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Studies of the Recoil Tritium Labeling Reaction. I. Glucose and Galactose[1]

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The reactions of $Li^6(n,\alpha)$ recoil tritons have been investigated in crystalline glucose and galactose. Approximately 12% of the tritium stopped in the organic phase is found in the non-labile C–H positions in otherwise unchanged hexose molecules. The tritium shows widely varying specific activities in the various non-labile positions. Possible reaction mechanisms for the incorporation of tritium into hexoses are discussed.

Introduction

In previously reported studies, it has been demonstrated that tritium recoiling from the nuclear reaction in which it was formed can react chemically with its environment to produce labeled organic compounds.[2] The technique for carrying out such a process consists simply of mixing a lithium compound with the hydrogenous material to be labeled and exposing the mixture to slow neutrons. A considerable fraction of the energetic tritium produced in the $Li^6(n,\alpha)T$ reaction will replace bound hydrogen in molecules of the stopping medium to form a radioactive form of the original hydrogenous molecule. However, little is known of the chemical reaction mechanisms involved.[3]

In order to investigate the specificity of the chemical reactions of recoil tritium, studies have been made in crystalline glucose and galactose. After purification, the active glucose and galactose obtained were chemically degraded to determine the distribution of the tritium among the various non-labile hydrogen positions.

Experimental

a. **Irradiation. Glucose.**—A finely powdered mixture of 81 g. of glucose and 88 g. of Li_2CO_3 was irradiated in the thermal column of the Brookhaven reactor for 65 hours at a flux of ~6 × 10^9 n/cm.^{2}-sec. Although the material was slightly brownish from radiation decomposition at the end of the irradiation, more than 75 g. of glucose eventually crystallized out of the purified sirup, indicating that considerably less than 7% of the original glucose was destroyed by radiation.

Galactose.—In order to obtain a higher specific activity it was decided to irradiate the galactose in the pile proper rather than in the thermal column. It is desirable, however, to keep the relative flux of fast neutrons low, so that radiation damage from neutron–proton collisions occurring in the sample is minimized. A mixture of 0.22 g. of Li_2CO_3 and 2.0 g. of galactose was therefore irradiated in a pile location about two feet from the nearest fuel elements. The slow neutron flux of this facility was measured by activation of gold foils and found to be 1.8 × 10^{12} neutrons/cm.^{2}-sec. with a Cd ratio of 25.

After a 27-hour irradiation the mixture was somewhat brownish and only 630 mg. of galactose could be crystallized out of it. This recovery of only 32% is presumably largely due to the increased radiation destruction of galactose caused by the more intense irradiation. Macro amounts of organic acids were separated during the purification of this sample.

In both of the irradiations the particle size of the mixture was of the order of 1 μ or less. As the range of the tritons is ~40 μ the probability of stopping a given triton in the organic or lithium phase is proportional to the stopping powers of the two phases. To a sufficient approximation the mass stopping powers of the two compounds can be taken to be equal. Consequently the fraction of the total tritons produced in the system that are stopped in the organic phase is simply the ratio of the weight of the sugar to that of the total sample. The total tritium activity produced is calculated from the flux, the time of irradiation, and the number of lithium atoms by taking 70 barns as the cross section of the $Li^6(n,\alpha)T$ reaction for natural lithium and 12.5 years as the half-life of tritium.

The major error that enters into these calculations is the uncertainty in the neutron flux. The 6 × 10^9 n/cm.^{2}-sec. flux employed in the glucose irradiation is probably known to ±20% while the 1.8 × 10^{12} n/cm.^{2}-sec. flux for the galactose irradiation is accurate to ±10%. These errors appear directly in the figures in Table II for the "% entry of tritons into hexose."

b. **Chemical Purification of Hexoses.**—The purification of this glucose sample has been described previously.[2] The irradiated galactose–Li_2CO_3 mixture was treated quite similarly. Although this mixture had been subjected to much more intense radiation, the same purification steps produced a solution from which the surviving galactose crystallized quite readily. Five hundred mg. of this galactose was then diluted with 9.5 g. of inactive galactose in order to furnish a larger sample for the subsequent chemical steps. This diluted galactose was converted to galactose pentaacetate and recrystallized three times. The subsequent reactions were performed on this recrystallized galactose pentaacetate.

c. **Hexose Degradation Scheme.**—The specific activity of tritium located in each of the non-labile positions of the hexose molecules can be determined by preparing, in addition to the hexose itself, a proper set of five derivatives, in each of which one or more of the original C–H bonds have been broken, thus removing any tritium that may have been present in those positions in the hexose molecule.

