Results and Discussion

Rhodium oxide reacts with lanthanum oxide at 1100° to form a lanthanum rhodium oxide, with a perovskite-like structure. Table II summarizes the *d*-values obtained for $LaRhO_3$. Calculations based on X-ray data show that $LaRhO_3$ belongs to the space group $D_{2h}(16)Pbnm$ with four formula weights per unit cell. The lattice constants are $a = 5.524$ Å., $b = 5.679$ Å., $c = 7.900$ Å. Determination of the number of formula weights per unit cell, and chemical analysis, indicate that the formula is $LaRhO_3$.

Lanthanum oxide reacts with cobalt carbonate to form lanthanum cobalt oxide, with a perovskite-like structure. Table III summarizes the *d*-values obtained for $LaCoO_3$. $LaCoO_3$ belongs to space group $D_{3d}(5)R\bar{3}m$ with two formula weights per unit cell. The dimensions of the rhombohedral pseudo-cell are $a = 7.64$ Å., $\alpha = 90°42'$. The dimensions of the primitive rhombohedral cell are $a_p = 5.436$ Å., $\alpha_p = 60°48'$. The multiple primitive hexagonal cell in terms of which the rhombohedral cell may be described has the dimensions: $a = 5.424$ Å., $c = 13.068$ Å.

The unit cell reported by Askham, Fankuchen and Ward,[6] is based on a unit cell one-half the size of that given here. The larger cell is based on data obtained by Geller[3-5] from isostructural materials in which two very faint lines necessitated doubling of the indices. These lines did not appear on the films of lanthanum cobalt oxide. However, by step-counting using a Norelco Diffractometer, over the region where these lines should appear, the stronger of the two lines was detected and had an intensity of 25% above background.

[Contribution from Department of Chemistry and Enrico Fermi Institute of Nuclear Studies, University of Chicago]

C^{14} Hot Atom Chemistry of *n*-Pentane and Isopentane[1]

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Reactions of C^{14} atoms of velocities corresponding to energies up to 40,000 electron volts have been studied in liquid *n*-pentane and isopentane at about room temperature. C^{14} atoms were generated at the Argonne National Laboratory pile through the reaction of thermal neutrons in the $N^{14}(n,p)C^{14}$ process. Aniline was most often used as the source of nitrogen, but substitution of aliphatic amines for the aniline gave similar results indicating that the products were characteristic only of the hydrocarbon solvent. A wide variety of hydrocarbons was formed. Hexane and pentane isomers were identified. Hexane isomers predominate, yields of individual compounds being up to 12%. The type and yield of compounds formed from *n*-pentane differ from those formed from isopentane. A mechanism is proposed based on previously developed hot atom kinetic theory which assures very rapid reactions of produced radicals before general diffusion takes place allowing all possible reactions to occur. The evidence appears to favor our more specific theory.

I. Introduction

Interest in C^{14} hot atom chemistry has risen both for itself and as a possible short route to production of C^{14} tagged organic compounds. Several studies of organic systems have been undertaken, the first being that of Yankwich, Rollefson and Norris.[4] Anderson, Penna-Franca and Wolf[5] have studied the production of C^{14}-labeled benzoic acid from nicotinic acid finding most of the activity in the ring. Wolf, Redvanly and Anderson[6] have reported the yield of C^{14}-benzoic acid from the irradiation of a benzene–nickel cyanide clathrate compound to be 1.44% in disagreement with the 4.0% reported by Zifferero.[7] When the irradiation of acridine was carried out by Wolf and Anderson[8] they found the yield of acridine to be 3.5% and that of anthracene to be 0.2%. The fact that this ratio of yields is about that expected for random substitution of ring carbon and nitrogen by C^{14} led them to hypothesize that substitution was indeed random. An analysis for C^{14} by position in acetic acid produced from irradiated acetamide was carried out by Wolf, Gordon and Anderson.[9] Substitution was not random. In acetic acid produced by acid hydrolysis from neutron irradiated acetamide they found 63.1% of the C^{14} in the carbonyl position and 36.9% in the methyl position; for basic hydrolysis 60.9% in the carbonyl position and 39.1% in the methyl position. Propionamide was also isolated as a product of the irradiation of acetamide, and the propionic acid produced from it was similarly analyzed. Acid hydrolysis gave 21.0% in the carbonyl carbon, 26.8% in the methylene position and 52.9% in the methyl position. Basic hydrolysis gave 23.9% in the carbonyl position, 23.1% in the methylene position and 52.9% in the methyl carbon. Toluene produced from a mixture of benzene and 2-methylpyrazine showed 86.1% of the C^{14} in the methyl group and 13.9% in the benzene ring. In all of these cases the fraction of the total C^{14} generated accounted for was small and the questions of over-all mechanism and the general behavior of high velocity C^{14} atoms remained unelucidated.

