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Hot Atom Chemistry of Carbon; Particularly in Aromatic Systems

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The reactions of radioactive C^{14} carbon atoms moving with the high velocities corresponding to energies up to 40,000 electron volts have been studied in aniline, benzene, methanol, triphenylamine, aniline hydrofluoride, ethylamine and methylamine hydrofluoride, all at about room temperature. The hot C^{14} atoms were generated by the reaction of thermal neutrons with nitrogen 14, $N^{14}(n,p)C^{14}$. For those substances, such as hydrocarbons, which do not contain nitrogen to serve as a source of C^{14} about 5 mole per cent. of a nitrogenous material such as aniline was dissolved in the substance and the solution irradiated and studied. It was demonstrated that the nature of the carbon hot atom reactions is essentially independent of the choice of nitrogenous solute and therefore most probably is characteristic of the solvent hydrocarbon. The irradiations were performed in the reactors at the Argonne National Laboratory. In all cases a variety of products differing from the molecules struck by the high velocity carbon atom was produced ranging from light gases to heavy molecules with a marked tendency to yield heavy materials in the case of aromatic compounds and solid phases. It is supposed that in the case of aromatic compounds the opened ring formed by the collision of the recoiling C^{14} atom with one of the ring CH groups is so reactive that it combines not only with the C^{14} atom which struck but avidly with the surrounding molecules of the system producing a highly aromatic substituted derivative of hexane.

I. Introduction

Hot Carbon Atom Research.—Ruben and Kamen irradiated ammonium nitrate solutions with neutrons as early as 1941, but they were concerned primarily with the production of carbon-14 activity rather than the study of hot atom chemistry.

The earliest carbon-14 hot atom chemistry reported as such was that observed by Yankwich, Rollefson and Norris.[1] They irradiated sealed cans of ammonium nitrate solution, ammonium nitrate crystals, urea solutions, urea crystals, hydrazine hydrochloride, glycine, pyridine and aniline, with neutrons from the 60-inch Berkeley cyclotron. After two years the samples were analyzed. Appreciable yields of radioactive carbon monoxide and carbon dioxide were obtained from the ammonium nitrate samples, radioactive hydrogen cyanide was obtained from the crystalline urea and hydrazine samples, and radioactive methanol was found in the glycine. Few products were detected in the other systems because of insufficient radioactivity. The over-all results did encourage Yankwich[2] to speculate as to the usefulness of hot atom chemistry in synthesizing carbon-14 labeled compounds.

Yankwich[3] later reported large yields of radioactive methane from neutron irradiated beryllium nitride. Apparently, hot carbon-14 atoms combined with beryllium to form the carbide, Be_2C^{14}. This yields methane when dissolved in water.

Norris and Snell[4] irradiated ammonium nitrate solutions in the Oak Ridge nuclear reactor and found radioactive carbon dioxide and monoxide to be the principal hot atom products. Less than 1% of the activity appeared as formic acid, formaldehyde and methanol.

Giacomello[5] has reported a study of carbon-14 hot atom chemistry in pyridine oxalate. Fifteen per cent. of the activity was said to be in benzene, phenol, carbon dioxide and carbon monoxide. Chemical species containing the remainder of the radioactivity were not identified.

Giacomello, Croatto and Maddock[6] have reported on their study of quinoline oxalate. Twenty per cent. of the total activity was said to be in naphthalene, naphthol, quinoline, oxalic acid, carbon dioxide and carbon monoxide.

Wolf and Anderson[7] irradiated acridine in the

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[1] P. E. Yankwich, G. K. Rollefson and T. H. Norris, *J. Chem. Phys.*, **14**, 131 (1946).

[2] P. E. Yankwich, G. K. Rollefson and T. H. Norris, *ibid.*, **14**, 131 (1946).

[3] P. E. Yankwich, *ibid.*, **15**, 374 (1947).

[4] L. D. Norris and A. H. Snell, *Nucleonics*, **5**, [3] 18 (1949).

[5] G. Giacomello, *Ric. Sci.*, **21**, 1211 (1951).

[6] G. Giacomello, U. Croatto and A. G. Maddock, *ibid.*, **21**, 1598 (1951).

[7] B. Wolf and R. C. Anderson, Amer. Chem. Soc. meeting, March 1953.

Brookhaven nuclear reactor and looked primarily for carbon-14 activity in acridine itself. They found 2.8 to 3.2% of the total activity in acridine, 2.2 to 4.0% in gaseous products, and about 0.2% in anthracene (the carbon analog of acridine). In further work the acridine was degraded and it was found that the substitution of carbon-14 for the ordinary carbon atoms was completely random. The proportional amount of activity in anthracene supports the view that substitution is random.