Table I lists the derivatives chosen for the hexose degradation analysis and also indicates which of the C–H bonds from the original sugar are preserved intact in each derivative. These derivatives are formed with yields of 70–95%. In a previous study it has been shown by the use of C^{14} tracers that the preparation of the derivatives, under the conditions described below, does not result in any rearrangement or exchange involving the skeletal carbons of the hexoses.[4] On the basis of this, it is reasonable to assume that the hydrogen atoms attached to these skeletal carbons also do not exchange under the same conditions. The self-consistent results on the tritium distribution obtained by using these derivatives indicate that this assumption is valid.

d. **Preparation of Derivatives.**—The crystalline hexoses were acetylated with acetic anhydride and sodium acetate by the usual procedure and the resultant penta-*O*-acetyl-D-hexoses recrystallized from an ethanol–water mixture. The radiochemically pure penta-*O*-acetyl-D-hexoses were deacetylated with dilute sulfuric acid[5] and the resulting sugars were used to prepare the phenylosazone, phenylosotriazole, 2-phenyl-4-formylosotriazole, 2-phenyl-4-carboxylic acid,

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[1] Research performed in part under the auspices of the U. S. Atomic Energy Commission.

[2] R. Wolfgang, F. S. Rowland and C. N. Turton, *Science*, **121**, 715 (1955).

[3] The chemistry of other recoil atoms has been extensively studied—mainly radioactive halogens, etc., produced by (n,γ) processes, and C^{14} from the N^{14} (n,p)C^{14} reaction. It is difficult to predict the applicability of these results to the tritium recoil system. See A. G. Schrodt and W. F. Libby, THIS JOURNAL, **76**, 3100 (1954), and A. P. Wolf and R. C. Anderson, *ibid.*, **77**, 1608 (1955), for the C^{14} reactions, and the excellent review articles by J. Willard in *Ann. Rev. Nuclear Sci.*, **3**, 193 (1953), and *Ann. Rev. Phys. Chem.*, **6**, 141 (1955).

[4] J. C. Bevington, E. J. Bourne and C. N. Turton, *Chem. and Ind.*, 1390 (1953).

[5] S. Abraham, I. L. Chaikoff and W. Z. Hassid, *J. Biol. Chem.*, **195**, 567 (1952).

TABLE I

TRITIUM ACTIVITY OF HEXOSE DERIVATIVES

	Derivative	Intact C–H bonds in derivative 1	2	3	4	5	6	6	Specific activities, dpm/μmole Glucose	Galactose[a]
(a)	Hexose	x	x	x	x	x	x	x	1216 ± 12	....
(b)	Hexose pentaacetate	x	x	x	x	x	x	x	1214 ± 6	2310 ± 10
(c)	Hexose phenylosazone	x		x	x	x	x	x	1136 ± 8	2160 ± 40
(d)	Hexose phenylosotriazole	x		x	x	x	x	x	1150 ± 16	2220 ± 20
(e)	Potassium hexonate		x	x	x	x	x	x	1166 ± 10	2100 ± 40
(f)	Dibasic acid		x	x	x	x			....	1650 ± 30
(g)	2-Phenyl-4-formylosotriazole	x		x					386 ± 6	676 ± 8
(h)	2-Phenyl-4-carboxylic acid osotriazole	x							36 ± 4	170 ± 30
(i)	Benzoyl glycolaldehyde semicarbazone					x	x	x	584 ± 10	774 ± 10
(j)	Formaldehyde dimedone						x	x	582 ± 10	532 ± 12

