After the addition of hydrogen to the C:N bond the R group is no longer in the plane of the cycle; further addition of hydrogen across the carbonyl double bond from the side opposite R, either with or without catalyst hindrance,[6] gives rise to the same racemic configurations as before.

These explanations are more clearly appreciated when seen with models. And an adaptation of these postulates explains the formation of (−)-ephedrine by the hydrogenation of (−)-phenylacetylcarbinol in the presence of methylamine.[10]

Experimental

The hydrogenation results with α-oximinopropiophenone and 1,3-diphenyl-2-oximino-1-propanone are described elsewhere.[1]

The reduction of oximinoacetophenone, and of the phenolic oximinopropiophenones in ethanolic HCl was repeated, the results agreeing substantially with those already published.[5a] Oximinoacetophenone hydrogenated in alkaline medium gave only small yields of phenylethanolamine, and there is indication that an appreciable amount of 2,5-diphenylpyrazine was formed.

Ethyl Ester of *erythro*-β-Phenylserine.—One-tenth mole (22.1 g.) of ethyl benzoyloximinoacetate was dissolved in 100 ml. of 3 *N* absolute ethanolic HCl and shaken with 2 g. of catalyst prepared from pure palladium and Nuchar as described by Hartung and Chang.[1] The reaction proceeded smoothly until 0.269 mole hydrogen was taken up. Crystals had formed in the flask. Crystals and catalyst were collected on a buchner funnel. The filtrate was allowed to evaporate to dryness in the open. The catalyst was extracted with hot water, first with 100 ml. and then 50 ml. The aqueous extracts were allowed to cool, and then used to dissolve the residue from the alcoholic filtrate, then treated with 30 ml. of concd. NH_3. The crystals which formed were filtered off and the filtrate was extracted with three 100-ml. portions of ether. The ether was volatilized and the residue added to the crystals, and the total crude base was crystallized from benzene crystals, m.p. 83–84°; obtained 15.4 g. Further recrystallization from dilute alcohol gave colorless crystals m.p. 85–86° (dec.); hydrochloride m.p. 170° (dec.). Reported values for *erythro*-phenylserine ethyl ester,[9a] base 85–86°, hydrochloride 176°.

Ten grams of phenylserine ethyl ester hydrochloride was dissolved in 20 ml. of warm water and to the solution was slowly added 40 ml. of 10% NaOH solution. A white crystalline mass separated, which quickly dissolved on shaking. The mixture was boiled for 2 minutes, cooled and carefully neutralized to litmus with dilute HCl, and then placed in a refrigerator overnight. Colorless, feather-like crystals were collected, dry weight 6.0 g. (82%), m.p. 180–184° (dec.). Recrystallization from 50% alcohol gave crystals m.p. 184–188° (dec.). Shaw and Fox[9b] report the free acid as m.p. 189–192° (dec.). A careful examination of all the hydrogenation products failed to reveal the presence of *threo*-isomer.

A twentieth mole of ethyl benzoyloximinoacetate in 100 ml. of 1.5 *N* absolute ethanolic HCl was reduced with 2 g. of Pd-on-Nuchar catalyst, as before. The reaction was interrupted when 0.104 mole of hydrogen had been taken up. Considerable crystallization had taken place, catalyst and crystals were removed by filtration; isolation and purification of product as before, showed presence of only unchanged oximino ketone and hydrochloride of the ethyl ester of *erythro*-β-phenylserine.

CHAPEL HILL, NORTH CAROLINA

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[10] C. Neuberg and co-workers, *Biochem. Z.*, **115**, 282 (1921); **128**, 610 (1922).

