when it is *p*-nitro. The fit of the data to these lines is quite poor, since k_H and k_{Cl} respond to the electronic influence of X differently. Nevertheless, the figure gives a capsule view of the electronic influences at work. For example, consider the case where the hydrogen donor is *p*-methoxytoluene. Resonance form Ib will be important, and electron-withdrawing X groups in the radical will stabilize this form still more. Thus, k_H would be expected to increase in going from TAT to NAT. Since k_{Cl} decreases from TAT to NAT, k_H/k_{Cl} should increase significantly in going from TAT to NAT. In agreement with this prediction, ρ is $+1$ (*i.e.*, the slope of the upper line in Figure 7 is $+1$).

When the hydrogen donor is *p*-nitrotoluene, both k_H and k_{Cl} would be expected to decrease in going from TAT to NAT. It is reasonable, however, to expect k_{Cl} to decrease more than does k_H (IIc is more important than is Ic), and the net effect is that k_H/k_{Cl} increases slightly in going from TAT to NAT. Figure 7 shows that ρ is 0.4 in this case.

A Limitation on k_H/k_{Cl} Values. One limitation which is implicit in the discussion in the preceding paragraph may warrant clarification. Values of k_H are relative only in a single vertical column in Table IX. For clarity, consider two radicals with two different ratios, k_H/k_{Cl} and k_H'/k_{Cl}'. To compare k_H and k_H' directly, the ratio of k_{Cl} to k_{Cl}' must be known. These data could be obtained by either measuring the ratio k_{Cl}/k_{Cl}' or by obtaining the absolute rate constants for chlorine abstraction for each of the radicals by some technique. Relative k_{Cl}/k_{Cl}' values cannot be obtained by studies of the type done here. If two different PAT-type initiators are allowed to decompose in the same solution in the presence of carbon tetrachloride, their different rates of reaction result in different steady-state concentrations of radicals, and k_{Cl}/k_{Cl}' cannot be obtained.

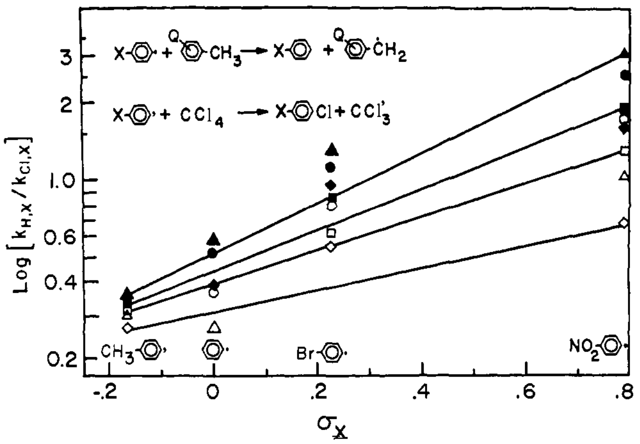


Figure 7. The effect of the electronic substituent in the phenyl radical on the rate of hydrogen abstraction from toluene and substituted toluenes. The log of the relative rate of abstraction of hydrogen is plotted on the vertical axis and the Hammett σ constant of the *substituent in the radical* on the horizontal axis. The points indicate the substituent in the hydrogen donors, coded as follows: ○, toluene; ▲, *p*-methoxytoluene; ■, *m*-xylene; △, *m*-bromotoluene; ●, *p*-bromotoluene; □, *p*-fluorotoluene; ◆, mesitylene; ◇, *p*-nitrotoluene.

Acknowledgment. The authors wish to thank S. C. Stodola and H. G. Guard for performing a large number of initial experiments. They also gratefully acknowledge helpful discussions with Professors C. Walling and Jack Kampmeier during the preparation of this manuscript.

Hydrogen Secondary Isotope Effects on the Radical Polymerization of Styrene[1,2]

William A. Pryor, Richard W. Henderson,[3a] Robert A. Patsiga,[3b] and N. Carroll[3c]

Contribution from the Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803. *Received October 18, 1965*

Abstract: It has generally been assumed that radical and ionic reactions will lead to similar hydrogen secondary isotope effects, but this assumption has not been tested in any detail, since very few studies on radical reactions have been reported. This paper reports isotope effects on the propagation step in the polymerization of styrene. The following substituted styrenes were studied: α-*d*, β-d_2, ring-d_5, α-*t*, and *trans*-β-*t*. All these isotopically substituted styrenes react faster than does normal styrene, *i.e.*, the isotope effects are all inverse. Table I gives values which approximate k_p/k_p' (*i.e.*, the isotope effect k_H/k_D on the propagation step) and Table III gives values of k_p/k_p'' (k_H/k_T for the propagation step).

Secondary hydrogen isotope effects are of theoretical interest and a large number of examples have now been reported.[4] These effects are divided into two types: those of the "first kind," in which the deuterium or tritium atom is substituted on an atom which undergoes a spatial (or hybridization) change during the

---

(1) This research was supported in part by a grant from the Air Force Office of Scientific Research.

(2) Reactions of Radicals. Part XIII. Most of these data were presented at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965.

(3) (a) An Undergraduate Research Participant; (b) a postdoctoral student on a National Science Foundation Summer Research Participation Program; (c) a postdoctoral student supported by a grant from the Air Force Office of Scientific Research.

(4) Reviews are given by (a) E. A. Halevi, *Progr. Phys. Org. Chem.*, **1**, 109 (1963); (b) L. Melander, "Isotope Effects on Reaction Rates," The Ronald Press Co., New York, N. Y., 1960; (c) J. Bigeleisen and M. Wolfsberg, *Advan. Chem. Phys.*, **1**, 15 (1958); (d) R. E. Weston, Jr., *Ann. Rev. Nucl. Sci.*, **11**, 439 (1961); (e) F. H. Westheimer, *Chem. Rev.*, **61**, 265 (1961); (f) K. B. Wiberg, *ibid.*, **55**, 713 (1955); (g) K. B. Wiberg, "Physical Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1964, p 351 ff.

reaction, and those of the "second kind," in which the isotopic hydrogen atom is substituted on a more remote carbon which does not undergo a formal change in bonding during the reaction.[5a]

In effects of the first kind, substitution of deuterium on a carbon which changes from sp^3 to sp^2 hybridization during the reaction produces a secondary kinetic isotope effect of about 12% per deuterium atom in the normal direction.[5b] That is, k_H/k_D has the value of approximately 1.1 per deuterium atom. Substitution of deuterium on a carbon undergoing a hybridization change in the reverse direction, from sp^2 to sp^3, produces an isotope effect of about the same magnitude but in the inverse direction ($k_H/k_D \cong 0.9$). Isotope effects of the second kind are generally smaller but in the same direction as would have been produced had the substitution been at the α carbon.[6] Data for deuterium and tritium can be related by the equation derived by Swain, *et al.*,[7a] and by Bigeleisen:[7b] $k_H/k_T = (k_H/k_D)^{1.44}$.

