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METHODS OF PREPARING FORMALDEHYDE - C^{14}

by

A. R. Van Dyken

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Part of the work on which this report is based was done at the Oak Ridge National Laboratory, part at the Argonne National Laboratory. The report will be submitted to the faculty of the University of Chicago as a thesis by the author, who is a candidate for the degree Ph.D. in Chemistry.

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METHODS OF PREPARING FORMALDEHYDE - C^{14}

A. R. Van Dyken

Introduction

The motive for this study was the need for a method of preparing formaldehyde containing isotopic carbon, particularly carbon-14. Up to the time at which this investigation started, radioactive formaldehyde had not been prepared, and in view of its importance as a key intermediate in the synthesis of various types of biologically important compounds, the lack of a workable process for its preparation constituted a serious handicap to the workers in this field.

Although the production of formaldehyde on a tonnage scale is a well-understood process and, moreover, the literature abounds in methods of preparation and reactions in which formaldehyde is formed, the special conditions pertaining to synthesis with radioactive materials severely limit the choice of method. Among the limitations thus imposed are: first, the scale of the operations which must be reduced to the milligram level; second, the choice of starting materials, carbon dioxide being the primary source of isotopic carbon; and, finally, the requirement that the product should be produced in anhydrous form. This latter requirement virtually eliminates methods in which formaldehyde is formed in dilute aqueous solution, since there is no known way of recovering anhydrous formaldehyde efficiently from such a solution except by the addition of inert carrier.

During the course of this work a number of different approaches to the problem were explored, beginning with attempts to accomplish the direct reduction of carbon dioxide to formaldehyde in acceptable yield. Thereafter a variety of indirect methods were considered, of which the most promising appeared to be one making use of the thermal decomposition of methyl triphenylmethyl ether into triphenylmethane and formaldehyde. This process was carried through to the stage of experimental trials with radioactive materials at tracer levels of activity. Results of these trials throw some light on the mechanism of the pyrolytic decomposition.

Survey of Previous Work

Reduction of Carbon Dioxide to Formaldehyde

The reduction of carbon dioxide to formaldehyde by catalytic hydrogenation has been claimed by many investigators. Bach(1) reported that an aqueous solution of carbon dioxide is reduced by hydrogen to formaldehyde in the presence of palladium. However, exhaustive studies, both theoretical and experimental, have refuted these claims. It is now known from the work of Newton and Dodge(2) that the equilibrium is very unfavorable and that hydrogenation catalysts will decompose formaldehyde almost completely to carbon monoxide and hydrogen.

Various chemical reagents have been reported to reduce carbon dioxide to formaldehyde, but yields were small. Of these reducing agents the most notable was lithium aluminum hydride,(3) which gave yields up to 25 per cent based on hydride consumed, when excess carbon dioxide was passed rapidly into an ether solution of the hydride. From the experimental observation that two moles of carbon dioxide react with one of lithium aluminum hydride, Finholt and Schlesinger were led to the conclusion, evidently erroneous, that formaldehyde was the sole product. On the basis of our results (reported later) and those of Nystrom and Yanko, based on analysis for formaldehyde, the observed stoichiometric ratio of 2:1 must have been the fortuitous result of the concurrent formation of methanol and formate in equivalent amounts.

Bromination of Salicyl Alcohol

In a study of the relative rates of bromination of several aromatic compounds, Francis(4,5) found that the SO_3H, COOH, CHO, and CH_2OH groups were eliminated from the ortho positions of substituted phenols and amines when the bromination was carried out above 40°. When the CH_2OH group was eliminated it was shown by qualitative tests to form formaldehyde. This presents the possibility of preparing formaldehyde containing isotopic carbon from carbon dioxide through the preparation of

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(1) Bach, Comp. Rendus 126, 479 (1898).

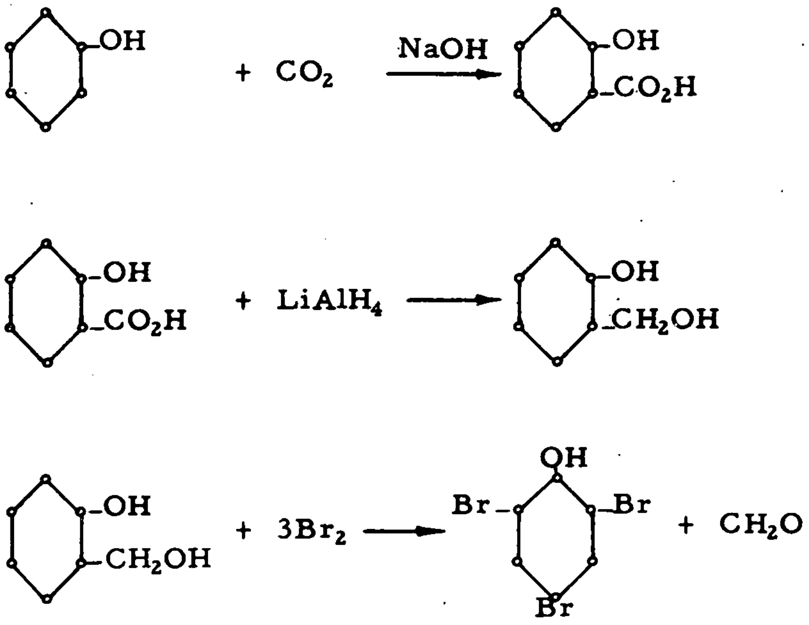
(2) Newton and Dodge, J. Am. Chem. Soc. 57, 4747-59 (1935).

(3) Nystrom, Yanko, and Brown, J. Am. Chem. Soc. 70, 441 (1948).

(4) Francis and Hall, J. Am. Chem. Soc. 46, 2498 (1924).

(5) Francis, J. Am. Chem. Soc. 48, 1631 (1926).

salicylic acid and subsequent reduction of the acid to salicyl alcohol with lithium aluminum hydride, according to the following equations:



Decomposition of Triphenylmethylcarbinol

The report by Schlenk and Ochs(6) that triphenylmethylcarbinol decomposes smoothly above its melting point, 109°, to yield triphenylmethane and formaldehyde is the basis of a method for the preparation of formaldehyde from carbon dioxide containing isotopic carbon. The carbinol was prepared by the reaction of triphenylmethylsodium with anhydrous formaldehyde. Danilov(7) reduced β, β, β-triphenylacetaldehyde with aluminum-amalgam to form the same carbinol, m.p. 110.5-111°. He made no mention of its decomposition, but said that the material prepared by Schlenk and Ochs was impure as shown by carbon and hydrogen analysis and melting point. Jones(8) modified the first method, using paraformaldehyde instead of the anhydrous monomeric form, and reported the melting point as 107°, with no mention of decomposition. If the decomposition, as reported by Schlenk and Ochs, actually occurs, a synthesis which would yield formaldehyde containing carbon-14 is given by the steps listed

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(6) Schlenk and Ochs, Berichte <u>49</u>, 608 (1916).

(7) Danilov, J. Russ. Chem. Soc. <u>51</u>, 123-25 (1920).

(8) Jones and Seymor, J. Am. Chem.Soc. <u>50</u>, 1152 (1928).

below, where the asterisk indicates the location of the carbon-14.

1) $(C_6H_5)_3CNa + \overset{**}{C}O_2 \rightarrow (C_6H_5)_3C\overset{*}{C}O_2Na$

2) $(C_6H_5)_3C\overset{*}{C}O_2Na + H^+ \rightarrow (C_6H_5)_3C\overset{*}{C}O_2H$

3) $(C_6H_5)_3C\overset{*}{C}O_2H + SOCl_2 \rightarrow (C_6H_5)_3C\overset{*}{C}OCl$

4) $(C_6H_5)_3C\overset{*}{C}OCl + LiAlH_4 \rightarrow (C_6H_5)_3C\overset{*}{C}H_2OH$

5) $(C_6H_5)_3C\overset{*}{C}H_2OH \rightarrow (C_6H_5)_3CH + \overset{*}{C}H_2O$

Step 4 was first carried out by Nystrom and the problem studied in this work was the decomposition of the resulting carbinol.

Decomposition of Ethers

Simple aliphatic ethers, in general, yield saturated hydrocarbons and aldehydes or ketones on decomposition. The decomposition of dimethyl ether has been studied extensively and the mechanism of its decomposition is understood better than that of any other ether. Hinshelwood and Askey(9) showed that the final products of its decomposition were methane, carbon monoxide, and hydrogen. At intermediate points in the decomposition formaldehyde was present; but, being unstable under the conditions of the decomposition, it eventually decomposed to carbon monoxide and hydrogen. They also showed that the rate of decomposition was first order between 557 and 771°, and pressures above 300 mm of Hg.

Rice and Johnson(10) detected free radicals in the decomposition of dimethyl ether by the Paneth technique and estimated the activation energy for the initial step of the reaction to be 80 Kcal. Much evidence has also been presented to prove that it is a chain reaction. The decomposition was retarded by an increase of the surface to volume ratio of the reaction vessel(11) and was inhibited by nitric oxide,(12) a characteristic of certain chain reactions. In addition. Leermakers(13) showed that the reaction was

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(9) Hinshelwood and Askey, Proc. Roy. Soc. (London) 115A, 215 (1927).