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY, HARVARD UNIVERSITY]

The Polymerization of Allyl Compounds. VI. The Polymerization of Allyl-1-d_2 Acetate and the Mechanism of its Chain Termination

BY PAUL D. BARTLETT AND FRED A. TATE[1]

RECEIVED JULY 25, 1952

Allyl acetate having deuterium at the α-position of the allyl group was polymerized by benzoyl peroxide in amounts from 0.25 to 2.00% by weight. The rates of polymerization were from 1.93 to 2.89 times those observed in identical experiments with undeuterated allyl acetate, and the average molecular weight of all the polymer so produced was 2.38 times as great for the deuterated as for the undeuterated material. These results confirm the conclusion previously reached on kinetic grounds that the chain terminating step in the polymerization of allyl acetate involves the transfer of hydrogen from the α-position of allyl acetate to a chain-carrying free radical. Assuming that all chains are terminated in this way, light hydrogen is estimated to be transferred in this atomic displacement reaction about three times as fast as deuterium. Chain transfer in the polymerization of allyl acetate must also proceed through the α-acetoxyallyl free radical.

The polymerization of allyl acetate shows a linear relation between the concentrations of monomer and of initiator throughout the consumption of the latter,[2] a behavior since observed also for α-methylstyrene,[3] isopropenyl acetate[4a,b] and vinylmesitylene.[5] The explanation originally suggested[2] appears to have gained general acceptance, although the evidence for it is entirely indirect. The kinetic chain is considered to be terminated by the transfer of a hydrogen atom to a growing radical from a monomer molecule with the formation of an acetoxyallyl radical, I

$$\underset{\text{I}}{CH_2{=}CH\dot{C}HOOCCH_3 \longleftrightarrow \dot{C}H_2CH{=}CHOOCCH_3}$$

which is so stabilized by virtue of its allylic structure that it resists reacting with a monomer long enough to combine instead with another radical either of its own or of the chain-propagating kind.

Through the use of the isotope-rate effect a tool has recently become available for testing the participation of a particular hydrogen atom in a hydrogen-transfer process. In a number of examples in which hydrogen is transferred as a proton, the rate of transfer for protium is found to be from four to ten times as great as for deuterium.[6a,b] Although this rate ratio for the hydrogen isotopes has not been thoroughly investigated for the

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[1] U. S. Rubber Company Fellow at Harvard University, 1950–1951.

[2] P. D. Bartlett and R. Altschul, THIS JOURNAL, **67**, 816 (1945).

[3] G. Smets and L. de Haes, *Bull. soc. chim. Belg.*, **59**, 13 (1950).

[4] (a) R. Hart and G. Smets, *J. Polymer Sci.*, **5**, 55 (1950); (b) N. G. Gaylord and F. R. Eirich, *ibid.*, **5**, 743 (1950).

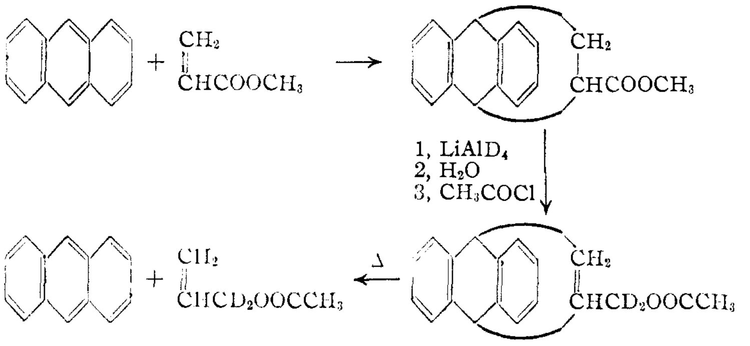
[5] A. de Pauw and G. Smets, *Bull. soc. chim. Belg.*, **59**, 629 (1950).

[6] (a) See W. F. K. Wynne-Jones, *J. Chem. Phys.*, **2**, 381 (1934); (b) F. H. Westheimer and N. Nicolaides, THIS JOURNAL, **71**, 25 (1949), and references there cited.

transfer of hydrogen in an atomic or free-radical reaction, it was reasonable to expect that deuteration of the α-position of the allyl group in allyl acetate would affect the rate of the chain termination step only if transfer of the α-hydrogen was involved in that step.[7] The kinetic chain length in the polymerization of allyl acetate is the ratio k_2/k_3 between the rate constants for chain propagation and termination; since the α-hydrogen atom is not concerned in the propagation process, deuteration should increase the kinetic chain length if the termination process is as we suppose it to be. We therefore undertook to determine the effect of α-deuteration upon the kinetic chain length of the polymerization of allyl acetate and upon the molecular weight of the resulting polymer.