These results have been rationalized as arising primarily from zero-point vibrational energy changes during the course of the reaction.[8]

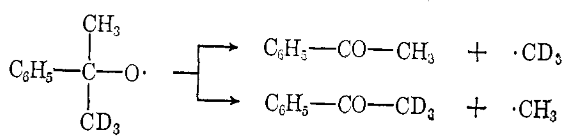
Secondary isotope effects usually have been studied in ionic reactions,[9] but it has been argued that they should be similar for ionic and for radical reactions.[10] However, if secondary isotope effects arise from both hyperconjugative and inductive forces, and if these forces often act in opposite directions, then secondary isotope effects on radical reactions will not always parallel those observed in ionic reactions. For this reason secondary isotope effects on radical reactions have special interest,[11] and we have begun a program of their study.

Very few data on secondary isotope effects in radical reactions have been reported. Denny and Tunkel[12] studied seven reactions of *trans*-dideuteriostilbene which involve destruction of the double bond. Most of the reactions are of complex mechanism and in some cases it is not clear whether or not radical intermediates are involved. However, at least one reaction, the addition of tetrachloro-*o*-benzoquinone to stilbene in benzene solution, does involve radicals, and it gives $k_H/k_D = 0.88$. The average isotope effect for the seven reactions is 0.88. If the reactions involve addition to one end of the double bond, then one of the carbon atoms changes from sp^2 toward sp^3 hybridization during reaction. Thus, the observed effect accords with the expectation of roughly a 12% inverse isotope effect for one deuterium atom. Implicit in such a calculation is the untested assumption that the variation of a carbon atom from olefinic to a radical or carbonium ion center does not produce an appreciable isotope effect.[13]

Seltzer has reported an isotope effect of 1.27 for the homolysis of azobis-α-phenylethane labeled in both α positions with deuterium. He concludes from this that both bonds break simultaneously and that this is an effect of 12% per atom.[10b]

A study of the pyrolysis of dimethylmercury has been reported by Weston and Seltzer.[14] Although the central carbon changes from sp^3 to sp^2 hybridization, the isotope effect is inverse, k_H/k_D being 0.93 for the normal *vs.* the hexadeuterated species at 366°. The authors explain this unexpected result as due to a large increase in the C–H stretching frequencies at the transition state and a very small change in the out-of-plane bending vibration frequency. As was first pointed out by Streitwieser[8b] in connection with a solvolysis reaction, the change in the out-of-plane bending vibration is usually dominant.

Zavitsas and Seltzer[15] studied the β scission of the radical shown. For this reaction, k_H/k_D is 1.17 at

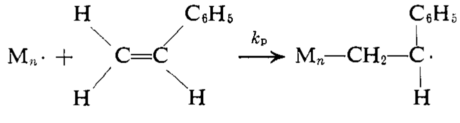


−9° and 1.12 at 75°, in accord with expectation. Apparently the dimethylmercury homolysis is atypical.

The addition of methyl or trifluoromethyl radicals to deuterated olefins has been studied by Feld, Stefani, and Szwarc.[16] In general, they find inverse effects of about 5% per deuterium atom for the addition of either radical to simple olefins. For example, the addition of the methyl radicals to either $CH_3—CH{=}CD_2$ or to $C_6H_5—CD{=}CD_2$ gives k_H/k_D of 0.89. In the reaction with styrene-d_3, addition to the terminal carbon atom changes the hybridization at that carbon; the other carbon changes from olefinic to a free-radical center.[13] On this basis, the isotope effect for both dideuteriopropene and trideuteriostyrene is about 5% per atom for two deuterium atoms.

In addition to these, a number of examples of Diels–Alder reactions have been studied. They all give isotope effects in accord with the rules given, but the radical nature of these processes is speculative.[17]

We here report the secondary isotope effects on the propagation step in the polymerization of styrene.



$$M_n\cdot + (H)(H)C{=}C(C_6H_5)(H) \xrightarrow{k_p} M_n—CH_2—C(C_6H_5)(H)\cdot$$

The following labeled styrene molecules have been studied: styrene-α-*t*, *trans*-styrene-β-*t*, styrene-α-*d*, styrene-β-d_2, and $C_6D_5—CH{=}CH_2$ (styrene-d_5).

Experimental Section

α-Bromostyrene.[18,19] Gaseous hydrogen bromide was generated, dried, and bubbled through an ice cold solution of phenylacetylene

---

(5) Reference 4a: (a) p 111; (b) p 172.

(6) This should particularly be true for radical reactions; for ionic reactions exceptions are known. See ref 4a, pp 171, 172, 192, 198, and 200; R. J. Cvetanovic, F. J. Duncan, W. E. Falconer, and R. S. Irvin, *J. Am. Chem. Soc.*, **87**, 1827 (1965).

(7) (a) C. G. Swain, E. C. Stivers, J. F. Reuwer, and L. J. Schaad, *ibid.*, **80**, 5885 (1958); (b) J. Bigeleisen, "Tritium in the Physical and Biological Sciences," Vol. 1, International Atomic Energy Agency, Vienna, 1962.

(8) (a) Reference 4; (b) A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey, and S. Suzuki, *J. Am. Chem. Soc.*, **80**, 2326 (1958); (c) also see L. S. Bartell, *ibid.*, **83**, 3567 (1961), and other papers in this series.

(9) This appears to be due to the fact that secondary isotope effects were first observed in ionic reactions, and also because of the intense current interest in the mechanism of the displacement reaction.

