A theoretical treatment has been prepared by Roginsky (26).

The relation between the mechanism of a reaction and the magnitude of the isotope effect for that reaction has been treated theoretically. On the basis of the absolute reaction rate theory developed by Eyring (14), the ratio of reaction rate constants for two isotopic molecules undergoing reaction in the same reaction vessel may be expressed as:

$$\frac{k_1}{k_2} = \frac{K_1}{K_2} \left[\frac{m_2^*}{m_1^*} \right]^{\frac{1}{2}} \frac{Q_{A_2}}{Q_{A_1}} \frac{Q_1^\ddagger}{Q_2^\ddagger} \frac{\delta_2}{\delta_1}$$

where:

k - rate constant

K - transmission coefficient

m* - effective mass of the activated complex along the coordinate of decomposition, usually calculated as the reduced mass $m_1 m_2 / (m_1 + m_2)$ of the two atoms involved in the bond being broken or formed in the rate-controlling step of the reaction

δ - length of the top of the potential energy barrier

Q - complete partition function

Q^\ddagger refers to the activated complex molecule and Q_A to the reactant molecule. The subscripts 1 and 2 refer to the properties of the two isotopic molecules respectively.

Bigeleisen and Mayer (4) have shown that the ratio of the partition functions of two isotopic molecules may be more simply expressed as a function of the vibrational energy levels of the molecules. Using various approximations, Bigeleisen (3) obtains the following equation for the ratio of reaction rates of isotopic molecules when the values of Δu are small and positive.

$$\frac{k_1}{k_2} = \left[\frac{m_2^*}{m_1^*} \right]^{\frac{1}{2}} \left[1 + \sum_i \frac{3N-6}{G(u_i)\Delta u_i} - \sum_i \frac{3N'-6}{G(u_i^\ddagger)\Delta u_i^\ddagger} \right]$$

$$G(u) = 1/2 - 1/u + 1/(e^u - 1)$$

$$u = \frac{h\nu}{hT} \quad \text{and} \quad \Delta u = \frac{h}{hT} (\nu_1 - \nu_2)$$

h - Planck constant

k - Boltzmann constant

T - Absolute temperature

The ν 's are the fundamental vibrational frequencies of the normal and isotopic molecules. $G(u)$ has been tabulated as a function of u (4).

In the above equation, it is assumed that the isotope effect on the potential energy surface of the reacting molecules is negligible and that the transmission coefficients are practically identical for the two isotopic molecules, so that $K_1 = K_2$ and $\delta_1 = \delta_2$.

Bigeleisen's equation separates the isotope effect on reaction rates into two factors:

(1) The "reduced mass effect" which expresses the effect of mass on the frequency of breaking or forming bonds in the activated complex.

(2) The "zero-point energy effect" which expresses the effect of mass change on the equilibrium between reactant molecules and the activated complexes.

It may be expected that the lighter isotopic molecule will have the greater reaction rate constant. The reduced mass effect factor $(m_2^*/m_1^*)^{\frac{1}{2}}$ is greater than unity (if the subscript 1 refers to the lighter molecule). Also, in bond cleavage the reacting molecules are usually more "tightly bonded" than the activated complex molecules. This means that:

$$\sum_i^{3N-6} G(u_i) \Delta u_i > \sum_i^{3N'-6} G(u_i^\ddagger) \Delta u_i^\ddagger$$

The maximum isotope effect will be obtained when the isotopic atoms are essentially free from bonding in the activated complex, i.e., when

$$\sum_i^{3N'-6} G(u_i^\ddagger) \Delta u_i^\ddagger = 0$$

When the isotope effect is less than the maximum calculated value, it indicates the occurrence of a three-center reaction in which the new bond is formed as the old bond is broken (32). In this case, the difference in zero-point energy in the activated complex in part cancels the difference in zero-point energy in the reactants. If bonding in the activated complex is as strong as that in the reactants then

$$\sum_i^{3N-6} G(u_i) \Delta u_i = \sum_i^{3N'-6} G(u_i^\ddagger) \Delta u_i^\ddagger$$

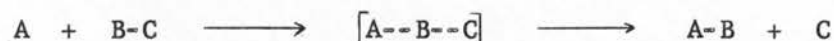
and only the reduced mass factor will remain in the evaluation of the isotope effect. In general, in any series of related reactions, the

reaction with the lowest activation energy will have the lowest isotope effect.

In order to calculate the theoretical isotope effect for a particular reaction it is necessary to evaluate the free energy functions $G(u_i)$ Δu_i for the normal molecule and the transition state. This calculation requires detailed knowledge of those vibrational frequencies of the molecule and of the activated complex that are affected by isotopic substitution. This information is often not available even for the normal molecule. Therefore the best that can be done from a theoretical point of view is to make approximate calculations based on some model of the transition state.

In the above expression for relative reaction rates of isotopic molecules, the reduced mass factor $(m_2^*/m_1^*)^{1/2}$ for a given reaction is evaluated as a simple bond rupture or bond formation. Since many reactions, such as substitution and displacement, involve simultaneous bond formation and rupture, Bigeleisen and Wolfsberg (5) (6) have extended the isotope effect equation to include the reduced mass factor for an isotopic three-center reaction.

In a three-center reaction of the type



the reaction coordinate, x_L , in the transition state may be expressed as

$$x_L = \alpha |r_B - r_C| - \beta |r_B - r_A|$$

where $r_B - r_C$ and $r_B - r_A$ are the separation of B - C and B - A respectively, and β/α determines the relative amount of bond formation between A - B to bond extension between B - C in the activated complex.

From these considerations, the isotope effect equation for simultaneous bond rupture and bond formation takes the form

$$\frac{k_1}{k_2} = \frac{\left[\frac{1}{m_{B_1}} + \frac{1}{m_{C_1}} \right] + p \left[\frac{1}{m_{B_1}} + \frac{1}{m_{A_1}} \right] + \frac{2p^{\frac{1}{2}}}{m_{B_1}}}{\left[\frac{1}{m_{B_2}} + \frac{1}{m_{C_2}} \right] + p \left[\frac{1}{m_{B_2}} + \frac{1}{m_{A_2}} \right] + \frac{2p^{\frac{1}{2}}}{m_{B_2}}} \left[1 + \sum_i^{3N-6} G(u_i) \Delta u_i^- + \sum_i^{3N'-6} G(u_i^\ddagger) \Delta u_i^\ddagger \right]$$

where $p = \beta^2/\alpha^2$ and $m_X =$ mass of atom X.

When p is equal to zero, the above equation reduces to the simple case of bond rupture, while, when $1/p$ is equal to zero, it becomes the combination of two atoms, molecules, or radicals.

Vinyl Polymerization

Vinyl polymerizations may be simply represented by the reaction



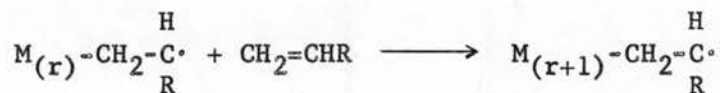
in which n is often in the range $10^2 - 10^5$. The polymer formed is essentially a saturated linear molecule, with monomer units connected by ordinary covalent linkages, and arranged in a head-to-tail fashion along the polymer chain (20). The polymers may be formed from the vinyl monomers using either free radical or ionic initiators. In this work, we shall be chiefly concerned with the propagation step in polymerizations by free radical and cationic mechanisms.

Free Radical Mechanism: Free radical addition polymerization is a chain reaction, consisting of the following basic steps (13).

1. Initiation



2. Propagation



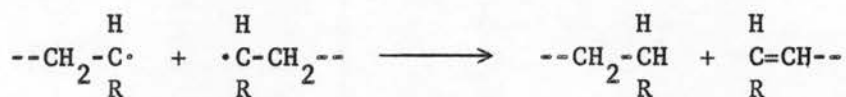
3. Termination



The polymerization is often initiated by the decomposition of compounds which easily form free radicals, such as benzoyl peroxide or azobis-isobutyronitrile. In thermal polymerization the initiation step is considered to be the formation of a diradical.

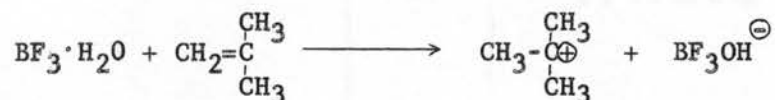


Once a free radical has been formed, a sequence of rapid propagation steps occurs. Experimental evidence indicates that the rate of propagation is independent of the chain length. The chain reaction is usually terminated by a coupling reaction as illustrated in the above termination reaction. However, disproportionation through transfer of a hydrogen atom may also cause chain termination to a lesser extent.

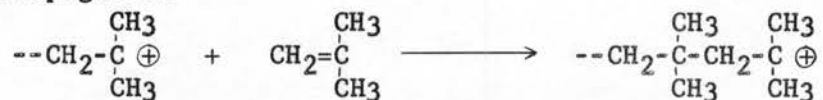


Cationic Mechanism: Certain vinyl monomers are readily polymerized by very small amounts of catalysts of the type used in Friedel-Crafts reactions (13). However, in many cases, these Lewis acid catalysts are ineffective without the presence of a co-catalyst such as water, alcohol, or acetic acid. The sequence of reactions for cationic polymerization may be represented by the polymerization of isobutylene in the presence of boron trifluoride monohydrate.

1. Initiation



2. Propagation



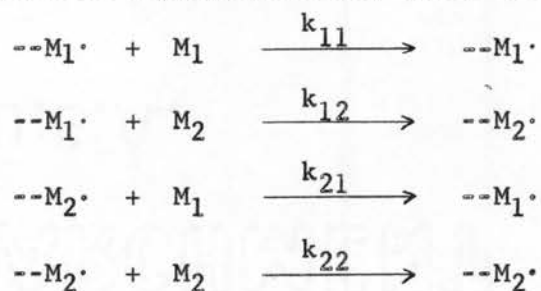
3. Termination



Many cationic polymerizations are characterized by high reaction rates at low temperatures. The temperature coefficients are low, or in some cases negative, i.e. the reaction rate actually decreases with rise in temperature. Evans and Polanyi (12) have stated that in solutions of relatively low dielectric constant the propagation step should not require any activation energy.

Copolymerization: When two different polymerizable monomers are mixed together, in the presence of an initiator, the resulting macromolecules generally contain monomer units of both types since the growing chain can attack either type of monomer. Such a reaction is called copolymerization and the resulting polymer a copolymer (1).

For the copolymerization of two monomers, the propagation step consists of four reactions, each with its own characteristic rate constant. For free radical copolymerization these are:



$\text{M}_1\cdot$ and $\text{M}_2\cdot$ represent chain radicals having monomers M_1 and M_2 respectively as their terminal, free-radical-bearing units. Under steady-state conditions, the ratio between the rates of disappearance of M_1 and M_2

is given by the equation

$$\frac{d[M_1]}{d[M_2]} = \frac{\left[\frac{[M_1]}{[M_2]} \right]}{\left[\frac{[M_1]}{[M_2]} + r_2 \right]} \left[r_1 \frac{[M_1]}{[M_2]} + 1 \right]$$

where r_1 and r_2 are monomer reactivity ratios defined as

$$r_1 = k_{11}/k_{12} \quad \text{and} \quad r_2 = k_{22}/k_{21}$$

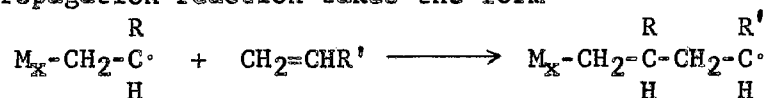
Thus r_1 represents the relative reactivity of a M_1^\cdot radical toward monomer M_1 as compared with monomer M_2 . Similarly, r_2 expresses the relative reactivity of a M_2^\cdot radical toward monomer M_2 as compared with monomer M_1 . If the two radicals M_1 and M_2 display the same relative preference for one of the monomers over the other then,

$$k_{11}/k_{12} = k_{21}/k_{22} \quad \text{and} \quad r_1 = 1/r_2 \quad \text{or} \quad r_1 r_2 = 1$$

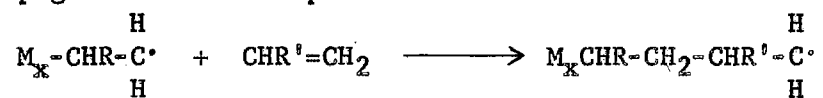
The reactivity ratio (r) expresses the relative reactivity of the "like" and "unlike" monomers for a given radical.