Anderson, Penna-Franca, and Wolf[8] have found carbon-14 labeled benzoic acid to be one product of neutron irradiation of nicotinic acid or nicotinamide. Most of the radiocarbon activity resides in the ring as would be expected. Degradation studies have shown a higher concentration of radioactivity in the position formerly occupied by the nitrogen atom than in the other ring positions. This is the situation to be expected if the formation of the benzoic acid is a hot reaction. Substitution in a hot collision is more likely to be successful if the masses of the atoms are equal.

Vaughan[9] has irradiated ammonium chloride and ammonium bromide and found methylamine to be the principal carbon-14 labeled product.

Rowland and Libby[10] have recently studied reactions of carbon-11 recoil atoms in systems of solid and liquid carbon dioxide. The only products were carbon monoxide and dioxide—equal amounts being produced in solid targets while liquid targets yielded only carbon monoxide. It is suggested that the solid phase targets will confine the radicals generated along the recoil track long enough for them to recombine, while in liquid samples the recoil carbon atom can diffuse away from the radicals and react with the carbon dioxide molecules.

II. Experimental Procedure

The CP-3′ nuclear reactor of the Argonne National Laboratory was used as the thermal neutron source for this research. Thirty-five samples were irradiated with fluxes ranging from 2.7×10^{11} to 4.6×10^{11} neutrons per square centimeter per second. The simultaneous exposure to gamma radiation ranged from 2×10^3 to 7×10^3 roentgens per minute.

TABLE I

LIST OF IRRADIATED SAMPLES

Chemical composition	No. irradiated	
Aniline	18 ml./ampoule	16
Aniline	300 ml./bulb	4
Aniline (8%) in benzene	15 ml./ampoule	2
Aniline (10%) in methanol	15 ml./ampoule	2
Aniline hydrofluoride	4 g./ampoule	2
Triphenylamine	10 g./ampoule	2
Ethylamine	20 ml./ampoule	3
Ethylamine hydrofluoride	3 g./ampoule	2
Methylamine hydrofluoride	3 g./ampoule	2

Most of the samples for irradiation, being primarily pure compounds or simple solutions, required no special techniques for their preparation. However, the amine salts, the hydrofluorides, did require special procedures and great care in their preparation. The fluoride salts were necessary for the research since the other amine salts readily available would be highly activated by the pile.

The quartz ampoules used to contain the samples were prepared from tubing having a maximum outside diameter of 20 millimeters and a wall thickness of one millimeter. Quartz was used because it is not appreciably activated by pile exposure. The largest sample containers were made from quartz florence flasks. The samples were degassed by repeated pumping and freezing in the case of liquids and simply by pumping in the case of solids, and then were sealed in the quartz containers. In one or two cases, air was purposely left in the samples to observe whether it had any effect on the distribution of radioactive products.

The sturdiness of the quartz ampoules, necessary to withstand the vapor pressures of the samples at the pile temperature, and any additional pressure of radiation decomposition products, makes them rather difficult to open in a comparatively fragile Pyrex vacuum line. A brass ampoule opener was prepared with a 29/42 standard taper, a side arm by which the opener could be attached to a vacuum line and a hardened pointed machine screw to facilitate fracture of the ampoule. An ampoule to be opened is placed in the glass vessel of the opener. The vessel is then capped with the brass block and connected to the vacuum line. After evacuation, methane is admitted and liquid nitrogen placed around the glass vessel. Methane condenses and serves as a heat transfer medium so that the ampoule contents can be rather quickly frozen. After freezing is complete, the methane is pumped off until only several centimeters mercury pressure remain at room temperature. The stopcock connecting the brass block to the line is closed and the whole block-and-vessel assembly is removed from the line. With appropriate motions the ampoule is thrown against the brass block until the ampoule is chipped open. The assembly then is returned to the line. The methane in the ampoule opener is vented into an evacuated bulb. Fresh methane is admitted and allowed to mix with any radioactive gas. The vessel is then reopened to the partially evacuated bulb. Several transfers of this sort effectively transfer all of the radioactive gaseous products to the storage bulb.

The various gaseous fractions were burned to carbon dioxide and precipitated as calcium carbonate for counting, *i.e.*, the measurement of the radiocarbon content. The combustion procedure involved displacement of the gas from the storage bulb with water. The gas was burned at the tip of the capillary tube sealed into the combustion chamber. The chamber exhausted into a series of traps. An inlet for oxygen was also provided close to the capillary tube. The combustion chamber and the traps were evacuated, then filled with oxygen. Liquid nitrogen baths were placed around the traps while oxygen continued to flow slowly into the system. An electric discharge was struck across two tungsten electrodes near the tip of the capillary to ignite the gas from the storage bulb as it was released through the capillary. Combustion of the gas to carbon dioxide is more than 95% complete in this procedure for methane, ethane, propane.

