ysis mixture was diluted with an equal volume of water, decolorized with carbon and acidified. The precipitate which appeared was removed from the hot solution by filtration and the filtrate on being cooled deposited 0.14 g. of tan solid which after three crystallizations from glacial acetic acid yielded yellowish-white crystals of m. p. 215–217° taken alone or mixed with the oxidation product (III) of 1-*p*-nitrophenyl-3-acetyl-5-methylpyrazole (II).

(b) **By Hydrolysis of Ethyl 1-*p*-Nitrophenyl-5-methyl-3-pyrazolecarboxylate** (V).—Five-tenths of a gram of the ester (V) was heated on the steam-bath with a mixture of 1 ml. of concentrated hydrochloric acid and 3 ml. of glacial acetic acid for four hours. The hydrolysis mixture was cooled, the solid which crystallized therefrom was separated and crystallized three times from aqueous alcohol to yield 0.15 g. of pure-white, crystalline 1-*p*-nitrophenyl-5-methyl-3-pyrazolecarboxylic acid of m. p. 216.5–217.5° taken alone or mixed with III.

Anal. Found: C, 53.5; H, 4.14.

(c) **By Hydrolysis of Ethyl 2-Acetyl-2-*p*-nitrophenylazolevulinate** (IV).—To one gram of the dye IV in 20 ml. alcohol and 5 ml. water at the boiling point was added 0.4 g. of potassium hydroxide in 5 ml. of water. After three hours of heating, the dark reaction mixture was acidified, and on being cooled the acidic solution deposited a gelatinous yellowish precipitate that was separated and treated with warm dilute solution bicarbonate solution. The cloudy bicarbonate solution was filtered and acidified to yield a yellowish-white precipitate that gave after separation and three crystallizations from glacial acetic acid 0.10 g. of 1-*p*-nitro-phenyl-5-methyl-3-pyrazole carboxylic acid in the form of white needles of m. p. 215.5–216.5° taken alone or mixed with III.

Summary

The furan nucleus of 2, 5-dimethylfuran on reaction with *p*-nitrobenzenediazonium chloride followed by acid hydrolysis of an initial, unstable coupling product is cleaved with the formation of 1-*p*-nitrophenyl-3-acetyl-5-methylpyrazole.

RECEIVED AUGUST 25, 1947

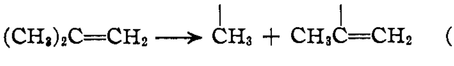
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE CATHOLIC UNIVERSITY OF AMERICA]

The Thermal Decomposition of Mono-olefins: Isobutylene

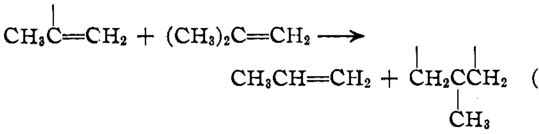
BY FRANCIS OWEN RICE AND W. STUART HAYNES[1]

The mechanism of the thermal decomposition of paraffin hydrocarbons from the free radical standpoint[2] has already been studied in considerable detail and appears to give a satisfactory interpretation of the complicated chemical changes that occur in the pyrolysis of saturated, open chain hydrocarbons. Even when this picture is applied to the decomposition of paraffins as high as the octanes, the amounts of products calculated are in reasonable agreement[3] both qualitatively and quantitatively with the amounts found experimentally.

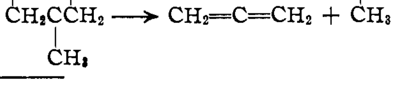
In contrast with the decomposition of paraffin hydrocarbons, the mechanism of olefin decompositions is not well understood in spite of a considerable amount of study. This is surprising because the predictions made on the basis of the free radical theory proposed by Rice[2] are rather straightforward and are shown for example in the case of isobutylene by the equations



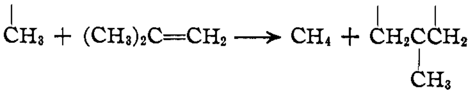
$$(CH_3)_2C{=}CH_2 \longrightarrow \overset{|}{C}H_3 + CH_3\overset{|}{C}{=}CH_2 \qquad (1)$$