[a] This sample diluted 20-fold with inactive galactose to facilitate chemistry and counting.

benzoyl glycolaldehyde semicarbazone and hexonic acid derivatives by previously described methods.[4] The formaldehyde dimedone derivatives were prepared by oxidation of sugar samples with sodium metaperiodate and precipitation of the resulting formaldehyde with dimedone.[6] Mucic acid was made from D-galactose by oxidation with nitric acid.

e. **Tritium Assay.**—Samples were assayed for tritium by converting them to gas which was then counted in a proportional counter. The method of Kaplan, Wilzbach and Brown was used for the gasification.[7] A standard aliquot of the resulting methane–hydrogen gas was introduced into a silver-walled glass counter with an active volume of 85 cc. To complete the counter filling either ethane (to 34 cm. pressure) or 90% argon–10% methane mixture (to 70 cm.) was added. For weights of sample (plus water) up to 15 mg., these fillings gave very good plateaus at about 2600 and 2000 volts, respectively. These measurements are reproducible to about 1% for samples of the same material, and to about 1–2% for samples of different compounds containing the same labeled groups. The absolute accuracy of the assays is probably good to about 5%.

Results

Both the glucose and the galactose crystallized from the irradiated samples were found to contain tritium. However, in view of the large activity of other tagged molecules that must also have been formed during irradiation it is necessary to verify the radiochemical purity of the compounds isolated. This was done by subjecting each sugar to a series of recrystallizations and reactions and assaying for radioactivity at each step. If the tritium is bound in the pure hexose, no loss of specific activity (measured in disintegrations per minute per micromole) will occur. However, any tritium associated with impurities will tend to fractionate with a resultant loss of activity.

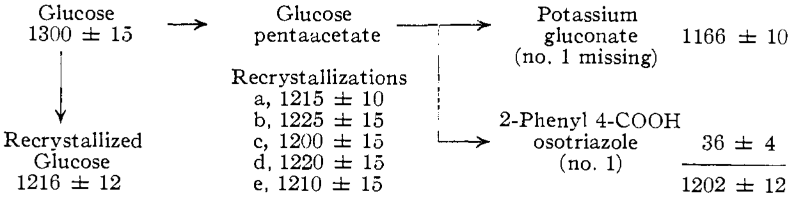

Fig. 1.—Radiochemical purity of glucose; specific activities in d.p.m. μmole.

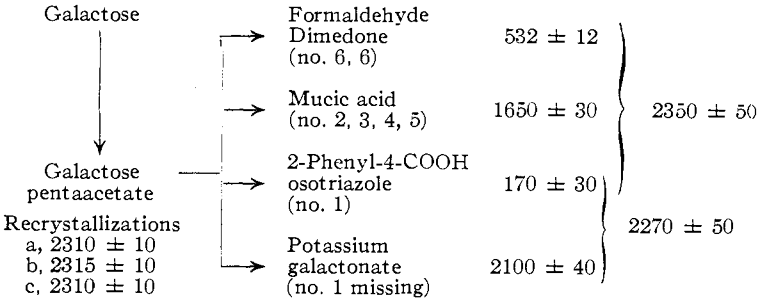

Fig. 2.—Radiochemical purity of galactose; specific activities in d.p.m./μmole.

The procedure followed for glucose is shown in Fig. 1. Recrystallization of both glucose and the pentaacetate derivative yielded constant and identical specific activities with only a 6% loss of the activity in the crude glucose. Two derivatives were then prepared, one containing only the hydrogen attached to carbon 1 of the glucose and the other containing all the C–H hydrogens of the glucose except that attached to carbon 1. The sum of the specific activities of these derivatives is again the same within the errors as the specific activity of recrystallized glucose.

A similar procedure for galactose is shown in Fig. 2.