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A comprehensive attempt at identifying a large number of the products resulting from production of energetic C^{14} atoms in organic media was made by Schrodt and Libby.[10] Aniline was chosen for investigation. Yields of C^{14}-aniline were low (3%), and other C^{14} active compounds definitely identified during the research still accounted for only 23.4% of the total activity. The authors attributed most of the products to the opening of the benzene ring as the result of collision with recoiling C^{14} atoms. The very reactive fragment thus created reacted to give high molecular weight compounds and only a minor fraction of the C^{14} atoms survived to form readily identifiable compounds. According to this theory, aliphatic compounds would not be expected to produce such reactive fragments, and so the authors carried out preliminary experiments on ethylamine, ethylamine hydrofluoride and methylamine hydrofluoride which showed that the C^{14}-containing compounds produced in aliphatic systems give a higher fraction of the C^{14} produced in identifiable products, and less in unidentifiable high polymers.

In the present research a more detailed study of particularly simple aliphatic systems, *n*-pentane and isopentane, was undertaken.

II. Experimental Procedure

The *n*-pentane and isopentane irradiated were pure grade Phillips hydrocarbon (99 mole % minimum). Carriers for compounds up to and including the hexane isomers were also pure grade with the exception of 2-methylpentane which was technical grade (95 mole % minimum). Carriers beyond the hexanes were used only to get an indication of the distribution of activity with boiling point. The aniline used as the nitrogenous source for C^{14} in the neutron field was Mallinckrodt analytical reagent. The propylamine was from the Eastman Kodak Company.

Quartz ampules were used for all irradiations. They were prepared from 28 mm. diameter quartz tubing of 1.5 mm. wall thickness and filled with the solution as described by Schrodt and Libby.[10] Twenty ml. of 5 mole % solution of amine in the hydrocarbon of interest was used for all irradiations. Aniline was the preferred amine because of its ease of handling and because of the fact that neither it nor the products of its hot atom chemistry[10] were in the low molecular weight hydrocarbon boiling range. Irradiation took place in the Argonne National Laboratory's CP-5 reactor at a neutron flux of about 10^{12} neutrons per cm.^{2}/sec. The accompanying gamma flux was 500 roentgens/sec. The exposures varied from 8 to 240 hours with 120 hours being the common time. The resultant spectrum of radiocarbon containing chemicals was independent of the exposure time within the analytical error.[10]

After irradiation, the sample was frozen, opened, swept out with methane, the methane collected and then burned to carbon dioxide according to the method of Schrodt and Libby.[10] A solution of carriers had been prepared previously. In most experiments the minimum amount of carrier used was 20 cc. for each compound for which analysis was intended. For short period irradiation a 10 cc. minimum of carrier was used to increase specific activity. The limit on amount of carrier added was set by the hold-up of the columns used in separation, the largest hold-up being 4.5 cc. at a through-put of 50 ml./hr. After breaking the ampule and removing the gases, the remainder of the sample was allowed to melt and was then transferred to a distillation flask by rinsing it from the irradiation ampoule with the already prepared mixture of carriers. The ampoule was then flushed three times with portions of the mixture of carriers and these too were added to the distillation flask. All carrier solution left was transferred to the flask and the sample was ready for distillation. A portion of this solution was reserved for the determination of total activity.

Distillation was done with three columns, a Podbielniak heli-grid packed column of 8 mm. inside diameter and 12 in. length which was rated at 50 theoretical plates with a hold-up of 2 ml., both at a through-put of 50 cc./hr., a Podbielniak concentric tube column of 8 mm. inside diameter and 60 cm. length rated at 70 theoretical plates with a hold-up of 3.2 cc., both at a through-put of 60 ml./hr.; a Podbielniak concentric tube column of 8 mm. inside diameter and 90 cm. length rated at 100 theoretical plates with a hold-up of 4.5 cc. at a through-put of 60 ml./hr. Separated fractions were identified by boiling point, or refractive index, or both. Refractive indices were taken on a Bausch and Lomb Abbe type refractometer. The refractometer was checked regularly with a glass standard.