(10) See (a) ref 8b, p 2329 and note 24; (b) S. Seltzer, *J. Am. Chem. Soc.*, **83**, 2625 (1961), especially note 28.

(11) See, for example, ref 4a, pp 123 and 153; and ref 4g, p 360.

(12) D. B. Denny and N. Tunkel, *Chem. Ind.* (London), 1383 (1959).

(13) See, for example, ref 4a, p 169.

(14) R. E. Weston, Jr., and S. Seltzer, *J. Phys. Chem.*, **66**, 2192 (1962).

(15) A. A. Zavitsas and S. Seltzer, *J. Am. Chem. Soc.*, **86**, 1265 (1964).

(16) M. Feld, A. P. Stefani, and M. Szwarc, *ibid.*, **84**, 4451 (1962).

(17) See, for example, S. Seltzer, *ibid.*, **85**, 1360 (1963); **87**, 1534 (1965); M. J. Goldstein and G. L. Thayer, *ibid.*, **87**, 1925, 1933 (1965); D. E. Van Sickle and J. O. Rodin, *ibid.*, **86**, 3091 (1964).

(18) J. U. Nef, *Ann.*, 308, 271 (1899).

(19) C. Dufraisse, *Ann. Chim.*, 17, 164 (1922).

(170 ml, 1.55 moles) in 100 ml of hexane over a period of 4 hr. The solvent was removed and the residue was distilled through a short, packed column to give recovered phenylacetylene (20 g, 0.19 mole, bp 28–29° (8 mm), and 180 g of an oil (bp 24–60° (0.5 mm)). A solution of this oil and 90 ml of saturated alcoholic potassium hydroxide was allowed to stand for 2 days at −15°. After separation of layers, the organic phase was washed, dried, and distilled to give 153 g of an oil, bp 40–55° (0.7 mm). This oil was mixed with 320 ml of water, 36 g of sodium carbonate, 46 g of hydroxylamine hydrochloride, and a small amount of ethanol and allowed to stand for 2 days at −15°. The organic phase was washed, dried, and distilled to give α-bromostyrene (139 g, 55% yield, bp 41–42° (0.7 mm)). In some experiments α-bromostyrene purchased from the Chemical Intermediates and Research Co. was used; it had essentially the same degree of purity as the material synthesized above, although the impurities were not identical.

Analysis by gas phase chromatography (gpc) indicated a composition of 94% α-bromostyrene, 5% β-bromostyrene, and 1% of an unidentified third material. The nuclear magnetic resonance spectrum (nmr) taken with a Varian A-60 instrument (20% in carbon tetrachloride; TMS internal standard) showed broad absorption from 7.0 to 7.6 ppm due to the aromatic protons, a pair of doublets with a splitting of 2 cps centered at 5.62 and 5.90 ppm from the two β protons, and a peak from an impurity at 4.1 ppm (not β-bromostyrene). Little or no styrene impurity containing an α proton is present. The infrared spectrum confirmed the identification.

Styrene-*α-d* was prepared from α-bromostyrene using a Grignard reaction in tetrahydrofuran (THF).[20] The Grignard salt was hydrolyzed using 25 ml of D_2O (99.8%, Nuclear Research Chemicals, Inc.) and worked up in the standard way, and the styrene was distilled to give 10.3 g (bp 32–33° (10 mm)).

The infrared spectrum of this styrene-*α-d* agreed with that reported by Kobayashi[21] except for the peak at 12.4 μ which is missing in our material. The nmr spectrum[22,23] shows a peak at 5.10 and one at 5.63 ppm due to the *trans*- and *cis*-β-protons, respectively, with a splitting of 2 cps, a peak at about 7.2 ppm due to the aromatic protons, and only low absorption at 6.3 to 6.9 ppm characteristic of α protons. Integration gives 118:3:24 for the areas of the aromatic, α, *cis*-β and *trans*-β protons, implying that normal styrene is present as an impurity to the extent of about 12%. The small amount of β-bromostyrene present in the α-bromostyrene and the equivalence of the areas of the two β-protons in the nmr spectrum indicates that no styrene-*β-d* is present. Thus, the material is 88% styrene-*α-d* and 12% styrene.

Styrene-*β-d*. Styrene-*β-d* and -*β-t* were prepared by identical procedures from β-bromostyrene and the *β-d* material was used to demonstrate the isotopic purity of the tritiated compound. β-Bromostyrene (Eastman) was relatively pure as purchased; recrystallization increased the ratio of *trans* to *cis* but did not otherwise affect purity. The material used here was estimated by gpc to be 90% *trans*. The infrared spectrum supports this, showing major peaks in agreement with those reported by Yoshino, *et al.*[23] The nmr spectrum has areas in the ratio of 5.0:1.0:1.0 for the aromatic, α, and β protons as expected. α-Bromostyrene definitely is not present.

The synthesis of styrene-*β-d* is described in the following section. The nmr spectrum of the styrene-*β-d* showed protons in the ratio of 5.0:1.08:1.09 for aromatic, α, and β protons. Therefore styrene-*α-d* was absent; the infrared spectra of α- and β-styrene-*d* confirmed this. Both the nmr and the infrared spectra showed the absence of phenylacetylene. The nmr spectrum demonstrated the stereochemistry of the β proton to be 74% *cis* to the phenyl. Therefore, the material is 74% *trans*- and 26% *cis*-styrene-*β-d* and contains less than 1% of α or ring deuteration.

Styrene-*β-t* and -*β-d*. The method of Yoshino, *et al.*,[23] was used to prepare both styrene-*β-t* and -*β-d*. Dry THF (20 ml) was added with stirring to 1.82 g of magnesium (0.078 g-atom) in a nitrogen-flushed flask. β-Bromostyrene (5.0 g, 0.027 mole) and ethyl bromide (4.46 g, 0.041 mole) were combined with 15 ml of THF and added dropwise with cooling over 1 hr, and the mixture was then allowed to stand at room temperature for 1 additional hr. A mixture of 40 μl of H_2O-*t* (2 mcuries; Nuclear Research Chemicals) and 1.22 ml of water (0.07 mole) was added to 15 ml of THF. The Grignard solution was diluted with 30 ml of additional THF, and the THF–water mixture was added to it over 45 min from a dropping funnel.