In most free-radical copolymerizations $r_1 r_2 \neq 1$; that is, the radicals display different selectivities in their choice of monomers. Also no free radical copolymerization has been found in which $r_1 r_2 > 1$. This means that the tendency of radicals to regenerate themselves never exceeds the tendency for alternation.

The order of reactivity of a given radical can be correlated with the stabilization of the product radical $M_x - \overset{\text{R}}{\underset{\text{H}}{\text{C}}} \text{CH}_2 \text{CH}^\cdot$ due to added opportunities for resonance offered by substituent R. From this it may be concluded that in head-to-tail propagation the radical will be located on the more substituted carbon owing to its increased resonance stability, and the propagation reaction takes the form



If the propagation reaction proceeded as



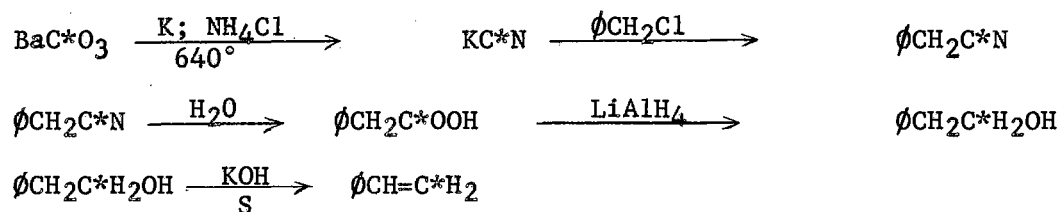
with the radical on the unsubstituted carbon, the substituents R and R' would have very little or no effect on radical reactivity. Hence, in this situation $r_1 r_2$ is approximately 1, which is not generally true for free radical polymerizations. The product $r_1 r_2$ approaches unity only in those cases in which the monomer substituents are similar to one another in their electron-attracting or -releasing capacities.

INTRODUCTION TO EXPERIMENTAL WORK

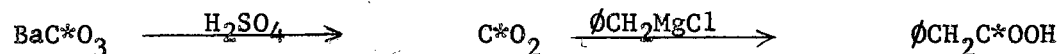
Monomer Syntheses

Styrene- β -C¹⁴: The carbon-14 used for this preparation was obtained as barium carbonate. It was therefore first necessary to develop an effective synthesis of styrene- β -C¹⁴ beginning with this material. Two methods of synthesis were considered as possible routes to the desired labeled styrene - a cyanide method and a Grignard method. The various steps of these syntheses were first carried out with "dead" materials in order to determine the method by which the radioactive styrene could be most efficiently obtained. These syntheses are represented by the following reactions.

For the cyanide method:



For the Grignard method:



Reactions from phenylacetic acid to styrene are the same as those for the cyanide method.

The formation of potassium cyanide from barium carbonate was carried out in a sealed tube in which a mixture of barium carbonate and ammonium chloride was heated to 640° in the presence of an excess of metallic potassium. The cyanide was recovered from the reaction mixture

by distilling the acidified reaction product into a potassium hydroxide solution.

The potassium cyanide solution that resulted was concentrated and the potassium cyanide then was caused to react with benzyl chloride to give phenylacetonitrile. The unpurified nitrile was hydrolyzed to phenylacetic acid, but with some difficulty. Neither sulfuric acid nor potassium hydroxide in glycerin was found to be an effective reagent for this hydrolysis. Somewhat better results were obtained when the hydrolysis was carried out in a mixture of sulfuric and phosphoric acids. However, the yields were not consistent and overall yields from potassium cyanide were only 50-60%.

The reduction of phenylacetic acid to phenethyl alcohol, with lithium aluminum hydride, proceeded smoothly with good yields.

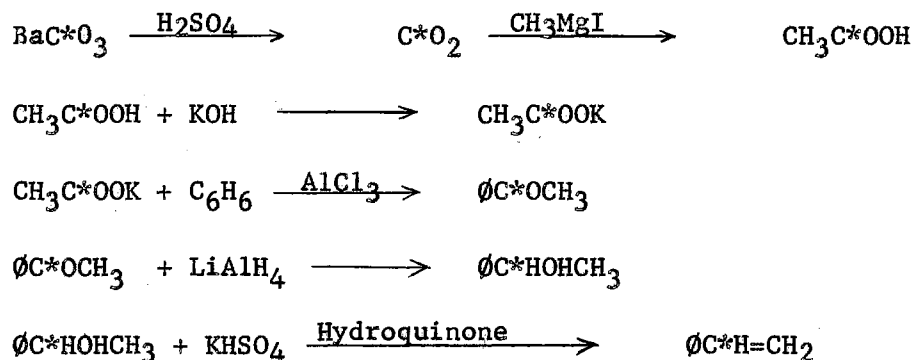
The conversion of the alcohol to styrene was carried out by heating phenethyl alcohol in the presence of a dehydrating agent and a polymerization inhibitor. Among the dehydrating agents used were potassium hydrogen sulfate, alumina, sodium hydroxide, and potassium hydroxide. Only potassium hydroxide in the presence of sulfur as a polymerization inhibitor was effective for this dehydration. A mixture of the alcohol, solid potassium hydroxide, and sulfur were heated to 170°. The styrene distilled as it was formed in the reaction. This styrene was suitable for polymerization without further purification.

In the Grignard method, the carbon dioxide was liberated from barium carbonate by the use of concentrated sulfuric acid. The carbon dioxide was condensed, by means of liquid nitrogen, in a tube containing benzylmagnesium chloride. The tube was sealed and the carbonation occurred upon warming to room temperature. This relatively simple procedure gave yields of about 90% phenylacetic acid based on barium carbonate.

Because the Grignard method was a simpler procedure which gave better overall yields, this method was chosen for the preparation of the styrene- β -C¹⁴. The "hot" run was similar to the trial runs except that corresponding "dead" compounds were added as scavengers during various extraction and transfer operations. These scavenger operations served to recover small amounts of the radioactive materials which would ordinarily be lost in these operations.

The styrene was prepared from the alcohol in small amounts as needed. This was done so that the bulk of radioactive material could be stored as a stable compound that would not polymerize upon standing.

Styrene- α -C¹⁴: The following synthesis scheme was used to prepare styrene- α -C¹⁴ from barium carbonate-C¹⁴:



Acetic acid was prepared using the procedure described above for phenylacetic acid except that methylmagnesium iodide was substituted for benzylmagnesium chloride. This procedure gave good yields of acetic acid in aqueous solution. Potassium hydroxide was then added to the acetic acid solution until a pH of 9.5 was reached. This basic solution was extracted with ether and the aqueous portion evaporated to dryness. The solid residue that remained was a very hygroscopic material, which made handling quite difficult. The yield of potassium acetate was low, probably owing to poor recovery of the acetic acid from the Grignard reaction mixture.

Acetophenone was obtained by a Friedel-Crafts synthesis with benzene and potassium acetate in the presence of a large excess of aluminum chloride. The acetophenone was purified by distillation on a vacuum line. Yields were 65-70% for this reaction.

The lithium aluminum hydride reduction of acetophenone to α -methylbenzyl alcohol proceeded smoothly with good yields.

The alcohol was converted to styrene by heating in the presence of potassium hydrogen sulfate and a polymerization inhibitor. A mixture of α -methylbenzyl alcohol, potassium hydrogen sulfate, and hydroquinone was heated first to 150-160°; after the initial reaction had subsided the temperature was raised to 190-195°. The styrene distilled as it was formed in the reaction. This styrene was suitable for polymerization without further purification.

As the overall radioactivity yield from this procedure was low, 0.5 millicuries of acetophenone carbonyl- C^{14} was purchased from Tracerlab and converted to styrene- α - C^{14} with good yields by the procedure described above.

Styrene Polymerization

Free Radical Polymerization: Styrene was polymerized thermally by placing sealed glass vials containing the monomer in an oil bath at 98-100°. At this temperature, thermal polymerization is reported to proceed at about 2% conversion per hour giving a polymer with an average molecular weight of about 400,000 (8). The polymerization rates for the labeled styrene monomers were generally higher than this, about 4-5% per hour at low conversions.

Unreacted monomer was removed from polymer by distillation on a vacuum line at about 1 micron pressure. The monomer-polymer mixture was heated with in infra-red lamp and the distilled styrene was collected

in a tube cooled with liquid nitrogen. Traces of monomer were still present in the polymeric product.

A white flocculent purified polymer was prepared by reprecipitation of the above material. The polymer was dissolved in 1,4-dioxane and the dioxane solution was added to a large amount of methanol. The precipitated polymer was removed and dried on a vacuum line at 1 micron pressure while heat was applied with an infra-red lamp.

Styrene containing about 1% benzoyl peroxide was polymerized in sealed glass vials immersed in an oil bath at 51-52°. The polymer formed at low conversion was removed from unreacted monomer by precipitation with methanol, followed by purification by reprecipitating a 1,4-dioxane solution of the polymer with an excess of methanol. The polymer formed at high conversion was dissolved in 1,4-dioxane and precipitated by adding the solution to an excess of methanol.

Cationic Polymerization: A solution of 2-3 mg. of anhydrous stannic chloride per gram of purified 1,2-dichloroethane was used as the catalyst-solvent system. The polymerizations were carried out by preparing a 20% by weight solution of styrene in the catalyst-solvent mixture, and allowing the resulting solution to react at room temperature. The degree of polymerization could be estimated from the amount of precipitate formed by adding a small drop of the reacting solution to methanol. The reaction was stopped by pouring the reactants into an excess of methanol. The precipitated polymer was removed by filtration and purified by reprecipitation from a 1,4-dioxane solution with methanol.

Copolymerization with Maleic Anhydride: For this study a one-to-one alternating copolymer of styrene with another monomer was desired. Maleic anhydride was chosen because it adds only to its comonomer and not to molecules of its own kind. Polymers of almost perfect alternation have

been reported (2) by a free radical copolymerization of styrene with maleic anhydride in large excess.

Mixed monomers of about 5 mole percent styrene and 95 mole percent maleic anhydride were copolymerized in benzene solution at reflux temperature in the presence of benzoyl peroxide. The copolymer precipitated as it was formed, therefore it separated from any soluble styrene polymer that might be present.

The precipitated copolymer was removed by filtration and washed with petroleum ether. This product was reprecipitated by dropwise addition of an acetone solution of the copolymer to vigorously agitated petroleum ether. The reprecipitated copolymer was dried in an evacuated drying pistol at 140° for 17 days.

Radioactivity Assay of Carbon-14 Labeled Compounds

Polymer samples of 5-10 mg. each were placed in small platinum boats and weighed on a microbalance. The samples were then transferred to a wet combustion apparatus and oxidized to carbon dioxide with hot Van Slyke solution (25). The radioactive carbon dioxide was flushed out with "dead" carbon dioxide and expanded into an evacuated stainless steel ionization chamber. The radioactivity assays were made on an Applied Physics Corporation Vibrating Reed Electrometer, Model 30.

Determination of the Observed Isotope Effect

The magnitude of the isotope effect may be evaluated from the equation of Stevens and Attree (29):

$$\frac{k^*}{k} = \frac{\ln(1-rf)}{\ln(1-f)}$$

where

k^*/k = ratio of reaction rate constant of labeled molecule to that of ordinary molecule

r = ratio of specific activity of product to specific activity of reactant

f = fraction reacted

For the preparations of labeled styrene polymers, two polymerizations were carried out for each determination of the isotope effect; one polymerization was stopped at a low conversion, the other was continued to high conversion. Because the radioactivity assays of liquid samples could not be obtained with good precision using the wet combustion method, the activity of the reactant in the form of styrene monomer was not determined. However, in the case of most styrene polymerizations, the activity of polymer at 100% conversion should equal that of the beginning monomer. Therefore, in this case the above equation could be applied as the specific activity of the high conversion (100%) polymer would be equal to the specific activity of the reactant.