In order to burn sizable samples of aniline rapidly and under controlled conditions a special burner was constructed. This device, similar to the gas burner above, permitted aniline vapor to be ignited and burned at a capillary tip in the presence of excess oxygen. The intense heat of the aniline flame made necessary the use of a Vycor enclosure. Combustion gases were passed over hot copper oxide and collected in ammonium hydroxide. Combustion of small liquid samples was accomplished by means of the Van Slyke technique.[11]

The carbon dioxide from the various combustions was precipitated as calcium carbonate. A readily filterable precipitate was formed by adding a hot solution of calcium chloride slowly with vigorous stirring, to a hot ammoniacal solution of the carbon dioxide.

The Geiger counters used in this research were the cylindrical thin wall flow counters previously described.[12] A typical size was 1.5 inches in diameter and 10 inches in active length. The wall thickness was 2 mg./cm.^{2} consisting of plastic sheeting coated with a thin layer of gold or aluminum metalized on the sheeting. The gas in the counter was

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[8] R. C. Anderson, E. Penna-Franca, and A. P. Wolf, Brookhaven National Laboratory Quarterly Progress Report, October 1–December 31, 1954.

[9] J. D. Vaughan, Dissertation, University of Illinois, 1954, University Microfilms publication #9159.

[10] F. S. Rowland and W. F. Libby, *J. Chem. Phys.*, **21**, 1943 (1953).

[11] D. D. Van Slyke, *J. Biol. Chem.*, **136**, 509 (1940).

[12] T. Sugihara, R. Wolfgang and W. F. Libby, *Rev. Sci. Instr.*, **24**, 511 (1953).

TABLE II

ANILINE EXTRACTION DATA

	Sample number							
	VII	VIII	IX	X	XI	XII	XIII	XIVPb
	Irradiation conditions							
Hole no. of pile	3A	8A	3A	5A	5B	5C	5D	8A
Neutron flux, n/cm.^{2}/sec. × 10^{-11}	4.6	3.4	4.6	2.7	1.3	0.63	0.31	3.4
γ-Intensity r/min. × 10^{-3}	....	7	...	2	2	2	2	7
Time (full power). sec. × 10^{-5}	0.036	0.288	1.56	4.3	4.3	4.3	4.3	0.65
Vol. aniline, ml.	18	18	20	20	20	20	20	20
Total d.p.m. measured × 10^{-5}	0.78	4.5	39	64	31	15	8.0	12
C^{14} produced, μg.	0.008	0.045	0.39	0.64	0.31	0.15	0.08	0.12
	Percentages of total activity							
Methane	....[a]	2.8	1.2	1.5	1.7	1.5	1.5	2.6
Water extract	8.1	7.9	...[a]	...[a]	...[a]	...[a]	...[a]	...[a]
Acetic acid, 1st ext.	5.5	6.2	12.2	13.8	14.2	15.0	14.0	14.2
Acetic acid, 2nd, 3rd ext.	....[a]	....[a]	3.5	3.2	3.9	2.8	3.5	2.9
0.1 N HCl, 1st ext.	38.4	40.2	34.7	33.5	32.4	31.9	32.2	30.2
0.1 N HCl, 2nd ext.	....[a]	7.7	7.0	6.6	7.2	7.4	7.4	6.5
1.0 N HCl	17.4	13.1	12.9	13.9	11.7	11.6	11.1	15.1
6.0 N HCl	....[a]	....[a]	...[a]	11.4	12.5	...[a]	...[a]	11.3
12.0 N HCl	....[a]	....[a]	...[a]	7.1	9.2	...[a]	...[a]	9.1
Benzene layer	25.2	20.5	23.2	3.0	3.3	26.4	26.8	4.2
Insol. residue	3.4	1.6	5.5	6.2	4.0	3.5	3.3	3.8

[a] Extraction not made.

a commercially available mixture of helium with 1.3% n-butane, known as "Q gas."[13]

Where only small samples were to be counted routinely and the versatility of the large counter is not needed, smaller counters were built and operated satisfactorily. All counters were shielded with anti-coincidence counters and massive iron closure to reduce the background to less than ten counts per minute. The low level techniques used were not absolutely essential to the research but were helpful in reducing the length of time required for counting and allowed absolute assays of the total radiocarbon content of the materials to be made. A check on the total recovery of radiocarbon is possible since the exposure time and the pile flux allows one to calculate the total number of radiocarbon atoms produced in the sample. The samples were disposed around the counter on cylindrical sample holders so that the geometry of the sample was uniform.

As has been shown elsewhere[14] C^{14}, like most other simple beta radioactivities, *i.e.*, β-ray transitions involving just two levels, one in the parent and one in the product nucleus, show exponential absorption under conditions in which the sample is close to the counter. This ensures that one can calculate the absolute specific activity by correcting for the self-absorption in the sample. For a thick sample in which the β-radiation emitted by the radioactive isotope involved has an effective absorption coefficient of $1/\lambda$, the effective thickness of the sample is just λ so that the count rate expected is given by equation 1

$$R(\text{c.p.m.}) = A\lambda\sigma/G$$

in which A is the area of the sample in cm.^{2}, λ is the reciprocal of the absorption coefficient in the material of the sample itself in mg./cm.^{2}, σ is the true absolute specific activity of the sample in disintegrations per minute per milligram, and G is the ratio of 4 π to the average solid angle subtended by the sensitive volume of the counter at the sample.

