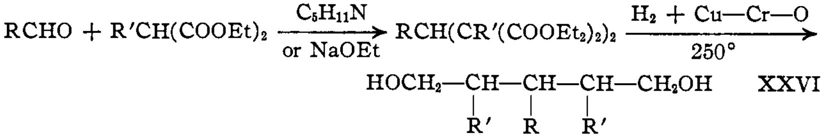

$$\mathrm{RCHO} + \mathrm{R'CH(COOEt)_2} \xrightarrow[\text{or NaOEt}]{C_5H_{11}N} \mathrm{RCH(CR'(COOEt_2)_2)_2} \xrightarrow[250^\circ]{H_2 + Cu—Cr—O} \mathrm{HOCH_2—\underset{R'}{CH}—\underset{R}{CH}—\underset{R'}{CH}—CH_2OH}$$

XXVIII

Summary[21]

A number of ethyl esters of dibasic acids containing four or more carbons, variously substituted, have been subjected to the action of hydrogen at 100 to 300 atmospheres at 250° over copper–chromium oxide. The isolation of the major products from these reactions has led to certain conclusions with regard to the relation of structure to susceptibility to cleavage of C to C and C to O linkages, and with regard to feasible methods for preparing various glycols and alcohols.

[21] I wish to record here my indebtedness to Charles Sumner Slichter who, as Dean of the Graduate School and Chairman of the University Research Committee, has for thirteen years unwaveringly supported me through the allotment of funds for the purchase of important apparatus and for the employment at various times of B. H. Nissen, W. A. Lazier, A. E. Broderick, Howard Cramer, Karl Folkers, Ralph Connor and Bruno Wojcik as research assistants.

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The Rates of the Thermal Decomposition of Certain Triphenylmethyl Alkyl Ethers[1]

BY JAMES F. NORRIS AND ARTHUR CRESSWELL

It has been shown[2] that ethers of the type $(C_6H_5)_3C—O—R$, in which R represents an alkyl radical, decompose under the influence of heat into triphenylmethane and a product formed from the alkoxyl group as the result of the loss of one hydrogen atom; in the case of the ethyl ether acetaldehyde is formed. The temperature at which pyrolysis begins to be evident is definite when an ether of this type is heated in such a way that the temperature is raised at a fixed rate. Under the same conditions the several ethers decompose at different temperatures.

Since pyrolysis takes place in a relatively simple way and the primary products are stable under the conditions used, it seemed probable that the study of the rates at which typical ethers of this structure undergo pyrolysis would yield information of value. The methyl, ethyl and isopropyl ethers derived from triphenylcarbinol were studied with the expectation that something would be learned in regard to the order of the decompositions, their temperature coefficients and the effect on the rate of the tem-

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[1] From a part of the thesis presented by Arthur Cresswell in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1932.

[2] Norris and Young, THIS JOURNAL, **52**, 753 (1930).

perature interval between the temperature at which pyrolysis begins and that at which the pyrolysis is effected.

It was found in the case of the ethyl ether that up to about 11% decomposition the velocity constant was of the first order—at 259° $K = 0.010$, at 269° $K = 0.021$. The rate of decomposition doubled approximately for a rise of 10°. Beyond this point the calculated velocity constant increased with the time.

The isopropyl ether showed the characteristics of a monomolecular reaction up to about 28% decomposition. The first order velocity constants were as follows: at 259° 0.016, at 270° 0.032, at 289° 0.080.

At 259° the first order constant for the ethyl ether was 0.010 and for isopropyl ether 0.014. This temperature is 17° above the cracking temperature[3] of the ethyl ether (242°) and 39° above that of the isopropyl ether (220°). At 270, 28 and 50 degrees, respectively, above the cracking temperatures, the constants were 0.021 and 0.028. It appears that the rates of decomposition of the two similar ethers are approximately equal at the same temperatures, although these temperatures bear a different relationship to the cracking temperatures of the two compounds.

At 270° the rates of pyrolysis increased with time after the ether had been heated for five hours. Since the increase in rate with time at a constant temperature was particularly marked in the case of the methyl ether, which showed this behavior at the lower temperatures, this ether was studied more fully in order to discover the cause of this behavior.

