b.p. 88–88.5°) and glacial acetic acid (200 ml.) were heated with stirring to the reflux temperature for 7 hours. At this time the yellow-green color of the solution had turned to a red-black and the reaction was complete. The Ascarite tubes at the exit end of the reflux condenser had absorbed 5.12 g. (44.7%) of CO_2; an inflammable gas (presumably methane[13]), was produced but the quantity not measured.

The black reaction mixture, when cool, was added slowly to 2.5 liters of rapidly stirred anhydrous ether. The ether solution was decanted from the sandy heavy mass of lead salts and eventually fractionated through a 20-plate Whitmore–Lux column after first stripping the ether through a 3-foot Vigreux column. The fraction b.p. 40–41° at 12.5 mm.(5.18 g., 19.5%) was acetic anhydride, n^{20}D 1.3882. When boiled with aniline gave acetanilide, m.p. and mixed m.p. 112.5–114°. Inspection of the pot residue and the mass of lead salts failed to yield any further identifiable products.

Oxidation of *n*-Butyl-*n*-Butyrate.—The lead tetraacetate (199 g., 0.45 mole), glacial acetic acid (200 ml.) and *n*-butyl-*n*-butyrate (120 g., 0.83 mole, b.p. 165–165.5°) were mixed and heated at the reflux temperature (124–129°) for 11 hours until reaction was complete. The Ascarite had absorbed 8.73 g. (44.1%) of CO_2. Again an inflammable gas (presumably methane[13]) was evolved. Two products were obtained by distillation: (1) 1-acetoxy-1-butyoxybutane, b.p. 95–97° (4.5 mm.), n^{20}D 1.4210. *Anal.* Calcd. for $C_{10}H_{18}O_4$: C, 59.38; H, 8.97; sapon. equiv., 101.1. Found: C, 58.76; H, 8.55; sapon. equiv., 98.9. Prolonged boiling with water yielded *n*-butyraldehyde, 2,4-dinitrophenylhydrazone m.p. and mixed m.p. 121–122°. (2) B.p. 138–140° (4 mm.), 7.48 g., 12.8%. *Anal.* Calcd. for $C_{12}H_{20}O_6$: C, 55.37; H, 7.73; sapon. equiv., 86.76. Found: C, 56.10; H, 7.79; sapon. equiv., 87.24. Attempts to prepare a derivative of the hydrolysis product failed. This substance is probably 1-acetoxy-1-butyroxy-2-acetoxybutane rather than the expected 1,1-diacetoxy-1-butyroxybutane (saponification equivalent 65.07).

Investigation of the pot residues and the lead salts failed to yield any other identifiable products.

Oxidation of Methyl Acetate.—The reaction flask in this run was fitted with a Dry Ice cooled reflux condenser. The gaseous reaction products were passed through a series of Ascarite tubes into a receiver designed to collect methane[13] by water displacement. Meticulously dried lead tetraacetate (200 g., 0.45 mole) was suspended in 200 ml. of glacial acetic acid (dried over Na_2SO_4) and the mixture heated to the reflux temperature (125°). Then freshly distilled methyl acetate (40 g., 0.54 mole) was added slowly over a period of 12 hours, whereupon the reflux temperature dropped gradually to 110°. After 35 hours at constant reflux, the lead tetraacetate was completely consumed. The Ascarite had absorbed 17.5 g. (69.7%) of CO_2 and a total of 6,550 ml. (51.3%) of inflammable gas (presumably methane[13]) was collected. Upon distillation (as described above) the only product which could be isolated was methylene diacetate (1.92 g., 2.6%), b.p. 55–60° at 10 mm.[14] This was hydrolyzed by boiling with $CaCO_3$ solution to formaldehyde (dimedon derivative m.p. and mixed m.p. 189–190°. The lead salts and pot residues were studied, but no further products could be obtained.