In the case of liquid samples which were of not too low specific activity, a method of absolute assay was developed which consists of absorbing the liquid samples on non-radioactive talc. After absorbing on the talc, the talc was thoroughly shaken and mixed and the count taken under known geometrical conditions. We then calculated the absolute specific activity of the mixture of liquid plus talc and then calculated the true specific activity of the liquid knowing the weight per cent. of the liquid in the talc mixture. For liquids of lower specific activity of which ample volume was available, a special sample cylinder consisting of metal to which cooling coils had been soldered and through which liquid nitrogen could be circulated was used. This device allowed the measurement of volatile low melting liquids such as pentane in a simple manner.

It should be pointed out that the value of the reciprocal of the absorption coefficient, λ, used in the calculation of the absolute specific activity must be the proper one for the material of which the sample is composed. Lerch[15] has shown that the absorption coefficient, or the reciprocal of λ, varies in proportion to the expression $(1 + \bar{M}/100)$ where $\bar{M}$ is the average atomic weight of the absorber. Therefore, a different value of λ must be used for talc samples than for ordinary organic derivatives. This is a correction of about 10% for organic compounds.

III. Experimental Results

Aniline.—Irradiated liquid aniline was tested for radio methane and other gaseous radioactive content, and was found to have only 2 or 3% of its radiocarbon in this form. It was shown next that the extraction of the liquid aniline which had had the gas removed from it with concentrated hydrochloric acid resulted in the removal of about 90% of the radioactive carbon into the acid layer if the liquid aniline was previously dissolved in benzene. This experiment established that nearly all of the products of the C^{14} hot atom chemistry were of essentially basic characteristic. A series of extractions were performed in other portions of the irradiated sample and a distribution of radiocarbon content among the basic compounds of various strengths determined. The results are given in Table II. Table II also contains data on the irradiation conditions for the various samples so one has evidence as to the lack of effect of various intensities of exposure on the distribution.

These data set an upper limit to the amount of activity to be found in the form of benzene and non-basic hydrocarbons. In addition, tests were made in which aniline, benzene, toluene, o-, m- and p-toluidine, benzylaniline and N-methylaniline

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[13] Nuclear Instrument and Chemical Company, Chicago.

[14] (a) W. F. Libby, *Anal. Chem.*, **19**, 2 (1947); (b) A. D. Suttle, Jr., and W. F. Libby, *ibid.*, **27**, 921 (1955).

[15] P. Lerch, *Helv. Phys. Acta*, **26**, 663 (1953).

were all added as carriers. Separation of these compounds showed that the percentage of the radioactivity occurring in these pure compounds is very small. Table III gives these results.

TABLE III

CARRIERS USED FOR RADIOACTIVE PRODUCTS FROM ANILINE

Carrier	% Total activity carried
Methane (representing all gaseous activity)	1.5
Aniline	3.0
Benzene	0.1
Toluene	0.7
Toluidine (*o*, *m* and *p*)	3.2
Benzylamine	0.8
N-Methylaniline	2.0
Methylbenzidine (*o*-methyl group)	2.6
N-Methyl-, N,N-diphenylamine	1.6
o, *m*, *p*-Methyl-, N,N-diphenylamine	3.7
N-Phenylbenzylamine	2.1
N,N′-Diphenylmethylenediamine	1.2
Benzalaniline	0.9
Acridine	0.0
Total activity account for	23.4

Other experiments in which the irradiated liquid aniline was simply distilled until the flask was essentially dry showed that only 10 to 15% of the radioactivity was removed in this manner, and that 90% of it remained as a small hardly visible film over the bottom of the distilling flask which was removable by a Van Slyke combustion. An attempt was made to limit the molecular weight by measuring the weight of this film and its absolute radioactivity. Assuming one C^{14} atom per molecule, the number limit could be calculated. The result was very high, some 65,000 units. This is not unreasonable. Other evidence indicated that the molecular weight probably was in the vicinity of about 600 units. It is clear that in decelerating the high velocity C^{14} atoms a considerable number of ordinary carbon atoms are given high velocity by collision and they, in turn, will suffer the same type of chemical effects that the C^{14} atom itself suffers so the minimum extent to which the C^{14} containing molecules must be diluted is given by the ratio of the number of knocked-on carbon atoms to the number of C^{14} atoms. In other words, the dilution will at least equal the number of knock on recoiling carbon atoms involved in the deceleration of a single C^{14} hot atom.