(10) Rice and Johnson, J. Am. Chem. Soc. 56, 214 (1934).

(11) Pease, J. Am. Chem. Soc. 59, 425 (1937).

(12) Stavely and Hinshelwood, Proc. Roy. Soc. (London) A159, 192 (1937).

(13) Leermakers, J. Am. Chem. Soc. 56, 1899 (1934).

sensitized by methyl radicals, which were produced by the photolysis of acetone which was mixed with the ether. Quantum yields up to 230 were obtained at low concentrations of acetone and low light intensities. Values for the activation energies for various steps of the methyl radical sensitized reaction were in good agreement with those given by Rice and Herzfeld(14) in the mechanism which they proposed for the thermal decomposition, as given below.

		E.,Kcal
1)	$CH_3OCH_3 \rightarrow CH_3 + CH_3O$	80
2)	$CH_3O + CH_3OCH_3 \rightarrow CH_3OH + CH_2OCH_3$	15-25
3)	$CH_3O \rightarrow HCHO + H$	20-45
4)	$H + CH_3OCH_3 \rightarrow H_2 + CH_2OCH_3$	10-15
5)	$CH_3 + CH_3OCH_3 \rightarrow CH_4 + CH_3OCH_2$	15
6)	$CH_2OCH_3 \rightarrow CH_3 + HCHO$	38
7)	$2\,CH_3 \rightarrow C_2H_6$	8
8)	$CH_3 + CH_2OCH_3 \rightarrow C_2H_5OCH_3$	8
9)	$2\,CH_2OCH_3 \rightarrow (CH_3OCH_2)_2$	8

Urey and Leifer(15) have shown by mass spectrographic analysis of the products of thermal decomposition that ethane was present to the extent of 0.8 per cent of ether decomposed, giving proof that methyl radicals are disappearing by reaction 7). Recently, Steacie and collaborators(16) have studied the mercury-sensitized decomposition of dimethyl ether at various temperatures. At 25° an important product of the reaction was ethylene glycol dimethyl ether, $(CH_3OCH_2)_2$, formed by the dimerization of the CH_3OCH_2 radical, which had been postulated by Rice and Herzfeld as an important chain carrying radical, but whose existence had not been proven.

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(14) Rice and Herzfeld, J. Am. Chem. Soc. 56, 284 (1934).

(15) Urey and Leifer, J. Am. Chem. Soc. 64, 994 (1942).

(16) Steacie, Darwent, and Marcus, J. Chem. Phys. 16, 987 (1948).

Decomposition of Triphenylmethyl Ethers

Norris and collaborators(17) showed that ethers of the type $(C_6H_5)_3$ COR, where R is a simple aliphatic radical, either primary or secondary, decompose at temperatures ranging from 215° to 262° to form triphenylmethane and an aldehyde or a ketone depending on whether R is primary or secondary. Of the various substances which lowered the temperature at which decomposition set in, aluminum oxide and potassium acid sulfate were the most effective, lowering the temperature, in the case of the methyl ether, from 262° without catalyst to 157° and 132°, respectively. The effect of the catalysts on the composition of the products was not mentioned. Reaction rates(18) were found to be initially first order, but increased with the extent of decomposition and passed through a maximum. The initial rate was increased by the addition of triphenylmethane.

The thermal decomposition of methyl trityl ether produced, in addition to formaldehyde and triphenylmethane, substantial amounts of methanol and carbon monoxide. Although the author stated that these were formed to the extent of 36 per cent, the experimental data reported are not consistent with this figure. In one experiment, in which 0.0925 moles of ether was decomposed at 280° to 300° over a period of 240 hours, there were formed 0.0329 moles of carbon monoxide and 0.0399 moles of methanol, together amounting to 78 per cent.

Decomposition of Other Methyl Ethers

It was reported by Hurd,(19) on the basis of unpublished work by Dunlay, that 9, 10-dihydro-9, 10-dimethoxy-9, 10-diphenylanthracene decomposed above 300° with the evolution of formaldehyde. No further reference to this was found.

Behavior of N-methylol Derivatives

The N-methylol derivatives of amides and of di-aryl amines decompose on heating with the liberation of formaldehyde, and according to Hurd(20) there is no known exception to this rule. N-methylolbenzamide decomposes slightly above its melting point (104°C) into benzamide and

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(17) Norris and Young, J. Am. Chem. Soc. 52, 753 (1930).

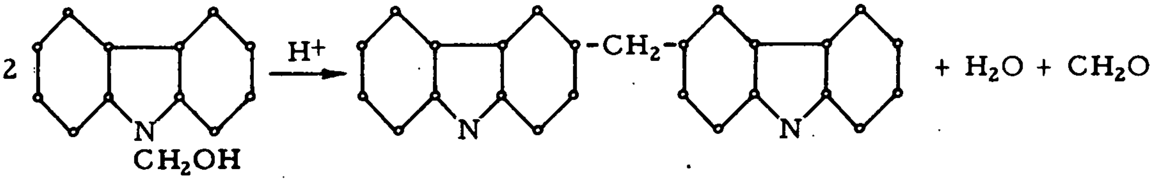
(18) Norris and Cresswell, J. Am. Chem. Soc. 55, 4946-51 (1933).

(19) Hurd, The Pyrolysis of Carbon Compounds (Chemical Catalog Co., New York, 1929) p. 200.

(20) Hurd, op. cit., p. 158.

formaldehyde;(21) similarly, N-methylolphthalimide reverts on heating to phthalimide and formaldehyde.(22) A similar fission occurs on heating in water solution and, in the case of N-methylolcarbazole(23) it has been reported that formaldehyde is liberated quantitatively in this manner.

In the presence of acids, the decomposition of N-methylolamines takes a somewhat different course as the consequence of a subsequent condensation reaction forming diphenylmethane derivatives, as in the following example:(24)



The decomposition of N-methylolamides occurs, in part, with the formation of N,N′-methylene derivatives and the recovery of formaldehyde is therefore not always quantitative.

The interest in N-methylol derivatives for the present investigation lies in the possibility of isolating formaldehyde from aqueous solutions as a derivative from which anhydrous monomeric formaldehyde can be generated with ease.

Summary of Experimental Results, and Conclusions

Reduction of Carbon Dioxide

Carbon dioxide was reduced by lithium aluminum hydride, using the technique of reverse addition, i.e., the stoichiometric amount of lithium aluminum hydride was added to a solution of carbon dioxide in ether at -80° in a closed vessel. The solubility of carbon dioxide in ether at this temperature was sufficient to make such a procedure feasible. However, the best yield was 25 per cent, not significantly different from that which had been observed previously under conditions presumably less favorable. When the solution was acidified no carbon dioxide was found. Either the reduction of the intermediate corresponding to the formaldehyde

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(21) Einhorn, Ann. 343, 224 (1905).

(22) Einhorn, Ann. 361, 113 (1908).

(23) Lange, Frdl., 11, 176 (1914)

(24) *Ibid.*

stage occurs much more rapidly than the reduction to that stage in the following scheme for the various steps in the reduction,

$$CO_2 \xrightarrow{\text{fast}} \text{formate} \xrightarrow{\text{slow}} \text{formaldehyde} \xrightarrow{\text{fast}} \text{methanol}$$

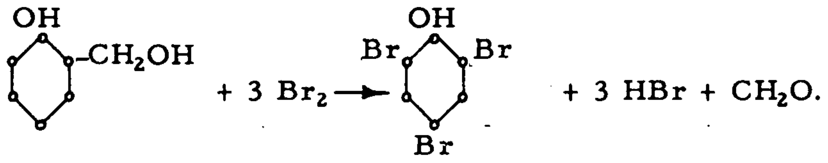
or the intermediate corresponding to the formaldehyde is in equilibrium with those of formate and methanol, as follows:

$$4(CH_2O_2)_2LiAl \rightleftharpoons (HCO_2)_4LiAl + 3(CH_3O)_4LiAl.$$

Bromination of Salicyl Alcohol

Salicyl alcohol was reacted with the quantity of bromine, calculated by the following equations:

$$KBrO_3 + 6HCl + 5\ KBr \longrightarrow 3\ Br_2 + 3\ H_2O + \underline{6}\ KCl \qquad (1)$$



(2)

Analysis of the resulting solution from the above bromination by precipitation of the formaldehyde condensation product with "methone" showed a 71 per cent yield of formaldehyde.

Decomposition of Triphenylmethylcarbinol

Contrary to the report of Schlenk and Ochs,(25) triphenylmethylcarbinol was found to be stable up to 200°C. After six hours of heating it gave no evidence of decomposition. However, in the presence of various added substances; zinc chloride, phosphorus pentoxide, and platinum black, the carbinol did decompose at lower temperatures, but no formaldehyde was obtained.