Methyl Acetate from Oxidation of Acetic Acid.—The reaction flask was fitted with an inefficient air-cooled reflux condenser for this experiment. To the outlet of the condenser was attached a series of three Ascarite-filled U-tubes, a Dry Ice cooled trap and a bubble counter.

Lead tetraacetate (217 g., 0.49 mole) was suspended in 520 ml. of glacial acetic acid and heated to the reflux temperature (116–122°). At the same time a moderately rapid stream of N_2 was passed through the reaction mixture to aid in sweeping out low-boiling products. After 26 hours, the solution turned from yellow to black and reaction was complete. The Dry Ice trap contained 0.46 g. (1.3) of methyl acetate, n^{20}D 1.3599. This was derivatized by reaction with anilinomagnesium bromide (Hardy[15]) to obtain acetanilide, m.p. and mixed m.p. 113–114°.

The amount of CO_2 produced was not determined. The function of the Ascarite tubes in this case was simply to absorb the acetic acid vapors swept over by the flow of N_2 gas and permit the methyl acetate to come into the Dry Ice trap in the pure state.

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(14) I. Heilbron, "Dictionary of Organic Compounds," Oxford Univ. Press, 1953, Vol. 3, p. 371.

(15) D. V. N. Hardy, *J. Chem. Soc.*, 398 (1936).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF KANSAS, LAWRENCE, KANS.]

The Reactions of Recoil Tritium Atoms with Unsaturated Acids

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Recoil tritium atoms substitute into all of the hydrogen positions of crystalline *cis*- and *trans*-cinnamic acid and of sodium *trans*-cinnamate. The specific activities of the different positions of the aromatic ring are within 25% of each other for the *trans* compounds (and benzoic acid), and decrease in the oder *ortho* > *para* > *meta*. The specific activity of the *o*-position in *cis*-cinnamic acid is about half that of the *m*- and *p*-positions, perhaps because of steric interference by the -COOH group. Replacement of non-labile hydrogen by recoil tritium in maleic and fumaric acids is accompanied by geometric *cis*–*trans* isomerization in less than 5% of the substitutions. Addition to the double bond to form succinic acid is about half as frequent as substitution for hydrogen in the parent molecule. Addition to the triple bond of phenylpropiolic acid leads to labeled cinnamic acid, more than 90% in the *trans* form. The substitution of tritium for hydrogen is explained in terms of high kinetic energy reactions involving a miniumum of atomic motion during substitution.

Introduction

Previous studies of $Li^6(n,\alpha)T$ recoil reactions have shown that energetic tritium atoms are able to substitute for H atoms in many organic compounds.[2] Intramolecular degradations, when performed, have shown that the tritium atoms are not uniformly substituted throughout the molecule, but are found in varying specific activities in all of the non-labile hydrogen positions.[3–6] The crystalline molecules thus far investigated have been too complex for interpretation of the variations; heavily irradiated samples have also shown different distributions in separate irradiations. The present work has been undertaken in order to determine the influence of certain

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(1) The results presented in this paper are taken from a thesis presented by R. Milford White to the Universty of Kansas in partial fulfillment of the requirements for the Ph.D. degree. This work was supported by Contract No. At-(11-1)-407 with the United States Atomic Energy Commission.

(2) F. S. Rowland and R. Wolfgang, *Nucleonics*, **14**, No. 8, 58 (1956).

(3) F. S. Rowland, C. N. Turton and R. Wolfgang, THIS JOURNAL, **78**, 2358 (1956).

(4) H. Keller and F. S. Rowland, *J. Phys. Chem.*, **62**, 1373 (1958).

(5) W. J. Hoff, Jr., and F. S. Rowland, THIS JOURNAL, **79**, 4867 (1957).