In practice, conversions of 100% are very difficult to achieve, especially in bulk polymerizations. Therefore, the Stevens and Attree equation was rearranged so that the magnitude of the isotope effect could be calculated from the specific activities of two polymer samples of different degrees of conversion from a given monomer. In this rearranged equation, derived below, the specific activity of the initial reactant need not be known.

$$\text{Let } K = \frac{\ln\left(1 - \frac{n_1}{x} f_1\right)}{\ln(1-f_1)} = \frac{\ln\left(1 - \frac{n_2}{x} f_2\right)}{\ln(1-f_2)}$$

where

$K = k^*/k$

x = specific activity of reactant

n_1 = specific activity of product at fraction reacted f_1

n_2 = specific activity of product at fraction reaction f_2

$$\ln\left(1 - \frac{n_1 f_1}{x}\right) = K \ln(1-f_1)$$

$$-\frac{n_1 f_1}{x} = (1-f_1)^K - 1$$

$$x = -\frac{n_1 f_1}{(1-f_1)^K - 1}$$

also,

$$-\frac{n_2 f_2}{x} = (1-f_2)^K - 1$$

Eliminating x

$$\frac{n_2 f_2}{n_1 f_1} \left[(1-f_1)^K - 1 \right] = (1-f_2)^K - 1$$

$$n_2 f_2 (1-f_1)^K - n_1 f_1 (1-f_2)^K = n_2 f_2 - n_1 f_1$$

and

$$(1-f_1)^K - \frac{n_1 f_1}{n_2 f_2} (1-f_2)^K + \frac{n_1 f_1}{n_2 f_2} - 1 = 0$$

This equation can be solved for K by a method of successive approximations.

EXPERIMENTAL DATA

Synthesis of Styrene- β -C¹⁴

Cyanide Method

Potassium Cyanide from Barium Carbonate: This procedure for the preparation of cyanide from carbonate was similar to that described by Sixma, et al (28).

A mixture of 202 mg. of barium carbonate and 100 mg. of ammonium chloride was placed in a 10-mm. diameter #172 Pyrex tube. One and two-tenths grams of metallic potassium was washed twice with dry ether and then added to the reaction mixture. The tube was evacuated and sealed and then heated to 100° to melt the potassium. After vigorous shaking to mix the liquid potassium with the other materials present, the tube was placed in a furnace at 640°. After heating for one hour, the tube was removed and allowed to cool to room temperature.

The tube was opened and excess potassium was decomposed by careful addition of ethanol. The resulting mixture, which contained considerable solid material, was transferred to a round-bottom flask. The reaction tube then was washed with 20 ml. of warm water and the water was added to the contents of the flask.

The reaction mixture was acidified with 10 ml. of 50% sulfuric acid and the hydrogen cyanide which formed was distilled at atmospheric pressure into a potassium hydroxide solution. The distillation was continued until about 10 ml. of distillate had been collected.

The amount of cyanide present in the potassium hydroxide solution was determined argentometrically. The titration indicated a yield of cyanide of about 110% based on the original barium carbonate. This excess cyanide probably resulted from reaction of metallic potassium with atmospheric carbon dioxide.

Preparation of Phenylacetonitrile: A 50-ml. three-neck flask was fitted with a reflux condenser and a separatory funnel. Two and one-half grams of potassium cyanide was placed in the flask and dissolved in 2.5 ml. of warm water. A solution of 8.25 g. of benzyl chloride in 10 ml. of ethanol was placed in the separatory funnel. This solution was slowly added to the cyanide and the reaction mixture was then refluxed for four hours.

The separatory funnel was removed from the reaction flask and it was replaced by a flash-distilling unit. The ethanol and water were distilled until 11 ml. of material had been collected. The crude phenylacetonitrile remaining in the flask was then hydrolyzed directly without purification.

Preparation of Phenylacetic Acid: Eighteen milliliters of 85% phosphoric acid and 3.6 ml. of concentrated sulfuric acid were added to the crude phenylacetonitrile prepared above. This hydrolysis mixture was refluxed for two hours. After cooling, the mixture was made basic by the addition of 20% sodium hydroxide solution. The basic material which contained considerable solids was extracted with three 50-ml. portions of ether to remove unreacted phenylacetonitrile.

The remaining basic solution was acidified with 50% sulfuric acid and extracted with four 50-ml. portions of ether. The ether was evaporated leaving a yellow oil which changed to a white solid upon drying.

The crude acid was recrystallized from petroleum ether. Yield: 2.98 g. (57% based on potassium cyanide). M.P. 70-72°.

Grignard Method

Phenylacetic Acid-Carboxyl-C¹⁴ from C¹⁴O₂: This reaction, in which benzylmagnesium chloride reacts with radioactive carbon dioxide in a sealed tube, was carried out according to the procedure described by Lamprecht and Rehberg (18).

Carbon dioxide was liberated from barium carbonate-C¹⁴ with sulfuric acid on a vacuum line, and condensed, by means of liquid nitrogen, in a tube which contained a benzylmagnesium chloride solution.

Fifteen milligrams of barium carbonate-C¹⁴ (1 mc.) and 575 mg. of barium carbonate were weighed into the carbon dioxide generating flask. A mat of glass wool was packed above the salt to prevent spattering when the acid was added. A pressure-compensated separatory funnel containing 3.2 ml. of concentrated sulfuric acid was attached to the flask and the total assembly connected to the vacuum line. Also connected to the vacuum line was a vial containing approximately a twofold excess of benzylmagnesium chloride in ether. The Grignard mixture was cooled with a liquid nitrogen bath and the whole system was then evacuated to about 1 micron pressure. The reaction system was shut off from the vacuum manifold and carbon dioxide was generated by carefully adding the concentrated sulfuric acid to the barium carbonate. After the evolution of gas had ceased, the flask was heated for a few minutes with a small flame to expel any remaining carbon dioxide. The reaction tube which now contained the Grignard reagent and condensed carbon dioxide was sealed with a hand torch. After sealing, the tube was slowly warmed to room temperature by allowing the liquid nitrogen in the bath to evaporate. After warming, the tube was vigorously shaken to insure complete reaction.

The reaction tube was opened and the contents were treated according to the extraction scheme illustrated in Figure I.

The scavengers added at the indicated places served to remove residual radioactive phenylacetic acid. The amounts of scavengers used were as follows:

I:	97.3 mg.
II:	94.4 "
III:	99.4 "
Total:	291.1 "

The total acid recovered after drying was 656.6 mg. of a white crystalline solid, m.p. 73-74°. The yield was 365.5 mg. after subtracting the total weight of added scavengers (89.8% based on barium carbonate).

Preparation of Phenethyl Alcohol- α -C¹⁴: The reduction of phenylacetic acid with lithium aluminum hydride was carried out according to the procedure outlined by Nystrom and Brown (22).

A 100-ml. round-bottom, three-neck flask was fitted with a pressure-compensated separatory funnel, a reflux condenser containing a drying tube, and a magnetic stirring apparatus. Three-tenths of a gram of lithium aluminum hydride was added to 15 ml. of anhydrous ether which had been placed in the reaction flask. A solution of the phenylacetic acid prepared above (656.6 mg.) in 15 ml. of anhydrous ether was placed in the separatory funnel.

The acid solution was added dropwise to the lithium aluminum hydride solution with vigorous stirring. After the addition of the acid, remaining lithium aluminum hydride was decomposed by the addition of a solution of 1.0034 g. of "dead" phenethyl alcohol in 10 ml. of dry ether. Then 2 ml. of water was carefully added to the reaction mixture. The complexes formed in the reduction were decomposed by the addition of

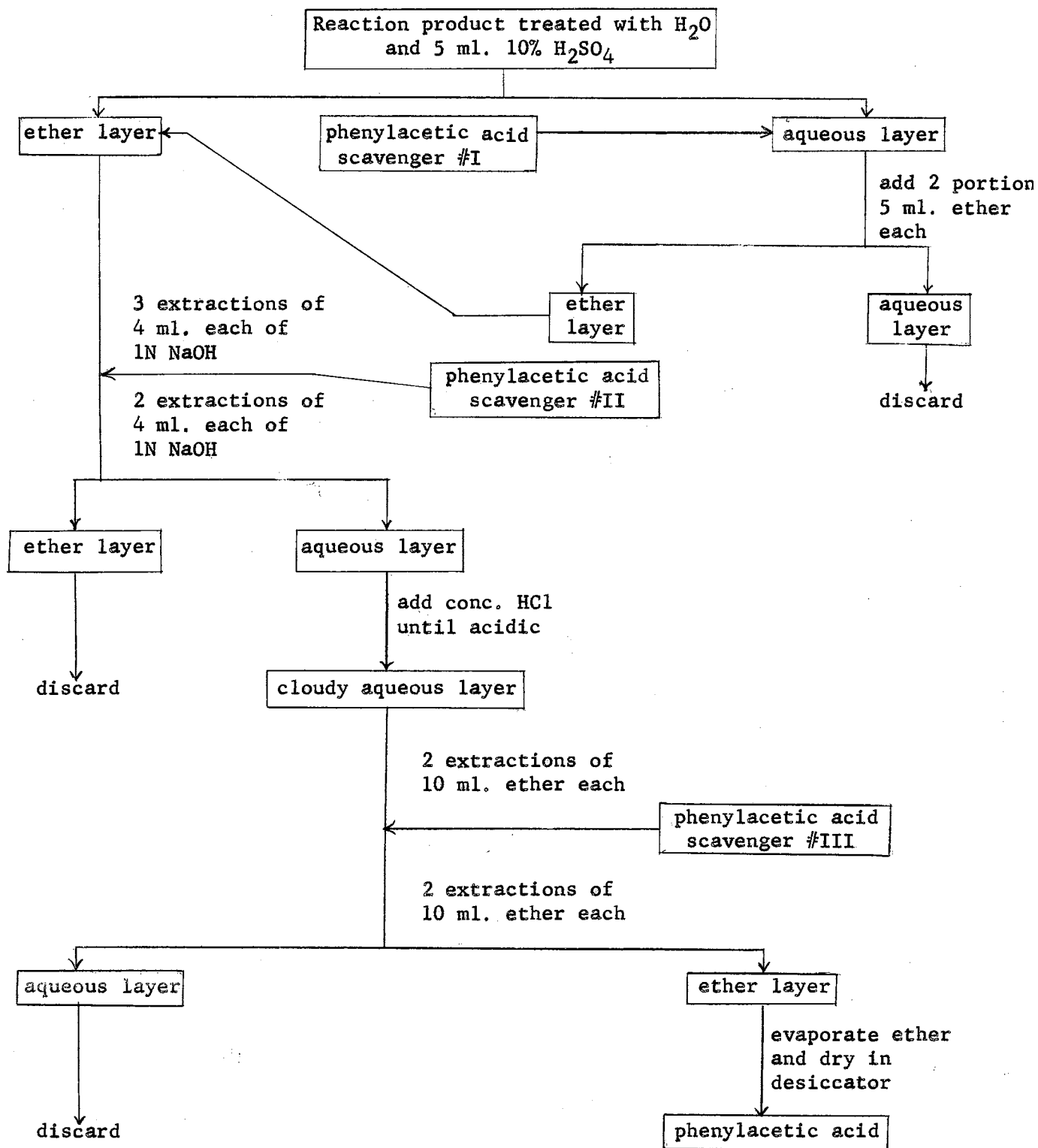


Figure I -- Extraction Scheme for Phenylacetic Acid-Carboxyl-C¹⁴ Preparation

12 ml. of 10% sulfuric acid.

The reaction products were separated according to the procedure outlined in Figure II. The weight of scavenger used in this separation was 0.2414 g.

The ether was evaporated from the phenethyl alcohol by adding successive small amounts of solution to a 20-ml. round-bottom flask to which a gentle suction was applied. The material remaining was a cloudy yellow liquid.

This crude alcohol was purified by distillation on a vacuum line. The flask containing the crude product was placed on the line which also contained a U-tube immersed in a dry ice-acetone bath. The crude alcohol was kept at room temperature with about 1 micron pressure for seven hours until distillation was complete.

A clear colorless liquid had collected in the U-tube. This was removed with a constricted pipette. Because considerable liquid adhered to the walls of the tube, 1.1916 g. of "dead" phenethyl alcohol was added and mixed with the remaining "hot" alcohol. This was then removed and added to the original sample. The total weight of alcohol was 2.8412 g. from which a value of 0.4048 g. was obtained by subtracting the total of the weights of added "dead" compound. The yield was 68.8% from phenylacetic acid. The overall yield from barium carbonate was 61.8%.

The radioactive alcohol was diluted to 14.64 g. with "dead" alcohol and assayed for radioactivity. An average of three samples assayed at 6.06 $\mu\text{c.}/\text{mmole}$. Assuming that 1 mc. of carbon-14 was present in the barium carbonate, the overall radioactivity yield was 72.6% for the phenethyl alcohol synthesis. The greater activity yield as compared with overall weight yield was probably caused by recovery of radioactive products from the scavenger operations.