It was found that decomposition of the pure carbinol could be brought about at much higher temperatures. Several experiments were carried out above 385°, and yields of formaldehyde up to 62 per cent were obtained in one hour, but the usual yield was between 45 and 50 per cent. At 350-360°,

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(25) Schlenk and Ochs, Berichte, 49, 608 (1916).

the decomposition is much slower and only a trace of formaldehyde was formed in several hours. The effects produced by various added substances, none of which led to better results than decomposition of the pure carbinol, are shown in Table I.

Table I

DECOMPOSITION OF $(C_6H_5)_3CCH_2OH$ IN THE PRESENCE OF VARIOUS SUBSTANCES

Substance		Wt. added per g. of carbinol	Temp. of heating bath	Yield of CH_2O	
0.	None		385-400°	50%	
1.	Pt (black)		385-400°	35%	
2.	Ag_2O		385-400°	Very small	(first reaction is reduction to Ag with accompanying evolution of CO_2)
3.	H_2O	5 cc H_2O .100 gm carbinol	310°	None	Carbinol was recovered
4.	Fluorenone	0.100 10.0	385-395°	38% 5%	(The b.p. of Fluorenone is 341° and lowers temp. of decomposition)
5.	$(C_6H_5)_3CH$	0.05 0.10	385° 385°	44.4% 45.7%	
6.	KOH	0.5	385°	None	
7.	KOH + $(C_6H_5)_3CH$	$\left.\begin{matrix}0.5\\10.0\end{matrix}\right\}$		5%	
8.	Al_2O_3	0.5	350°	None	Very rapid decomp.
9.	Cu	- -	385° 385°	44% 49%	Reaction carried out in copper tube (no glass)
10.	Quartz	-	385°	33%	Reaction carried out in quartz tube

The following observations support the conclusion that triphenylmethylcarbinol may decompose by reactions other than that yielding triphenylmethane and formaldehyde.

(1) The weight lost by the carbinol during decomposition is much greater than that accounted for by the formaldehyde formed.

(2) No triphenylmethane was obtained from the residue, nor was any other substance isolated or identified.

(3) In the presence of aluminum oxide, the decomposition takes place very readily, but no formaldehyde is formed. The residue from such a decompositon was found by combustion to contain only carbon and hydrogen.

These facts suggest that dehydration is the predominant reaction. The most probable product would be triphenylethylene formed by the migration of one phenyl group during dehydration. A rearrangement of this kind is known to occur when β, β-diphenylethyl alcohol is treated with phosphorus pentoxide in benzene solution, the product being stilbene.(26)

Pryolysis of Methyl Triphenylmethyl Ether

In view of the possibility of using this ether to prepare formaldehyde-C^{14} and the uncertainty in the published literature as to the relative amounts of the various products, plus the lack of information on the effect of catalysts on the products, a study of the decomposition of this ether was undertaken. Effects especially studied were those of time, temperature, and catalysts on the reaction. Also, a careful material balance was made with emphasis on the volatile products. Table II gives the data for the effects of time and temperature on the reaction. Since the boiling point of the ether is approximately 385°, bath temperatures much above this mean that refluxing would be much more vigorous without much increase in temperature. The most favorable conditions for decomposition, as established by these experiments, are to heat the mixture at bath temperatures above 390° for at least 90 minutes.

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(26) Rampart and Amagat, Ann. chim. [10], 8, 263-328 (1927).

Table II

DECOMPOSITION OF METHYL TRIPHENYLMETHYL ETHER

Temperature of bath	Time	% of theor. wt. loss	Yields	
			CH_2O*	CH_3OH
340-345°C	150 min.	74	48.0%	15.0%
390-400	60	88	66.5	13.0
390-400	90	102	72.5	15.5
440-450	35	87.5	73.5	9.6

*These yields are based on the actual weights lost from the ether.

In a more detailed study of volatile products from a decomposition carried out under optimum conditions of time and temperature, the yields of volatile products were formaldehyde 64 per cent, methanol 17.8 per cent, and carbon monoxide 12.7 per cent, accounting for 95 per cent of methoxyl-group carbon of the original ether.

The effect of various added substances on the decomposition and on the amount of formaldehyde formed is summarized in Table III. None of these substances increase the yield, and some of them decrease it considerably.

Decomposition of Methyl Tribiphenylmethyl Ether

This ether, a new compound, was observed to decompose above 300°C. A pyrolysis experiment carried out at 385°C brought about complete decomposition and a material balance of 99 per cent for methoxyl-group carbon was obtained. However, carbon monoxide was the predominant product, amounting to 68.4 per cent, while yields of formaldehyde and methanol were 16.8 and 14.7 per cent, respectively.

Table III

EFFECT OF VARIOUS SUBSTANCES ON THE DECOMPOSITION OF METHYL TRIPHENYLMETHYL ETHER

Added Substance	Conditions of Decomposition	Yields		
		CH_2O	CH_3OH	CO
Aluminum oxide	Complete in 25 minutes at 350°C	6%	16%	32%
Triphenylmethyl peroxide, 10%	a) Heated slowly up to 400°C	58.5	--	--
	b) Heated rapidly up to 400°C	60.3	--	--
Triphenylcarbinol, 10%	Heated at 385 ± 5° for 1 1/2 hrs.	67.0		
Triphenylchloromethane, 10%	Heated at 385 ± 5° for 1 1/2	None	45	32

Decomposition of 9,10-Dihydro-9, 10-dimethoxy-9, 10-diphenylanthracene

The reported evolution of formaldehyde from this ether above 300° was confirmed,(27) but methanol was the major product as shown by the results of a decomposition carried out at 385°, in which the yields of methanol, formaldehyde, and carbon monoxide were 64.0, 21.6, and 7.4 per cent, respectively. Since the stable residual product is 9, 10-diphenylanthracene formed by the loss of two methoxyl groups, the predominance of methanol in the volatile products is a consequence of the requirements for a hydrogen balance. Formaldehyde and carbon monoxide can only be formed by disproportionation reactions in which the hydrogen atoms lost by methoxyl groups appear as methanol.

Experiments with Methyl-C^{14} Triphenylmethyl Ether

To gain further information concerning the pyrolysis, ether containing carbon-14 in the methyl group was prepared from methanol-C^{14} and was decomposed in the apparatus shown in Figure 3. Both chemical and radioactive measurements were made on each of the products of the

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(27) Hurd, op. cit., p. 200.

decomposition, and the results are given in Table IV. The residue from this decomposition was analyzed for undecomposed ether by means of the isotope dilution technique and was found to contain 2.0 per cent of the original amount.

Table IV

DECOMPOSITION OF METHYL-C^{14} TRIPHENYLMETHYL ETHER

Substance	Chemical Analysis		Radiochemical Analysis	
	Amount	% Yield	Molar Activity uc x 10^3 per mol	Total Activity
I. Starting materials				
a. Methanol	-	-	11.07 ± 0.15	22.14
b. Ether	2.00 mmoles	-	11.16 ± 0.15	22.32
II. Volatile products				
a. Formaldehyde	0.80 mmoles	40	11.0 ± 0.15	8.82
b. Methanol	0.707 mmoles	35.4	11.05 ± 0.15	7.82
c. Carbon monoxide	0.367 mmoles	18.4	10.83 ± 0.15	4.00
		92.8		20.64 or 92.8% of total activity
III. Residual products				
a. Soluble in benzene	0.486 gm			0.795*
b. Insoluble in benzene	0.004 gm			0.026
				0.821 or 3.6% of total activity

*Of this 0.795 microcuries, 0.441 was undecomposed ether.

It is of interest to consider if a mechanism similar to that proposed by Rice and Herzfeld for dimethyl ether can be formulated to account for the experimental observation found in the decomposition of triphenylmethyl ether. Such a mechanism can be represented by the following equations:

1) $(C_6H_5)_3COCH_3 \rightarrow (C_6H_5)_3C + CH_3O$

2) $(C_6H_5)_3COCH_3 + CH_3O \rightarrow CH_3OH + (C_6H_5)_3COCH_2$

3) $(C_6H_5)_3COCH_3 + (C_6H_5)_3C \rightarrow (C_6H_5)_3CH + (C_6H_5)_3COCH_2$

4) $(C_6H_5)_3COCH_2 \rightarrow (C_6H_5)_3C + CH_2O$

5) $CH_3O + CH_2O \rightarrow CH_3OH + CHO$

6) $CH_3O + CHO \rightarrow CH_3OH + CO$

7) $(C_6H_5)_3C + CH_2O \rightarrow (C_6H_5)_3CH + CHO$

8) $(C_6H_5)_3C + CHO \rightarrow (C_6H_5)_3CH + CO$

9) $(C_6H_5)_3C \rightarrow$ other reactions.

Salient points in this scheme are the following:

1. We assume that formaldehyde is formed by the decomposition of a radical $(C_6H_5)_3\,COCH_2$, which is in turn formed by two different reactions as shown in equations 2) and 3).
2. Reactions 3) and 4) constitute a chain.
3. Reactions 7) to 9) are chain breaking reactions.
4. Equations 5) to 8) account for the formation of carbon monoxide.