(6) W. G. Brown and J. L. Garnett, *Intl. J. Appl. Rad. and Isotopes*, **5**, 114 (1959).

structural groups upon the reactions of recoil tritium atoms. The investigations reported here have centered around the presence of an unsaturated carbon–carbon bond in the molecule, and the effects which arise from it. The molecules whose reactions with tritium have been studied are *cis*-cinnamic acid, *trans*-cinnamic acid, sodium *trans*-cinnamate, maleic acid, fumaric acid and phenylpropiolic acid, all in the crystalline state. The purified parent compound and some other closely related products have been isolated from each irradiation sample. The intramolecular distributions of tritium in the cinnamic acids (and benzoic acid, for comparison) have been obtained by suitable degradations of the purified acids.

Experimental

Irradiations.—One gram each of thoroughly-mixed powders, containing 3% by weight Li_2CO_3 plus the appropriate parent organic compound, were used for each irradiation. Each sample was wrapped in aluminum foil, permitting the escape of all radiation-produced gases. The irradiations were carried out at 25–30°, under differing flux and time conditions as shown in Tables I and II.

Chemicals.—C.P. grades of *trans*-cinnamic acid and benzoic acid were used without further purification. C.P. maleic anhydride was hydrolyzed to maleic acid and recrystallized several times from water. Technical grade fumaric acid was purified by repeated crystallization from 1 *N* HCl. Sodium *trans*-cinnamate was obtained by neutralization of C.P. *trans*-cinnamic acid with NaOH and evaporation to dryness. Technical grade phenylpropiolic acid was recrystallized from CCl_4 and dilute alcohol alternately until the literature melting point was obtained. *cis*-Cinnamic acid was prepared as below.

Preparation of *cis*-Cinnamic Acid.—An equimolar amount of hydrogen was added to phenylpropiolic acid in methanolic solution with a palladium–charcoal catalyst. After filtration of the catalyst and evaporation of the methanol, the crude *cis*-cinnamic acid was extracted with hexane, converted to the aniline salt, and recrystallized from a benzene–hexane mixture. Acidification of the purified salt yielded *cis*-cinnamic acid (m.p. 68°). Several efforts to prepare the other two crystalline forms of *cis*-cinnamic acid were unsuccessful.

Purification of Irradiated Maleic and Fumaric Acids.—Each irradiated acid was divided into three aliquots: parent carrier (50:1) was added to the first, the geometric isomer (10:1) to the second and succinic acid (10:1) to the third aliquot.

Maleic acid was precipitated as the barium salt by addition of 0.1 *N* $BaCl_2$ to an ammoniacal solution of the carrier maleic acid aliquot. The barium maleate was counted without further purification. Less than 0.5% of the fumaric acid activity was carried by inactive barium maleate precipitated in the presence of labeled fumaric acid.

Fumaric acid and succinic acid were purified from their aliquots by recrystallization from 1 *N* HCl and dilute alcohol, respectively.

Exchange was found to be about 50% complete for maleic acid refluxed in tritiated water for one hour. All heating steps were therefore avoided in the purification of maleic acid. A similar experiment with fumaric acid showed only 2% exchange in one hour.

Purification of Aromatic Acids.—Inactive parent carrier was added (in the ratio of 50 g. of carrier to 1 g. of irradiated material) to each of the cinnamic acids and the salt, phenylpropiolic acid, and benzoic acid. After heating with decolorizing charcoal, the acids were converted to the ammonium salts and purified by displacement chromatography on Dowex 1-X anion exchange resin. This treatment removed some radioactive impurities very difficult to remove by recrystallization. The acids were then recrystallized to constant specific activity with water and various organic solvents.

Active *cis*-cinnamic acid was refluxed 0.5 hour in dilute alcohol and active *trans*-cinnamic acid was refluxed 5 hours in water to check for isotopic exchange. Successive aliquots which were withdrawn from each after various time intervals showed no loss (<1%) of specific activity.