Commercial styrene (40 ml) was added and the volatile material was removed at 2 mm. The forecut was largely THF and was discarded, and a 20-ml fraction boiling at 27° (5 mm) was collected. This was combined with 40 ml of additional styrene and redistilled (27° (6 mm)). The specific activity of this material was approximately 1.6×10^8 counts per 5 min per mole, a 5% yield of theory based on tritium. This material was prepolymerized[24] at 100° and redistilled.

In the preparation of styrene-*β-d*, 10 ml of D_2O in 20 ml of THF was added and styrene was distilled from the reaction mixture as before.

Styrene-*α-t* was prepared by a similar procedure using 0.72 g of magnesium and 3.0 g of α-bromostyrene. Hydrolysis was accomplished by adding 75 μl of H_2O-*t* (3.75 mcuries) in 0.23 ml of water and 10 ml of THF over 20 min from a dropping funnel; 50 ml of styrene was added and the middle fraction was collected at 27° (6 mm). The yield was 20 ml of material with an activity of approximately 3.0×10^9 counts per 5 min per mole, a 25% yield based on tritium. This material was diluted with 100 ml of styrene and redistilled; the center cut was prepolymerized and redistilled to afford 60 ml of purified monomer.

Styrene Ring-*d*$_6$. Benzene-d_6 (50 g) (Merck Sharp and Dohme, 99.5%) in 115 ml of carbon disulfide was added to aluminum chloride (94 g); acetic anhydride (30 g) was added over 15 min with rapid stirring and the mixture was heated at 100° for an additional 30 min, and then hydrolyzed by pouring onto ice and water.[25] The organic phase was washed, dried, and distilled to give a 45% yield of acetophenone-d_5. Benzene-d_6 was recovered and the synthesis was repeated on the same scale.

An ether solution of acetophenone (35 g in 65 ml) was added slowly to a slurry of lithium aluminum hydride (4.0 g) in 100 ml of ether, and then heated under reflux for 2 hr. The flask was cooled, the mixture was hydrolyzed with 10% sulfuric acid, the organic layer was separated and dried, and the ether was removed. The residual liquor was distilled slowly from a mixture of picric acid (0.3 g) and *p*-toluenesulfonic acid (0.3 g) at 100 mm while the temperature of the distillation flask was maintained at 150°. The organic layer was separated and dried and redistilled to give 26 g of styrene-d_5. The nmr of this material showed it to be 94.8% deuterated in the ring. Synthetic styrene was prepared by the same procedure for use as a control in the polymerization runs.

Styrene-*β*-d_2. This material was a generous gift of Dr. Leo A. Wall of the National Bureau of Standards. Its preparation has been described.[26] The material was prepolymerized and distilled twice before use. Its nmr spectrum showed it to be 97.3% deuterated at the β position.

Polymerization Techniques. Polymerizations were conducted in sealed ampoules and polymers were isolated either by precipitation with methanol or by freeze drying. In a typical polymerization, a measured amount of a benzene solution of azobisisobutyronitrile (AIBN) was introduced into a 10-ml ampoule and the benzene was pumped off. The required amount of monomer was added, and the ampoule was de-aired and sealed in the usual way. The reaction mixture was diluted with an equal volume of benzene and then poured into twice its volume of ice cold methanol. The polymer was filtered from the precipitation mixture, dissolved in 5 ml of benzene, and freeze dried.[27] The dry, fluffy polymer was redissolved in 5 ml of benzene and the procedure was repeated four times. If exact weights of polymer were needed, the polymerization

---

[20] W. Burlant and J. Neerman, *J. Org. Chem.*, **26**, 3602 (1961).

[21] M. Kobayashi, *Bull. Chem. Soc. Japan*, 33, 1416 (1960).

[22] The nmr spectrum of styrene is given in J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1965, p 106. The following spectra are given in the Varian Associates nmr spectra catalogs: phenylacetylene, β-bromostyrene, 4-chlorostyrene, α-methylstyrene, α,β-dibromostyrene, and ethylbenzene. None of these materials were present in either the α-bromostyrene or the styrene-*α-d*-prepared here.

[23] T. Yoshino, Y. Manabe, and Y. Kikuchi, *J. Am. Chem. Soc.*, **86**, 4670 (1964).

[24] Prepolymerization was effected by maintaining the styrene at 100° for 4 hr in a nitrogen-flushed flask.

[25] C. R. Noller and R. Adams, *J. Am. Chem. Soc.*, **46**, 1889 (1924).

[26] L. A. Wall and D. W. Brown, *J. Phys. Chem.*, **61**, 129 (1957), and private communications. We are indebted to Dr. Wall for supplying details of his method of converting phenylethanol to styrene which we used in preparing styrene-d_5

[27] This is a modification of the method of F. M. Lewis and F. R. Mayo, *Ind. Eng. Chem.*, 17, 134 (1945). A freeze–dry cycle consists of freezing the polymer–benzene solution and then pumping off benzene; as long as benzene is being evolved, the mixture remains cold enough to stay solid. Usually 1–2 hr is required.

mixture was quantitatively transferred to a weighed erlenmeyer flask by washing with benzene. Freeze drying was performed in the usual way, and the polymer weights were obtained.

A control showed that the methanol precipitation procedure gave a loss of less than 1% of the polymer from a mixture of 14 ml of styrene polymerized to about 10% conversion at 60° using 0.0244 g of AIBN. A control using hot monomer and cold polymer showed that four cycles of the freeze-dry procedure left less than 100 ppm of the monomer in the final polymer.