After an initial distillation with the packed column the fractions obtained whose boiling point and refractive indices correspond most closely to a pure carrier were selected for more efficient distillation with the concentric tube columns. These columns were equilibrated for 24 hours. They were run at a minimum boil-up rate and the take-off rate was held to between 0.1 and 0.2 cc. per hour. In this way cuts were isolated whose refractive indices agreed accurately with the literature values in all cases for all the various pentane and hexane isomers with one exception in some runs. The exception was 2-methylpentane so the results for this substance must be taken to be less accurate than for the other products. Part of each fraction finally was converted to carbon dioxide over hot copper oxide, precipitated as calcium carbonate, and counted. The purified fractions then were checked for constant specific activity by further distillation. When it was not possible to obtain a cut of 2-methylpentane whose refractive index agreed with the literature value, the cut of refractive index closest to that value was chosen to represent it. The sample's refractive index was then compared to a prepared set of standards of known composition, the diluent being assumed to be 2,3-dimethylbutane, and the value of the radioactivity was corrected for dilution by the inactive compound. This procedure undoubtedly introduced an appreciable error. Estimating the error of determination of the refractive index ordinarily to be 0.0001 unit, it was estimated that impurities of 5% would be identifiable. Thus fractions were at least 95% pure compounds and their specific radiocarbon contents were established to within about 7% of the value since the counting error was normally about 5% also on an absolute basis. The error in the case of 2-methylpentane probably was about 20%.

After all the light carriers and finally the *n*-hexane cut were distilled off, the remaining less volatile solution was vacuum distilled through a 15 in. Vigreux column to determine the general approximate distribution of heavier radioactive compounds. The highest boiling carrier used was *n*-hexadecane (288°). All distillation flasks as well as the original irradiation ampule were rinsed out with successive washes of carbon tetrachloride until a final wash which contained little activity was obtained. The activity in this rinse was designated as polymer. Some of these samples were combusted by the Van Slyke wet combustion method.[11] Irradiations were conducted at a few degrees above room temperature for 120 hours duration at a neutron flux of about 10^{12} neutrons/cm.^{2}/sec. Agreement among determinations of a given compound in separate runs was within 10% for pentane and hexane isomers in almost all runs. Frequently it was better. Exceptions to this were 2-methylpentane, the most difficult compound to separate, and activities lower boiling than isopentane where the low boiling point made efficient separation difficult. Here results varied as much as 20%. Eight hour and 240 hour irradiations gave substantially the same results, as did replacement of aniline by propylamine. All except polymer were counted as calcium carbonate. The polymer was taken up on talc as described by Schrodt and Libby[10] and counted in this way. Counting was done with the cylindrical thin-wall flow counter of Sugihara, Wolfgang and Libby,[12] a 10 in. counter of 1.5 in. diameter being used. The flow gas was "Q" gas, a mixture of 2% butane in helium available from the Nuclear Chicago Company. The counter wall was an aluminum filmed Mylar plastic foil of 0.87 mg./cm.^{2} total thickness and the counter was shielded with a standard anti-

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coincidence ring and iron shield. Samples were mounted on cylindrical sample holders of Lucite tubing $1^7/_8$ in. in inside diameter.

Absolute disintegration rates were determined from observed count rates by the method of Suttle and Libby.[13] These investigators have determined that for close cylindrical geometry beta emitters with a simple decay scheme follow an exponential absorption law. For an infinitely thick sample ($>> \lambda$ as defined below) the following expression is used

$$\sigma = \frac{RG}{A\lambda} e[(l_w/\lambda_w) + (l_a/\lambda_a)]$$

in which σ is the specific activity of the sample in total disintegrations per minute per gram (d.p.m./g.); R is the observed count rate in counts per minute; G is the effective geometry, corrected for average 15% back-scattering effect, the ratio of 4π to the average solid angle subtended by the sensitive volume of the counter at the sample multiplied by 0.85; A is the sample area in cm.^{2}; l_w is the thickness of the counter wall; l_a is the thickness of air between sample and counter wall, both in mg./cm.^{2}; λ, λ_w and λ_a are the reciprocals of the absorption coefficients in the sample material, the wall and air, respectively. Later work[14] has shown that the G factor should include corrections for the roughness of any crystalline powder sample, as well as the geometry and back-scattering factors as described above. The roughness correction becomes important when the crystal size becomes of the order of or larger than the mean thickness for the radiation, as in the case for soft betas ($\lambda < 10$ mg./cm.^{2}). This roughness factor is effective for soft beta emitters only about 1.8 over that based on purely smooth sample surface geometry. Thus, for soft beta emitters, if the radius of the inner surface of the counter wall be ρ, and the radius of the cylinder described by the inner surface of the sample be x, then for soft betas, such as C^{14} emits, the G is given by