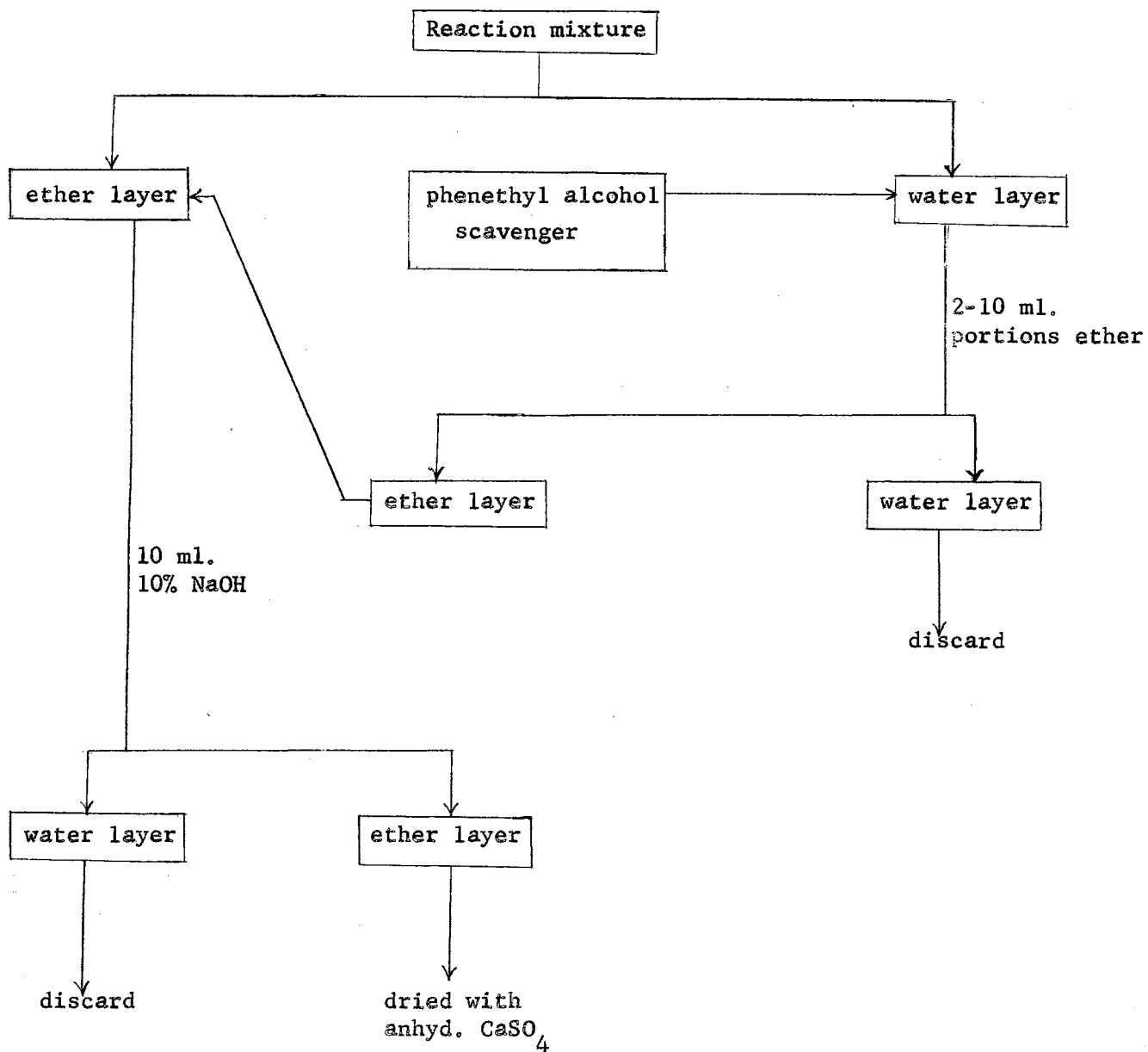


Figure II -- Extraction Scheme for Phenethyl Alcohol- α - C^{14} Preparation

Preparation of Styrene- β -C¹⁴: In this reaction, water was removed from phenethyl alcohol- α -C¹⁴ by the action of solid potassium hydroxide at an elevated temperature. The reaction product, styrene, was removed from unreacted alcohol by distillation as it was formed.

A mixture of 2.16 g. of the radioactive phenethyl alcohol, 1.19 g. of solid potassium hydroxide, and 0.045 g. of sulfur was placed in a 10-ml. reaction tube which was then immersed in a dibutyl phthalate bath. To the reaction tube was attached a distilling head and a condenser. The entire outer surface of the distilling head was wrapped with heating tape.

The dibutyl phthalate bath was heated to 170° and the distilling head was maintained between 150-160° with the heating tape. Styrene began to collect as distillate after about one-half hour of heating. Styrene and water continued to distill for about three hours at that temperature. The water layer was then removed from the distillate with a micro-pipette leaving 1.396 g. of styrene (yield 75.9%).

Synthesis of Styrene- α -C¹⁴

Acetic Acid-Carboxyl-C¹⁴ from C¹⁴O₂: This synthesis was similar to that described for the preparation of phenylacetic acid-carboxyl-C¹⁴. Barium carbonate (587 mg.) containing about 1 mc. of carbon-14 was reacted with 3.2 ml. of concentrated sulfuric acid. The carbon dioxide evolved was condensed into a tube containing 7 ml. (6 mmoles) of an ether solution of methylmagnesium iodide.

After completion of the reaction, the tube was broken and the contents were mixed with 15 ml. of water, and then 5 ml. of 10% sulfuric acid was added. The ether layer was removed and the aqueous layer was extracted with four 20-ml. portions of ether. Acetic acid (169.1 mg.)

was added to the water layer after the first ether extraction to serve as a scavenger. The ether was removed from the combined extracts by evaporation at room temperature.

Preparation of Potassium Acetate-Carboxyl-C¹⁴: The residue from the above ether extracts was taken up on 20 ml. of water. A dark red precipitate remained which probably was iodine that originated from the Grignard reagent. The liquid portion was decanted and the residue was washed with 15 ml. of water.

The combined aqueous solutions were neutralized with 10% potassium hydroxide and the end-point was determined by a pH meter. The end-point was exceeded at the first neutralization and 52.4 mg. of acetic acid was added. The potassium hydroxide solution was then added dropwise until a pH of 9.5 was reached. The resulting solution was yellow in color. This coloration was removed by extracting with two 20-ml. portions of ether.

The resulting potassium acetate solution was placed in an evaporating dish and the water was allowed to evaporate at room temperature first in the hood, then under vacuum after most of the water had been removed. The resulting solid was very hygroscopic and liquified after exposure to air for a short time. The solid was removed from the evaporating dish and 198.7 mg. of potassium acetate scavenger was added to the evaporating dish along with 5 ml. of water. This solution was then evaporated and the remaining solid was removed and combined with the original product. The final product consisted of 585.9 mg. of a slightly yellow solid. The weight yield was 69% from barium carbonate assuming equal recovery of scavenger and radioactive material.

Preparation of Acetophenone-Carbonyl-C¹⁴: The preparation of acetophenone was accomplished by a Friedel-Crafts reaction of benzene

with potassium acetate (15).

The reaction was carried out in a 50-ml. three-neck flask fitted with a stirrer, thermometer, and a reflux condenser that contained a calcium-sulfate drying tube.

The potassium acetate-carboxyl-C¹⁴ (see above) was mixed with 1.378 g. of "dead" potassium acetate. This material (1.964 g.) was placed in the reaction flask and dried in a vacuum desiccator for one-half hour.

After drying, the reaction apparatus was assembled. Seven and nine-tenths grams of dry benzene and 11.02 g. of aluminum chloride were added to the potassium acetate. Upon gentle heating, the aluminum chloride dissolved to give an olive-green solution. The reaction mixture was heated until it refluxed gently, whereupon the solution turned brown and hydrogen chloride was evolved. After 9.5 hours of refluxing, the contents were cooled to room temperature and the aluminum chloride complexes were decomposed by mixing with crushed ice. After being acidified with concentrated hydrochloric acid, the reaction product consisted of a straw-yellow water layer and a red-brown benzene layer. The benzene layer was separated and extracted twice with 10-ml. portions of 2% potassium hydroxide followed by 10 ml. of water. The benzene layer was then dried with calcium sulfate and the crude acetophenone-carbonyl-C¹⁴ was obtained by vacuum evaporation of the benzene at room temperature.

The crude product was purified by a vacuum line distillation at room temperature and about 1 micron pressure. The acetophenone was collected in a dry ice-ethanol cooled receiver; more volatile materials were further distilled into a receiver which was cooled with liquid nitrogen. The yield of acetophenone-carbonyl-C¹⁴ was 65%.

Preparation of α -Methylbenzyl Alcohol- α -C¹⁴: A 100-ml. round-bottom three-neck flask was fitted with a pressure-equalizing separatory funnel,

a reflux condenser with a drying tube containing calcium sulfate, and a magnetic-stirring setup. Acetophenone-carbonyl- C^{14} (1.89 g.) was dissolved in 25 ml. of dry ether and the solution was placed in the separatory funnel. The reaction flask contained a mixture of 0.4 g. of lithium aluminum hydride in 15 ml. ether.

The ether solution of acetophenone was added dropwise with vigorous stirring. After this addition, the remaining lithium aluminum hydride was decomposed by the careful dropwise addition of 5 ml. of water followed by 12 ml. of 10% sulfuric acid. The ether layer was removed and the water layer was washed with three 10-ml. portions of ether. The combined ether solutions were evaporated at room temperature, leaving the crude α -methylbenzyl alcohol. The alcohol was purified by a vacuum line distillation at room temperature and about 1 micron pressure. The yield for the lithium aluminum hydride reduction was 97%; the overall yield from barium carbonate was 43%.

The radioactive alcohol was diluted to 6.126 g. with "dead" alcohol. This material assayed at 2.06 $\mu\text{c.}/\text{mmole}$ for an average of three determinations. If it is assumed that 1 mc. of carbon-14 was present in the barium carbonate, the overall radioactivity yield was only 10.3% for the α -methylbenzyl alcohol- α - C^{14} synthesis. The loss in activity probably occurred during the extraction of acetic acid or during the drying and recovery of potassium acetate.

Preparation of Styrene- α - C^{14} : In this reaction water was removed from α -methylbenzyl alcohol- α - C^{14} by the action of potassium hydrogen sulfate at elevated temperature (7). The styrene was removed from the unreacted alcohol by distillation as it was formed.

A mixture of 2.20 g. of radioactive α -methylbenzyl alcohol, 0.02 g. of potassium hydrogen sulfate, and 0.02 g. of hydroquinone was placed

in a 10-ml. reaction tube which was immersed in a dibutyl phthalate bath. To the reaction tube was attached a distilling head and a condenser. The distilling head was wrapped with heating tape which kept its temperature at 150-160°.

The bath was heated to 150-160° for about 20 minutes until the vigorous boiling subsided. The temperature was then raised to 190-195°. Styrene and water continued to distill for about two hours at that temperature. The water layer was removed from the distillate with a micro-pipette, leaving 1.49 g. of styrene- α -C¹⁴ (yield 79%).

Polymerization of Styrene

The procedures for polymerizations as given below are examples of the preparations of polymers in low conversion. Polymers of high conversion were prepared and processed similarly. Reaction times for high conversion polymerizations were generally 40-80 times the corresponding reaction times for low conversion polymerizations. The procedures for obtaining styrene- α -C¹⁴ polymers were the same as those given below for the styrene- β -C¹⁴ polymerizations.

Thermal Polymerization of Styrene- β -C¹⁴: A sample of the radioactive styrene (1.0106 g.) was weighed into a vial made from 8-mm. Pyrex tubing. The tube was then immersed in a liquid nitrogen bath, evacuated, and sealed with a small torch. The styrene was polymerized thermally in an oil bath at 98-99° for four and one-fourth hours.

After this time the vial was cooled to room temperature and opened. The open vial was then placed in a tube which was attached to the vacuum-line distilling apparatus. The unreacted monomer was removed by distillation and collected in a tube immersed in liquid nitrogen. The monomer-polymer mixture was heated with an infra-red lamp. After three hours of heating at a pressure of about 1 micron, the polymer was

removed from the apparatus, broken up, and then replaced for another hour of heating under similar conditions. Polymer remaining after this purification weighed 0.2142 g.; this represents 21.2% conversion from monomer.

The polymer was further purified by a reprecipitation procedure (8). The above material was dissolved in 8.6 ml. of 1,4-dioxane and then precipitated by adding the dioxane solution to 125 ml. of methanol. The precipitate was digested by heating the mixture with an infra-red lamp and was then separated from the liquid by filtration, for which a fritted-glass crucible of fine porosity was used.