Experimental observations that are consistent with the proposed mechanism are:

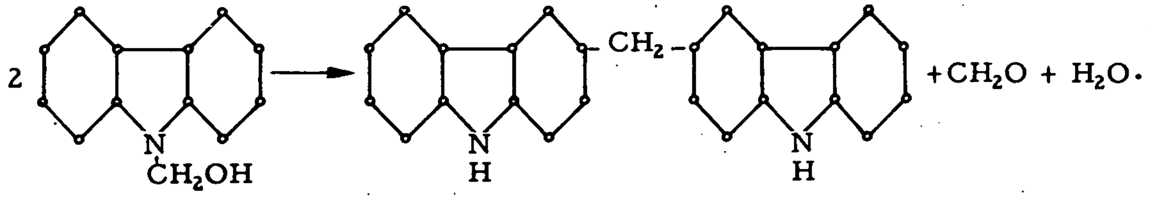
1. No hydrogen is formed during the reaction.
2. The observed ratio of approximately 3:2 for the formation of methanol and carbon monoxide can be accounted for by considering the relative importance of reactions 7) and 8) as compared to 5) and 6). If all the carbon monoxide were formed by reactions 5) and 6), the ratio of methanol to carbon monoxide would be 2:1. Therefore a considerable

fraction of carbon monoxide must be formed by reactions 7) and 8). Any chains initiated by reaction 2) result in additional methanol and require that more carbon monoxide be formed by reaction 7) and '8) for the observed ratio of methanol and carbon monoxide.

Methoxy and triphenylmethyl radicals are formed in equal numbers, but, in view of the fact that more methanol than carbon monoxide is formed, it follows that triphenylmethyl radicals must disappear by reactions other than hydrogen capture leading to triphenylmethane. This is supported by the fact that during a decomposition in which more than 95 per cent of the ether was decomposed the yield of triphenylmethane was less than 80 per cent.

Decomposition of N-methylol Derivatives

N-methylolphthalimide decomposed smoothly below 160° to yield 92 per cent formaldehyde. The decomposition of N-methylolcarbazole resulted in a 43 per cent yield of formaldehyde; some of the available formaldehyde being used in the formation of 3, 3′-methylenedicarbazole, according to the equation:



With 9-methylol-3, 6-dichlorocarbazole in which it was expected that the formation of the 3-methylene derivative would be hindered, the yield of formaldehyde was 90 per cent. These compounds are very useful for the generation of anhydrous formaldehyde but cannot be applied to the preparation of formaldehyde-C^{14} until syntheses of these compounds from methanol or carbon dioxide are devised.

Experimental

Part I. Reactions Yielding Formaldehyde

Determination of Formaldehyde

The "Methone Method" described by Walker(28) was used for the quantitative determination of formaldehyde in this work. It is based on the fact that formaldehyde and methone, 5, 5-dimethylcyclohexanedione-1, 3 react quantitatively in neutral, alkaline, or mildly acidic solution to form methylene bis-methone, a compound which is soluble to the extent of only 0.5-1.0 mg in 100 ml of water at 15-20° and much less soluble in the presence of excess methone.(29) A neutral or mildly acidic aqueous solution of formaldehyde was mixed with an excess of aqueous methone solution having a concentration of 0.4 g per 100 ml. The product, which was allowed to form overnight at room temperature, was collected on a sintered glass filter and determined gravimetrically.

The Reduction of Carbon Dioxide with Lithium Aluminum Hydride

The apparatus used in this experiment was constructed so that an ether solution of lithium aluminum hydride could be added to a solution of carbon dioxide in ether at -80°. It consisted of a reaction system, of approximately 125 ml capacity, to which was attached by means of a stopcock a calibrated volume of 416 cc, and through which the whole system could be evacuated by a mercury diffusion pump. The reaction system included a removable 100 ml flask and a buret with a delivery tube, the bottom of which was U-shaped so that it would be submerged in the solution with the exit above the surface. In this way the solution from the buret was cooled as it passed through the delivery tube.

The reaction flask containing 40 ml of dry diethyl ether was placed on the reaction system and cooled to -195°, after which the system was evacuated. Carbon dioxide that was generated from 1.993 g of barium carbonate was collected in the calibrated volume, yielding 9.84 millimoles of gas at a pressure of 441 mm of Hg. This gas was allowed to come in contact with the ether at -80°, giving a final pressure of 31 mm. Then 13.9 ml of 0.036 molar lithium aluminum hydride solution in diethyl ether was added to the ether solution of carbon dioxide over a period of fifteen minutes. The mixture was allowed to react for fifteen minutes at this temperature, while being agitated with a magnetic stirrer. The reaction

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(28) Walker, Formaldehyde (Reinhold Publishing Co., New York, 1944) pp. 263-266.

(29) Weinberger, Ind. Eng. Chem., Anal. Ed. 3, 365 (1931).

mixture was cooled to -195°, and the inert gases removed by evacuation. The remaining carbon dioxide which was condensed in a trap in the calibrated volume during evacuation had a final pressure of 38 mm at room temperature. It was condensed in the reaction flask at -195°, which was then isolated from the calibrated volume and the mixture allowed to react for ten minutes at -80°. The reaction mixture was then allowed to warm to room temperature and helium gas admitted to the system. A flow of helium gas was maintained through the system, the exit gas being passed through a bubbler containing 0.1 molar barium hydroxide solution. Ten ml of water and five ml of ten per cent sulfuric acid were added to the mixture, which was stirred until all the precipitate was dissolved. No precipitate was formed in the barium hydroxide solution, indicating that the gas passing through it contained no carbon dioxide.

The ether and aqueous layers were separated and the ether washed with 5 ml of water. The combined aqueous solution was made alkaline with sodium hydroxide; sufficient acetic acid was added to dissolve the aluminum hydroxide formed; and the solution was diluted to 50 ml. Two 5.0 ml aliquots yielded 0.0686 and 0.0688 g of methylene bis-methone respectively, which is equivalent to a 24 per cent yield of formaldehyde.

Bromination of Salicyl Alcohol

Salicyl alcohol was brominated by adding 10 ml of 6 N hydrochloric acid to 5 ml of aqueous solution containing 1 millimole (0.124 g) of the alcohol, m.p. 85°, 1 millimole (0.167 g) of potassium bromate, and an excess of potassium bromide (1.184 g).(30) The reaction was complete, as indicated by the decolorization of the bromine, in 30 minutes at 40-50°. The tribromophenol was removed by filtration, and the solution was neutralized with sodium hydroxide. Subsequent analysis by the method described resulted in the formation of 0.2083 g of methylene bis-methone, m.p. 188-189°, which represents a 71.4 per cent yield of formaldehyde.

The Decomposition of N-methylol Derivatives

The apparatus used in the decomposition of these compounds consisted of a series of three traps of the type represented by B and B′ in Figure 3. The first trap contained the material to be decomposed and the two succeeding traps contained 10 ml of water each. The first trap was heated by a bath at the desired temperature and nitrogen gas was swept through the system carrying the volatile products with it. The formaldehyde was absorbed from the gas stream by the water in the two succeeding traps, and the resulting aqueous solution was analyzed for formaldehyde by the method described.

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(30) Francis, J. Am. Chem. Soc. 48, 1631 (1926).

A 0.2808 g portion of N-methylolphthalimide, which had been recrystallized from benzene, m.p. 142-143°, was decomposed in the manner described above. The temperature was kept between 135° and 145° for thirty minutes and then slowly raised to a maximum of 190°. Analysis of the resulting aqueous solution by the method described showed the presence of 0.0435 g of formaldehyde, a yield of 92 per cent.

N-methylolcarbozole, m.p. 133°, was decomposed in the manner described by heating a 0.5028 g sample from 140° to 190° in three hours. Analysis of the resulting aqueous solution showed that it contained 0.0332 g of formaldehyde, a yield of 43.3 per cent based on the formation of one mole of formaldehyde from each mole of N-methylolcarbazole. The weight loss during decomposition was 0.0644 g and the residue of the decomposition melted in the range from 280 to 290°. These two facts, (1) the difference between the weight loss and the amount of formaldehyde found and (2) the melting point of the residue, indicate that 3, 3′-methylene dicarbazole, m.p. 287°,(31) was formed during the decomposition, since the decomposition of 2 moles of N-methylolcarbazole would then yield one mole of 3, 3′-methylene dicarbazole, one of formaldehyde, and one of water.

Preparation and Decomposition of N-methylol-3, 6-dichlorocarbazole

This new compound was prepared from 3, 6-dichlorocarbazole by the method described by Lange(32) for N-methylolcarbazole. A 2.32 g portion of 3, 6-dichlorocarbazole, m.p. 201-202.5°, and 1.0 g of potassium carbonate were mixed with 10 ml of absolute ethyl alcohol. To this mixture was added 1.0 ml of 38 per cent formalin solution. The mixture was heated for ten minutes on a steam bath, during which time the 3, 6-dichlorocarbazole went into solution. The solution was filtered hot and allowed to stand overnight. The product, which crystallized from solution, was collected on a filter. Recrystallization from benzene yielded 1.5 g of product, m.p. 151-153°, in a closed tube. Analysis: calculated for $C_{13}H_9NOCl_2$: C, 58.70; H, 3.40; Cl, 26.6; N, 5.26. Found: C, 58.54; H, 3.20; Cl, 26.4; N, 5.22.