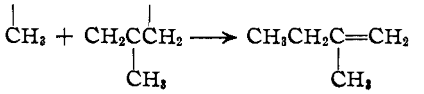
$$CH_3\overset{|}{C}{=}CH_2 + (CH_3)_2C{=}CH_2 \longrightarrow CH_3CH{=}CH_2 + \overset{|}{C}H_2\underset{\underset{CH_3}{|}}{\overset{|}{C}}H_2 \qquad (2)$$



$$\overset{|}{C}H_2\underset{\underset{CH_3}{|}}{\overset{|}{C}}H_2 \longrightarrow CH_2{=}C{=}CH_2 + \overset{|}{C}H_3 \qquad (3)$$



$$\overset{|}{C}H_3 + (CH_3)_2C{=}CH_2 \longrightarrow CH_4 + \overset{|}{C}H_2\underset{\underset{CH_3}{|}}{\overset{|}{C}}H_2 \qquad (4)$$



$$\overset{|}{C}H_3 + \overset{|}{C}H_2\underset{\underset{CH_3}{|}}{C}H_2 \longrightarrow CH_3CH_2\underset{\underset{CH_3}{|}}{C}{=}CH_2 \qquad (5)$$

The initial step produces radicals and the final step removes them. Reactions (3) and (4) constitute the chain which yields equal molecular quantities of methane and allene. If the chain is fairly long (50 or more chain cycles), we would expect methane and allene to be the predominant products and to be accompanied by only negligible amounts of other compounds. If, however, the chain is short and consists of only a few cycles, the amount of propylene, methane and other molecules resulting from the non-chain radical reactions would be increased. There are several other non-chain radical reactions that can be written but we have omitted them since they should produce only a small proportion of the decomposition products.

The pyrolysis of isobutylene has been the subject of a number of investigations.[4] Methane, hydrogen, ethylene and propylene were found to constitute the bulk of the gaseous products. Although the conditions were varied widely, allene was found to be completely absent or, at most, present in traces. In all cases the decomposition was accompanied by considerable quantities of oily and tarry material, containing benzene and

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[1] This is taken from the dissertation presented by W. Stuart Haynes for the degree of Doctor of Philosophy in The Catholic University of America.

[2] F. O. Rice and K. K. Rice, "The Aliphatic Free Radicals," The John Hopkins Press, Baltimore, Md., 1935.

[3] A. Kossiakoff and F. O. Rice, THIS JOURNAL, **65**, 590 (1943).

[4] (a) Hurd and Spence, *ibid*, **51**, 3561 (1929); (b) Hurd and Eilers, *Ind. Eng. Chem.*, **26**, 776 (1934); (c) Tropsch, Parrish and Egloff, *ibid.*, **28**, 581 (1936); (d) Hurd and Blunck, THIS JOURNAL, **59**, 1869 (1937).

its homologs and various polynuclear aromatic ring systems.

In view of this last observation we decided to undertake a new investigation of the isobutylene decomposition with the hope of finding conditions for avoiding the formation of tar and oil. These can only have resulted from successive reactions involving the first products of the decomposition and if we are to understand the mechanism we must be able to identify the primary products of the decomposition before they react further, either with themselves or with the substrate to produce finally tars and oils.

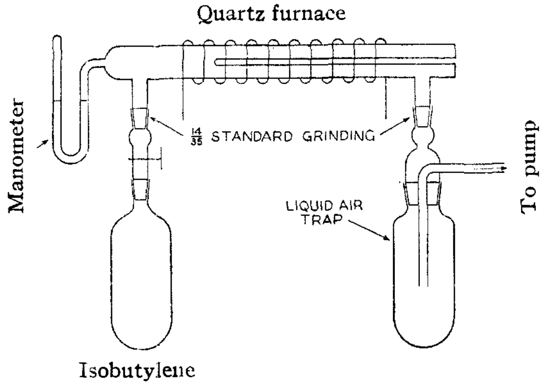

Fig. 1.—Thermal decomposition of isobutylene.

A flow system was used in which the isobutylene was passed through a quartz furnace 8″ × 1″, as shown in Fig. 1. The gases leaving the furnace were passed through two liquid air traps and the non-condensable portion was pumped out through a glycerol pump and collected over a solution of zinc sulfate.