The polystyrene was dried first in a vacuum desiccator and then on the vacuum line at 1 micron pressure. During the vacuum drying the polymer was heated with an infra-red lamp. The final product was a white, very flocculent solid polymer.

Benzoyl Peroxide Initiated Polymerization of Styrene- β -C¹⁴: A sample of styrene- β -C¹⁴ (0.8554 g.) was weighed into an 8-mm. Pyrex vial and 8.6 mg. of benzoyl peroxide was added. The vial was immersed in a liquid nitrogen bath, evacuated, and sealed with a small torch. The vial was then placed in an oil bath at 51-52° for 12 hours.

After this time the vial was opened and its contents were added to 50 ml. of methanol in order to precipitate the polymer. After drying, the polymer was dissolved in 6 ml. of 1,4-dioxane and the resulting solution was poured into 110 ml. of methanol. The precipitated polymer was digested by heating the mixture with an infra-red lamp. The polymer was then separated by filtration followed by drying in a vacuum desiccator. The yield of polystyrene, after purification, was 0.1339 g. representing 15.7% conversion from monomer.

Cationic Polymerization of Styrene- β -C¹⁴: The cationic polymerization of styrene was based on a procedure given by Pepper (24) in which styrene was polymerized in the presence of stannic chloride with 1,2-dichloroethane as the solvent.

A solvent-catalyst solution was prepared by dissolving 0.042 g. of anhydrous stannic chloride in 17.26 g. of redistilled 1,2-dichloroethane. Four milliliters of the catalyst solution were mixed with 1.103 g. of styrene- β -C¹⁴ that had previously been dried over anhydrous calcium sulfate. The polymerization was carried out in a 20-ml. flask equipped with a condenser and drying tube. The flask was immersed in a water bath at room temperature and the contents were agitated with a magnetic stirrer. The extent of polymerization was estimated by adding a small drop of the reaction mixture to methanol and observing the amount of precipitate formed. After two hours reaction the polymerization was stopped by pouring the reaction mixture into 50 ml. of methanol. The method of purification of the polymer was the same as that used for polystyrene obtained by thermal initiation. The yield of polymer was 0.078 g. or 7% conversion from monomer.

Copolymerization of Styrene- β -C¹⁴ and Maleic Anhydride: The copolymers were prepared according to a procedure described by Alfrey and Lavin (2). Maleic anhydride (9.63 g.), recrystallized from chloroform, was dissolved in 90 ml. of thiophene-free benzene. A small amount (0.25 g.) of material, probably maleic acid, was insoluble and was removed by filtration. The solution was placed in a 300-ml. flask equipped with a reflux condenser and 0.647 g. of styrene- β -C¹⁴ was added. This represents 6.1 mole per cent styrene and 93.9 mole per cent maleic anhydride. One and one-half milligrams of benzoyl peroxide was added and the resulting solution was heated to reflux temperature. After a few

minutes of boiling the solution became turbid. It then was refluxed for another 15 minutes. The mixture was then cooled to room temperature with a water-bath and the precipitated copolymer was removed by filtration. The copolymer was washed with petroleum ether and dried in a vacuum desiccator.

The dried polymer was dissolved in 20 ml. of reagent-grade acetone and the solution was transferred to a dropping funnel. This solution was then added dropwise to 125 ml. of petroleum ether with vigorous stirring. A white flocculent copolymer precipitated. It was separated by filtration and dried in an evacuated drying pistol for 17 days at 140°. The yield of product was 0.320 g. or 25% based on styrene; this assumes a one-to-one alternating copolymer.

A polymer of 100% conversion based on styrene was obtained similarly with one hour reflux after initial cloudiness.

RESULTS

The Observed Kinetic Isotope Effect

The radioactivity assays were made on a vibrating reed electrometer. Readings were obtained in millivolts, which were converted to microcuries/millimole ($\mu\text{c}/\text{mmole}$) with the aid of the following constants:

- 1.39 x 10^{-16} coulombs/disintegration (for carbon-14 in CO_2)
- 3.7 x 10^{10} disintegrations/second for one curie
- 0.96 x 10^{10} ohms (resistance of electrometer)

From the above constants a value of $2.025 \times 10^{-2} \mu\text{c}/\text{millivolt}$ is obtained.

In most cases, the polymer activities as used in the calculation of the isotope effect were averages from five assays on each polymer. When the isotope effect for a certain polymerization was to be determined, it was found that best results were obtained when the individual assays for polymers of low and high conversion were intermixed chronologically. This intermixing of samples tended to minimize errors caused by slow drifts in the vibrating reed electrometer.

The individual activity measurements given below are averages of 15-20 converted millivolt readings as obtained from the strip chart of the recording apparatus. The specific activities were averaged for each polymer and 95% confidence levels of the means were determined using the Student-t distribution (33).

Thermally Initiated Polymerization: The isotope effects were obtained for three thermal initiated polymerizations. These determinations included two polymerization studies with styrene- $\beta\text{-C}^{14}$ and one with styrene- $\alpha\text{-C}^{14}$.

The results for the first thermal polymerization run with styrene- β -C¹⁴ at 98-99° are tabulated below. The activities as given for each polymer represent separate determinations on aliquots from the same sample.

<u>Polymer of 21% Conversion</u>		<u>Polymer of 92% Conversion</u>	
$\mu\text{c./mmole}$		$\mu\text{c./mmole}$	
4.40		4.49	
4.36		4.55	
4.32		4.51	
4.31		4.49	
4.33		4.56	
4.344 \pm 0.045	mean	4.520 \pm 0.041	
0.09	range	0.07	
0.0326	std. dev.	0.0297	

isotope effect, $k^*/k = 0.94_1$

After the above assays were made, the operation of the vibrating reed electrometer was improved by the installation of a turret switch containing three resistances of 10^8 to 10^{12} ohms. Previously the resistances were changed manually; this procedure could easily alter their resistivity and thus alter a series of readings. Therefore, the activities of the above polymers were redetermined with the following results:

<u>Polymer of 21% Conversion</u>		<u>Polymer of 92% Conversion</u>	
$\mu\text{c./mmole}$		$\mu\text{c./mmole}$	
4.33		4.61	
4.37		4.61	
4.35	mean	4.61	

isotope effect, $k^*/k = 0.91_5$

These determinations were made before the technique of intermixing individual samples was adopted. The re-evaluated result is probably the better, as the resistivity of the instrument may have been altered

somewhat by handling of the 10^{10} ohm resistor previous to the original assays of the 92% conversion polymer.

A second thermal polymerization of styrene- β -C¹⁴ was run at 97-99° in order to confirm the above determination. The results of this polymerization study are as follows:

<u>Polymer of 19% Conversion</u>			<u>Polymer of 96% Conversion</u>	
$\mu\text{c./mmole}$			$\mu\text{c./mmole}$	
4.44			4.72	
4.44			4.67	
4.47			4.72	
4.40			4.73	
4.40			4.75	
4.430 \pm 0.037	mean		4.718 \pm 0.037	
0.07	range		0.08	
0.0268	std. dev.		0.0264	

isotope effect, $k^*/k = 0.92_0$

This value of the isotope effect is in good agreement with the re-evaluated data from the first thermal polymerization study with styrene- β -C¹⁴.

Styrene- α -C¹⁴ was polymerized by thermal initiation at 98-100°. The results of radioactivity assays of polymers of low and high conversion are tabulated below.

<u>Polymer of 18% Conversion</u>			<u>Polymer of 92% Conversion</u>	
$\mu\text{c./mmole}$			$\mu\text{c./mmole}$	
4.28			4.42	
4.37			4.44	
4.33			4.39	
4.33			4.46	
4.34			4.40	
4.330 \pm 0.040	mean		4.422 \pm 0.036	
0.09	range		0.07	
0.0290	std. dev.		0.0256	

isotope effect, $k^*/k = 0.97_0$

The isotope effect for the thermal polymerization of styrene- α -C¹⁴ has also been determined by Ingley et al (16). In their work, the labeled styrene was polymerized at 120° to various degrees of conversion and the monomer and polymer phases were separated. The active polystyrene was compression molded into circular plates for counting. The recovered styrene monomer was first polymerized at 98+% conversion and then molded for counting. The radioactivity of each sample was measured with a thin-windowed Geiger tube, using an infinite thickness of the sample to eliminate self-absorption corrections. An isotope effect (k^*/k) of 0.979 ± 0.004 was found for a series of six determinations.

Benzoyl Peroxide Initiated Polymerization: Styrene- β -C¹⁴ was polymerized at 51-52° in the presence of 1% benzoyl peroxide. Radioactivity assays for the polymer samples are tabulated below.

<u>Polymer of 16% Conversion</u>			<u>Polymer of 85% Conversion</u>	
$\mu\text{c./mmole}$			$\mu\text{c./mmole}$	
4.47			4.75	
4.51			4.76	
4.51			4.75	
4.53			4.68	
4.51			4.75	
4.506 \pm 0.027	mean		4.738 \pm 0.041	
0.06	range		0.08	
0.0196	std. dev.		0.0293	

isotope effect, $k^*/k = 0.91_5$

Cationic Polymerizations: The isotope effects were obtained for three polymerizations catalyzed with stannic chloride. These runs included two styrene- β -C¹⁴ polymerizations and one styrene- α -C¹⁴ polymerization.

The results tabulated below are for the first stannic chloride polymerization run with styrene- β -C¹⁴ at 25°.

Polymer of 7% Conversion

$\mu\text{c.}/\text{mmole}$	
4.59	
4.60	
4.63	
4.60	
4.55	
4.594 \pm 0.036	mean
0.08	range
0.0258	std. dev.

Polymer of 92% Conversion

$\mu\text{c.}/\text{mmole}$	
4.75	
4.76	
4.79	
4.74	
4.82	
4.772 \pm 0.041	mean
0.08	range
0.0293	std. dev.

isotope effect, $k^*/k = 0.95_0$

Another set of stannic chloride catalyzed polymerizations of styrene- $\beta\text{-C}^{14}$ were run in a similar manner. The results of these radioactivity determinations are given below.

Polymer of 9% Conversion

$\mu\text{c.}/\text{mmole}$	
4.73	
4.66	
4.71	
4.74	
4.75	
4.718 \pm 0.044	mean
0.09	range
0.0319	std. dev.

Polymer of 96% Conversion

$\mu\text{c.}/\text{mmole}$	
4.82	
4.88	
4.83	
4.90	
4.82	
4.850 \pm 0.046	mean
0.08	range
0.0335	std. dev.

isotope effect, $k^*/k = 0.096_7$

The following results were obtained for the stannic chloride catalyzed polymerization of styrene- $\alpha\text{-C}^{14}$ at 25°:

Polymer of 15% Conversion

$\mu\text{c.}/\text{mmole}$	
5.07	
5.00	
5.09	
5.02	
5.08	
5.052 \pm 0.049	mean
0.09	range
0.0355	std. dev.

Polymer of 96% Conversion

$\mu\text{c.}/\text{mmole}$	
5.05	
5.03	
5.12	
5.03	
5.12	
5.070 \pm 0.058	mean
0.09	range
0.0415	std. dev.

isotope effect, $k^*/k = 1.00$

Copolymerization of Styrene- β -C¹⁴ and Maleic Anhydride: In the copolymerization runs the concentrations of maleic anhydride in the original comonomer mixture were 93.9 and 94.1 mole per cent for preparations to low and high conversions respectively. Differences in the concentrations of styrene in the copolymers of low and high conversions were not detected by infra-red analysis. Radioactivity assays for these copolymer products are tabulated below.

Polymer of 25% Conversion

$\mu\text{c./mmole}$
 2.328
 2.333
 2.331
 2.358
 2.376

2.345⁺0.026
 0.048
 0.0187

mean
 range
 std. dev.

Polymer of 100% Conversion

$\mu\text{c./mmole}$
 2.474
 2.446
 2.442
 2.459
 2.445

2.449 \pm 0.024
 0.052
 0.0172

isotope effect, $k^*/k = 0.95_1$

Summary of Observed Isotope Effects

The results of the observed isotope effects obtained for the various polymerizations are compiled in Figure III.