Experimental

Attempts to reduce acrylic acid, its esters or its salts directly in a manner suitable for the preparation of allyl-1-d_2 acetate failed because of accompanying polymerization, and the following scheme was therefore adopted for protecting the double bond during reduction.



Addition of Methyl Acrylate to Anthracene.—A mixture of 100 g. (0.56 mole) of 95% anthracene, purchased from the Eastman Kodak Company, 150 g. (1.74 mole) of methyl acrylate from the same source and 1600 ml. of nitrobenzene was heated under reflux for four hours. The black solution was concentrated by removal of the solvent and excess methyl acrylate at 80° under the pressure of the water-pump, and was poured into 200 ml. of ether. The porous cake resulting was washed with ether to remove the color. Crystallization once from ether and twice from an 80-20 mixture of ether and petroleum ether (20-40°) gave a product melting sharply at 117°. The yield by combining several crops with this melting point was 70% of methyl 9,10-ethanoanthracene-11-carboxylate.

Anal. Calcd. for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 82.00; H, 6.23.

9,10-Ethanoanthracene-11-carboxylic acid was obtained both by alkaline hydrolysis of the methyl ester and by addition of acrylic acid to anthracene. Precipitated from the solution of its sodium salt, it melted at 187°.

Anal. Calcd. for $C_{17}H_{14}O_2$: C, 81.56; H, 5.64. Found: C, 81.49; H, 5.87.

9,10-Ethanoanthracene-11-methanol-13-d_2.—In a 1-l. flask equipped for stirring was put 1 g. (0.024 mole) of lithium aluminum deuteride (purchased from Metal Hydrides, Inc., Beverly, Mass., on allocation from the Atomic Energy Commission, assaying 92.5% active and 99.8% of its hydrogen deuterium) and 600 ml. of carefully dried tetrahydrofuran. The mixture was heated to reflux and 9.29 g. (0.0352 mole) of the ester, methyl 9,10-ethanoanthracene-11-carboxylate, was added slowly with vigorous stirring over a two-hour period. Reflux and stirring were continued overnight. The product was hydrolyzed with 10% sulfuric acid. The tetrahydrofuran was removed near room temperature under diminished pressure and the residue was extracted four times with a total of 600 ml. of ether. The extracts were washed with a sodium carbonate solution and dried over potassium carbonate, then concentrated and decolorized with "Nuchar." Crystallization and recrystallization from an ether-petroleum ether mixture yielded the product as hard, clear rhombic crystals melting at 110°.

Anal. Calcd. for $C_{17}H_{16}O$: C, 86.40; H, 6.83. Found: C, 86.37; H, 7.00.

The best yield was 85.7% based on the ester used. Attempts to diminish the excess of the hydride did not improve its utilization.

The deuterated and undeuterated compounds have indentical appearance, melting point and mixed melting point.

9,10-Ethanoanthracene-11-methyl-13-d_2 Acetate.—The above alcohol (5.82 g., 0.024 mole) was dissolved in 50 ml. of Merck and Co., Inc., acetone. The solution was heated to reflux and 10 g. (0.127 mole) of acetyl chloride was added through the condenser. After boiling for 15 minutes, during which time the solution became canary yellow, the mixture was poured over 800 ml. of ice. The reactor was rinsed with acetone and the rinsings were added to the ice solution. The product, a white amorphous mass, was broken up, filtered and dried at 40°. After decolorizing with Nuchar the product crystallized from ether in thick clear needles. Further recrystallization from ether gave a product melting at 121° whether deuterated or not. The yields were about 95%.

Anal. Calcd. for $C_{19}H_{18}O_2$: C, 81.99; H, 6.52. Found: C, 81.76; H, 6.63.