Counting Procedure. A Packard Model 314X Tricarb liquid scintillation counter was used. The liquid scintillation counting solution was toluene containing 0.100 g of POPOP and 4.00 g of PPO per 800 g of dry toluene. Counting was done for 5-min periods (about 5×10^4 total counts) after a 5-hr dark-adaptation period. Each sample was counted at least eight times and the values were averaged. Styrene quenched severely; its activity could be determined by counting samples as small as 1 to 5 μl and using a channels ratio method[28] to correct for quenching. The specific activity of the styrene was confirmed by counting toluene-*t* in the presence of varying amounts of inactive styrene and preparing a graph of per cent quenching *vs.* microliters of styrene added per 18 ml of scintillation solution. In practice a third method was used which gave substantial agreement with these two. Styrene was converted as completely as possible to polymer, and this high-conversion polymer was counted simultaneously with runs under the standard conditions and was used to calculate the specific activity of the monomer. This is considered to be the most direct way of comparing the specific activity of monomer and low conversion polymers. Conversions of about 95% could be obtained in the high conversion runs, and the specific activity of this polymer could be corrected by the small amount necessary (about 1%) to convert it to the specific activity of 100% polymer. (See below for further discussion.) Standard samples of 10 to 100 mg of polymer were counted, and a channels ratio correction was made for the small amount of quenching which occurred (usually less than 5%).

Discussion

Deuterium Isotope Effects. The experiments using deuterated monomers involve duplicate runs in which normal and deuterated styrenes were separately polymerized. In all cases, the deuterated monomers were prepolymerized twice and distilled at least three times. For styrene-*α-d* and styrene-d_5, synthetic normal styrene was prepared by the same technique as was used for the labeled compound and was shown to give the correct rate of thermal polymerization[29] at 60°. This test rigorously demonstrates the purity of the monomer, since the rate of thermal polymerizations is sensitive to very small amounts of inhibitor or initiator impurities. (For example, an initiator would be detected at a concentration as low as 2×10^{-5} *M*.) Therefore, the isotope effects observed are not due to adventitious initiators in the deuterated species.

The mechanism of polymerization of styrene is[30]

$$\text{AIBN} \xrightarrow{k_d} 2\text{R}\cdot \tag{1}$$

$$\text{R}\cdot + \text{M} \xrightarrow{k_i} \text{M}\cdot \tag{2}$$

$$\text{M}\cdot + \text{M} \xrightarrow{k_p} \text{M}\cdot \tag{3}$$

$$2\text{M}\cdot \xrightarrow{k_t} \text{polymer} \tag{4}$$

where M is styrene, M· is a styryl or polystyryl radical (rate constants are assumed to be independent of radical size), and transfer is neglected. The usual assumptions of a steady state in radical concentrations, long kinetic chains, and bimolecular termination lead to the following expression for the rate of formation of polymer R_P

$$R_P = k_p(\text{M})(R_i/2k_t)^{1/2} = \Delta(\text{M})R_i^{1/2}/2^{1/2} \tag{5}$$

where $\Delta = k_p/k_t^{1/2}$ and R_i is the total rate of initiation of polymerization. Under conditions where the rate initiated by AIBN is large enough so thermal initiation can be ignored, and assuming a steady state in R·, $R_i = 2k_d(\text{AIBN})$ and

$$R_P = \Delta(M)[k_d f(\text{AIBN})]^{1/2} \tag{6}$$

If the rates of polymerization of ordinary styrene R_P and deuterated styrene R_P' are compared at identical styrene and AIBN concentrations, and if $k_d f$ has the same value in normal and deuteriostyrene, then

$$\left(\frac{R_P}{R_P'}\right)_{\text{AIBN}} = \frac{\Delta}{\Delta'} \tag{7}$$

where primed quantities refer to deuterated styrene. Since the activation energy for termination is small, k_t/k_t' will be nearly unity,[31] and the square root of this ratio will be even closer to unity. Therefore, eq 8 should be an excellent approximation

$$\frac{\Delta}{\Delta'} \cong \frac{k_p}{k_p'} \tag{8}$$

Thus, the comparison of the rates of polymerization of styrene and a deuterated styrene under conditions such that the rate of initiation is the same in both gives a rate ratio which should closely approximate the isotope effect on the propagation step.

The question of whether or not an identical concentration of AIBN in styrene and deuteriostyrene leads to an identical rate of initiation is worth discussion. If a steady state in R· radicals is assumed, then R_P values are not sensitive to any possible isotope effect on reaction 2. Therefore, it must simply be shown that both the decomposition rate constant, k_d, and the efficiency of initiation of polymerization, *f*, are the same in both styrene and styrene-*d*. The constancy of k_d appears certain; AIBN has a rate of decomposition which is remarkably independent of solvent.[32] The constancy of *f*, however, requires that the same fraction of the R· radicals initiates the polymerization in both cases. It is conceivable that AIBN concentrations might exist such that the isotope effect on reaction 2 leads to a larger fraction of the primary R· radicals undergoing primary radical termination or dimeriza-

---

[28] E. T. Bush, *Anal. Chem.*, **35**, 1024 (1963).

[29] The rates of these thermal polymerizations have been reported: W. A. Pryor, R. Henderson, N. Carroll, and E. Ciuffarin, Abstracts of Papers presented at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, p 7S. They were measured as part of a study of the mechanism of thermal initiation in styrene. We have further experiments in progress which bear on the mechanism of this reaction, and we plan to discuss these experiments and the isotope effect on thermally initiated polymerizations in a later paper.

[30] Background references are summarized by (a) C. H. Bamford, W. G. Barb, A. D. Jenkins, and P. F. Onyon, "Kinetics of Vinyl Polymerization by Radical Mechanisms," Butterworth and Co. (Publishers) Ltd., London, 1958, pp 55–72; (b) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 63 ff; (c) W. A. Pryor, "Free Radicals," McGraw-Hill Book Co., Inc., New York, N. Y., 1966.

[31] The activation energies for termination and propagation are 2 and 8 kcal/mole; see ref 30a, p 71. Isotope effects are generally smaller for reactions with smaller activation energies.