To two additional aliquots of the irradiated phenylpropiolic acid, *cis*- and *trans*-cinnamic acids were added, respectively (10 parts carrier to 1 part irradiated material). Phenylpropiolic acid was removed from each cinnamic acid aliquot by displacement chromatography on a Dowex 1-X column. *trans*-Cinnamic acid was purified by recrystallization from carbon tetrachloride. The *cis*-acid was purified by recrystallization of the aniline salt from a benzene–hexane mixture.

Isolation of Styrene, Acrylic Acid and Labile Tritium from *trans*-Cinnamic Acid.—Ten ml. of styrene and 1.0 g. of irradiated *trans*-cinnamic acid were dissolved in alcohol, evaporated to remove alcohol, and then washed with 5% KOH. Fresh inactive *trans*-cinnamic acid was added and washed away two additional times. After drying and vacuum-distillation of the styrene, dibromostyrene was prepared and crystallized to constant specific activity.[7] Exchange in a control experiment was less than 0.1%.

Ten ml. of a 50% aqueous acrylic acid solution was added to 1.0 g. of the irradiated acid, and then dissolved in alcohol–water solution. *trans*-Cinnamic acid was added to saturation at the boiling point, and then crystallized out by cooling; several repetitions removed most of the active *trans*-cinnamic acid. The residue was made anhydrous by several distillations after toluene addition, and the *p*-toluidide was then formed as described by Cheronis and Entrikin.[7] Approximately 13% exchange was observed during the toluene distillations for acrylic acid containing labile tritium. Less than 0.1% exchange was observed in the formation of the *p*-toluidide.

The labile tritium activity was determined by distillation of water from an aqueous solution of an aliquot of irradiated acid.

Oxidation to Benzaldehyde.—Cinnamic acid was partially oxidized with $KMnO_4$. The benzaldehyde was steam distilled from 50 ml. of 0.5 *M* $KMnO_4$ simultaneous with the slow addition of cinnamic acid (1 g. as the sodium salt) to the solution. The benzaldehyde phenylhydrazone was formed by adding the distillate to a dilute solution of phenylhydrazine in acetic acid, and was recrystallized from dilute alcohol (yield 50%). Less than 0.1% exchange was observed when this reaction was performed in tritiated water.

Oxidation to Benzoic Acid.—A solution of the sodium salt of the acid (10 g.) was slowly added to a gently refluxing solution of potassium permanganate (40g.) in very dilute sodium hydroxide solution(250 ml.). After refluxing 30 minutes, the manganese dioxide was filtered and the benzoic acid precipitated from the filtrate by the addition of cold dilute sulfuric acid (yield 60%). Benzoic acid obtained by the oxidation of *trans*-cinnamic acid in the presence of tritiated water showed <0.1% exchange.

Degradation of Benzoic Acid.—The experimental details for the formation from benzoic acid of benzamide, acetanilide, *p*-bromoacetanilide, tribromoaniline and 3,5-dinitrobenzoic acid have been given previously.[8–10] Control experiments on the degradation procedure showed less than 0.5% tritium exchange with the solvent in any of these steps.

The *p*-toluidide and *p*-phenylphenacyl ester of *trans*-cinnamic acid were prepared according to standard procedures.[7]

Tritium Assay.—Aliquots of the pure solid compounds were converted to gas by the zinc combustion method. Tritium assay was then performed by gas proportional counting in a 100-ml. silver-walled glass counter brought to 40 cm. total pressure with propane.[11]

Results

The tritium activity found in each parent molecule after purification to constant specific radio-

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(7) N. D. Cheronis and J. B. Entrikin, "Semimicro Qualitative Organic Analysis," Interscience Publishers, Inc., New York, N. Y., 1957. R. Shriner, R. Fuson and D. Curtin, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1956.

(8) W. Bonner, THIS JOURNAL, **79**, 2469 (1957).

(9) R. Milford White and F. S. Rowland, *ibid.*, **83**, 4713 (1960).

(10) R. Milford White, Ph.D. Thesis, University of Kansas, 1960.