The gases condensed in the traps, consisting of C_1 to C_4 hydrocarbons, were distilled at low temperature in a Podbielniak column and separated into different fractions. Three of our fractions boiled within ±0.3° of the boiling points of methylacetylene, allene and propylene which are reported respectively as −23.3°, −34.3° and −47.7° at 760 mm. pressure. We obtained in this way a fairly good analysis of the condensable products, but in each case the fraction was analyzed in a Shepherd type gas analysis apparatus.[5] The gases not condensed by liquid air were also measured and analyzed.

The identification of the C_3 hydrocarbons was accomplished by hydrogenating a portion of each fraction in the gas analysis apparatus over a nickel catalyst. The lowest boiling fraction (propylene) had one double bond whereas both the other fractions proved to be hydrocarbons having either one triple bond or two double bonds. Additional evidence was obtained by showing that the methylacetylene fraction gave an immediate and copious precipitate with an aqueous solution of ammoniacal silver nitrate. On the other hand, the allene fraction gave a white precipitate with an aqueous solution of mercuric chloride but no precipitate with the ammoniacal silver nitrate solution.

In the series of experiments reported in this paper, the conditions were such that there was practically complete absence of tar or carbon throughout the course of a run. This was accomplished by adjusting the temperature, pressure and contact time to values at which there was no formation of carbonaceous material on the glass walls at the outlet of the furnace. In experimental runs 2, 3, 9 and 10, evidence of some tar formation was noticed, the greatest amounts relative to the quantity of isobutylene used appearing in runs 2 and 10. One observes that in these runs occur the highest temperatures, the greatest contact times, or the highest pressures. Thus by fixing two of these variables and increasing the third, one would get a critical value for each at which incipient tar formation occurs, followed by abundant tar formation for higher values of this variable. The three variables would obviously be interdependent with respect to the conditions under which tar formation will occur.

Table I contains a summary of all the results on the isobutylene decomposition. Figure 2 shows the relation between the pressure and the yield of the various hydrocarbon products. From these results it appears likely that isobutylene decomposes through a free radical mechanism but the chain is rather short since there are appreciable quantities of propylene formed, presumably by some non-chain reaction such as reaction (2). We would not be able to detect the presence of

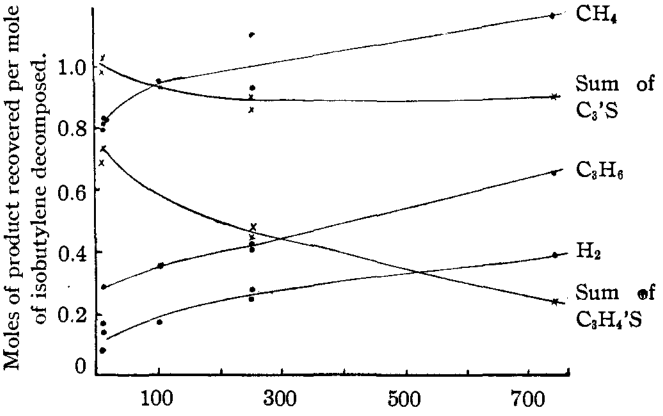

Fig. 2.—Curves showing the relation between the pressure in the furnace and the moles of different products recovered per mole of isobutylene decomposed. Experiments 2 and 3 have been omitted because of the large fraction of isobutylene decomposed and experiment 6 has been omitted because of loss of material.

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(5) Shepherd, *J. Research Nat. Bur. Standards*, **6**, 121 (1931).

TABLE I

DECOMPOSITION OF ISOBUTYLENE

The last ten rows of figures contain the number of moles of the respective substance recovered per mole of isobutylene decomposed. In Experiment 6 the furnace broke near the end of the run and some material was lost.