Decomposition of this compound was carried out in the manner described above. A 0.100 g sample was heated for one hour raising the temperature from 150-200°. Analysis indicated that 0.0102 g of formaldehyde were obtained, or a yield of 90 per cent based on one mole of formaldehyde from one of the carbazole.

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(31) Dutt, J. Chem. Soc. 125, 802 (1924).

(32) Lange, Frdl. 11, 197 (1912-1913).

Preparation of Triphenylmethylcarbinol

Triphenylacetylchloride was prepared by the action of excess thionyl chloride on 17.5 g of triphenylacetic acid by the method of Norris and Cresswell,(33) yielding 12.7 g of the product, m.p. 126-127°. A 9.5 g portion of the chloride was added in two and one-half hours to a 50 per cent excess of lithium aluminum hydride by the technique of Nystrom and Brown(34) for substances only slightly soluble in ether, using a modified Sohxlet extractor. The product, recovered by the normal procedure, was 8.4 g of material, m.p. 103-104°, a yield of 99 per cent. The melting point of the product after recrystallization from petroleum ether (70-90°) was 104°, which is different from the 109° and 110.5-111° reported by Schlenk and Ochs(35) and Danilov,(36) respectively. The product obtained in this laboratory by the reaction of triphenylmethylsodium and formaldehyde, according to the method of Schlenk and Ochs, melted at 104°. The melting point of the mixture of the two products also melted at 104°. When this material was heated to 105-106° it resolidified to a form melting from 108-109°. Recrystallization of this higher melting form from petroleum ether yielded the form melting at 104°. It was concluded that the substance obtained in this work was a lower melting form of triphenylmethylcarbinol. This was substantiated by the fact that the acetate prepared from this substance melted at 135° compared to the melting point of 136° reported for the acetate of triphenylmethylcarbinol by Danilov.

The thermal decomposition of the carbinol was carried out by the method described for the N-methylol derivatives. The carbinol was heated in a trap and the volatile products carried by a stream of nitrogen through two traps containing water which absorbed any formaldehyde formed. In one such decomposition, 0.500 g of carbinol reported above was heated for two hours at 380-400° and the resulting aqueous solution was found to contain 0.02175 g of formaldehyde, a yield of 40 per cent. The residue was then heated for an additional eight hours at this temperature and no more formaldehyde was found.

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(33) Norris and Cresswell, J. Am. Chem. Soc. 56, 473 (1934).

(34) Nystrom and Brown, J. Am. Chem. Soc. 69, 1197 (1947).

(35) Schlenk and Ochs, Ber. 49, 608 (1916).

(36) Danilov, J. Russ. Chem. Soc. 51, 123 (1920).

Thermal Decomposition of Ethers

The thermal decomposition of ethers was also carried out by heating the substance in a trap by means of a bath at the desired temperature and flushing the volatile products from the reaction tube with a stream of nitrogen gas. The outer tube of the trap used for decomposition (see B in Figure 3) was approximately twelve inches long and the inlet tube for the nitrogen gas extended only four inches into it. Only the lower two inches of the tube were heated by a salt bath so that the entry point of the nitrogen gas was above the heated zone of the trap. In this way the less volatile products of the decomposition, e.g. triphenylmethane, were not entrained in the gas stream and carried from the decomposition tube; and the weight lost during the decomposition could be used as a measure of the extent of decomposition.

The stream of nitrogen gas was then passed through two consecutive traps each containing 10 ml of water, cooled with an ice water mixture, for the purpose of absorbing formaldehyde and methanol. The gas was then passed through copper oxide heated to 700° in a combustion tube, oxidizing the carbon monoxide to carbon dioxide, which was absorbed in a barium hydroxide solution. The quantity of carbon monoxide formed during decomposition was determined from the weight of barium carbonate precipitated.

Analysis of formaldehyde and methanol was carried out by diluting the aqueous solution to 100 ml and using 10 or 20 ml aliquots for separate determination. The formaldehyde was determined by the methone method previously described. For the determination of methanol a differential method was used. The total amount of methanol and formaldehyde in an aliquot was determined by oxidation with potassium permanganate by the method described by Oesper,(37) and the result expressed as milliequivalents of total material oxidized. The number of milliequivalents of formaldehyde present in the aliquot as determined for a separate aliquot by the previous method was subtracted from the total and the remainder considered as milliequivalents of methanol.

The efficiency of absorption of methanol was shown by a separate determination of the quantities of these two substances absorbed in the first and second traps during decomposition. From the decomposition of 1.0008 g of methyl triphenylmethyl ether, the water from the first trap was found to contain 0.070 g of formaldehyde and 0.0194 g of methanol, and that from the second trap no formaldehyde and only 0.0009 g of methanol. Therefore, the only material found in the second trap was 4.5 per cent of the methanol.

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(37) Oesper, Newer Methods of Volumetric Analysis (Van Nostrand Co., New York, 1938) pp. 55-66.

In a decomposition of methyl triphenylmethyl ether by the method described above, 1.0008 g (3.65 millimoles) of ether heated for three hours between 385 and 395° lost 0.110 g. The barium carbonate precipitated was 0.0917 g (0.465 millimoles), or a yield of carbon monoxide of 12.7 per cent. The formaldehyde in two 10 ml aliquots from a total volume of 100 ml each formed 0.0682 g of methylene bis-methone, which is equivalent to 0.0700 g of formaldehyde in the total volume or a yield of 64.0 per cent. It was found that 1.334 milliequivalents of potassium permanganate was reduced by one-tenth aliquots of the solution of formaldehyde and methanol. The formaldehyde present in this volume, 0.233 millimoles, would reduce 0.932 milliequivalents of potassium permanganate. Therefore, 1.334 minus 0.932, or 0.402 milliequivalents of potassium permanganate was reduced by the methanol present, which is equivalent to 0.0669 millimoles of methanol or 0.669 millimoles for the total volume, which is a yield of methanol of 18.3 per cent. The total yield of formaldehyde, methanol, and carbon monoxide represents a 95.0 per cent recovery of methoxyl carbon on a molar basis.

Methyl tribiphenylmethyl ether was decomposed in the same manner. In this experiment 0.5008 g (0.996 millimoles) of the ether was heated for two hours between 380 and 390°, and lost 0.0333 g. Analysis of the products by the methods described showed that 0.684 millimoles of carbon monoxide, 0.168 millimoles of formaldehyde, and 0.146 millimoles of methanol were obtained which is a total recovery of methoxyl carbon of 0.998 millimoles.

A dimethoxy ether, 9, 10-dihydro-9, 10-dimethoxy-9, 10-diphenylanthracene was also decomposed. A 0.3984 g (1.016 millimole) sample was heated for one hour between 380 and 390° and lost 0.0638 g in weight. Analysis of the products by the same methods showed that 0.148 millimoles of carbon monoxide, 1.30 millimoles of methanol, and 0.433 millimoles of formaldehyde were formed, or yields based on methoxyl carbon of 7.3, 64.0, and 21.4 per cent, respectively.

Preparation of Ethers

The methyl triphenylmethyl ether used in the decomposition was prepared by the method of Norris and Young,(38) giving a product melting at 82.5-83°. A method for preparing this ether from equal molar quantities of methanol and triphenylmethylbromide will be described in detail in the synthesis of methyl-C^{14} triphenylmethyl ether.

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(38) Norris and Young, J. Am. Chem. Soc. 52, 753 (1930).

The dimethoxy ether, 9, 10-dihydro-9, 10-dimethoxy-9, 10-diphenylanthracene, m.p. above 300°, with decomposition, was prepared by the method given by Schlenk and Bergmann(39) from the corresponding monomethoxy compound, 9-hydroxy-10-methoxy-9, 10-dihydro-9, 10-diphenylanthracene, m.p. 247°.

Methyl triphenylmethyl ether, a new compound, was prepared by dissolving 2.0 g of tribiphenylcarbinol, m.p. 206-208°, in 20 ml of hot benzene and adding 50 ml of methanol containing 0.5 ml of concentrated sulfuric acid at reflux. The solution turned pink but became colorless on cooling to room temperature and the ether crystallized from solution. Collection of the crystals on a filter yielded 1.9 g of the ether, m.p. 163-163.5°. Analysis: Calculated for $C_{38}H_{30}O$: C, 90.80; H, 6.01. Found: C, 90.95; H, 6.11.