TYPE OF POLYMERIZATION PROPAGATION	MONOMER	INITIATOR	TEMPERATURE	OBSERVED ISOTOPE EFFECT
Free Radical	Styrene- β -C ¹⁴	Heat	97-99°	0.92 ₀
			98-99°	0.91 ₅
		Benzoyl Peroxide	51-52°	0.91 ₅
	Styrene- β -C ¹⁴ and Maleic Anhydride	Benzoyl Peroxide	80°	0.95 ₁
	Styrene- α -C ¹⁴	Heat	98-100°	0.97 ₀
			120°	0.97 ₉ *
Cationic	Styrene- β -C ¹⁴	Stannic Chloride	25°	0.95 ₀
			25°	0.96 ₇
	Styrene- α -C ¹⁴	Stannic Chloride	25°	1.00

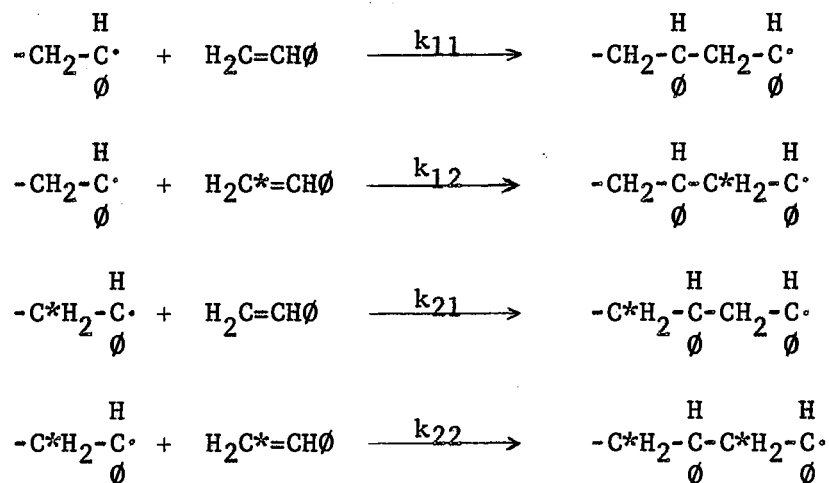
* Ingley et al (16)

Figure III -- Observed Isotope Effects for Styrene- β -C¹⁴ and
Styrene- α -C¹⁴ Polymerizations

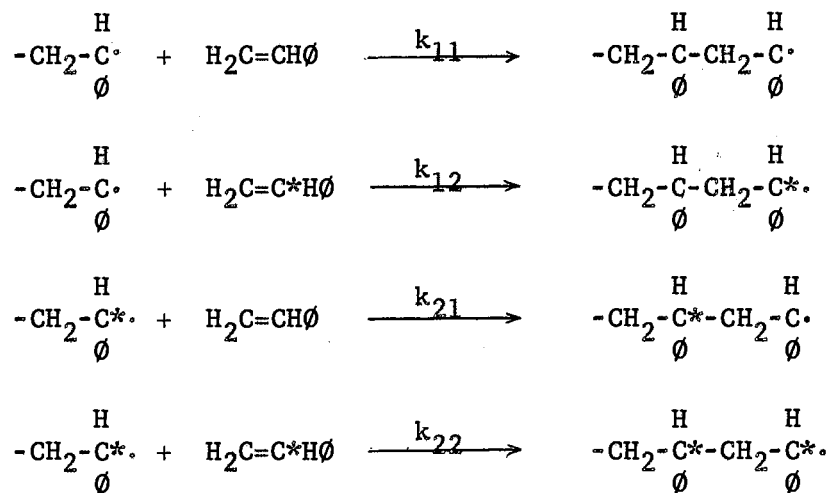
DISCUSSION OF RESULTS

Application of Copolymerization Scheme

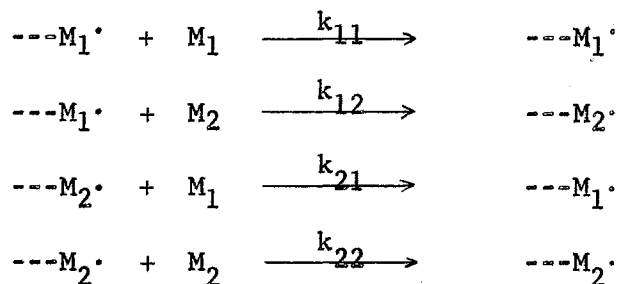
The polymerization of styrene with styrene- β -C¹⁴ may be treated according to the usual copolymerization scheme for propagation.



The scheme for the copolymerization system of styrene and styrene- α -C¹⁴ may be represented in a similar manner.



Let us consider the general copolymerization equations



from which the following expression may be obtained:

$$\frac{d [M_1]}{d [M_2]} = \left[\frac{[M_1]}{[M_2]} \right] \left[\frac{r_1 \frac{[M_1]}{[M_2]} + 1}{\frac{[M_1]}{[M_2]} + r_2} \right]$$

where $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$

The above equation may now be multiplied by $1/[M_1] / 1/[M_1]$ to give,

$$\frac{d [M_1]}{d [M_2]} = \frac{r_1 \frac{[M_1]}{[M_2]} + 1}{\frac{[M_1]}{[M_2]} + r_2} = \frac{r_1 \frac{[M_1]}{[M_2]} + 1}{1 + r_2 \frac{[M_2]}{[M_1]}}$$

Now let M_2 be styrene- β - C^{14} or styrene- α - C^{14} in tracer quantities;

then, $[M_2] \ll [M_1]$

and

$$\frac{d [M_1]}{d [M_2]} = r_1 \frac{[M_1]}{[M_2]}$$

Substituting back into the original copolymerization rate expression,

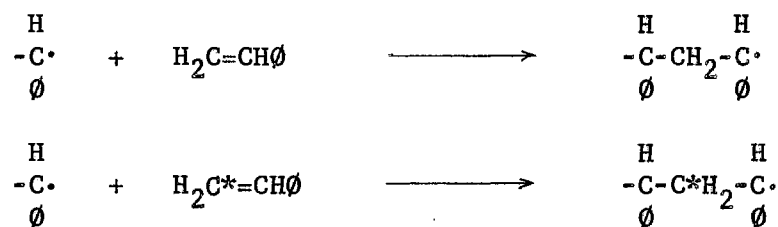
$$r_1 \frac{[M_1]}{[M_2]} = \left[\frac{[M_1]}{[M_2]} \right] \left[\frac{r_1 \frac{[M_1]}{[M_2]} + 1}{\frac{[M_1]}{[M_2]} + r_2} \right]$$

$$r_1 \frac{[M_1]}{[M_2]} + r_1 r_2 = r_1 \frac{[M_1]}{[M_2]} + 1$$

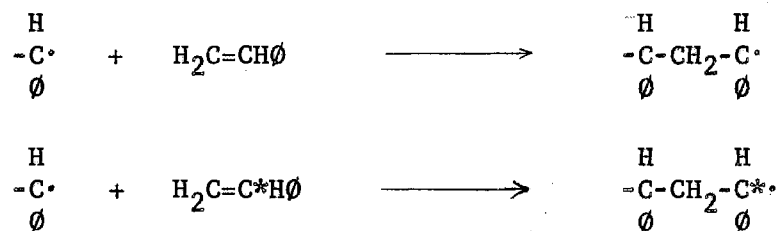
therefore, $r_1 r_2 = 1$ or $k_{11}/k_{12} = k_{21}/k_{22}$

Therefore, the two radicals $M_1\cdot$ and $M_2\cdot$ display the same selectivities in their choice of monomers. In the styrene - styrene- α -C¹⁴ case studied here, we may therefore assume that the relative reactivity of ---C \cdot radicals toward styrene and styrene- α -C¹⁴ monomers is the same as the relative reactivity of ---C¹⁴ radicals toward the same monomers. Thus, we may assume no isotope effect from those carbon-14 atoms which are located in the propagating radical. We may now reduce the copolymerization equations to the following:

For styrene- β -C¹⁴



For styrene- α -C¹⁴



We may now attack the problem of chemical composition of copolymers of a relatively high degree of polymerization according to the treatment of Wall (30) in which two propagation steps are involved. Let M_1 and M_2 represent the initial concentrations of labeled and normal styrene molecules respectively, and x_1 and x_2 be the corresponding amounts reacting in time t . Then we have

$$\frac{dx_1}{dt} = k_1 (M_1 - x_1) \qquad \frac{dx_2}{dt} = k_2 (M_2 - x_2)$$

$$\frac{dx_1}{dx_2} = \frac{k_1 (M_1 - x_1)}{k_2 (M_2 - x_2)} = \theta \frac{(M_1 - x_1)}{(M_2 - x_2)}$$

where θ is the ratio of two velocity constants.

Integrating the above expressions we have

$$k_1 = \frac{1}{t} \ln \frac{M_1}{M_1 - x_1} \quad \text{and} \quad k_2 = \frac{1}{t} \ln \frac{M_2}{M_2 - x_2}$$

$$\theta = \frac{\ln \frac{M_1}{M_1 - x_1}}{\ln \frac{M_2}{M_2 - x_2}}$$

Now let

$$M_1/M_2 = a \qquad x_1/x_2 = a' \qquad a'/a = r$$

then,

$$M_1 = aM_2 \qquad x_1 = a'x_2 = arx_2$$

If the copolymerization is allowed to proceed until $x_2/M_2 = f$, then,

$$\theta = \frac{\ln \frac{aM_2}{aM_2 - arx_2}}{\ln \frac{M_2}{M_2 - x_2}} = \frac{\ln \frac{1}{1 - rf}}{\ln \frac{1}{1 - f}} = \frac{\ln (1 - rf)}{\ln (1 - f)}$$

where r is equivalent to the ratio of activity of polymer at fraction reacted f to the activity of the monomer.

This expression is now identical with the Stevens and Attree equation (29) which forms the basis for the evaluation of the magnitude of the isotope effect from experimental data. Therefore, the isotope effects as experimentally determined represent the ratio of reaction rates for

propagation of polymerization.

Cationic copolymerization may be treated in a similar manner for styrene and its labeled comonomers giving similar equations to those above except that the unpaired electron is replaced with a positive charge.

Theoretical Evaluation of the Kinetic Isotope Effect

The following qualitative relations may be obtained from the observed isotope effects (see Figure III).

(1) No significant difference exists in the isotope effects for free-radical polymerization of styrene- β -C¹⁴ by thermal initiation or by benzoyl peroxide catalysis. This is the expected result because in either polymerization the propagation step consists of the radical attack of a growing chain upon a monomer unit. Because of the high degree of polymerization, any isotope effects involved in the initiation or termination steps would not be detected.

(2) The isotope effect for a given styrene- β -C¹⁴ polymerization is greater than the isotope effect for the corresponding polymerization with styrene- α -C¹⁴.

(3) The isotope effect for the cationic polymerization of a given labeled monomer is less than the isotope effect for the free radical polymerization with the corresponding labeled monomer. The Bigeleisen equation predicts that in any series of related reactions, the reaction with the lowest activation energy will generally have the lowest isotope effect (3). Therefore, the difference in isotope effect is probably due to the lower activation energy for the propagation reaction in cationic polymerization. It has been shown that in solutions of relatively low dielectric constant the reaction between the propagating ion and the monomer (neutral molecule) requires little or no activation energy (12).

The activation energy for propagation in free radical styrene polymerization has been found to be about 7 kcal./mole (9).

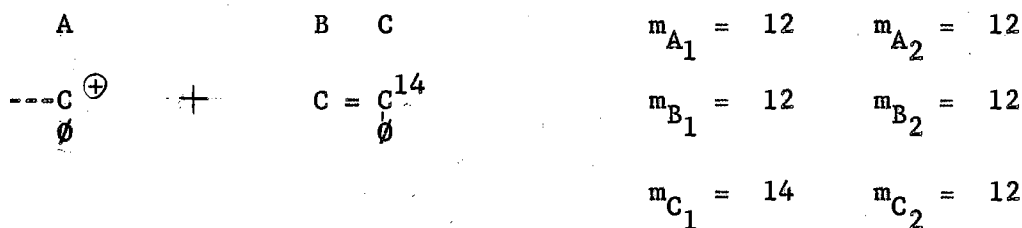
Three-center Reaction with no Activation Energy: If we assume no activation energy for the cationic polymerization, the isotope effect may be calculated from the reduced mass effect portion of the Bigeleisen three-center reaction equation. The zero-point energy factor need not be considered in the case of no activation energy because

$$\int_0^{\infty} G(u_i) \Delta u_i = \int_0^{\infty} G(u_i^\ddagger) \Delta u_i^\ddagger$$

The theoretical isotope effect for the cationic polymerization of styrene- α -C¹⁴ and styrene- β -C¹⁴ may now be calculated for various values of p. An example of such a calculation for styrene- α -C¹⁴ at p = 1 is given below.

$$\frac{k_1}{k_2} = \left[\frac{\left[\frac{1}{m_{B_1}} + \frac{1}{m_{C_1}} \right] + p \left[\frac{1}{m_{B_1}} + \frac{1}{m_{A_1}} \right] + \frac{2p^{1/2}}{m_{B_1}}}{\left[\frac{1}{m_{B_2}} + \frac{1}{m_{C_2}} \right] + p \left[\frac{1}{m_{B_2}} + \frac{1}{m_{A_2}} \right] + \frac{2p^{1/2}}{m_{B_2}}} \right]^{1/2}$$

The subscript 1 refers to the heavier molecule.