[32] See ref 30b, p 512. The efficiency of AIBN is discussed by L. M. Arnett and J. H. Peterson, *J. Am. Chem. Soc.*, **74**, 2031 (1952); J. P. Van Hook and A. V. Tobolsky, *ibid.*, **80**, 779 (1958); A. V. Tobolsky, C. E. Rogers, and R. D. Brickman, *ibid.*, **82**, 1277 (1960); J. C. Bevington, *Trans. Faraday Soc.*, **51**, 1392 (1955); J. C. Bevington and D. E. Eaves, *ibid.*, **55**, 1777 (1959); J. C. Bevington, *Makromol. Chem.*, **34**, 152 (1959); J. C. Bevington and H. G. Troth, *Trans. Faraday Soc.*, **58**, 186 (1962).

tion in styrene compared with styrene-*d*. To avoid this, the lowest AIBN concentrations were used for which the thermal initiation rate is a negligible portion of the initiated rate.[33]

Tritium Isotope Effects. The equations for tritium are particularly simple. Since the isotopic atom is present at tracer levels, the end monomer unit in the growing radicals is essentially never labeled, and radioactivity is incorporated into the polymer by the competition of the growing chain between adding a normal or a labeled styrene.[34] Thus the isotope effect reflects the competition between the two reactions

$$M_n\cdot + \text{styrene} \xrightarrow{k_p} M_{n+1}\cdot \tag{9}$$

$$M_n\cdot + \text{styrene-}t \xrightarrow{k_p''} M_{n+1}\cdot \tag{10}$$

where k_p'' refers to the step with tritium in the monomer and the attacking radical is the same in both reactions.

The equation for calculating k_p/k_p'' is[34]

$$\frac{k_p}{k_p''} = \log(1 - x_2)/\log(1 - rx_2) \tag{11}$$

where r is the ratio of the specific activity of the polymer to that of the monomer and x_2 is the fraction of the unlabeled monomer converted to polymer (*i.e.*, the macroscopic fraction reacted). At low conversions and for small isotope effects eq 12 is an excellent approximation[34] to eq 11.

$$\frac{k_p}{k_p''} = \frac{1}{r} \tag{12}$$

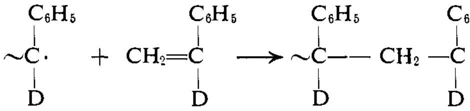
Since styrene quenches severely and also in order to keep counting procedures standard, the specific activity of the monomer was determined by converting it to polymer (see the Experimental Section). The procedure used, therefore, was the following. The tritiated monomer (4 ml) was converted as nearly completely as possible to polymer by heating in an ampoule for 4 days at 100°. (The thermal rate at 100° is 2% per hour.) Polymer was isolated by the freeze–dry method and the extent of reaction x_2 was determined. It varied from 94 to 96%. An aliquot of this material was counted, and this was taken as a first approximation for the specific activity of the monomer (SAM). The polymer from a run of low conversion (about 5%) was taken as the specific activity of the polymer (SAP). This gives a first approximation for r = SAP/SAM, and eq 12 was used to calculate a first approximation to k_p/k_p''. This value was then used to correct the value of SAM to that which would have been obtained had the polymerization been carried to 100% rather than 94–96%. The equation is[34a]

$$r = \text{SAP/SAM} = (1/x_2)[1 - (1 - x_2)^{k_p''/k_p}] \tag{13}$$

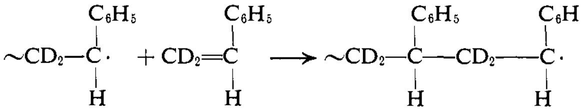
Equation 13 shows that for values of $x_2 \cong 0.95$ and $k_T/k_H \cong 1.1$, $r \cong 1.014$. Thus, the specific activity of the polymer at 95% conversion is some 1% greater than the true specific activity of the monomer due to the inverse isotope effect. Therefore, the specific activity of the 95% conversion polymer was divided by the calculated value of r to give the true specific activity of the monomer. This value and eq 11 were used to calculate k_p/k_p'' from low conversion runs.

Results

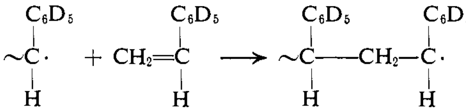
Deuterium Isotope Effects. Table I shows the deuterium runs, and the data indicate an inverse isotope effect at each position. The reactions and transition states for the three deuterated monomers are shown. If radical centers are considered sp² and if



$$\sim\underset{D}{\overset{C_6H_5}{C}}\cdot + CH_2{=}\underset{D}{\overset{C_6H_5}{C}} \longrightarrow \sim\underset{D}{\overset{C_6H_5}{C}}-CH_2-\underset{D}{\overset{C_6H_5}{C}}\cdot \tag{14}$$



$$\sim CD_2-\underset{H}{\overset{C_6H_5}{C}}\cdot + CD_2{=}\underset{H}{\overset{C_6H_5}{C}} \longrightarrow \sim CD_2-\underset{H}{\overset{C_6H_5}{C}}-CD_2-\underset{H}{\overset{C_6H_5}{C}}\cdot \tag{15}$$



$$\sim\underset{H}{\overset{C_6D_5}{C}}\cdot + CH_2{=}\underset{H}{\overset{C_6D_5}{C}} \longrightarrow \sim\underset{H}{\overset{C_6D_5}{C}}-CH_2-\underset{H}{\overset{C_6D_5}{C}}\cdot \tag{16}$$

secondary isotope effects of the second kind are ignored, then the values of R_P/R_P' for reactions 14 and 15 are predicted to be aout 0.90 and $0.9^2 = 0.81$, compared with the observed 0.91 and 0.88. The expected isotope effect for reaction 16 is harder to estimate, but the observed 0.82 does not appear large when ascribed to either a 4% per atom effect for five deuterium atoms or a 2% effect per atom for ten deuteriums. Effects of nuclear deuteration on side-chain reactions are well known.[35]

Table I. Polymerization of Styrene and Deuterated Styrenes at 60°[a]

Monomer	(AIBN)	$R_P \times 10^6$	$R_P' \times 10^6$	$R_P/R_P' \cong k_p/k_p'$
C_6H_5—CD=CH_2	0.0145	85[b]	92[c]	0.91[f]
C_6H_5—CH=CD_2	0.0142	85[d]	96[e]	0.88[g]
C_6D_5—CH=CH_2	0.0220	108	127	0.85
	0.0295	107	134	0.80

[a] Rates in moles/liter/sec. [b] One determination only of synthetic α-H styrene. [c] One determination only of synthetic α-D styrene. [d] An average of four determinations using commercial styrene: 92.7, 81.4, 83.1, 82.4. [e] Determined on material furnished by Dr. L. A. Wall. An average of three values: 99.4, 97.3, 92.7. [f] Professor H. J. Harwood of the University of Akron has informed us that he and Mr. B. F. Losekamp have obtained $R_p/R_p' = 1.0$ for both thermal- and AIBN-initiated styrene polymerizations using styrene-α-*d* at 70°. [g] G. S. Hammond and K. R. Kopecky, *J. Polymer Sci.*, **60**, S54 (1962), have reported $R_p/R_p' = 1.0$ for both thermal and benzoyl peroxide polymerizations of styrene-β-d_2.