The relative ease with which these sugars have been radiochemically purified is apparently characteristic for labeled compounds made by the tritium recoil method. This must be partly due to the relatively large fraction of the tritons that are incorporated into the active parent molecule. (Including the labile hydrogens this fraction can be estimated to be 20% in the case of sugars.) Moreover, experiments on other systems, now in progress, indicate that a large part of the remaining tritium becomes incorporated in easily separable molecules, chiefly HT.

The results obtained with the undegraded hexoses are summarized in Table II. The amount of tritium activity entering the organic phase of the irradiated sample is calculated from the bombardment conditions as indicated previously. Column 2 lists the specific activity of the purified undiluted sugar. The third column represents the probability that a recoil tritium atom brought to rest in the crystalline sugar will replace a non-labile

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(6) R. E. Reeves, THIS JOURNAL, **63**, 1476 (1941).

(7) K. Wilzbach, L. Kaplan and W. G. Brown, *Science*, **118**, 522 (1953).

hydrogen atom of the hexose molecule without causing any other permanent change in that molecule.

TABLE II

HEXOSE ACTIVATION BY TRITIUM RECOIL

	Activity T entering organic phase, d.p.m./mg.	Activity T hexose, non-labile, d.p.m./mg.	% Entry of tritons into hexose
Glucose	67,000	6,700	10 ± 2
Galactose	2,100,000	250,000	12 ± 1

It should be noted that the highest activity obtained (250,000 d.p.m./mg.) is by no means the maximum that could be obtained in hexoses by the recoil triton labeling method. In these experiments no particular effort was made to provide the optimum irradiation conditions for minimizing radiation destruction, so that higher specific activities could be obtained through longer irradiations.

The specific activities of tritium present in the various hexose derivatives are given in Table I. The specific activity of individual C–H positions is obtained from these derivatives as follows (see Fig. 3): the tritium activity attached to carbon positions 1 and 6 is obtained directly from (h) and (j), respectively; 2, 3, and 5 from (a) or (b) minus (c) or (d), (g) minus (h), and (i) minus (j), respectively; and 4 is obtained by the difference of (a) or (b) and the sum of the other positions. Separate checks on the accuracy of the resultant distribution are then available through the potassium hexonate and the dibasic acid.

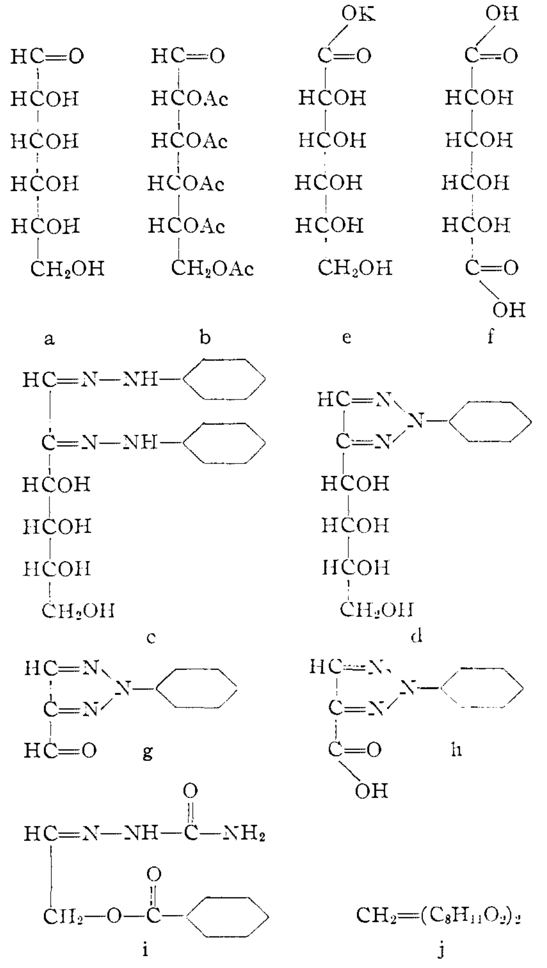

Fig. 3.—Hexose degradation scheme.