The rates of decomposition of the methyl ether (cracking temperature 262°) were determined at 268, 277, 280 and 298°. In all cases the rate increased with time.

Large scale complete decompositions of the methyl and the ethyl ethers were made to determine the products of decomposition so that the effect of the latter on the rate could be investigated. Previous work had shown that the chief products of the decomposition of all the ethers of this type are triphenylmethane and an aldehyde when the radical is a primary one and a ketone when it is secondary.

The ethyl ether yielded the expected products and a small amount of carbon monoxide, which indicated that about 4% of the ester had decomposed in a way to give this gas. The methyl ether gave carbon monoxide and methyl alcohol in addition to triphenylmethane and formaldehyde. It appears from these results that the methoxyl group can yield products which result from at least two modes of decomposition

$$CH_3O\text{—} = CH_2O + (H)$$
$$2CH_3O\text{—} = CH_3OH + CO + 2(H)$$

The hydrogen atoms are used up in the formation of triphenylmethane.

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(3) The cracking temperatures given are the temperatures at which the ethers first show signs of decomposition when the temperatures at which they are heated are raised at the rate of one degree per minute.

About 40% of the methyl ether produced in its decomposition methyl alcohol and carbon monoxide. This difference between methyl and ethyl ethers is shown in the case of other compounds which are not being studied.

In order to determine whether the products of the pyrolysis of the methyl ether had an effect on the rate of its decomposition the rates were determined in the presence of triphenylmethane, methyl alcohol and formaldehyde. When a mixture of the ether and hydrocarbon in the molecular ratio of 2 of the former to 1 of the latter was pyrolyzed at 268° the decomposition at the end of two hours was twice that of the ether alone; at the end of five hours 1.3 times as great. At 280° at the end of two hours the rate was 3.6 and of five hours 2.2 times as great. The greater effect at the beginning of the decomposition is what would be expected. In the presence of methyl alcohol the pyrolysis was slightly retarded. With formaldehyde the results were not conclusive.

The Effect of the Presence of Oxygen on the Rate of Pyrolysis.—All the results stated above were obtained when the ethers were pyrolyzed in the presence of a small volume of air. The tubes used were of such a size that the volume of the air present was approximately 5 cc. In order to determine whether the oxygen present affected the rate of cracking, parallel experiments were carried out with the methyl ether at the same time in the presence of and in the absence of air. In the latter case the tubes containing the ether were evacuated and filled with nitrogen three times before being sealed. In two experiments at 268° in the presence of air the percentage decomposition at the end of six hours was 12.66 and 12.78; in the presence of nitrogen the percentages were 1.83 and 1.83. The difference found must be due to the catalytic influence of oxygen since the weight of the gas present could produce an almost negligible effect if ordinary oxidation were involved. These results led to a further study in this Laboratory of the effect of the presence of traces of oxygen on rates of pyrolysis and cracking temperatures. This work will be reported later. It has been shown in the case of ethers derived from diphenylcarbinol that the cracking temperatures and rates of decomposition are markedly affected.

Experimental Details

Compounds Used.—The ethers were made by the method of Norris and Young.[2] It was found that triphenylmethyl methyl ether could be distilled without decomposition under diminished pressure; it boiled at 163° (2 mm.), 183° (4 mm.) and 195° (5 mm.). The ether, after crystallization, melted at 82.6–82.9° as reported in the earlier work in which the ether was not distilled. A large sample of the ether, which had this melting point and was prepared in the spring, was found to melt at 95.5–96° in the following autumn. All samples subsequently prepared in the same way melted at the higher point. This behavior of the ether will be further studied. The ethyl and the isopropyl ethers did not show a similar change in melting point. The samples used melted at 81.2–81.8, and 111°, respectively.

Experimental Method.—In determining the rates of pyrolysis, accurately weighed samples of the ether (approximately 0.5 g.) were placed in tubes of glass (internal diameter 10 mm., length 120 mm., drawn out tip 20 mm.) which were sealed. A number of tubes were placed in a thermostat which was electrically heated and controlled, contained a fan, and held the temperature constant with a maximum variation of 0.5°. The tubes were removed at intervals of one hour and examined. A small flame was held in contact with the tip until a small hole was formed. The tube was connected with a vacuum pump, rotated, heated to 100°, cooled and weighed. This procedure was repeated until the weight became constant. Two blank determinations were made in a similar way with tubes which contained triphenylmethane only. The change in weight was not greater than 0.2 mg.