Tritium Isotope Effects. Table II gives the data for tritium-labeled styrenes. Theoretically, it should not matter whether the polymerizations are initiated with AIBN or are thermally initiated; the activity is incorporated in the propagation step and the initiation is immaterial. Hodnett[34b] had previously shown this to

---

(33) Concentrations of 10^{-2} to 10^{-3} *M* at 60° satisfy these requirements. See G. Henrici-Olivé and S. Olivé, *Makromol. Chem.*, **37**, 71 (1960); T. Manabe, T. Utsumi, and S. Okamura, *J. Polymer Sci.*, **58**, 121 (1962).

(34) (a) Reference 4b, pp 48–58; (b) E. M. Hodnett and A. W. Jensen, *J. Polymer Sci.*, **43**, 183 (1960).

(35) Reference 4a, pp 158 and 182; A. Streitwieser and H. Klein, *J. Am. Chem. Soc.*, **86**, 5170 (1964), have reported an example of nuclear deuteration producing an effect opposite in direction to side-chain deuteration.

Table II. Isotope Effects for Styrene-α-*t* and -β-*t* at 60 and 100°

Conditions No.	Temp, °C	Time, hr	(AIBN) × 10^3	Specific activity $\times 10^{-6\,a}$	Polymer, g	Conversion, %	Channels ratio efficiency^b	Polymer counted, mg	k_H/k_T
					Styrene-α-*t*				
J1	100	96	...	4.10970	2.5543	98.5	97.5	17.0	...
J2	100	96	...	4.18774	2.5543	98.5	97.5	12.4	...
H1	60	2.00	9.71	4.20845	0.2098	5.79	97.7	12.9	0.98_6
H2	60	2.00	9.71	4.14439	0.2098	5.79	98.0	10.7	1.00_1
I1	60	2.00	9.71	4.19312	0.2072	5.72	97.3	17.9	0.98_9
I2	60	2.00	9.71	4.18687	0.2072	5.72	96.3	14.4	0.99_1
G1	100	3.32	...	4.13275	0.2828	7.82	96.3	13.1	1.00_4
G2	100	3.32	...	4.13838	0.2928	7.82	95.0	15.0	0.99_2
					Styrene-β-*t*				
A1	100	96	...	1.42846	2.6087	96.3	96.2	41.7	...
A2	100	96	...	1.42535	2.6087	96.3	96.2	98.8	...
B1	60	2.5	8.48	1.51266	0.3080	6.79	96.7	15.8	0.93_5
B2	60	2.5	8.48	1.51210	0.3080	6.79	94.7	70.9	0.93_4
C	60		8.48	1.51215	0.3088	6.80	97.0	21.4	0.93_4
D	60	36	...	1.52309	0.2141	5.90	96.0	52.0	0.92_6
E	100	2.5	...	1.52578	0.3465	9.57	92.5	59.8	0.92_4
F	100	2.5	...	1.54193	0.3880	10.71	97.2	36.2	0.91_4

[a] Counts per 5 min. [b] Toluene-*t* was counted with 13% efficiency and this was taken as defining 100% efficiency in the channels ratio (CR) method. Polymer samples which gave less than about 95% of this CR efficiency were discarded.

be the case for styrene-β-C^{14}, and Table II shows it to be the case for styrene-β-*t* at 60°. With this simplification, the average tritium isotope effects from Table II are shown in Table III.

Table III. Tritium Isotope Effects, k_p/k_p''

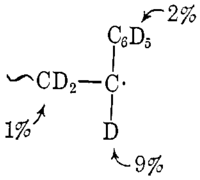
	60°	100°
Styrene-α-*t*	0.99_1	0.99_8
Styrene-β-*t*	0.93_2	0.91_9

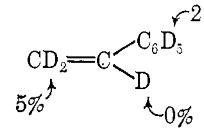
These effects accord well with expectations. Isotopic substitution at the α carbon should not lead to an isotope effect if the vibrational frequencies of the α hydrogen are similar in an olefinic and radical-bearing carbon. This confirms that the isotope effect for styrene-α-*d* is due to the deuterium label in the attacking radical rather than that in the monomer. The isotope effect for styrene-β-*t* is in good agreement with expectation based on Szwarc's data[16] for methyl radical additions to styrene-d_3, where 5% per atom was observed.

Conclusions. The isotope effect for the reaction of an *unlabeled* polystyryl radical with styrene-β-d_2 can be calculated from the result for styrene-β-*t;* the value for the tritiated monomer is converted to the value for styrene-β-d_1 using the equation of Swain[7] and this is squared.

$$\frac{k_p}{k_p'} = (k_p/k_p'')^{2/1.44} = 0.93^{1.39} = 0.90$$

Since the observed effect for styrene-β-d_2 is 0.88, the two deuteriums β to the radical center in reaction 15 must contribute an inverse isotope effect of 1% per atom. The isotope effect for all the deuteriums in the hypothetical transition state shown below can then be assigned as the inverse isotope effects (per atom)





The 9% isotope effect for the deuterium atom on the α carbon of the radical is in agreement with the effects found (or postulated) for the reverse process in which homolysis of a bond occurs.[10b,15] The 5% per atom effect for the deuteriums on the end of a terminal double bond agrees with Szwarc's data on the addition of methyl radicals to olefins,[16] although it is surprising that methyl and polystyryl radicals should be so similar. It is perhaps too early to propose a detailed rationale for the difference between the effects for the deuteriums on the two carbons between which bond formation is occurring (9 and 5%).

Temperature Effects. It has been recognized recently that isotope effects do not always arise from an activation energy term as might be expected for an effect due to zero point vibrational changes.[36] Leffek recently reviewed the evidence for secondary effects and found that they are due to a preexponential term as often as to an activation energy term. The tritium effect for styrene-β-*t* becomes more inverse as the temperature is raised, contrary to the simple theoretical expectation.