With this group of derivatives, the specific activities of carbon atoms 2 and 4 are normally obtained by small differences of large numbers and therefore are not as accurately known as the others. In the case of glucose, the activity of carbon position 5 is also somewhat uncertain because of its low activity and the high activities in the two positions attached to carbon 6. It would be desirable to isolate other derivatives which give a more direct measure of the radioactivity in these positions, but attempts to isolate additional suitable derivatives for these positions have not yet been successful.

Table III gives the results of this analysis together with estimated errors. It appears that the recoil tritium atoms possess a remarkable specificity for the different C–H positions in the hexoses. It is also noteworthy that the very similar molecules, glucose and galactose, yield substantially different patterns of tritium distribution.

TABLE III

TRITIUM DISTRIBUTION AMONG C–H POSITIONS IN HEXOSES

	Glucose		Galactose[a]	
Hydrogen attached to carbon no.	Spec. act., d.p.m./μmole	% Total activity in C–H positions	Spec. act., d.p.m./μmole	% Total activity in C–H positions
1	36 ± 4	3	180 ± 30	8
2	74 ± 10	6	120 ± 40	5
3	350 ± 15	29	500 ± 30	22
4	170 ± 20	14	750 ± 50	32
5	2 ± 15	0	250 ± 10	11
6	290 ± 10	24	260 ± 10	11
6	290 ± 10	24	260 = 10	11

[a] This sample diluted 20-fold with inactive galactose to facilitate chemistry and counting.

Discussion

In considering the chemical fate of a recoil triton or tritium atom,[8] we can safely ignore that part of its path where it still has a large amount of kinetic energy. Although in this energy range large numbers of ions and radicals are produced in the stopping medium, they are too far from the end of the range of the tritium atom to affect its final chemical combination. Thus we need to be concerned only with the events occurring very near the end of the range. Here there are several possible mechanisms by which the tritium atom can enter chemical combination. First, the energetic atom may strike a molecule and immediately combine with a part of it to give a new, stable, tritiated molecule. Walden inversions and pick-up of a hydrogen atom (to form HT) would be examples of such non-radical reactions where the tritium enters its final combination immediately upon reaching the end of its range. Secondly, the tritium may

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(8) The original triton produced in the nuclear reaction is, of course, an ion. It will pick up an orbital electron when its kinetic energy drops into the range in which the velocity of the ion is of the order of magnitude of the velocity of an orbital electron. This electron pick-up begins at about 10^5 e.v. for tritons and is complete at energies far above those of concern in chemical reactions.

create one or more radicals at the very end of its range and then combine with it (or them). Or, thirdly, the tritium may reach thermal energy and, not reacting immediately, diffuse around the medium, finally to abstract a hydrogen atom and form HT,[9] or perhaps to meet and combine with a free radical. It is also possible that such tritium may not combine into a stable molecule until dissolution of the crystal. These classes of mechanisms differ significantly in the length of time taken by the tritium to enter final combination after reaching chemical bond energies. Our classification of the second type of mechanism with the first as a "hot atom" mechanism, while calling the third a thermal process, is therefore admittedly somewhat arbitrary.

The salient experimental results bearing on a possible choice of mechanism can be summarized as follows.

(1) A large fraction of the recoil tritium can replace non-labile hydrogen in crystalline hexoses without causing any other permanent change in the molecule.

(2) The labeled, but otherwise unchanged, hexoses formed show wide variation in the specific activity at the six different non-labile positions.

(3) Although glucose and galactose are diastereomers, the distribution of recoil tritium within them differs markedly.

The experimental results from the hot atom chemistry of halogens activated by the (n,γ) process have led to the formulation of two separate theories, which may be characterized as the "billiard ball-epithermal" and the "brush-heap" or "random fragmentation" hypotheses.[3] The random fragmentation mechanism postulates that the recoil atom is trapped in a cage formed by the packed molecules of the condensed medium while it still has a considerable amount of energy. This energy is dissipated by breaking bonds in a rather indiscriminate fashion in the immediate vicinity of the energetic atoms. Finally when the energy of the recoil atom has been reduced below bond breaking energies, it may combine with any one of the many radicals or atoms it has formed to give a stable molecule.