Allyl-1-d_2 Acetate.—The above ester, 9,10-ethanoanthracene-11-methyl-13-d_2 acetate (7.54 g., 0.027 mole) was placed in a 150-ml. pear-shaped flask and a Vigreux column, insulated with glass wool, and provided with a standard-taper thermometer, was fitted in place. A Wood's metal-bath at 350-360° was brought just above the level of the melted ester. Three or four minutes later the allyl acetate began to distil, at a vapor temperature of 103°. The pyrolysis was discontinued when the rate of distillation had dropped to one-fifth of that at the peak of the reaction. The yield of allyl acetate by this procedure was 88.2%.

In each case, although the melting points and crystal forms of the deuterated and undeuterated compounds were identical, their infrared spectra, determined over the range 2-16 μ with a Baird recording spectrometer, showed numerous points of difference. This fact made it possible to perform experiments such as the following to test the existence of isotope exchange when the cyclic alcohol is heated with lithium aluminum deuteride.

Treatment of 9,10-Ethanoanthracene-11-methanol with Lithium Aluminum Deuteride.—The undeuterated alcohol (3 g.) was added to 1 g. of lithium aluminum deuteride in 600 ml. of refluxing dried tetrahydrofuran, with rapid stirring. Refluxing and stirring were continued overnight. Isolation in the same manner as in the preparation of the alcohol yielded a product identical in melting point and in infrared spectrum with the original undeuterated alcohol. This rules out one possible mechanism by which the amount of deuterium in the ultimate product might be different from that calculated.

Deuterium Analysis of Allyl-1-d_2 Acetate.—Dr. David Rittenberg of Columbia University was kind enough to perform a mass spectrographic analysis of the product. The immediate precursor of allyl-1-d_2 acetate, 9,10-ethanoanthracene-11-methyl-13d_2 acetate, was mixed with undeuterated material in the proportion of 0.1075 to 1.6779 g. and the melt pyrolyzed as described above. The resulting partially deuterated sample of allyl acetate, n^{25}D 1.4020, was subjected to quantitative combustion in the usual manner, the water was converted to hydrogen by passing over zinc at about 400°, and this hydrogen was investigated in the mass spectrograph. The deuterium content was: calcd., 1.49; found, 1.34, 1.36. This corresponds to 90.6% deuteration at the α-position of the allyl group.

Another set of analyses was kindly carried out for us by using a gradient density tube[9] calibrated at the time of use by Dr. V. J. Shiner, Jr.,[8] of this laboratory by

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[7] This test was suggested to us by Dr. Harold Kwart.

[8] du Pont Postdoctoral Fellow, 1951-1952.

[9] C. Anfinsen in A. O. Wilson, A. O. C. Nier and S. R. Reimann, "Preparation and Measurement of Isotopic Tracers," J. W. Edwards, Ann Arbor, Michigan, 1946.

samples of known deuterium content. An analysis of the combustion water from the bicyclic precursor of the labeled allyl acetate was carried out without dilution and indicated 10.64 atom per cent. deuterium (calculated, 11.10 atom per cent.). Two samples of the allyl acetate used were diluted, one with distilled water (hydrogen dilution factor 3.72) and one with absolute ethanol (hydrogen dilution factor 3.33), and subjected to combustion. Analysis of the combustion water indicated for the allyl acetate 24.40 and 24.25 atom per cent. deuterium (calculated, 25.00). These figures correspond to a deuteration at the α-position of the allyl acetate of 96.0, 97.6 and 97.1%.

Titration for Unsaturation.—The unsaturation of the deuterated allyl acetate was determined by titration with bromide–bromate solution of a sample diluted with acetic acid. A sample weighing 0.5620 g. was diluted to 10.00 ml. with glacial acetic acid and 2-ml. aliquot portions were titrated. The results were

Ml. of 0.1003 N bromide–bromate	Ml. of 0.09915 N thiosulfate	Moles per kilogram of ester
36.50	14.73	9.79
37.78	16.03	9.79

The 90.6% deuterated ester should have 9.81 moles per kilogram.