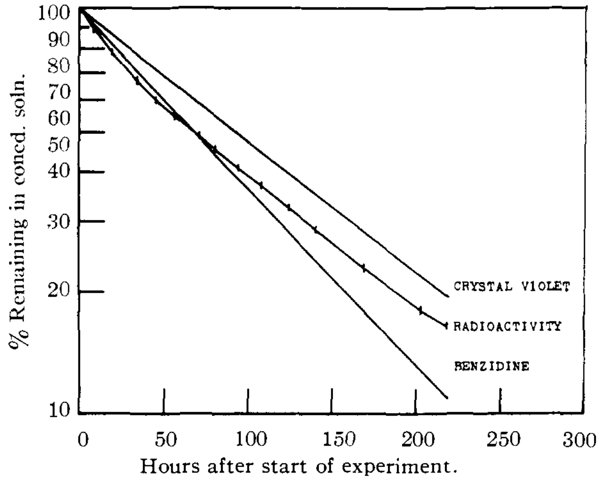


Fig. 1.—Diffusion of radioactive products from aniline and comparison with known compounds.

In order to obtain a more accurate molecular weight figure than that previously estimated, diffusion experiments were conducted. It was suspected on the basis of the understanding of hot atom reactions gained in previous experiments that the principal result of the collisions of C^{14} atoms with aniline molecules would be obtained by the opening of the aromatic ring and adding several amine molecules to the highly unsaturated free radical so produced. Such a molecule should have a molecular weight no greater than about 600. By diffusion experiments it is possible to distinguish between compounds of very high molecular weight and those on the order of 600 or less. A simple diffusion cell was standardized with crystal violet which has a molecular weight of 390. Using the cell constant obtained in this standardization, the average molecular weight of the radioactive products was determined to be in the neighborhood of about 500. Benzidine was also used as a calibrating system. The cell consisted of a simple glass frit serving as a membrane from which samples were removed from time to time and analyzed for crystal violet and benzidine, as well as for radiocarbon. Stirring was accomplished by rotating the cell assembly.

Although this is a rather crude molecular weight determination it does seem to be sufficient to indicate that the extremely large molecules such as aniline black do not make up any appreciable portion of the radioactive products and that the probable molecular weight range for the radioactive carbon containing molecules is in the hundreds rather than in the thousands.

In order to test for the absence of γ-radiation effects in aniline, several ampoules of aniline were irradiated in the pile for different lengths of time to determine whether or not the radioactive products of the pile irradiations were truly hot atom products, and to see if there was any build-up of radioactive products due to radiation damage. The shortest irradiation was for a period of one hour, while the longest irradiation was for a period of 120 hours. The distribution of products among compounds of differing basicity was unchanged by different irradiation periods. A series of four ampoules were laid end to end in the same hole of the pile and irradiated for the same period of time but at different fluxes. The distribution of products from these ampoules was the same as for those irradiated for various lengths of time. In addition, one ampoule was encased in 1.5 inches of lead to alter the neutron–gamma ratio during the bombardment. Again the same distribution of products was observed. In Table II the data from these various irradiations is reported. Each percentage figure is accurate to 10%. Since the results from all of these irradiations are essentially the same, it can be concluded apparently that the observed products are indeed independent of the γ-radiation, and that they are due only to the reactions of the C^{14} atom created within the systems. In cases where an extraction was omitted, the amount of activity expected for that extract was found in the next extraction actually made.

The distribution of radioactivity by the acid extraction indicated a mixture of primary, secondary and tertiary amines. Benzenesulfonyl chloride was added to the mixture in the presence of sodium hydroxide solution. The product of this reaction with primary amines is soluble in basic aqueous solution, while the product from secondary amines is insoluble in the basic solution and tertiary amines do not react. Both the secondary amine product and the unreacted tertiary amine may be dissolved in benzene, and may be separated from the product of the primary reaction by extraction with basic aqueous solution from benzene solution. The carriers used in the application of this technique to the products of the radiation of aniline were, of course, only similar to the radioactive products and not identical, so the apparent radioactivity distribution might not be a completely faithful representation of the actual character of the radioactive molecules. The unreacted tertiary amine was separated from the compound formed with the secondary amines by extraction of the benzene solution with strong acid. In this way, the primary, secondary and tertiary amines were separated. The percentages obtained were 21% primary amines, 55% secondary amines, and 24% tertiary amines. These percentages are to be compared with 18% which extracted into water and acetic acid and should therefore be characteristic of primary amines, 57% of which extracted not into water and acetic acid but into 0.1 *M* HCl and 1.0 *M* HCl, and therefore probably are secondary amines and 25% of which resisted the extraction into water and acetic acid and 0.1 *M* HCl but extracted into 6.0 and 12.0 *M* HCl.