This theory has been advanced to explain the reactions of very much larger recoil atoms than the recoil triton, and can perhaps not be expected to hold for tritium. Because of the relatively high velocity, small size and low mass of the tritium atom, it seems plausible that it can penetrate a condensed medium readily without being trapped until it has reached quite low energies. In any event, the random fragmentation mechanism seems not be applicable in the case of recoil tritium. In order to react with the hot tritium atom, a hexose molecule must exist within the energetic spot at the end of the range. It is extremely unlikely that the large hexose molecule would retain its structure and configuration in the midst of an energetic collection of radicals. A complex mixture of isomers, derivatives and degradation products should result, and a high yield of labeled, but otherwise unchanged hexose would not be expected.

It appears instead that when the recoil triton is finally stopped, it has only a few electron volts of energy left. This is sufficient to eject a hydrogen atom from the hexose while doing little additional damage in the same vicinity. The ejection of the hydrogen could proceed either by Walden inversion or through the formation of radicals. A Walden inversion mechanism can be excluded for those tritons that attain chemical combination in the otherwise unchanged hexose molecule, for such an inversion would necessarily produce a labeled diastereomer of the irradiated sugar (*e.g.*, galactose labeled at the 4 hydrogen would result from glucose). Therefore, one important tritium reaction process must be formation of a hexose radical by rupture of a C–H bond, followed by reaction with this radical. Investigation of diastereomer production in hexose irradiations may furnish additional information on this process.

This picture is essentially consistent with the "epithermal mechanism" proposed by Libby and his associates for the reactions of recoil halogens.[10] In that mechanism also, the recoil atom is postulated to reach the end of its range with only a few electron volts remaining, there to react with one of the few radicals it produces.

The model of the recoil tritium reaction mechanism proposed so far, while it can account for the high gross entry of tritium into hexoses, is not sufficient to explain the variations in specific activity for certain hydrogen positions. The explanation for this effect presumably involves two factors. First, the hydrogen positions in the crystalline hexose differ in the degrees of steric shielding by other groups. If the recoiling triton has been reduced to a few electron volts or less, the energy required to penetrate a steric barrier may be quite important, making less likely the replacement of such shielded hydrogen atoms. Secondly, there may be a short time interval between the formation of a hexose radical and the reaction of the tritium with it to form a stable molecule. During this interval, the radical may isomerize structurally. The probability of such isomerization would be expected to depend on which hydrogen was missing in the radical.

The experimental observation that galactose shows a different pattern of tritium distribution from glucose is consistent with this reaction model. The galactose configuration differs from that of glucose only by an inversion around the number four carbon position, and yet has a substantially different tritium distribution. This difference may indicate that configuration and crystalline form are important factors in determining activity distribution, or perhaps that the distributions are seriously altered by differences in irradiation conditions, for

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[9] Gas phase studies of many compounds indicate that thermal hydrogen atoms primarily react with stable molecules by abstracting hydrogen. See "Atomic and Free Radical Reactions," by E. W. R. Steacie, Reinhold Publ. Corp., New York, N. Y., 1954.

[10] L. Friedman and W. F. Libby, *J. Chem. Phys.*, **17**, 647 (1949); M. S. Fox and W. F. Libby, *ibid.*, **20**, 487 (1952); F. S. Rowland and W. F. Libby, *ibid.*, **21**, 1495 (1953). The billiard-ball mechanism set forth in these and preceding papers by W. F. Libby proposes that some reactions do take place in the 100 e.v. region by the almost complete transfer of the recoil atom's momentum to an atom of very similar mass in the medium. Since no atom in these systems approximates the mass of the triton, this mechanism is completely inapplicable in the present system.

example, in samples with heavy radiation damage.

It should be emphasized that investigation of only the fate of those tritons which are finally incorporated in otherwise unchanged hexose molecules, a selected sample of the recoil atoms is being considered which may not be representative of the behavior or mechanism of reaction of the other recoil tritons. Nevertheless, this does not affect the rather general and incomplete reaction mechanism thus far formulated. Studies are now in progress, on this and other systems, to determine the yields of a wider range of products under several experimental conditions. These results may serve to extend the ideas set forth in this paper.