(11) F. S. Rowland, J. K. Lee and R. M. White, "Oklahoma Conference—Radioisotopes in Agriculture," TID-7578, U. S. Govt. Printing Office, 1960.

activity is shown in Tables I and II. Table I also shows the tritium found in other labeled compounds isolated from irradiated maleic, fumaric, phenylpropiolic and *trans*-cinnamic acids, given as d.p.m./mg. of irradiated parent molecule. The labeled succinic acid from fumaric acid proved difficult to purify, and the 6000 d.p.m./mg. represents the extrapolation of a series of recrystallizations not quite to constant activity. Since control experiments indicate some exchange of tritium with the solvent in the purification of acrylic acid from *trans*-cinnamic acid, the specific activity of acrylic acid is approximate. The other data represent the average of three or more recrystallizations whose specific activities all were within ±1% of the mean. The excess of the crude radioactivity over the sum for purified compounds represents unidentified products such as labile tritium, HT trapped in the crystalline lattice and released upon solution, etc. Labile tritium activity is shown to be an important product in these systems by its substantial measured yield from *trans*-cinnamic acid.

TABLE I

TRITIUM RADIOACTIVITY OF COMPOUNDS ISOLATED FROM RECOIL REACTIONS WITH SEVERAL UNSATURATED ACIDS

Irradiated compound Irradiation conditions	Phenyl-propiolic acid	Maleic acid	Fumaric acid	*trans*-Cinnamic acid
	2 hours at 5 × 10^{12} n./cm.^{2}/sec.			
	Specific radioactivity (d.p.m./mg. of parent)			
Calculated total activity (d.p.m./mg.)	145,000	145,000	145,000	145,000
Crude irradiated material	112,000	105,000	120,000	96,600
Phenylpropiolic acid	51,200	.....	.....	.....
trans-Cinnamic acid	8,510	.....	.....	42,700
cis-Cinnamic acid	660	.....	.....	.....
Maleic acid	.....	14,900	660	.....
Fumaric acid	.....	590	17,300	.....
Succinic acid	.....	7,690	Est. 6,000	.....
Styrene	.....	.....	.....	2,910
Acrylic acid	.....	.....	.....	~2,000
Labile activity	.....	.....	.....	26,700
Radioactivity found as parent, %	35	10	12	30

The radioactivities of degradation products from benzoic and cinnamic acids are shown in Table II. Each of these also represents the average of two or more recrystallizations in agreement with each other. Since previous experiments with very heavily radiation-damaged sugars have shown that the distribution of radioactivity within the molecule is somewhat dependent on post-irradiation treatment,[4] two aliquots of a thoroughly mixed fraction of *trans*-cinnamic acid were dissolved in carbon tetrachloride and ethyl alcohol, respectively. These samples were each brought to constant specific activity; the tritium assays of these separately purified samples agreed within 1%.[12]

The percentage of tritium observed in the parent molecule, as compared to the total production of tritium in the sample calculated from lithium concentration and nominal neutron flux, is shown in Tables I and III. Without independent flux monitoring in each sample of a larger group, we do not attribute more than ±20% significance to the listed percentages. This is especially true in view of the variety of irradiation conditions employed in these experiments.

The intramolecular tritium distributions indicated by the radioactivity of the degradation products are shown in Table III. The distributions have been calculated on the basis of the sum of the five aromatic hydrogen activities equal to 100. The specific activity of the cinnamic acids from phenylpropiolic acid was insufficient to warrant degradation except to benzoic acid.

These intramolecular distributions are most accurate in relative *ortho–meta–para* distributions, and less dependable for the olefinic hydrogens. Benzoic acid can be shown to be free from radioactive impurities by comparison of the sum of the activities of tribromoaniline and 3,5-dinitrobenzoic acid, as well as by the agreement with benzamide and acetanilide. The agreement is quite good for benzoic acid from the *trans*-cinnamic acid and salt, while a slight impurity is indicated for the purified benzoic acid parent.