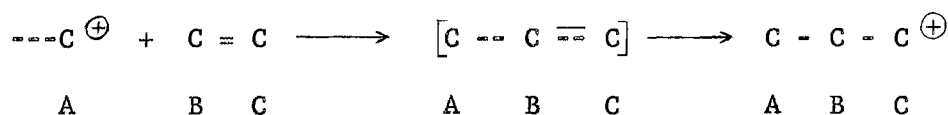
$$\frac{k_1}{k_2} = \left[\frac{1/12 + 1/14 + 1/12 + 1/12 + 2/12}{1/12 + 1/12 + 1/12 + 1/12 + 2/12} \right]^{1/2} = \left[\frac{82}{84} \right]^{1/2} = 0.988$$

Isotope effects have been similarly determined at various values of p for both styrene- α -C¹⁴ and styrene- β -C¹⁴ cationic polymerizations. The results are tabulated below.

p	Styrene- α -C ¹⁴	Styrene- β -C ¹⁴
0.00	0.964	0.964
0.25	0.979	0.953
0.44	0.983	0.952
1.00	0.988	0.951
2.25	0.992	0.952
4.00	0.995	0.953
6.25	0.996	0.954
16.00	0.998	0.957
∞	1.00	0.964

The change of isotope effect with change of p values is shown graphically in Figure IV.

The graph indicates that at relatively high p values the calculated isotope effects approach those found experimentally for cationic polymerizations. In the propagation reaction,



the value of p may be considered as a measure of the ratio of the amount of bond formation between A and B to the amount of bond extension between B and C in the transition state. The bond extension between B and C for cationic propagation involves the transition from a double bond to a single bond. Therefore, the amount of bond extension between B and C may be considered relatively small in comparison to the amount of bond formation between A and B in the transition state. The value for p would be relatively large in this situation. It may be seen from Figures III and IV that the isotope effect calculations fit experimental results best for $p > 5$.

Three-center Reaction Including Activation Energy Term: In order to calculate the isotope effect for the propagation step in free radical polymerization, the zero-point energy term must be considered. In this case,

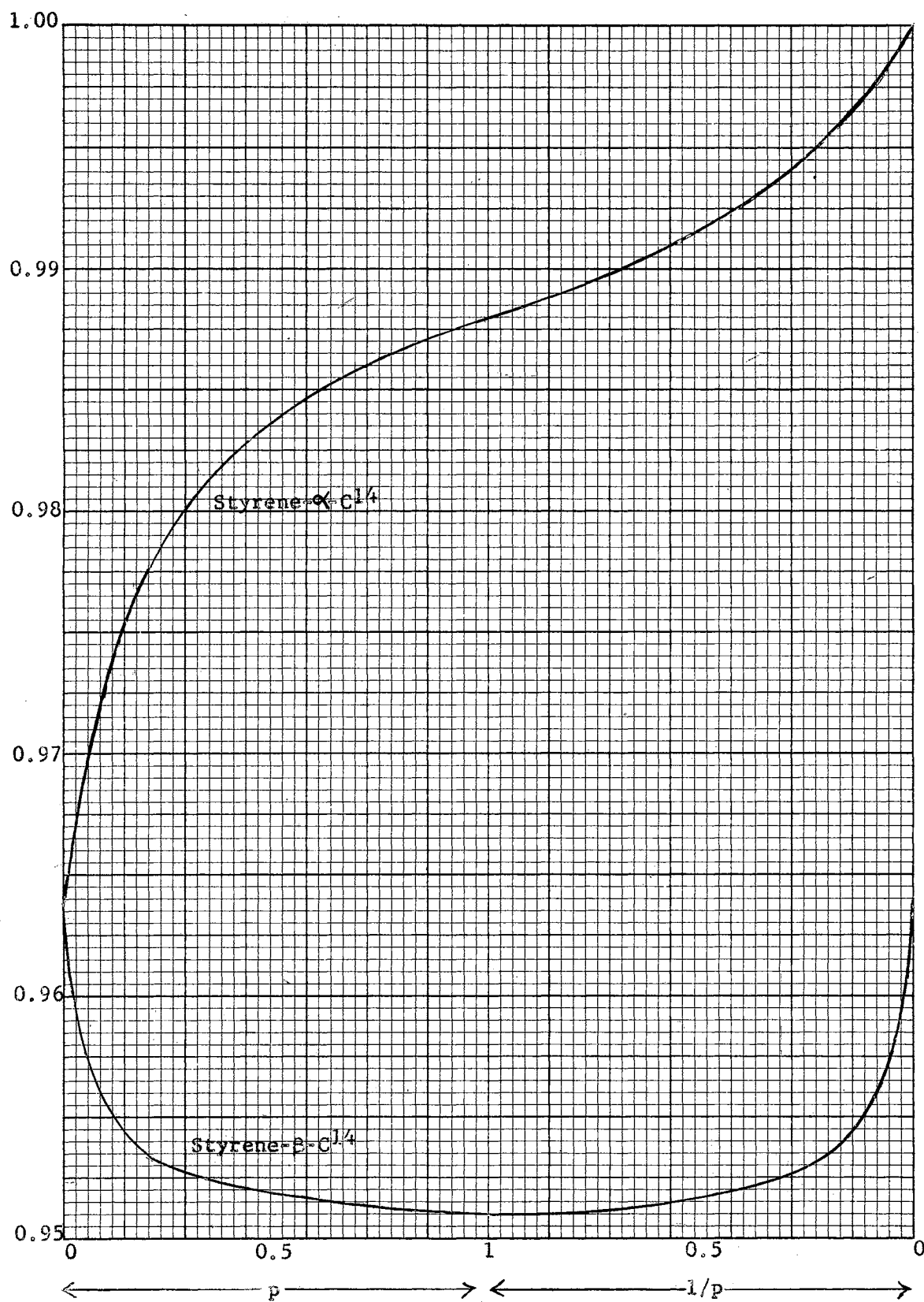
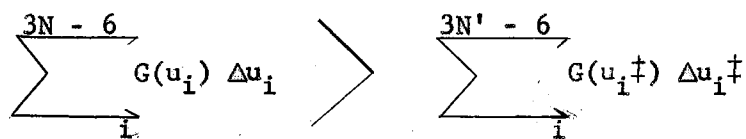


Figure IV -- Variation in the Isotope Effect with Change of p for Cationic Polymerizations of Styrene



since energy is required to form the activated complex for the propagation reaction. Therefore the calculated isotope effect will now consist of the reduced mass term as determined above multiplied by the function

$$f/f^\ddagger = \left[1 + \sum_i^{3N-6} G(u_i) \Delta u_i - \sum_i^{3N'-6} G(u_i^\ddagger) \Delta u_i^\ddagger \right]$$

In order to calculate the isotope effect for free radical polymerization of styrene it will be necessary to evaluate the free energy functions $G(u_i) \Delta u_i$ for the normal molecules and the transition states. For this calculation one requires knowledge or an assumption of the fundamental vibrational frequencies of the molecule and the transition state as affected by isotopic substitution. As this information is often not available even for the normal molecule, the best that can be done from a theoretical point of view is to make some approximate calculations based on models of the transition state. The fundamental vibrational frequencies involving carbon-14 bonds have not been determined, but they may be approximated from the frequencies of the corresponding carbon-12 bonds by application of the following equation (11).

$$\frac{W_2}{W_1} = \left[\frac{m_1}{m_2} \right]^{\frac{1}{2}}$$

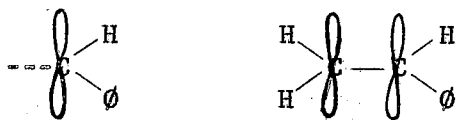
where W = vibrational frequency

m = reduced mass

The isotope effect for free radical propagation of styrene polymerization has been calculated for three models of the transition state. As the free energy functions are temperature-dependent, the

calculations were made at those temperatures at which the isotope effects were experimentally determined.

Transition State Model #1: For the first model, assume the simple case in which the π electrons associated with the vinyl group are unpaired in the transition state. The model may be represented as



in which the C-C vibrational frequency is assumed to be that found in the polymeric molecule. A skeletal stretching frequency of 1070 cm^{-1} has been assigned for the C-C bond in the polystyrene chain (19). If we assume this frequency for the C-C bond in the above transition complex, we may then proceed with the calculation of the isotope effect. The vibrational frequency for the monomeric styrene C=C side-chain bond is 1636 cm^{-1} (8).

$$\frac{k_1}{k_2} = \left[\text{reduced mass term} \right]^{\frac{1}{2}} \left[1 + \sum_i^{3N-6} G(u_i) \Delta u_i - \sum_i^{3N^\ddagger-6} G(u_i^\ddagger) \Delta u_i^\ddagger \right]^{-1}$$

$$u = \frac{hcW}{kT} \quad \text{and} \quad \Delta u = \frac{hc}{kT} (W_2 - W_1)$$

$$G(u) = 1/2 - 1/u + 1/e^{u-1}$$

h - Planck constant (6.62×10^{-27} erg sec.)

k - Boltzmann constant (1.38×10^{-16} erg/deg.)

c - velocity of light (3.00×10^{10} cm./sec.)

W - vibrational frequency expressed in cm^{-1}

T - absolute temperature

The reciprocal of the free energy term is used in this case in order to obtain the isotope effect in terms of k_1/k_2 with the subscript 1 referring to the heavier molecule. The free energy term will be the same for styrene- α - C^{14} and styrene- β - C^{14} polymerizations using this

particular model of the transition state. Various constants required in the calculations of the free energy term are tabulated below.

Fundamental Vibrational Frequencies

$\nu_{C^{12}=C^{12}}$	1636 cm^{-1}
$\nu_{C^{12}=C^{14}}$	1576 "
$\nu_{C^{12}-C^{12}}$	1070 "
$\nu_{C^{12}-C^{14}}$	1031 "

<u>T</u>	<u>hc/kT</u>
323°	0.004456
373°	0.003858
393°	0.003662

An example of the calculation of the free energy term is given below.

at 50°C.

$$u = 0.004456 \times 1636 = 7.290$$

$$G(u) = 0.3635$$

$$\Delta u = 0.004456 \times (1636 - 1576) = 0.2674$$

$$u^\ddagger = 0.004456 \times 1070 = 4.768$$

$$G(u^\ddagger) = 0.2988$$

$$\Delta u^\ddagger = 0.004456 \times (1070 - 1031) = 0.1738$$

$$\left[1 + \sum_i^{3N-6} G(u_i) \Delta u_i - \sum_i^{3N'-6} G(u_i^\ddagger) \Delta u_i^\ddagger \right]^{-1} = [1 + 0.3635 \times 0.2674 - 0.2988 \times 0.1738]^{-1} = 0.957$$

The free energy term may be calculated similarly for the other temperatures. The following values were obtained:

0.963 at 100°C.

0.965 at 120°C.

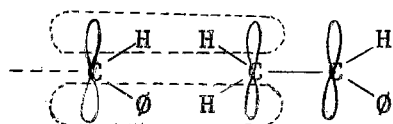
These values may now be combined with the reduced mass term for a three-center reaction to give the calculated isotope effect. If the p values as used in the reduced mass term are similar for cationic and free

radical propagation, the reduced mass effect may be taken from the table on page 47 at some p value which approximates the observed isotope effects found for cationic polymerization. Using $p = 6.25$ in the reduced mass term, the calculated isotope effects for free radical propagation based on the above model of the transition state are tabulated below.

monomer \ temperature, °C.	50	100	120
Styrene- α -C ¹⁴	-	0.959	0.961
Styrene- β -C ¹⁴	0.913	0.919	

These calculations are in good agreement with experimental results for styrene- β -C¹⁴ free radical polymerization, but are somewhat low compared with the isotope effects determined for the corresponding polymerizations with styrene- α -C¹⁴.

Transition State Model #2: For a second model of the transition state, consider that upon the approach of a polymer chain radical to a monomer unit, there occurs a simultaneous unpairing of monomer π electrons along with an interaction between a monomer π electron and the unpaired electron from the approaching radical. The transition state may be represented as follows:



The fundamental vibrational frequency of the monomer C-C bond will be considered the same as that assumed for the transition state in Model #1. A vibrational frequency which will represent the monomer-radical π bond interaction may be estimated as the difference in the fundamental vibrational frequencies between a normal C=C bond and C-C bond.