Rates of Pyrolysis.—It will be seen from the table that the calculated first order velocity constants for the methyl ether increase with time. In the cases of the other ethers the increase is noticeable at the higher percentage decompositions.

RATES OF PYROLYSIS OF TRIPHENYLMETHYL ALKYL ETHERS

Methyl Ether

Time, hours	% decomp. at 268°	First order vel. const.	% decomp. at 277°	First order vel. const.	% decomp. at 280°	First order vel. const.	% decomp. at 298°	First order vel. const.
2	1.1	0.005	1.8	0.009	2.9	0.005	3.8	0.019
3	..	...	4.0	.014	6.2	.021	10.9	.038
3.4	3.8	.011	..	...	..	...	..	...
4	..	...	7.7	.020	11.1	.030	29.7	.088
4.1	4.9	.012	..	...	..	...	..	...
5	6.6	.014	10.1	.021	16.5	.037	43.1	.11
6	11.3	.020	15.5	.022	23.9	.047	..	...

Ethyl Ether

Time, hours	% decomp. at 259°	First order vel. const.	% decomp. at 269°	First order vel. const.	% decomp. at 270°	First order vel. const.
2	2.3	0.010	4.1	0.021	4.1	0.021
3	3.0	.010	7.6	.025	6.1	.021
4	3.9	.010	8.4	.021	7.2	.018
5	..	...	10.3	.021	9.2	.018
6	..	...	11.1	.019	13.6	.023
	Average	.010		.021		.020

Isopropyl Ether

Time, hours	% decomp. at 259°	First order vel. const.	% decomp. at 270°	First order vel. const.	% decomp. at 289°	First order vel. const.
1	1.8	0.018	2.9	0.029	6.3	0.065
2	2.7	.014	6.4	.033	14.8	.080
3	..	...	5.7	.020	23.7	.090
3.25	5.0	.016	..	...	..	...
4	5.3	.014	..	...	27.5	.080
4.1	..	...	11.7	.030	..	...
5	7.2	.015	14.7	.031	38.1	.093
6	9.2	.016	..	...	..	...
6.4	..	...	22.4	.040	..	...
	Average	.016		.032		.080

Complete Pyrolysis of Triphenylmethyl Methyl and Triphenylmethyl Ethyl Ethers.—A sample of the methyl ether (25.24 g.) was heated at 280–300° in an apparatus designed to collect and measure the gaseous and liquid products of the decomposition. The rate of decomposition increased to a maximum between the 88th and 137th hours, decreased, and was complete in 240 hours. There was obtained 1.6 g. of a liquid boiling at 64–65° which was identified as methyl alcohol by the melting point of the *p*-nitrobenzoate prepared from it (95°). A mixed melting point confirmed the conclusion. The gas measured 934 cc. (24° and 761 mm.) and was shown by analysis to contain 87.2% of carbon monoxide; the remaining gas which was not combustible and which contained only a trace of carbon monoxide was evidently the nitrogen present in the apparatus. The residue, of a brown color, was shown to be triphenylmethane and a trace of a colored substance. From 0.0925 mole of ether were obtained 0.0329 mole of carbon monoxide and 0.0399 mole of methyl alcohol; 36% of the ether yielded these products and triphenylmethane and the rest formaldehyde and the hydrocarbon. Fifteen grams of the ethyl ether was pyrolyzed under the same conditions. The carbon monoxide formed measured 50 cc., which corresponds to a decomposition of about 4% to produce this gas.

Effect of the Products of Decomposition on the Rate of Pyrolysis.—Since the increase in the rate of pyrolysis with time was most marked in the case of the methyl ether, the influence of the presence of triphenylmethane on the rate was studied with this compound. A mixture of the ether and the hydrocarbon in the molecular ratio of 2:1 was melted and stirred to ensure homogeneity. After solidification weighed portions were heated and analyzed in the manner described above. The results were as follows: at 269° the ratios between the percentage decomposition in the presence and in the absence of the hydrocarbon were at the end of two hours 2.0, four hours 1.5 and five hours 1.3. At 280° the ratios after the same time intervals were 3.6, 2.5, and 2.3, respectively. The results show that the presence of the chief product of the pyrolysis markedly accelerates the rate of pyrolysis and are consistent with the fact that when the ether alone is used the rate of decomposition increases with time.