The agreement among *trans*-cinnamic acid and the *p*-toluidide and *p*-phenylphenacyl ester indicates essential radiochemical purity prior to partial oxidation to benzaldehyde. The olefinic hydrogens may be expected to exchange more readily with solvent hydrogen than do the ring hydrogens, and the choice of purification procedures is consequently somewhat limited. Further, if the permanganate oxidation of benzaldehyde overshoots, a substantial tritium isotope effect can be expected leading to preferential oxidation of unlabeled benzaldehyde, and an increased specific activity of the remaining aldehyde. For these reasons, there is less quantitative validity to the assay of olefinic hydrogen than to the ring hydrogens.

Discussion

Radiation Damage.—Recoil tritum irradiations of systems such as these can lead to labeled compounds either by direct reaction of the tritium atom with the parent organic molecule, or by indirect reactions depending on radiation degradation of labeled molecules or by direct reaction with radiation products. The high percentage yield of a labeled parent molecule by direct reaction with it implies that indirect radiation products can only seriously perturb the observations when destruction of the parent molecule is very heavy—20% to 50% or more. None of these samples was irradiated long enough to destroy a large percentage of the parent molecules. The damage to benzoic acid which received by far the largest neutron dose, can be estimated as 15% from the data of Markowitz, Rowland and Wolfgang, quoted in reference 2.

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[12] Similar experiments by Mr. V. Anselmo in our laboratory have failed to detect any differences in specific activity greater than 5% in lightly irradiated naphthalene or benzoic acid. The small observed differences can be explained by inhomogeneities in neutron flux resulting from self-shielding and/or incomplete mixing of the original lithium carbonate mixture.

TABLE II

TRITIUM RADIOACTIVITY OF BENZOIC ACID, CINNAMIC ACIDS AND DEGRADATION PRODUCTS FROM $Li^6(n,\alpha)H^3$ REACTION

(DPM/μmole)

Irradiated compound Irradiation conditions	Benzoic acid 1 week ~10^{12}	*cis*-Cinnamic acid 2 hours 5×10^{12}	*trans*-Cinnamic acid ~12 hours 5×10^{11}	Sodium *trans*-cinnamate 8 hours 1.3×10^{12}	Phenylpropiolic acid 2 hours 5×10^{12}	
Compound isolated		Parent compound		Parent + *trans*-acid	*cis*-Cinnamic acid	*trans*-Cinnamic acid
cis-Cinnamic acid		3200			97	
trans-Cinnamic acid			4820	6920		1260
p-Phenyl phenacyl ester			4790			
p-Toluidide			4710			
Benzaldehye phenylhydrazone			4410	5650		
Benzoic acid	41,100	2800	4160	4810	16	130
Benzamide	41,300	2800	3940	4840		
Acetanilide	39,800	2820	3860	4840		
p-Bromoacetanilide	31,400	2070	3060	3850		
3,5-Dinitrobenzoic acid	24,800	1470	2550	3150		
Tribromoaniline	14,200	..	1470	1670		
Total radioactivity found in molecule, %	~16	15	~30	27	0.5	6

TABLE III

INTRAMOLECULAR DISTRIBUTIONS OF TRITIUM ACTIVITY IN AROMATIC ACIDS

Irradiated compound	Specific activity (d.p.m./μmole)[a] and relative activity (total ring = 100) Benzoic acid		*cis*-Cinnamic acid		*trans*-Cinnamic acid		Sodium *trans*-cinnamate	
Hydrogen position	Specific	Relative	Specific	Relative	Specific	Relative	Specific	Relative
ortho	17,100 ± 700	43/2	720 ± 50	25/2	1590 ± 40	41/2	2180 ± 50	45/2
meta	14,200 ± 200	36/2	1350 ± 40	48/2	1470 ± 20	38/2	1670 ± 20	35/2
para	8,400 ± 400	21	750 ± 50	27	800 ± 50	21	990 ± 60	20
α-H		..	380 ± 60	13	360 ± 60	9	1270 ± 90	26
β-H		..			550 ± 60	14	810 ± 70	17

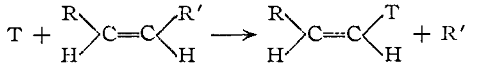
[a] Acetanilide is used for total ring activity.