Aniline Hydrofluoride.—The distribution of products from the hot atom chemistry of C^{14} in aniline hydrofluoride was compared with the distribution from pure aniline by means of the successive acid extractions. The percentages of activity in compounds of differing base strengths are tabulated below alongside of the typical distribution for pure aniline. Particularly notable is the decrease in yield of secondary amines which are to be found in the 0.1 *M* HCl extract. A nearly sixfold increase in insoluble products, presumably extremely high polymers, is observed.

TABLE IV

ANILINE HYDROFLUORIDE EXTRACTION DATA

Fraction	$C_6H_5NH_2{\cdot}HF$	$C_6H_5NH_2$, %
Gaseous activity	1.3	1.5
Aqueous extract Acetic acid extract	24.0	16
0.1 *M* HCl extract	20.0	32
1.0 *M* HCl extract	5.2	13
6.0 *M* HCl extract	11.1	11
12 *M* HCl extract	13.0	9
Benzene layer	2.4	3.5
Insoluble	23.0	4

Aniline in Benzene.—The eight mole per cent. solution of aniline in benzene yielded a unique distribution of activity when extracted with various concentrations of acid. It is evident that much of the radioactivity now resided in non-basic compounds. This indicates that the C^{14} atoms do not seek out the amine molecules, but for the most part react with the hydrocarbon environment as it is found when they are stopped.

Although little success was expected, a few carrier experiments were conducted with the results shown in Table VI.

TABLE V

DISTRIBUTION OF ACTIVITY BY SOLVENT EXTRACTION FOR 8 MOLE PER CENT. ANILINE IN BENZENE

Fraction	% of total activity	Fraction	% of total activity
Methane	1.5	6.0 *N* HCl extractable	6.6
Acetic acid extract	4.3	12 *N* HCl extractable	2.5
0.1 *N* HCl extractable	3.9	Remaining Bz layer	62.5
1.0 *N* HCl extractable	6.5	Insoluble residue	12.2

TABLE VI

CARRIERS USED FOR 8% ANILINE IN BENZENE PRODUCTS

Carrier	% of total activity
Benzene	2.5
Toluene	1.7
Diphenylmethane	3.2
Triphenylmethane	2.1

Apparently more complex molecules are the predominant products of this system, just as was the case with pure aniline.

Simply boiling off the benzene, after extracting the basic components from the solution, yielded a minute residue of low volatility containing more than 75% of the total radioactivity. The radioactive components of this residue apparently boil higher than triphenylmethane, b.p. 359°.

Triphenylamine.—Triphenylamine was irradiated as the solid in a granular form. No detectable activity escaped from the granules as gas. One gram of the irradiated triphenylamine was dissolved in benzene and extracted with acid solutions. The following distribution of radioactivity was obtained.

TABLE VII

TRIPHENYLAMINE EXTRACTION DATA

Extract	% of total activity	Extract	% of total activity
Gaseous	1.8	12.0 *M* HCl	17.1
Acetic acid	1.7	Remaining benzene layer	68.7
0.1 *M* HCl	2.4	Insoluble residue	7.4
1.0 *M* HCl	0.9		

Aniline in Methanol.—A 4.25 mole % solution of aniline in methanol was irradiated. The results are given in Table VIII. It is clear that the hot atom reaction yields a variety of radioactive alcohols in the system. The gaseous activity is very high. Presumably this is due in large part to ethane formed by substitution of the C^{14} for the oxygen in the methanol. The masses are not so dissimilar as to make substitution unlikely. Comparing these data with those for methylamine given later, one notices considerably more gaseous activity in the methanol system. Probably carbon oxides contributed to the gaseous activity in the methanol system.

TABLE VIII

4.25 MOLE % ANILINE IN METHANOL DATA

Carrier	B.p., °C.	Samples or derivatives, g.	Boiling range, °C.	Absolute D.P.M.	% of total activity
Methane	−184	4.8	−195 to 25	48,700	34.3
Methanol	65	10.4	25–72	22,500	15.9
Ethanol	78	7.9	72–84	11,930	8.4
n-Propanol	97	8.0	84–105	13,000	9.1
n-Butanol	118	8.1	105–122	8,750	6.2
Isoamyl alcohol	130	8.1	122–150	7,000	4.9
Higher alcohols	184	1.4	150	16,000	11.3
Aniline (basic cpd.)	...	..	....	14,100	9.9

Aliphatic Systems.—In view of the apparent complexity of the products of the C^{14} hot atom chemistry and aromatic systems apparently due to the extremely reactive character of the open benzene rings, the examination of aliphatic systems seemed to be attractive. Therefore, ampoules of pure ethylamine, ethylamine hydrofluoride, methylamine hydrofluoride, were irradiated. The samples were all processed in a similar manner, that is, carriers were added having a range of boiling points, after which the mixture was distilled and the fractions counted. Results are given in Tables IX to XI.