Similar experiments were made in which methyl alcohol and formaldehyde were added to the ether before pyrolysis. In the case of the former there appeared to be a slight retarding effect, but the results were such that a definite statement is not warranted. When formaldehyde was used the results were not conclusive.

Effect of Air and Oxygen on the Rate of Pyrolysis.—All the experiments recorded above were carried out in sealed tubes which contained in addition to the ethers approximately 5 cc. of air. Determinations of rates were made simultaneously with tubes that contained air and others that were evacuated and filled with nitrogen three times before sealing. In the case of the methyl ether at 268° the percentage decomposition in the presence of air at the end of three hours was 6.3 times that in the presence of nitrogen only; at the end of six hours it was 7.0 times as great. The amount of oxygen in the tubes containing air was so small that if it brought about oxidation to carbon dioxide the loss of weight resulting would be equivalent to 0.9%; if a volatile or non-volatile substance were formed the change in weight would be correspondingly small. At the end of six hours in the presence of air 12.7% of the ether had decomposed. The effect of oxygen is apparently catalytic and probably takes place through the intermediate formation of a peroxide.

To gain further information in regard to the influence of oxygen on pyrolysis the methyl ether was heated in tubes which were exhausted and filled with oxygen three times. The pyrolysis was carried out at 263°, which is one degree above the temperature at which the ether first shows signs of decomposition when it is heated in such a way that the temperature rises at the rate of one degree per minute. Control experiments were carried out at the same time with tubes filled with nitrogen. At the end of two, four and five hours the ratios of the percentage decomposition in the presence of oxygen and of air were 3.2, 4.4 and 2.8, respectively. The percentage decomposition in the presence of oxygen at the end of five hours was 32.5.

Summary

1. The rates of pyrolysis of the methyl, ethyl, and isopropyl ethers derived from triphenylcarbinol have been determined at several temperatures.

2. The ethyl ether at the lower temperatures and up to about 11% decomposition showed the characteristics of a reaction of the first order and the rate doubled for a rise of 10 degrees. Similar results were obtained with isopropyl ether up to about 28% decomposition.

3. The calculated first order velocity constants in the case of the methyl ether increased rapidly with time. It was shown that triphenylmethane, a product of the decomposition, had a marked accelerating effect on the decomposition.

4. The presence of a small amount of air increased greatly the rate of pyrolysis.

CAMBRIDGE, MASSACHUSETTS

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Basis for the Physiological Activity of Onium Compounds. XV. Sulfonium Compounds[1,2]

BY R. R. RENSHAW AND D. S. SEARLE

In earlier work[3] it was found that one of the derivatives of the sulfur analog of choline (acetylthioformocholine) produced a very marked lowering of the blood pressure (muscarine action) and that this action was not complicated, as is the case with most of the choline derivatives, by the evidence of any stimulating nicotine action. The need of an effective product having this type of action is considerable in therapeutics. The authors, in coöperation with Reid Hunt, have, therefore, undertaken to investigate a number of sulfonium derivatives.

The successful preparation of sulfonium compounds by the direct addition of a halide to a sulfide is in general restricted to the relatively simple compounds. One difficulty, as has been pointed out in an earlier paper,[4] is the tendency of the unsymmetrical sulfonium structures to dissociate in two or more ways and of the products then to recombine to produce a mixture difficult or impossible to separate. Often, too, the dissociation is

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(1) This problem is being carried out in coöperation with Dr. Reid Hunt of the Harvard Medical School. The physiological data are the basis of another series of papers published elsewhere by him.

(2) This is the first paper from a thesis presented by D. S. Searle, June, 1930, for the degree of Doctor of Philosophy at New York University.

(3) Hunt and Renshaw, *J. Pharm. Exptl. Therap.*, **25**, 315 (1925).

(4) Renshaw, Bacon and Roblyer, THIS JOURNAL, **48**, 517 (1926).