Polymerization Measurements.—The polymerizations were carried out in Adams brand, Wintrobe hematocrit tubes of total volume 1 ml. and graduated in millimeters, which fitted interchangeably into the vapor thermostat shown in Fig. 1. The temperature was held at 80.0 ± 0.2° with boiling benzene. The samples could thus be kept free from access of oxygen and the polymerizations followed by watching the considerable volume change which attends the process.[2] It was assumed that the fractional shrinkage on polymerization was the same for deuterated as for undeuterated allyl acetate. By greasing the upper half of the ground joint with either "Silicone" or "Lubriseal" grease it was possible to limit the 24-hour loss of ester to only that (1.2%) which would be anticipated from the vapor pressure of allyl acetate at 80°. Corrections were made for this observed rate of loss in interpreting the volume measurements.

Solutions were made up by weight in a tared, stoppered serum bottle of 10-ml. capacity. After preparation of the solution of benzoyl peroxide in the monomer, the solution was degassed by evacuating and admitting nitrogen in turn seven times, through a 20-gage hypodermic needle, with shaking between cycles. The inner member of the thermostat assembly, containing the hematocrit tube, was also evacuated and refilled with nitrogen separately. After introduction of a portion of the solution into the reaction tube through a nitrogen-filled hypodermic syringe against a stream of nitrogen from the inlet tube, a further precautionary degassing at 0° was carried out, the loss in volume being noted and corrected for. The inlet tube was replaced by a standard taper stopper and the heating was begun. After about four minutes, when temperature equilibrium had been established, the time and volume were noted. The heating was continued until there was no more than 0.1% volume change in three hours. Thus the shrinkage in any run registers the amount of polymerization produced by the peroxide present during its total disappearance.

Molecular Weight Comparisons.—In order to compare the molecular weights and degrees of polymerization of the samples of the deuterated and undeuterated polyallyl acetate it is only necessary to compare the viscosity numbers[10] of their benzene solutions; for the weight-average and number-average molecular weights of these polymers are strictly proportional to each other. The polymer samples from the kinetic runs were pooled and the flow times of their solutions in reagent quality benzene were determined at 25 ± 0.05°, using an Ubbelohde viscometer.

Results

Table I summarizes the results of seven comparisons carried out, in each of which identical solutions of benzoyl peroxide in undeuterated and deuterated allyl acetate were polymerized under identical conditions. In the table the quantity called A is the per cent. volume shrinkage in the deuterated allyl acetate, and B is the per cent. shrinkage in the undeuterated sample containing the same concentration of initiator.

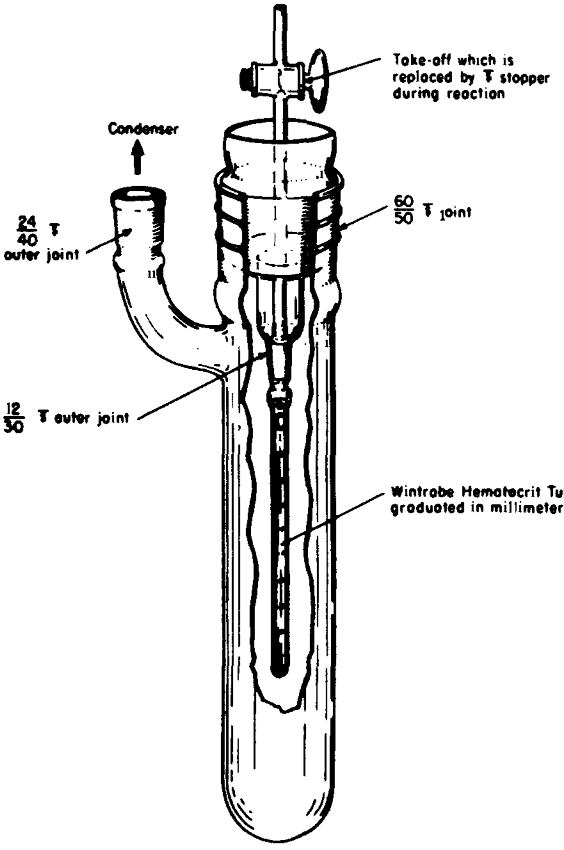

Fig. 1.—Thermostat.