TABLE IX

ETHYLAMINE DATA

Carrier	Carrier b.p., °C.	Boiling range, °C.	Sample or derivative, g.	Absolute D.P.M. × 10^{-5}	% of total activity
Methane	−195	−195 to −6	4.5	1.7	6.8
Ethylamine	16.6	−6 to 25	56	5.5	21.5
n-Propylamine	48.7	25–49	23.7	2.8	10.9
n-Butylamine	78	49–78	21.1	3.1	12.1
Di-*n*-propylamine	110	78–110	17.3	2.7	10.5
t-Octylamine	140	110–140	15.1	2.1	8.2
3-Isopropylamine propylamine	156	140–156	16.2	2.6	10.1
Tributylamine	214	156–215	13.8	3.6	14.0
Di-2-ethylhexylamine	255	215–256	11.8	1.4	5.5
N-Methyldiphenylamine	293	256	5.4	0.1	0.4

TABLE X

ETHYLAMINE HYDROFLUORIDE DATA

Carrier	Carrier b.p. °C.	Range, °C.	Sample or derivative g.	Absolute D.P.M. × 10^{-5}	% of total activity
Gaseous	−195	−195 to −6	4.5	1.8	7.1
Ethylamine	16.6	−6 to 20	4.9	4.1	16.1
n-Propylamine	48.7	20–49	6.4	3.8	14.7
n-Butylamine	78	49–78	3.6	1.8	7.0
Di-*n*-propylamine	110	78–110	1.5	1.3	5.1
n-Hexylamine	128	110–132	7.0	0.8	3.1
t-Octylamine	140	132–140	7.8	0.9	3.5
3-Isopropylamine propylamine	156	140–156	7.6	2.5	9.8
Tributylamine	214	156–215	7.8	2.5	9.8
Di-2-ethylhexylamine	255	215–256	7.7	2.3	9.0
Methyldiphenylamine	293	256	5.3	3.8	14.8

TABLE XI

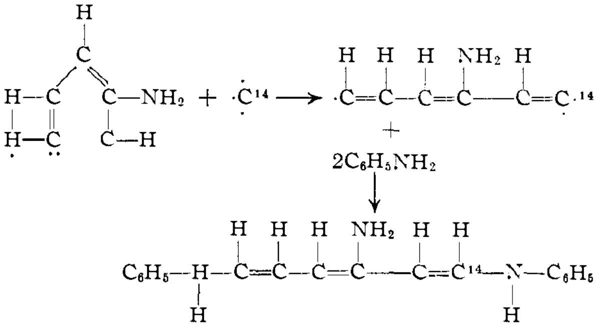
METHYLAMINE HYDROFLUORIDE DATA

Carrier	Carrier b.p., °C.	Boiling range, °C.	Sample or derivative, g.	Absolute D.P.M. × 10^{-5}	% of total activity
Gaseous	−195	−195 to −10	4.5	2.3	18.5
Methylamine	− 6.5	−10 to 15	21.4	1.97	15.8
Ethylamine	16.6	15–45	28.0	1.99	16.0
n-Propylamine	48.7	45–75	23.7	1.25	10.0
n-Butylamine	78	75–100	21.1	0.27	2.2
n-Amylamine	104	100–125	26.0[a]	1.24	10.0
n-Hexylamine	128	125–150	17.8	0.23	1.8
3-Isopropylamine propylamine	156	150–200	16.2	0.50	4.0
Tributylamine	214	200	13.8	2.70	21.7

[a] Includes talc.

IV. Discussion

We understand the hot atom chemistry of aromatic compounds by envisaging a collision of the high velocity C^{14} atom with the benzene ring which displaces one of the carbon atoms of the ring, thus opening the chain to form a highly unsaturated radical. This radical is formed in the immediate vicinity of the stopped C^{14} atom and may undergo a series of reactions such as (2)



The molecules resulting from this reaction may possibly react further adding one or two more solvent molecules to the double bonds. And so a highly substituted derivative of hexane with various numbers of primary, secondary and possibly tertiary nitrogen atoms involved may be formed, which could well fall in a molecular weight range of five to six hundred.

If collisions successful in the incorporation of the C^{14} atoms have not occurred before the full energy of the recoil is expended, the C^{14} atom at the end of its range will have been decelerated to the point where collisions with molecules as a whole will be successful in stopping it and so a general disruption of the molecule or of two or three molecules in succession may lead to the opening of several aromatic rings in the immediate vicinity of one another.[16] These could result in the formation of products of very high molecular weight.[16] It is, we believe, this type of reaction which results in the radioactivity which seems to be of high molecular weight. In the case of the aniline hydrofluoride system this fraction is observed to increase to about 23% of the total amount of radiocarbon. This is in keeping with the earlier observation that such polymerization in the "epithermal" region[16] is favored in the solid phase. In other words, a large increase in insoluble products observed in the aniline hydro-

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[16] M. S. Fox and W. F. Libby, *J. Chem. Phys.*, **20**, 487 (1952).

fluoride system probably is due to this phase effect. The several rings opened in the vicinity of one another lead to combinations among themselves and adjacent molecules in the case of the solid aniline hydrofluoride because the free radicals are trapped together for a longer time in the solid than they are in the liquid cage.