Carbon-14 Isotope Effect. Hodnett[34b] finds k_{12}/k_{14} for styrene-β-C^{14} to be 1.09 and for styrene-α-C^{14} to be 1.03. Thus, the carbon isotope effects are normal, whereas the deuterium and tritium effects are inverse. Weston and Seltzer[14] have observed the same pattern for homolysis of dimethylmercury; there the carbon k_{12}/k_{13} ratio is 1.04, and k_H/k_D is 0.93. In the styrene propagation step, the inverse hydrogen isotope effect can be rationalized using the usual arguments involving the out-of-plane bending vibration which moves to a higher frequency as the carbon moves

---

(36) Reference 4a, p 193; K. T. Leffek and J. W. MacLean, *Can. J. Chem.*, 43 40 (1965).

toward sp^3 hybridization. The normal carbon isotope effect must result from the weakening of vibrational frequencies as the carbon bonding moves from a double to a single bond.

Acknowledgment. We wish to thank Dr. Ennio Ciuffarin for assistance at the beginning of this work and Dr. Fred J. Impastato of the Ethyl Corporation, Baton Rouge, La., for some of the nmr measurements.

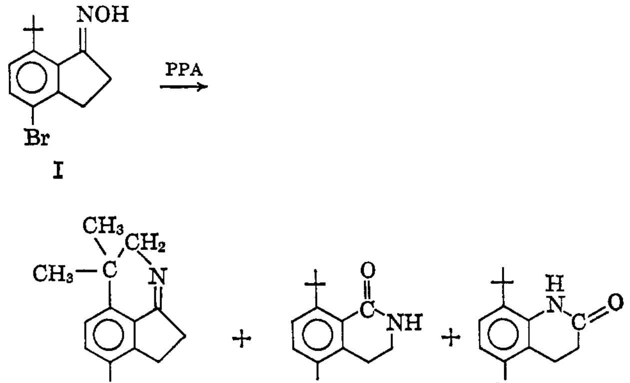
Further Studies of Bond Insertion and Nonstereospecific Beckmann Rearrangements in 7-Alkyl-1-indanone Oximes[1]

Peter T. Lansbury[2a] **and Norman R. Mancuso**[2b]

Contribution from the Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214. *Received October 2, 1965*

Abstract: The reaction of 8-*t*-butyl-5-bromo-1-tetralone oxime (II) with polyphosphoric acid results only in Beckmann rearrangement with aryl migration and no C–H bond insertion, as had been observed with 7-*t*-butyl-4-bromo-1-indanone oxime (I). Both 4,7-dimethyl-1-indanone oxime (IV) and 4,7-diethyl-1-indanone oxime (IX) undergo C–H bond insertion at the benzylic carbon atom. The strained imines expected from these reactions were not isolable but were converted to acylated amino ketones for identification. Lactams resulting from Beckmann rearrangement accompanied the above iminium ion insertion products but the predominance of alkyl migration *via* net *cis* migration was of particular novelty. Mechanistic aspects of the above Beckmann reactions, as well as related Schmidt reactions and hydrazone diazotizations, are discussed. It is concluded that bond insertion and nonstereospecific rearrangement of 1-indanone derivatives is attributable to iminium ion intermediates.

Recently we studied the Beckmann and Schmidt reactions of 4-bromo-7-*t*-butyl-1-indanone and its oxime (I), in connection with our search for intramolecular alkyl group migrations between two nonbonded atoms.[1] The above compound was chosen[1] because of the rigid juxtaposition of the *t*-butyl group and the incipient iminium cation, because oxime fragmentation seemed unlikely and also because aryl migration to nitrogen was expected to be greatly retarded as a resultant of torsional strain. The usual Beckmann rearrangement in polyphosphoric acid (PPA) was in fact largely replaced by formation of a basic product which proved to be the result of insertion by the intermediate iminium cation into a proximal C–H bond.



I

major

minor

It was also interesting to find that the major lactam obtained was that derived from alkyl migration,[1] although 1-tetralone oxime (as well as other arylalkyl ketoximes) gives mainly the lactam resulting from aryl migration.[3] We then sought to extend our investigation of the insertion reaction to include the following questions. (1) Would bond insertion into the *t*-butyl group (giving a six-membered cyclic imine ring) occur if the oxime group were incorporated into a flexible tetralone ring, rather than the rigid indanone? (2) Would replacement of 7-*t*-butyl by a 7-methyl group in a 1-indanone oxime result in bond insertion to give a highly strained five-membered cyclic imine ring? (3) If insertion at a benzylic carbon did in fact occur, would attack by the iminium cation on a 7-ethyl group occur at the α- or β-C–H bond? In addition to the above aspects of the insertion reaction, we wished to further elucidate the conditions necessary for observing predominant alkyl migration in Beckmann and Schmidt reactions of 2,3-benzcycloalkanones, since our earlier results[1] suggested nonstereospecificity in a reaction previously considered to be a stereospecific *trans* migration.[4]

In this paper the Beckmann and Schmidt reactions of 5-bromo-8-*t*-butyl-1-tetralone, 4,7-dimethyl-1-indanone, and 4,7-diethyl-1-indanone are discussed. These systems, plus several additional selected compounds, were chosen to provide information on the points raised above.

Results and Discussion

In order to prepare 5-bromo-8-*t*-butyl-1-tetralone we converted β-(2-bromo-5-*t*-butylphenyl)propionic acid[1] into the diazoketone and transformed the latter into γ-(2-bromo-5-*t*-butylphenyl)butyric acid by the photo-

---

(1) For the previous paper in this series, see P. T. Lansbury, J. G. Colson, and N. R. Mancuso, *J. Am. Chem. Soc.*, **86**, 5225 (1964).

(2) (a) Alfred P. Sloan Foundation Fellow, 1963–1967; (b) DuPont Teaching Fellow, 1964–1965.

(3) L. J. Briggs and G. C. Ath, *J. Chem. Soc.*, 456 (1937); (b) P. T. Lansbury and N. R. Mancuso, *Tetrahedron Letters*, 2445 (1965).

(4) P. A. S. Smith, "Molecular Rearrangements," Vol. 1, P. deMayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp 457–528, and references cited therein.