With this transition state model, the calculation of the free energy term for styrene- α -C¹⁴ polymerization is the same as that calculated for transition state Model #1, since the labeled carbon of the monomer is not involved with the monomer-radical π electron interaction. The isotope effect for the free energy term for styrene- β -C¹⁴ using this transition state model is calculated from the following data:

Fundamental Vibrational Frequencies

C ¹² =C ¹²	1636 cm ⁻¹
C ¹² =C ¹⁴	1576 "
C ¹² -C ¹²	1070 "
C ¹² -C ¹⁴	1031 "
C ¹² --C ¹² (π)	500 "
C ¹² --C ¹⁴ (π)	482 "

The following values were obtained for the free energy term for styrene- β -C¹⁴ polymerization.

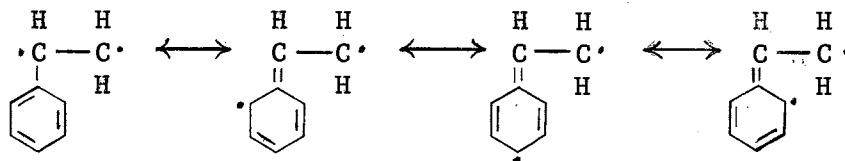
0.969 at 50°C.
0.973 at 100°C.

The calculated isotope effects for transition state Model #2 are compiled below. The reduced mass effects included in these calculations are the same as those used for Model #1.

Monomer \ Temperature, °C.	50	100	120
Styrene- α -C ¹⁴	-	0.959	0.961
Styrene- β -C ¹⁴	0.924	0.928	

The agreement of the above values with those found experimentally for styrene- β -C¹⁴ polymerizations are not so good as the calculations based on transition state Model #1.

Transition State Model #3: In this transition state model we consider the additional resonance forms that become possible when the π electrons on the side chain of styrene are unpaired.



In this model the C-aromatic bond will be shortened in the transition state owing to its increased double bond character.

The unpaired π electron associated with the labeled carbon atom in styrene- β -C¹⁴ is not involved with the resonance structures. Therefore, the evaluation of the free energy term for styrene- β -C¹⁴ polymerization based on this transition state model will be the same as the corresponding calculation made from Model #1.

In order to calculate the free energy term for styrene- α -C¹⁴ polymerization from this transition state model, vibrational frequencies for the C-aromatic bond must be assigned for both the normal molecule and the transition complex. These frequencies may be estimated from the observation that the force constants for the bonds C-C, C=C, and C \equiv C are approximately in the ratio 1:2:3 (17). The force constant, k , for a particular bond is defined as

$$k = 0.05877mw^2$$

where m = reduced mass of the pair of atoms forming the bond

w = vibrational frequency in cm^{-1}

The force constant for the C-C bond in ethane at 1187 cm^{-1} is 4.96×10^5 dyne/cm.

The bond length for the C-aromatic bond in styrene has been calculated as 1.44 \AA by the molecular orbital method (10). A C-C bond of this length

has 25% double bond character according to the Pauling equation (23).

From the above mentioned force constant relation, we may approximate the force constant of the styrene C-aromatic bond as

$$k = 4.96 \times 10^5 \times 1.25 = 6.20 \times 10^5 \text{ dyne/cm}$$

The vibrational frequency for the C-aromatic bond is 1326 cm^{-1} as calculated from the above force constant.

It has been found that the styrene radical is stabilized to the extent of about 20 kcal. by added resonance opportunities offered by the benzene ring (21). This would indicate a greater amount of double bond character for the C-aromatic bond in the transition state. If we assume 1.5 double bond character in this case,

$$k = 4.96 \times 10^5 \times 1.5 = 7.44 \times 10^5 \text{ dyne/cm}$$

and

$$W = 1453 \text{ cm}^{-1}$$

The isotope effect may now be calculated for styrene- α - C^{14} polymerization based on transition state Model #3 and the following vibrational frequencies:

$\text{C}^{12}=\text{C}^{12}$	1636 cm^{-1}
$\text{C}^{12}=\text{C}^{14}$	1576 "
$\text{C}^{12}-\text{C}^{12}$	1070 "
$\text{C}^{12}-\text{C}^{14}$	1031 "
C^{12} -aromatic (normal)	1326 "
C^{14} -aromatic (normal)	1278 "
C^{12} -aromatic (transition)	1453 "
C^{14} -aromatic (transition)	1400 "

The following values for the free energy term are obtained:

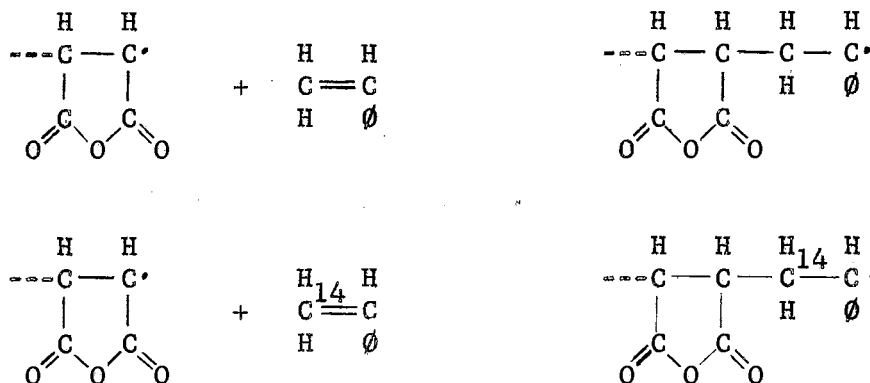
$$\begin{aligned} &0.972 \text{ at } 100^\circ\text{C.} \\ &0.973 \text{ at } 120^\circ\text{C.} \end{aligned}$$

Including the mass term for $p = 6.25$ we have,

Monomer	Temperature, °C.		
	50	100	120
Styrene- α -C ¹⁴	-	0.968	0.969
Styrene- β -C ¹⁴	0.913	0.919	

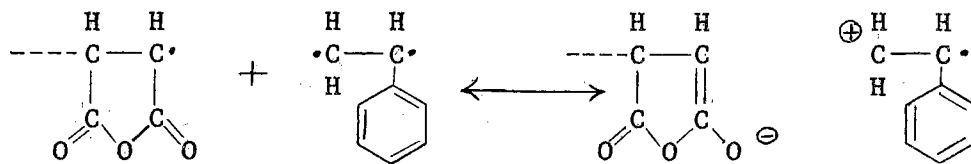
The values obtained using this transition state most nearly approximate the isotope effects found experimentally for the free radical polymerizations.

Styrene - Maleic Anhydride Copolymerization: The isotope effect for the free radical copolymerization of styrene- β -C¹⁴ and maleic anhydride was somewhat less than the corresponding polymerization of styrene- β -C¹⁴ by itself. For a one-to-one alternating copolymerization, the equations representing the reaction of the isotopic substituent may be represented as follows:



From these equations it would appear that the isotope effect should not differ significantly from the case where the attacking radical is another styrene unit, i.e., ordinary styrene- β -C¹⁴ polymerization. However, there is evidence which indicates the activation energy of propagation may be lowered by the participation of transition state resonance structures in which electron transfer has occurred between

radical and olefin (31).

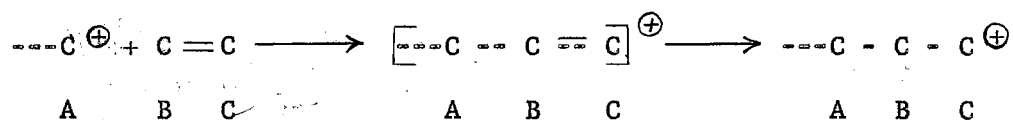


The theoretical treatment of the isotope effect predicts that for two related reactions, the reaction with the lower activation energy should have the lower isotope effect. Therefore, the lower observed isotope effect for the styrene - maleic anhydride copolymerization may be explained by the lower activation energy for chain propagation.

CONCLUSIONS

The theory of the kinetic isotope effect predicts that for two isotopic molecules undergoing reaction in the same reaction vessel, the lighter molecule will have a greater rate constant if the isotopic center is involved in the rate-determining step of the reaction. The magnitude of this difference in reaction rate constants is determined by the nature of the reacting system in the transition state. In this work, the propagation reactions for cationic and free-radical polymerizations of styrene were studied. The following conclusions were formed from a comparison of experimentally obtained isotope effects with theoretical considerations.

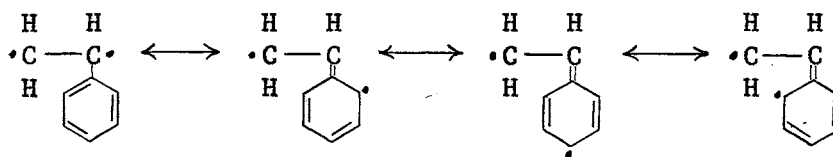
(1) For cationic propagation of styrene polymerization, where little or no activation energy is involved, the experimental isotope effects from styrene- α -C¹⁴ and styrene- β -C¹⁴ indicate a three-center reaction of the type



The theoretical isotope effect evaluations which best fit experimental data are those in which the amount of bond formation A - B in the transition state is relatively large in comparison to the amount of bond extension B - C. This would seem reasonable in that upon the approach of ion A, the maximum bond extension B - C may be considered to be that difference which exists between a C=C double bond and a C-C single bond.

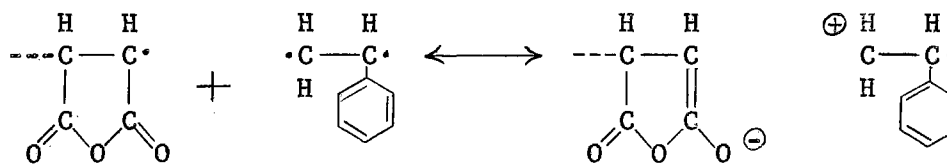
(2) In free radical polymerization of styrene, the theoretical calculation of the isotope effect is further complicated by a definite activation energy for propagation. Theoretical considerations indicate that greater isotope effects should be obtained for free-radical propagation than for the corresponding cationic polymerizations as a result of the difference in activation energies for propagation. This is in agreement with experimental results.

The theoretical isotope effects for polymerizations with styrene- α -C¹⁴ and styrene- β -C¹⁴ were approximated for various models of the transition state. The calculation which best fit experimental data was based on the following transition state model,



in which the π electrons of the monomer vinyl group are unpaired with subsequent stabilization of the biradical by three quinonoid resonance structures.

(3) The isotope effect for styrene- β -C¹⁴ free radical polymerization was greater than that for the free-radical one-to-one alternating copolymerization of the same tagged monomer with maleic anhydride. This indicates there is less activation energy involved in the reaction of styrene monomer with a maleic anhydride radical than in its reaction with a radical of its own kind. This may be explained by increased resonance stabilization arising from the following radical-monomer interaction in the transition state.



The contribution of this interaction involving electron transfer from monomer to radical is in addition to the resonance stabilization contributions of the three quinonoid structures which may be written for the biradical and the radical-ion.

SUMMARY

The kinetic isotope effects were studied for the propagation steps in free radical and cationic polymerizations of two carbon-14 labeled monomers, styrene- α -C¹⁴ and styrene- β -C¹⁴. The tagged monomers were obtained by synthesis from barium carbonate containing carbon-14. Free-radical mass polymerizations were initiated either thermally or with benzoyl peroxide. Cationic polymerizations were carried out in 1,2-dichloroethane solutions at room temperature in the presence of anhydrous stannic chloride. The free-radical initiated one-to-one alternating copolymerization of maleic anhydride with styrene- β -C¹⁴ was also studied.

The isotope effects were determined from radioactivity assay data obtained from polymer samples of both low and high conversions. The magnitude of the isotope effects for the propagation steps in these polymerizations are tabulated below.

Free radical, styrene- β -C ¹⁴	0.92 ₀ ; 0.91 ₅ ; 0.91 ₅
Free radical, styrene- α -C ¹⁴	0.97 ₀
Cationic, styrene- β -C ¹⁴	0.95 ₀ ; 0.96 ₇
Cationic, styrene- α -C ¹⁴	1.00
Styrene- β -C ¹⁴ - maleic anhydride copolymerization	0.95 ₁

Isotope effects for these reactions were calculated from theoretical considerations and compared with those obtained experimentally. Structures for the transition states for propagation of the polymerizations were proposed on the basis of these data.

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