TABLE I

Wt. % benzoyl peroxide	A	B	A/B
2.00	10.8	5.6	1.93
1.76	12.9	5.8	2.22
1.00	8.1	2.2	2.77
1.00	8.9	3.7	2.41
0.55	5.5	1.9	2.89
0.54	5.4	1.9	2.84
0.25	2.5	(0.9)	2.78
Sum (used in calculating A/B for combined sample)	54.1	22.0	Wtd. av. 2.46

It is immediately apparent that there is substantially more polymerization for a given amount of initiation in the deuterated than in the normal monomer. The ratio A/B, a measure of relative initiator efficiencies toward the isotopically different monomer, is definitely greater for the lower concentrations of benzoyl peroxide, and the last entry in the table represents an attempt to evaluate this ratio for a peroxide concentration so low that the shrinkage of the undeuterated sample could not be accurately determined. The figure in the table for B is accordingly an estimate obtained by extrapolating the data of Bartlett and Altschul.[2]

In Table II are recorded the viscosity measure-

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(10) Report on Nomenclature in the Field of Macromolecules of the International Union of Pure and Applied Chemistry, *J. Polymer Sci.*, **8**, 270 (1952).

ments on the combined polymers from the kinetic experiments.

TABLE II

VISCOSITY OF ALLYL ACETATE POLYMERS

Polymer	Concentration, g./100 ml.	Flow time, min.	$\frac{\eta - \eta_0}{\eta_0}$	Viscosity number
None	0.000	6.778	....	....
Normal	2.0392	7.213	0.0642	0.0315
Normal	1.0196	6.975	.0292	.0286
Normal	0.6797	6.904	.0186	.0274
Deuterated	.5022	6.975	.0291	.0579
Deuterated	.2511	6.875	.0143	.0569
Deuterated	.1674	6.843	.0096	.0573

From these results $[\eta]_H = 0.0251$, $[\eta]_D = 0.0567$, and $[\eta]_D/[\eta]_H = 2.26$.

Since the molecular weight of polyallyl acetate ($\bar{P} = 14$) falls well within the range where the Staudinger equation applies[11] this ratio of limiting viscosity numbers is equal to the ratio of molecular weights. The samples measured are made up of the total products of the kinetic runs, the different products thus being present in a numerical proportion which is the same as that of the shrinkages observed in the several runs. It is accordingly possible to calculate what the molecular weight ratio should be for this combined polymer in the absence of nondegradative[2] chain transfer, that is, assuming that all the difference between the amounts of polymerization in the identical deuterated and undeuterated samples is due to the difference in degree of polymerization of the polymer. The ratio so calculated is 54.1/22.0 = 2.46. Thus the ratio of molecular weights lags behind the ratio of initiator efficiencies by 8%.

Discussion

In a general way the results confirm that an α-hydrogen atom of the allyl group is transferred in the chain-terminating step in the polymerization of allyl acetate. It is of interest to see how far beyond this we can go in using this result to interpret some of the fine points in the polymerization.

The Corrected Isotopic Rate Ratio for the Chain-Terminating Step.—If, as indicated by the deuterium analyses, our heavy allyl acetate was incompletely deuterated at the α-position, the experimental rate ratio can be corrected to that for the pure deuterated material as follows. Let the experimental and corrected ratios be r and R, respectively, r being taken as 2.73, the mean of the observed ratios for all experiments where the peroxide concentration was 1% by weight or less. Let k_3 be the rate constant for the chain-terminating transfer of hydrogen from normal allyl acetate. Then the rate constant for this reaction in allyl-1-d_2 acetate will be, to a close approximation, k_3/R. The removal of the isotopic species *in polymerization* will be random and will not alter the isotopic ratio; but the removal of the isotopic species *in chain termination* will be selective, and will tend to concentrate the deuterated ester in the remaining unattacked monomer. A further complication is that we do not know the origin of the small fraction of protium in the α-positions. However, if 9.4% of protium (the largest amount shown in an analysis) is randomly distributed among the α-positions, 7.6% is in molecules containing one α-deuterium and 1.8% is in molecules containing no deuterium at all. The latter molecules will be attacked in chain termination with $2R$ (more than 5) times the probability of the doubly deuterated molecules and in the process one of the two protium atoms will find itself in some molecule other than allyl acetate without having entered into chain-terminating transfer. Even if the resulting compound is not capable of acting as a chain terminator like allyl acetate, it can be shown that in the system under investigation this depletion effect is small. A sample of allyl acetate containing 1% by weight of benzoyl peroxide will involve 8.1 g. per kilogram or 0.81% of the monomer in terminating chain transfer. The molecules so consumed will include only 1.9% of the original ester molecules having α-protium, altering the fraction of deuteration by the end of the polymerization (in the most unfavorable case) only to 90.7 instead of 90.6%. We therefore neglect the isotopic fractionation attendant upon polymerization and calculate the corrected isotopic transfer ratio R by the equation