Other molecules received approximately one-tenth the irradiation dose, but probably have larger G-values than the 0.6 calculated for benzoic acid under heavy ion bombardment—we estimate the maximum damage as ~5%.

The yields of other products become more susceptible to radiation interference as the percentage of total activity decreases. The ring activity of *cis*-cinnamic acid isolated from irradiated phenylpropiolic acid represents <0.1% of the calculated total tritium production in the sample, and can readily be attributed to radiation damage. The corresponding ring radioactivity of *trans*-cinnamic acid is probably at least in part also a result of radiation damage.

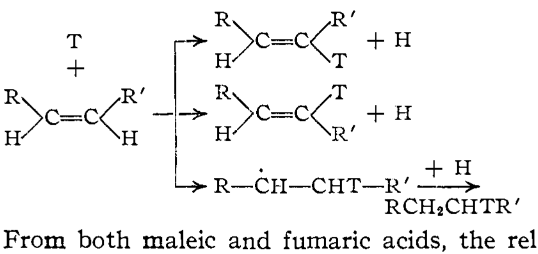
Reactions with Unsaturated Molecules.—Extensive studies of the gas phase reactions of recoil tritium with olefinic hydrocarbons have shown that most T for H substitutions occur while the recoil T atom still possesses high kinetic energy.[13,14] Some products (*e.g.*, propylene, butene-1 from *trans*-butene-2) are observed that are consistent with the decomposition of an excited *sec*-butyl radical formed in the initial reaction of the recoil tritium with the olefin; others (*e.g.*, *n*-butane) are consistent with the reactions of thermal *sec*-butyl radicals. In the gas phase, the time between radical formation and collision with another molecule can be varied by changing the pressure, and such a change results in alteration of the quantitative yields.[14] The observed changes are those expected when the relative yields of the decomposition products and addition products for *sec*-butyl radicals are dependent upon a competition between decomposition and collisional de-excitation.

The initial stages of hot tritium reactions probably are very similar in all phases. However, in condensed phases, only ~10^{-12} second is available before collisional de-excitation should be expected for any entities such as the *sec*-butyl radical. A reaction such as 1 which frequently has a relatively


(1)

low activation energy and may proceed well with sufficient time, can be severely suppressed by de-excitation in condensed phases. While the yield of labeled propylene is 0.6–0.8 that of the parent from *cis*- or *trans*-butene-2, the yields of both acrylic acid and styrene from *cis*-cinnamic acid in these experiments are only ~0.05 time the parent yield.

The specific activities of Table I also furnish comparisons for the relative likelihood of reactions 2, 3 and 4


(2)
(3)
(4)

From both maleic and fumaric acids, the relative yields of (2) and (3) are given by the radioactivity

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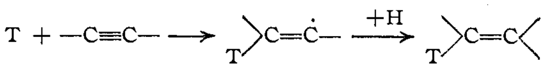
[13] D. Urch and R. Wolfgang, THIS JOURNAL, 81, 2025 (1959).

[14] J. K. Lee, B. Musgrave and F. S. Rowland, *ibid.*, 82, in press (1960).

of the parent and the opposite isomer, respectively, while that of (4) is measured by the succinic acid yield.