Part II. Experiments Using C^{14}

Measurements of C^{14}

An ionization chamber was used for the determination of C^{14} in this work. The chamber, Figure 1, which was constructed of stainless steel, had a volume of approximately 225 cc. All ion-currents were measured with the chamber filled to atmospheric pressure with carbon dioxide. The carbon dioxide obtained from the material containing the C^{14} was introduced into the evacuated chamber by expansion from a U-tube in which it had been condensed at -195°, and the pressure brought to atmospheric with inactive carbon dioxide which was passed into the chamber through the U-tube. It was assumed that the gas remaining in the U-tube during the expansion, a small fraction of that in the chamber, was carried into the chamber by the inactive carbon dioxide.

A vibrating reed electrometer(40) was used to measure the currents from the ionization chamber. The apparatus consisted of an Applied Physics Corporation Model 30 Vibrating Reed Electrometer, having four linear scales reading 1.0, 10, 100, and 1000 millivolts full scale; a Brown "Electonik" recording potentiometer recommended for use with the electrometer; a high resistance; and a Leeds and Northrup Single Range Portable Potentiometer, No. 8667, 111 millivolts full scale. Measurements were made by the steady deflection method, in which the voltage across the high resistance, connected as shown in Figure 2, was measured by the electrometer and recorded by the "Electronik" potentiometer. When the voltage reading was at the lower end of a scale, e.g. at 11.2 millivolts,

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(39) Schlenk and Bergmann, Ann. 463, 156 (19).

(40) Palevsky, Swank, and Grenchik, Rev. Sci.,Inst. 18, 298 (1947).

which made accuracy difficult, but too high to be read on the next more sensitive scale, a suitable portion was balanced out by the Leeds and Northrup potentiometer and the remainder read on a more sensitive scale.

The voltage supply for the ionization chamber consisted of eleven 45 volt batteries arranged in series so that increments of 45 volts from 45 to 495 volts could be applied to the chamber. In each measurement saturation currents were obtained by increasing the voltage across the chamber until there was no change in the current with further increase in voltage.

Actual voltages measured by the electrometer give relative values for C^{14} activity which are self-consistent. In order to express these values in units of radioactivity, disintegrations per second or microcuries, two factors must be used: (1) the value of the resistance used, and (2) the factor for the conversion of ion-current to activity. Two different input resistors were used, one having a resistance of 1.092×10^9 ohms, as determined by the Instrument Division of Argonne National Laboratory, and the second having a resistance of 1.56×10^{10} ohms, as determined by comparison with the former by means of the electrometer. From the values of these resistances the ion-current from the chamber can be calculated, and the disintegration rate calculated using the factor 1.17×10^{-16} coulombs per C^{14} disintegration, which was determined by W. B. Leslie(41) for a chamber of identical dimensions filled with carbon dioxide at a pressure of one atmosphere. The results reported in microcuries, are estimated to have a relative accuracy of better than 2 per cent, but due to the uncertainty of the value of the resistors, which is 5 per cent, the absolute values are estimated to be correct to within 10 per cent.

Conversion of Samples to Carbon Dioxide for Radioactive Measurements

Carbon dioxide was obtained from solid samples by dry combustion with oxygen in a microcombustion tube containing copper oxide and heated to 700°. The excess oxygen and the carbon dioxide were condensed in an evacuated trap cooled at -195°, after removal of the water by passage through a trap at -80°. When the combustion was completed, the trap containing the oxygen and carbon dioxide was attached to a vacuum system and the oxygen removed by evacuation of the trap which was cooled to -195°. The carbon dioxide was determined manometrically and introduced into the ionization chamber, which was connected to the same vacuum system.

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(41) Leslie, W. B., private communication.

To obtain carbon dioxide from an aqueous solution of methanol and formaldehyde, the solution was oxidized with an excess of alkaline potassium permanganate and then acidified with dilute sulfuric acid. The carbon dioxide was carried from the solution by a stream of helium, which was passed through two traps, the first at -80° to remove the water and the second at -195° to condense the carbon dioxide. Carrier carbon dioxide, formed by the addition of sodium bicarbonate to the solution, was then flushed from the solution by the stream of helium and condensed in the trap at -195°. The C^{14} activity of the carbon dioxide was measured in the ionization chamber and the activity of the methanol could be calculated from the total by subtraction of the activity of the formaldehyde, which had been determined in a separate experiment.

Preparation of Methyl-C^{14} Triphenylmethyl Ether

Methanol-C^{14}, which had been assayed to contain approximately 11.5 microcuries per millimole, was obtained from Oak Ridge National Laboratory. A 0.224 millimole sample of methanol was introduced into an ionization chamber and the pressure brought to atmospheric by the addition of carbon dioxide. Ion-current measurement showed its activity to be 2.494 microcuries, or 11.13 microcuries per millimole. In a second determination, 0.441 millimoles of methanol was shown to contain 4.84 microcuries, or 11.0 microcuries per millimole.

A portion of this methanol, 0.2461 g (7.68 millimoles) was placed in a storage vessel on a vacuum system, from which it could be transferred to a reaction vessel. A 2.4746 g (7.68 millimoles) sample of triphenylmethylbromide, m.p. 151-152°, was dissolved in 15 ml of benzene in a 50 ml round-bottom flask, and 1.0 g of dry pyridine was added.(42) After solution had taken place, the flask was placed on the vacuum system, cooled to -195°, and evacuated. The methanol was transferred from the storage vessel to the reaction flask, which was then isolated from the vacuum line and the mixture was allowed to react at room temperature for one hour. The solution was agitated by a glass-covered magnetic stirring bar. After reaction the volatile substances were removed by distillation on the vacuum line; the reaction flask was taken from the vacuum line; and 10 ml of water and 10 ml of benzene were added to the mixture. Following thorough mixing the water layer was separated and the benzene solution extracted with an additional 5 ml of water. The benzene solution was filtered through an alumina adsorption column (1 cm in diameter and 30 cm in length).. An additional 25 ml of benzene was filtered through the column, followed by 25 ml of absolute alcohol. The benzene filtrate was collected in three successive fractions of 15, 10, and 10 ml which after evaporation of the benzene yielded 1.9225, 0.0087, and 0.0067 g of product,

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(42) Swain, J. Am. Chem. Soc. 70, 1126 (1948).

respectively. The material obtained from the first benzene fraction, 1.9225 g of methyl triphenylmethyl ether, m.p. 82-83°, represented a 91.3 per cent yield from methanol.

Combustion of a 0.0225 g sample of the ether yielded 1.66 millimoles of carbon dioxide containing 0.930 microcuries, or 11.20 microcuries per millimole of ether. A second sample, 0.0304 g, yielded 2.22 millimoles of carbon dioxide containing 1.235 microcuries, or 11.13 microcuries per millimole of ether.

The Thermal Decomposition of Methyl-C^{14} Triphenylmethyl Ether

Methyl-C^{14} triphenylmethyl ether was decomposed in the apparatus shown in Figure 3. The volatile products of the reaction were carried from the decomposition tube, A, by a stream of helium and the methanol and formaldehyde were absorbed in water in traps B and B′. Iodine pentoxide heated to 110-120° in trap D oxidized the carbon monoxide to carbon dioxide which was condensed in trap C′. Any combustible gases not condensable at -195° would be oxidized in the combustion tube containing copper oxide at 900°, and the resulting carbon dioxide condensed in trap C′′.

In the decomposition, 0.5482 g, 2.00 millimoles, of the active ether reported above was heated between 384 and 394° for eighty minutes and the system flushed with helium gas for an additional forty-five minutes. Trap D was found to contain 0.367 millimoles of carbon dioxide which represents an 18.35 per cent molar yield of carbon monoxide from the decomposition of the ether. This gas was found to have an activity of 3.98 microcuries, or 10.83 microcuries per millimole.

The combined aqueous solution from traps B and B′ was diluted to 100 ml and aliquots were analyzed. Two 10 ml aliquots yielded 0.0235 and 0.0232 g of methylene bis-methone respectively, which is equivalent to 0.80 millimoles of formaldehyde in the total volume, or a yield of 40 per cent. The C^{14} activity of the formaldehyde was determined from the carbon dioxide formed by the combustion of the methylene bis-methone formed. Two samples, 0.01285 and 0.0157 g, were found to contain 0.489 and 0.588 microcuries, respectively, or an activity of 11.0 microcuries per millimole of formaldehyde. Chemical analysis for methanol showed 0.708 millimoles, or a yield of 35.4 per cent. The C^{14} activity of the aqueous solution of formaldehyde and methanol was determined by the method described to be 16.75 microcuries, or an activity of 11.1 microcuries per millimole.

Of the residue which remained in the decomposition tube, 0.4858 g was removed by solution in benzene. The remainder, carbonaceous material which adhered to the tube, was removed by combustion, which was accomplished by heating the tube while a stream of oxygen was passed through it. The resulting carbon dioxide, 0.3075 millimoles, contained 0.026 microcuries of C^{14} activity. Combustion of 0.0169 g of the benzene soluble residue yielded 1.291 millimoles of carbon dioxide containing 0.027 microcuries, or an activity of 0.795 microcuries for the entire amount. Results of this experiment are summarized in Table IV.

Analysis of the Thermal Decomposition Residue for Methyl-C^{14} Triphenylmethyl Ether.