$$\frac{k_3}{r} = Hk_3 + \frac{Dk_3}{R}, \text{ or } R = \frac{D}{(1/r) - H}$$

where H and D are the fractions of protium and deuterium, respectively, in the allyl acetate. The corrected value of R is 3.33 for 90.6% deuteration (mass spectrometer) or 2.89 for 96.6% deuteration (density method).

The Nature of Chain Transfer in the Polymerization of Allyl Acetate.—Bartlett and Altschul[2] concluded that in the polymerization of allyl acetate with 5.9% by weight of p-chlorobenzoyl peroxide there was 23% of chain transfer to monomer indicated by that proportion of polymer molecules having no fragment from the peroxide attached. Their work gave no basis for deciding whether the chain transfer represented a different mode of attack of growing free radical upon monomer from that to which the chain termination was ascribed, or whether it was due to the possession by the acetoxyallyl radicals of some feeble power of chain propagation, a mode of reaction occurring too seldom to alter the essentially terminating nature of the hydrogen transfer from monomer to chain carrier. This possibility of chain transfer occurring through some of the acetoxyallyl radicals had to be borne in mind, since these radicals proved entirely capable of attacking maleic anhydride and carrying on the copolymerization chains.[12] Now if chain transfer is occurring by some other mechanism than attack on the α-hydrogen atoms of the allyl group, this transfer will be isotopically unselective and will occur with the same frequency relative to chain propagation in the deuterated as in the undeuterated allyl acetate. Thus if we estimate from the above case that the chain transfer constant of allyl acetate in this mode of reaction is 0.0176 and this leads, as in the previous case cited, to a degree of polymerization of 13.3 in the undeuterated polymer, we predict that in the deuterated polymer the degree of polymerization will be given by

$$1/\bar{P} = \frac{0.0576}{2.73} + 0.0176; \ \bar{P} = 25.8$$

This would correspond to a ratio of molecular weights in the deuterated and undeuterated cases of 25.8/13.3 = 1.94 instead of 2.73 observed for the polymerization rates. The fact that the molecular weights and rates are in the same ratio within 8% instead of there being this 29% difference indicates that most of the chain transfer responds to isotopic substitution in the same manner as the rates of chain termination. This is evidence that the chain transfer proceeds through the acetoxyallyl radicals. If such chain transfer ever became a

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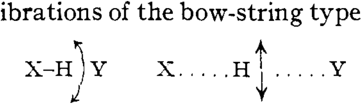
(11) T. E. McGoury and H. Mark, in A. Weissberger, "Physical Methods of Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1950, Vol. 1, Part 1, p. 349.

(12) P. D. Bartlett and K. Nozaki, THIS JOURNAL, **68**, 1495 (1946).

much larger element in the polymerization, it would tend to vitiate the linear relationship between monomer and peroxide concentration; as it is, the further reactions of the acetoxyallyl radicals with the monomer on the one hand and with the peroxide on the other probably account for the change in dM/dP and in the first-order rate constant for decomposition of benzoyl peroxide as the concentration of the peroxide is varied.[13] Chain transfer with the monomer, being competitive with radical–radical interaction, will increase the monomer consumption at low initiator concentrations, while chain transfer with the peroxide will increase the wastage of the latter at high concentrations of initiator.