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The Vibration–Rotational Spectrum of Methyl-d_3 Fluoride[1]

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The Raman and infrared spectra of methyl-d_3 fluoride have been obtained. The Q sub-band structure of the perpendicular bands was resolved and lead to the values 2258.0, 1073.3 and 911.0 for the "apparent" band centers and 0.179, −0.286 and 0.241 for the Coriolis coupling constants of ν_4, ν_5 and ν_6, respectively.

Introduction

The spectra of a number of fluorinated hydrocarbons have been studied in this Laboratory[2] to aid in obtaining an understanding of their interesting chemical and physical behavior.

The observed fundamental frequencies have been the primary experimental source of information for the force field of a molecule. However, additional information is available from Coriolis coupling constants.[3-6] In order to utilizet he information obtainable from such constants, methods have been developed for obtaining their values from band envelopes when the bands corresponding to degenerate vibrations are unresolved.[7,8] These methods have been applied recently to some simple molecules including CF_4, CF_3H and CF_3D.[7-9] The infrared spectrum of methyl fluoride, CH_3F, has been studied previously in some detail.[10-12] A study of the vibration–rotational spectrum of CD_3F was undertaken to provide the remaining data required for a systematic study of the force fields in the fluorine derivatives of methane. This paper deals with the Raman and infrared spectra of CD_3F.

Experimental

The starting point in the preparation of methyl-d_3 fluoride was the conversion of 1–2 propylene carbonate by lithium aluminum deuteride to methyl-d_3 alcohol.[13] It, in turn, was converted to methyl-d_3 *p*-toluenesulfonate, which gave the desired product upon reaction with potassium fluoride.[13] The sample was analyzed mass spectrographically and consisted of 94.4% CD_3F and 5.6% CD_2HF.[14]

The infrared spectrum was obtained with a Perkin-Elmer Model 21 spectrophotometer and under higher resolution with an instrument built about a Perkin-Elmer Model 99 double pass monochromator. The frequency range 880–3420 cm.$^{-1}$ was studied with NaCl and LiF prisms. Ammonia,[16] water vapor,[16] carbon monoxide,[16] hydrogen iodide,[16] hydrogen bromide,[15] and methane[15] were used as calibration substances. The calibration curves were based on the average of three runs. The spectrum of CD_3F was scanned from five to nine times, depending on the region being studied, and the results were averaged. The somewhat large number of runs appeared to be essential for obtaining a higher precision for the Q sub-band spacings of the perpendicular bands. A 10-cm. gas cell, equipped with KBr windows, was used. The spectra were taken at pressures ranging from 25 to 760 mm. Each band of CD_3F was scanned with a constant slit. The corresponding calibration spectra were under the same slit conditions.

The Raman spectrum of CD_3F was taken with an Applied Research Laboratories spectrograph which has a dispersion of 15.4 Å./mm. at 4358 Å. The spectra were obtained for the substance in the gas phase, using a multiple reflection cell[17] whose mirrors had a focal length of 50 cm. The pressure was one atmosphere. The spectrum of argon[18] was used for the calibration of the Raman films.

A_1 Fundamentals.—CD_3F has six normal modes of vibration, *i.e.*, three non-degenerate type A_1 vibrations and three doubly degenerate type E vibrations. The assignment of the fundamental frequencies is easily accomplished on the basis of band contours, band intensities and the reported results for the spectra of CH_3F,[10-12] CD_3Cl,[19-23] CD_3Br[19,22-25] and CD_3I.[22-24,26]

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[1] Presented before the 128th Meeting of the American Chemical Society, Minneapolis, Minnesota, September, 1955.

[2] For the latest publications the reader is referred to W. F. Edgell and C. E. May, *J. Chem. Phys.*, **22**, 1808 (1954); W. F. Edgell and C. J. Ultee, *ibid.*, **22**, 1983 (1954).

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