It was demonstrated that triphenylmethane and methyl triphenylmethyl ether could be separated by selective absorption on alumina. A mixture of 0.1293 g of the ether and 0.1592 g of triphenylmethane was dissolved in 10 ml of petroleum ether (60-90°) and the solution filtered through an alumina adsorption column (1 cm in diameter and 30 cm in length). Twenty ml of petroleum ether and 30 ml of benzene were then filtered through the column. It was found that three successive 10 ml fractions of petroleum ether had eluted 0.0190, 0.1363, and 0.0098 g of triphenylmethane, respectively, and that the three successive 10 ml fractions of benzene had eluted 0.042, 0.0621, and 0.0236 g of the ether, respectively.

The quantity of methyl-C^{14} triphenylmethyl ether remaining in the residue from the decomposition reported was measured by making use of the fact that it can be separated from triphenylmethane by selective adsorption, and the fact that inactive carrier ether can be added to make isolation and purification easier. A 0.465 g portion of the residue from the thermal decomposition was dissolved in 10 ml of petroleum ether and the solution filtered through the alumina adsorption column. Forty ml of petroleum ether was filtered through the column, followed by 40 ml of benzene and 20 ml of ethyl alcohol. The material eluted by the petroleum ether was inactive as shown by a preliminary count with a thin-window beta counter. The material which had been eluted by the benzene and alcohol, 0.2800 g, was shown to contain activity by a count with the same thin-window beta counter. To this 0.2800 g of eluent was added 0.100 g of pure inactive methyl triphenylmethyl ether and the mixture separated on the adsorption column. The mixture was dissolved in petroleum ether and filtered through the column. Additional petroleum ether filtered through the column until no more solid was eluted with the filtrate. Then a mixture of 20 per cent benzene in petroleum ether was filtered through the column which eluted 0.146 g of impure methyl triphenylmethyl ether, melting from 78-82°. This ether was recrystallized from methanol, since it was shown previously that the methoxy group of the ether does not exchange with hot methanol, and 0.078 g of ether, m.p. 82-83°, was obtained. This ether was found to contain 0.44 microcuries of C^{14} activity, or 1.08 microcuries per millimole. On the basis of the addition of 0.100 g of inactive ether and this measured activity, the residue contained 10.8 g of ether of the original activity, 2.0 per cent of the starting amount.

Abstract

Various methods of preparing formaldehyde-C^{14} were investigated. Since the primary source of C^{14} was carbon dioxide, various methods of converting it to formaldehyde were investigated. Later, when methanol-C^{14} became available, conversion of it to formaldehyde was investigated. The desirability of preparing anhydrous formaldehyde was considered important and the scale of the reaction was limited to the millimole range.

The direct reduction of carbon dioxide was carried out by adding, in ether solution, a stoichiometric amount of lithium aluminum hydride for reduction to formaldehyde to a solution of carbon dioxide in diethyl ether at -80 ; but a yield of only 25 per cent formaldehyde was obtained. The bromination of salicyl alcohol, which forms formaldehyde by elimination of the methoxyl, - CH_2OH, group suggests a method of converting carbon dioxide - C^{14} to formaldehyde - C^{14} , through carbonation of phenol to yield salicylic acid which would be subsequently reduced to salicyl alcohol. The bromination of salicyl alcohol at 40-50° resulted in the formation of 71 per cent formaldehyde, but it was obtained as an aqueous solution from which it would have to be isolated.

Triphenylmethyl carbinol is reported to decompose above its melting point, 109°, to yield formaldehyde and triphenylmethane. Triphenylmethyl carbinol-C^{14} , which would yield formaldehyde-C^{14} on decomposition, could be prepared by the carbonation of triphenylmethyl magnesium bromide or triphenylmethyl sodium with carbon dioxide-C^{14} , followed by reduction of the resulting triphenylacetic acid with lithium aluminum hydride. However, triphenylmethyl carbinol did not decompose to yield formaldehyde until heated above 375°. Consistent yields of only 45-50 per cent formaldehyde were obtained and the use of various substances which might act as catalysts for the decomposition did not increase the yields. There is evidence that dehydration of the carbinol is a competing reaction.

N-methylol derivatives are also reported to yield formaldehyde when heated. Two of these, N-methylolphthalimide and N-methylol-3, 6-dichlorocarbazole were found to yield 92 and 90 per cent formaldehyde from the methylol group respectively. Although this method is not useful for the preparation of formaldehyde-C^{14} unless a satisfactory method of synthesizing these compounds from available C^{14} compounds is devised, it is a very good method for the generation of anhydrous formaldehyde.

Methyl triphenylmethyl ether yields triphenylmethane, formaldehyde, methanol, and carbon monoxide on thermal decomposition. At optimum conditions, heating at 390-400° for at least 90 minutes, a 65-70 per cent yield of formaldehyde is obtained, which with the methanol and carbon monoxide formed accounts for 95 per cent of the original methoxyl group. The decomposition of two other ethers, methyl tribiphenylmethyl ether and 9, 10-dihydro-9, 10-dimethoxy-9, 10-diphenylanthracene was studied but the former yielded predominantly carbon monoxide and the latter methanol

rather than formaldehyde. Methyl-C^{14} triphenylmethyl ether was prepared from methanol-C^{14} and triphenylmethyl bromide in 91 per cent yield, based on methanol. The products from the thermal decomposition were quantitatively determined both chemically and radiochemically. The results agreed within the estimated accuracy of the methods, 2 per cent. Of the various methods of preparing anhydrous formaldehyde-C^{14} studied, the decomposition of methyl-C^{14} triphenylmethyl ether seems to be the most satisfactory.

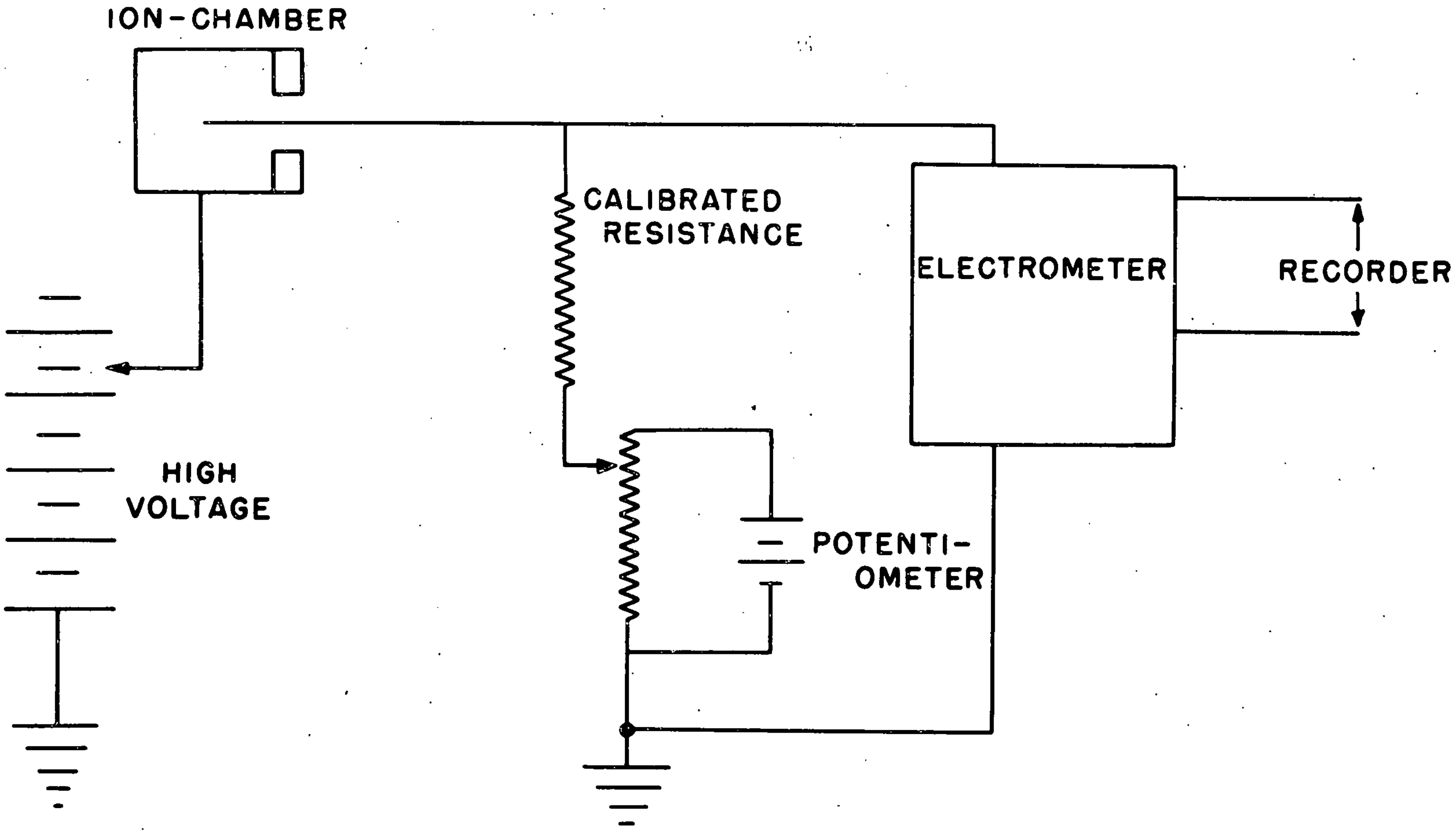

ION-CHAMBER
CALIBRATED RESISTANCE
ELECTROMETER
RECORDER
HIGH VOLTAGE
POTENTI-OMETER

FIGURE I.