$$G = \frac{1.8\pi}{\pi/2 - \cos^{-1}(\rho/x)}$$

In close contact between the sample and counter when ($\rho = x$), $G = 3.6$, and for $\rho = 1.90$ cm. and $x = 2.20$ cm., $G = 5.5$. In our case the factor $e^{(l_w/\lambda_w + l_a/\lambda_a)} = 1.35$ since $\lambda_w = \lambda_a = 3$ mg./cm.^{2} for C^{14}. Thus for our arrangement

$$\sigma\ (\text{d.p.m./mg.}) = \frac{7.4\ R\ (\text{c.p.m.})}{A\lambda}$$

λ in all cases was corrected to the value proper for the material involved according to the relation of Lerch.[15] He has shown that the absorption coefficient, the reciprocal of λ, is proportional to $(1 + \bar{M}/1000)$, where $\bar{M}$ is the average atomic mass of the absorber. This relation has recently been further verified for a number of substances by Libby.[11]

If we were to repeat the research we would use the gas chromatographic technique of Martin for the separation. Willard[16] has described its application to hot atom chemistry research.

III. Experimental Results

Radiocarbon yields of hydrocarbons of boiling point below 69° are given in Table I for both *n*-pentane and isopentane. Percentages are per cent. of the total radiocarbon activity generated in the irradiation which is carried by the particular compound. The total activity usually was about 10^6 d.p.m. For *n*-pentane products they are the average of three runs, for isopentane the average of two.

In work of this type a common source of error is contamination by trace quantities of compounds differing only slightly in structure and properties from the compound for which analysis is being carried out and which are therefore quite difficult to separate from the desired compound. The use of all possible pentane and hexane isomers as carriers together with repeated distillation with large amounts of fresh carriers for compounds other than that of interest to dilute out impurities have certainly eliminated this difficulty for the pentane isomers in this research and very likely for the hexane isomers too. The fact that *n*-hexane out of isopentane is found in relatively low yield would seem to reinforce this conclusion, since *n*-hexane is the hexane isomer most likely to be contaminated by branched heptane isomers for which no carriers were used. Olefins are of minor importance. Bromination removed less than 15% of the activity in a typical fraction, a result in general agreement with that of Wolf, *et al.*, for toluene irradiations where more stringent purification with sulfuric acid was employed.[17]

Table I

Low Boiling Hydrocarbons (% of C^{14})

n-Pentane irradiated, %	Product	Isopentane irradiated, %
2.1	Gas	1.4
5.7[a]	"Butane"	4.0
2.4	*neo*-Pentane	3.2
3.6	Isopentane	3.8
2.1	*n*-Pentane	1.3
0.1	2,2-Dimethylbutane	5.6
0.2	2,3-Dimethylbutane	4.5
4.5	2-Methylpentane	6.7
8.3	3-Methylpentane	8.7
12.2	*n*-Hexane	1.0

[a] Two runs only.

Table II

High Boiling Activity Distribution

n-Pentane Boiling range, °C.	%	Carrier	Isopentane %	Boiling range, °C.
69–125	4.7	*n*-Heptane, *n*-octane	3.8	69–117
125–139	3.4	*n*-Octane	4.0	117–138
139–151	7.2	Cumene	4.5	138–149
151–168	3.5	Cumene, *n*-decane	3.9	149–170
168–210	7.1	*n*-Decane, decalin	7.7	170–212
210–245	3.7	Decalin, *n*-dodecane	1.0	212–245
245–274	4.0	*n*-Tetradecane	0.8	245–275
<274	3.0	*n*-Hexadecane	6.1	<275
	25.6	Polymer	27.9	

Table II gives the activity distribution with boiling point above 69° for typical runs with *n*-pentane and isopentane. The general similarity of distribution is not surprising in view of the fact that the two mother molecules differ only by the positioning of a methyl group and consequently give compounds of similar structure and proximate boiling point as products.

IV. Discussion

These results are consistent with a theory of hot atom chemistry previously developed.[18] A newly born C^{14} recoiling with an initial energy of 40,300 electron volts ruptures all chemical bonds, 2,700 e.v. being available for the breaking of even a C–H

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[18] W. F. Libby, This Journal, **69**, 2523 (1947); M. S. Fox and W. F. Libby, *J. Chem. Phys.*, **20**, 487 (1952); F. S. Rowland and W. F. Libby, *ibid.*, **21**, 1495 (1953).

bond.[19] It is quite possible that initially the recoiling carbon atom is charged, but its velocity is too low to allow it to maintain this charge and so it will be effectively neutralized in the first few collisions.[20]