Expt.	1	2	3	4	5	6	7	8	9	10
Moles C_4H_8 through furnace	1.21	0.354	0.69	2.89	3.38	2.88	2.98	2.76	1.76	1.30
Per cent. decomposed	2.6	49.5	43.9	7.8	5.6	7.1	5.7	3.6	9.8	5.5
Temp. furnace, °C.	885	945	897	790	790	717	773	714	753	630
Press. in furnace, mm.	8	10	12	8	9	20	100	250	250	743
Contact time, sec.	0.07	0.56	0.29	0.026	0.301	0.053	0.46	0.43	0.42	2.1
H_2	0.17	0.61	0.23	0.08	0.14	0.11	0.17	0.25	0.28	0.39
CH_4	0.81	1.58	0.94	0.73	0.83	0.61	0.95	1.10	0.93	1.16
C_2H_6	0.02	0.00	0.01	0.05	0.03	0.01	0.02		0.03	0.06
C_2H_4	0.07	0.29	0.11	0.05	0.03	0.02	0.04	0.025[a]	0.125	0.27
C_2H_2	0.01	0.19	0.05	0.03	0.02	0.02	0.01		0.01	0.02
C_3H_6	0.20	0.25	0.20	0.29	0.29	0.11	0.35	0.42	0.41	0.66
$CH_2{=}C{=}CH_2$	..	0.07	0.05	0.37	0.49	0.25	0.21	0.23	0.21	0.14
$CH_3C{\equiv}CH$	..	0.36	0.20	0.325	0.25	0.23	0.38	0.26	0.24	0.10
ΣC_3H_4	0.80	0.43	0.25	0.695	0.74		0.59	0.49	0.45	0.24
ΣC_3's	1.00	0.68	0.45	0.985	1.03		0.94	0.91	0.86	0.90

[a] This is the sum of C_2H_6, C_2H_4 and C_2H_2.

pentenes because they would be present in only small quantity and since they boil at a higher temperature than isobutylene, they would be reported as this substance.

We are inclined to think that the methylacetylene is formed from allene by means of a radical chain. A free methyl radical, for example, reacting either with methylacetylene or allene would, in each case, give the same radical $\overset{|}{C}H_2{-}\overset{|}{C}{=}\overset{|}{C}H$. When this radical removes a hydrogen atom from an organic molecule, methylacetylene is formed, if a hydrogen atom attaches itself to the left-hand side of the molecule and allene is formed if a hydrogen atom is attached to the right-hand side of the molecule. We plan to investigate this point in a later paper.

Summary

1. The thermal decomposition of isobutylene probably proceeds through a short chain, producing methane and allene.

2. Under proper conditions of temperature, pressure and contact time, the decomposition of isobutylene occurs without appreciable production of carbonaceous and tarry material.

3. Both allene and methylacetylene are major products of the reaction. It has not yet been determined whether the methylacetylene is produced by isomerization of allene or by molecular dehydrogenation of the isobutylene.

4. Under best conditions there were about 60 moles per cent. yields of allene–methylacetylene based on the decomposed isobutylene.

WASHINGTON, D. C. RECEIVED JULY 25, 1947

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Apparent Molal Expansibilities of Potassium, Barium and Lanthanum Chlorides as a Function of Concentration and Temperature[1]

BY GRINNELL JONES,[2] E. FOLGER TAYLOR[3] AND RICHARD C. VOGEL[4]

The apparent molal thermal expansibility of a solute may be defined by the equations

$$\phi \bar{E}_2 = V_s\alpha_s - V_w\alpha_w = \left(\frac{\partial \phi V_2}{\partial T}\right)_P \qquad (1)$$

where V_s is the volume of solution containing one mole of solute, V_w is the volume of water used, α_s and α_w are the thermal coefficients of expansion of the solution and water, respectively, and ϕV_2 is the apparent molal volume of the solute.

Gucker[5] has obtained the limiting law for the partial molal expansibility, $\bar{E}_2$ of the solute as a function of the concentration from the Debye–Hückel theory, when $\bar{E}_2$ is defined by the equation

$$\bar{E}_2 = (\partial \bar{V}_2/\partial T)_P \qquad (2)$$

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(1) This paper represents part of the thesis material submitted by E. Folger Taylor and by R. C. Vogel in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Harvard University, Cambridge, Massachusetts.

(2) Deceased, June 23, 1947.

(3) Present address: Du Pont Company, Waynesboro, Virginia. E. Folger Taylor is responsible for the development of the mercury dilatometer described in this paper and for the studies carried out on water and on solutions of potassium chloride from 20 to 80°.

(4) Present address· Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois. R. C. Vogel was the grateful holder of an Allied Chemical and Dye Corporation Fellowship. He conducted experiments on water and solutions of barium chloride and lanthanum chloride from 20° to 60°.

(5) F. T. Gucker, Jr., THIS JOURNAL, 56, 1017 (1934).