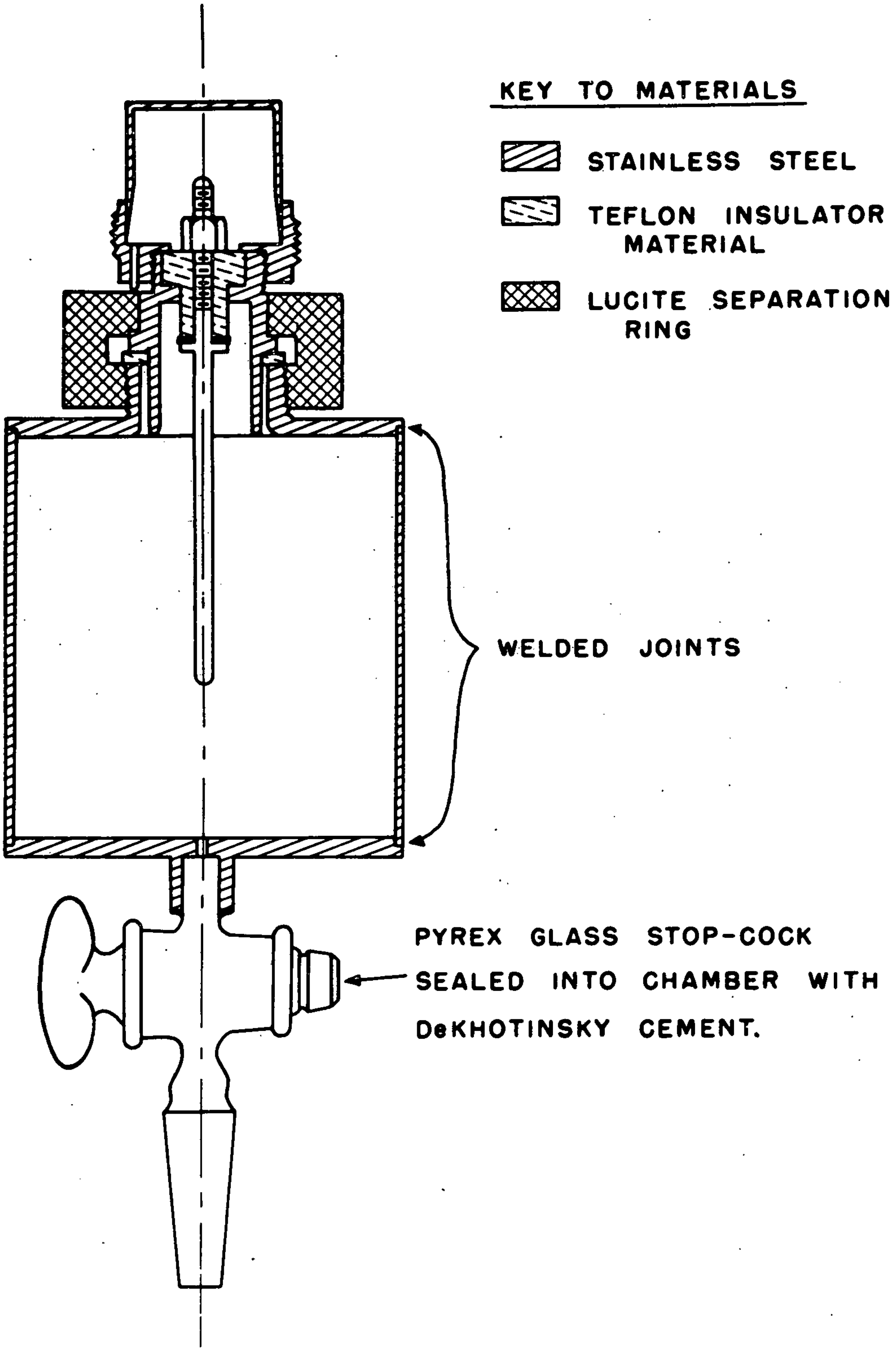
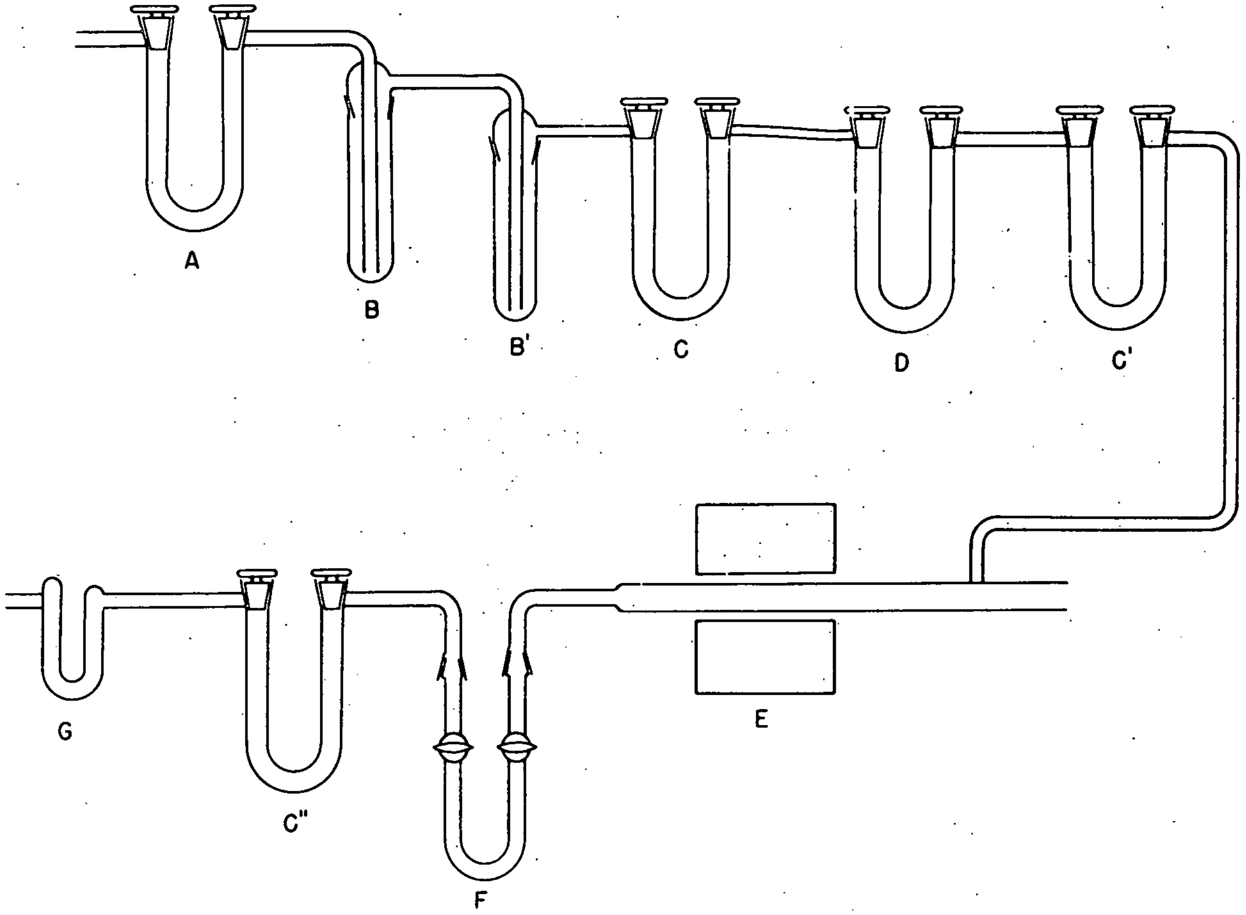


FIG. 2. CROSS-SECTIONAL DIAGRAM OF STAINLESS STEEL IONIZATION CHAMBER USED TO MEASURE CARBON-14 ACTIVITY.



A DECOMPOSITION TUBE, HEATED BY A SALT BATH.

B, B' TUBE EACH CONTAINING 10 cc. WATER, COOLED WITH ICE WATER.

C, C', C" TRAPS COOLED WITH LIQUID NITROGEN.

D TRAP CONTAINING IODINE PENTOXIDE HEATED AT 110-120 °C.

E QUARTZ TUBE HEATED AT 900 °C. CONTAINING COPPER OXIDE.

F TRAP COOLED WITH DRY ICE TRICHLOROETHYLENE.

G BUBBLER TUBE.

FIGURE 3.

1- 34