The aliphatic amines did not show the complex behavior of aniline and benzene. It seems reasonable that open aliphatic chains will be far less reactive than open aromatic rings. The appreciable yield of the parent molecule lends considerable support to this view. It indicates that a type of direct substitution occurs. The C^{14} atom which was stopped in the collision effectively replaces the atom displaced which carried off the momentum of the incoming C^{14} atom.

For the aliphatic amine salts, the distribution of products is like that expected from the irradiation of the pure solid amine with an increase of the higher molecular weight product observed due to the "phase effect."[16]

The higher yield of gaseous products from methylamine hydrofluoride suggests that ethane may be formed by substitution of C^{14} for N^{14}.

The results with the methanol system suggest oxygen substitution by the C^{14} atoms to give ethane. The higher yield of gaseous products from this system than from methylamine suggests that carbon oxides may make a fair fraction of the gaseous products. Production of labelled aliphatic alcohols seems entirely feasible.

Results given in this paper seem to support in a general way the hot atom theory developed previously.[16-18]

It is clear that radiation chemical effects seem not to be serious in this system. A method of synthesis of aliphatic organic compounds by direct pile irradiation seems to have been found.

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(17) W. F. Libby, THIS JOURNAL, **69**, 2533 (1947).

(18) F. S. Rowland and W. F. Libby, *J. Chem. Phys.*, **21**, 1940 (1953).

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The Primary Quantum Yield of Hydrogen Peroxide Decomposition[1]

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In aqueous hydrogen peroxide–formic acid solutions a chain reaction is initiated by ionizing radiation or by 2537 Å. light absorbed by the hydrogen peroxide. The principal gaseous product is carbon dioxide. This reaction is inhibited by oxygen, and from the quantum yield of oxygen consumption the primary quantum yield of hydrogen peroxide dissociation at 2537 Å. is deduced to be 0.49 ± 0.065. From this yield and a comparison of the photochemical experiments with those in which the reaction is induced by gamma rays, we calculate a *G* value of 3.06 water molecules decomposed to radicals per 100 e.v. of absorbed energy. These results suggest that the higher primary quantum yield of Dainton and Rowbottom and the high *G* value based on it are in error. A mechanism is proposed which fits the experimental data.

Dainton and Rowbottom[2] have measured at 2537 Å. the limiting quantum yield at high light intensities for aqueous hydrogen peroxide decomposition. By the accepted mechanism the primary quantum yield of hydrogen peroxide dissociation is one-half this limiting yield. These authors found the limiting yield to be 1.9 ± 0.1 and therefore the primary yield to be about 1.0. Next they compared at lower intensities the rates for the chain decomposition of aqueous hydrogen peroxide induced by 3660 Å. light and by CO^{60} γ-rays. Since the initiation rate for light had been determined the rate of radical production by γ-rays followed from the comparison and was estimated as 12.6 ± 1.8 water molecules decomposed per 100 e.v. of absorbed γ-rays at 0°.

Since the *G* value quoted for water decomposition to radicals is about fourfold that obtained by many workers[3a] and since Hunt and Taube[3b] find the limiting quantum yield for aqueous hydrogen peroxide at 2537 Å. to be 0.98 ± 0.05 at 25° for 0.017–0.186 M H_2O_2, we thought a redetermination of the primary quantum yield to be important. The system most suitable for this determination appeared to be the aqueous hydrogen peroxide–formic acid chain reaction inhibited by oxygen. The radiation chemistry of this system has been studied by Hart.[4] His results indicated that, if this system were irradiated with light absorbed by the hydrogen peroxide, then the quantum yield of oxygen consumption would measure the primary quantum yield of hydrogen peroxide dissociation.

Our hopes with respect to this system appear to have been justified, and this paper presents an investigation of the photochemistry of the aqueous hydrogen peroxide, formic acid, oxygen system. The primary quantum yield obtained agrees with that of Hunt and Taube, and this result would decrease by a factor of 2.0 the *G* value reported by Dainton and Rowbottom.

Experimental

For photochemical experiments a fused silica mercury resonance lamp (Type SC-2537, Hanovia Chemical and

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(1) Based on work performed under the auspices of the United States Atomic Energy Commission.

(2) F. S. Dainton and J. Rowbottom, *Trans. Faraday Soc.*, **49**, 1160 (1953).

(3) (a) See Table I, E. J. Hart, *Ann. Rev. Phys. Chem.*, **5**, 139 (1954); (b) J. P. Hunt and H. Taube, THIS JOURNAL, **74**, 5999 (1952).

(4) E. J. Hart, *ibid.*, **73**, 68 (1951).