Isotopic Rate Ratio and Reaction Type.—The early examples of differences in rate of transfer between the isomers of hydrogen concerned proton transfer between two nucleophilic centers and revealed rate ratios k_H/k_D between four and ten.[14] The ratios for the transfer of hydrogen and deuterium *atoms* are less well known, but some have been reported which are very much smaller than those prevailing in proton transfer.[15] A recent example in which hydrogen is transferred as a hydride ion between two electrophilic centers[16] shows a remarkable reversed isotope effect, in which the deuterium is transferred almost six times as fast as protium. The discoverers of this effect point out that it must indicate a degree of bonding of hydrogen in the transition state exceeding that in the starting material, and that this must be a consequence of the hydride character of the moving atom.

This point may well be one of considerable generality. The transition state in a proton transfer is subject to the same limitation of covalency as any "hydrogen bond," in that there can be no orbital common to all three atoms which will accommodate all four of the bonding electrons which are attracting the proton; hence the binding force in the transition state for proton transfer, as in the typical hydrogen bond, is largely coulombic and relatively weak. In the transfer of a hydride ion, however, between two electrophilic centers there is only a single pair of electrons concerned in the binding of the hydrogen before, after, and in the transition state. These electrons can be fully accommodated in the 1s orbital of the hydrogen and it is entirely possible that a comparatively strong molecular orbital can be formed linking together simultaneously with covalent forces a hydride ion and two electrophilic centers, one on either side of it. Naturally this strongly bonded species would not be a transition state, but if it were in general an intermediate in hydride-transfer reactions, then the transition state leading to it would also be one in which the hydrogen nucleus was subject to stronger restoring forces than in the starting material, and this is the criterion for a more positive increment in zero-point energy on reaction of the deuterium than of the protium compound, hence a higher rate for the D compound. According to this picture the increase in zero-point energy attending the formation of the transition state would reside not in vibrations along the reaction coördinate but in the vibrations of the hydrogen atom perpendicular to that direction, which are converted from simple bending (I) to the higher-frequency vibrations of the bow-string type (II).



I II

There are several reasons for thinking that in general "hydride bonds" are substantially stronger than conventional "hydrogen bonds." From its solubility behavior one would judge lithium aluminum hydride to be a highly covalent compound, and the only thing preventing it from being highly ionic must be the "hydride bond" Li–H–Al. The highly developed bridging power of hydrogen in the boranes might perhaps be advantageously described in terms of such three-center orbitals, and hydride-ion character is suggested by the rather high dipole moments of pentaborane[17] and decaborane.[18] The extraordinary ease with which it is sometimes possible to transfer hydride hydrogen from a tertiary position in a paraffin[19] also argues a substantial degree of bonding in the transition state.

As so often happens with free radical phenomena, the behavior of hydrogen in *atomic* transfer takes up a middle position between its behavior in proton and hydride transfer processes. It is as if the bonding power of the central hydrogen atom deduced theoretically for the H_3 intermediate in the ortho–para interconversion is general for atomic transfers of hydrogen and in some cases almost compensates at the transition state for the lost zero-point energy of the starting material.

CAMBRIDGE 38, MASSACHUSETTS

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[13] P. D. Bartlett and R. Altschul, ref. 2; K. Nozaki and P. D. Bartlett, THIS JOURNAL, **68**, 1686 (1946).

[14] Reference 6; also C. Reitz, *Z. physik. Chem.*, **A176**, 363 (1936); C. Reitz and J. Kopp, *ibid.*, **A184**, 429 (1939).

[15] W. H. Urry, paper presented at the 12th National Organic Symposium, Denver, Colorado, June 13, 1951.

[16] H. Gilman, G. E. Dunn and G. S. Hammond, THIS JOURNAL, **73**, 4499 (1951); see, however, L. Kaplan and K. E. Wilzbach, *ibid.*, in press.

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