The net result then is to have carbon atoms stripped of all hydrogen atoms recoiling through the solution at high velocity. We divide the track of the recoiling atom into two portions—the initial part is called the hot region and the final or end portion is called the epithermal region. The type of chemical effects in the hot region are very different in many ways from those at the end of the track. The division between the hot and epithermal region is made when the recoil energy is reduced to about 10 e.v.—two or three chemical bonds. What are the chemical consequences of this situation? Initially the C^{14} has such a high velocity that "billiard ball" mechanics, in which chemical bond effects are negligible, apply.[18] It can be stopped in a single collision only by a head-on collision with a C^{12} atom in the hydrocarbon molecules, transferring nearly all its energy to the C^{12} atom. The result is to leave the C^{14} trapped in a solvent cage with the three fragments left behind by the departed C^{12}. If the walls of the solvent cage were effectively impervious to hydrogen atoms, the target molecule containing C^{14} might be re-formed by appropriate combination of the fragments trapped in the solvent cage. This is not too probable a process, hence the low yield of the hydrocarbon of the irradiated system—*n*-pentane for *n*-pentane irradiations, isopentane for isopentane irradiations, benzene for benzene irradiations, etc., as normally found and reported previously.[5–8,10]

What competing process is possible in the hot region of the track? The bare carbon atom, stopped by a head-on collision and presumably a voracious seeker for hydrogen, exists in a solvent cage whose walls are hydrogen rich. It appears reasonable then that this carbon atom would abstract hydrogen from several wall molecules successively, becoming a $\cdot C^{14}H_3$ radical in the process and creating several organic radicals. The $\cdot C^{14}H_3$ radical could in our case of pentane irradiations then combine with one of these radicals producing a radioactive hexane isomer in a one step process. Such a process would allow formation of only those hexane isomers which can be produced by a net replacement of a hydrogen atom by a methyl group. This is in keeping with the experimental observation that 2,2-dimethylbutane and 2,3-dimethylbutane are observed only from isopentane while *n*-hexane arises in good yield only from *n*-pentane. The observed deviation of the yields from that which would result from statistical replacement of hydrogen atoms by methyl radicals may be attributed in general to the recognized greater reactivity of secondary and tertiary hydrogen relative to primary hydrogen in abstraction reactions, although the preference for 3-methylpentane out of *n*-pentane is not explained. This mechanism predicts the locations of the C^{14} in several of the radioactive products; *e.g.*, in *n*-hexane out of *n*-pentane the C^{14} should be in the end positions.

This proposed mechanism also gives a clue as to why isopentane might be a moderately important product from *n*-pentane irradiations, while *n*-pentane is a far less important product out of isopentane. Hits on end carbons of *n*-pentane give butyl radicals as a product. Abstraction of hydrogen by the C^{14} atom at the secondary carbons of this radical leaves a radical with the potentiality of forming isopentane. To form *n*-pentane out of isopentane by a similar process primary hydrogen abstraction is required. *neo*-Pentane production from each of the other pentanes is also possible, although the yield from *n*-pentane appears to be unreasonably high. In addition all C_1 to C_4 isomers are expected. (The "butane" yield reported certainly reflects more than *n*-butane.) It is even conceivable that products higher than C_6 are produced by the type of collision of a high velocity C^{14} atom—the hot region of the track of the atom as it decelerates. Thus, in this system a wide variety of products from collisions in the hot region of the track are possible.

By the time the recoiling carbon has reached the end of its track—the epithermal region—by collisions none of which was head-on with a C atom, it has very likely picked up one or more hydrogen atoms becoming in the process a $:C^{14}H$, or even a $:C^{14}H_2$ radical, and it will be trapped in due course in a solvent cage. Then it will abstract hydrogen atoms from one or more wall molecules creating radicals in the process, and forming a CH_3 radical or possibly methane. In the case of methyl radicals, it can react with the radicals formed by the H abstraction to form hexane isomers as in the hot region. As an alternative the $:C^{14}H_2$ radical can be incorporated into final chemical form without a hydrogen abstraction step as postulated by Doering, *et al.*[21] The same products result. It is in this epithermal region that polymeric products arise also according to the theory as the result of the close proximity of many radicals contained together in solvent cages.

The above mechanisms account for the main observations made in this work. The theory has several consequences which may be tested experimentally. For instance, the prediction that all C_5 and lower molecular weight molecules arise in the hot region while hexane isomers are produced in both hot and epithermal regions is susceptible to test by the phase effect.[18] Furthermore the mechanism would lead to C^{14} incorporation into *n*-hexane only in the end position.

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