In the crystalline state, the T for H substitution proceeds almost entirely through an asymmetric intermediate to give reaction 2, and maintaining the original isomeric structure.[15] Less than 5% of these substitutions are accompanied by a reversal in orientation as in reaction 3. The substitution of T for H by reactions 2 and 3 differ chiefly in that less actual atomic movement is required in the former: the atomic motion is essentially confined to the tritium and the replaced hydrogen atoms. Reaction 3 at least requires the additional motion of R′, and would probably pass through the symmetrical $R-\dot{C}H-CHT-R'$ radical. Assuming approximately equal production of both geometric isomers from such a radical, less than 10% as many substitution reactions occur through such a radical as react asymmetrically by (2). It seems quite probable that many true "hot" atom reactions will also follow mechanisms which involve "economy of atomic motion"—the observed strong preference for retention of configuration in the substitution of recoil tritium for hydrogen at an asymmetric carbon atom can similarly be described with the motion of fewer atoms than can the unobserved inversion of configuration.[16,17]

There is no direct T for H substitution reaction corresponding to (2) for phenylpropiolic acid, but addition to the triple bond by reaction 5 accounts for approximately the same fraction of the calculated total tritium production as does addition to the double bond by reaction 4



(5)

In this case, unlike the succinic acid product of maleic and fumaric acids, two isomeric forms are possible. The energetically more stable *trans*-cinnamic acid is preferentially formed. This preference could easily arise in the addition of the second hydrogen atom to form the stable olefinic molecule; alternately, the stereochemistry of the addition process may be controlled by the crystal structure of the parent compound in which the cinnamic acid is formed.

Ortho, meta, para **Distributions.**—The distribution of radioactivity among *ortho*, *meta* and *para* positions is most accurately known for sodium *trans*-cinnamate, for which the checks on radiochemical purity are especially satisfactory. In this molecule the specific activities of the various ring positions are similar, but clearly different from each other, decreasing in activity in the order *ortho* > *para* > *meta*. A very similar distribution was also found for *trans*-cinnamic acid and benzoic acid. The accuracy of the data is insufficient to indicate whether any measurable difference in distribution occurs among these three compounds—certainly, no large deviation occurs. A similar degradation of recoil-tritium labeled toluene showed 44.1, 37.5 and 18.4% as the relative tritium activity in the *ortho*, *meta* and *para* positions, respectively.[18]

The distribution of ring tritium in *cis*-cinnamic acid is markedly different from that obtained from the other three molecules. The distribution is approximately that to be expected from the other compounds if one *o*-position contributed no radioactivity. The obvious hypothesis follows that the –COOH group in a position *cis* to the aromatic ring effectively interferes with the substitution reaction at the adjacent *o*-position by some form of steric effect, leaving substitution at the *o*-position across the ring as the mechanism for obtaining the *o*-tritiated molecule. Steric effects might arise from alterations either in the ratio of recoil tritium attack on different molecular positions, or from markedly different decomposition paths for similar positions. Neither hypothesis seems excluded by the observations on *cis*-cinnamic acid.

The intramolecular distributions of Table III indicate that T for H substitutions at each olefinic position is approximately as frequent as substitution at the various aromatic hydrogen positions. There are indications of real differences in the specific activities of non-equivalent olefinic hydrogens, but the data are not as certain as with the aromatic positions. Previous comparisons of various hydrogen positions have indicated relatively little preference for reaction with aromatic, olefinic or saturated carbon–hydrogen positions,[6,14] and are quite consistent with the assumption that recoil tritium reactions, occurring at high kinetic energies, are insensitive to differences in activation energy for the various reactions.[14,19]

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[15] Urch and Wolfgang, in a private communication, report a similar, but less pronounced preference for the original molecule over its geometric isomer in gas phase irradiations of *cis*- and *trans*-dichloroethylenes plus He^3.

[16] H. Keller and F. S. Rowland, *J. Phys. Chem.*, **62**, 1373 (1958).

[17] J. Kay, R. Malsan and F. S. Rowland, THIS JOURNAL, **81**, 5050 (1959).

[18] M. Zifferero, *Energia Nucleare*, **4**, 479 (1957).

[19] P. Estrup and R. Wolfgang, THIS JOURNAL, **82**, 2661, 2665 (1960).