cc. of trimethylethylene, 150 cc. of reagent alcohol, 0.1 g. of iron-containing catalyst, rate of shaking 300 per minute, initial gage pressure of hydrogen 39–40 lb. per sq. in.

In one experiment in which ferrous sulfate was added to an iron-free catalyst so that the time was extended to thirty-three minutes, the plot of hydrogen pressure against time was not linear except perhaps during the first minute.

The addition of two drops of C. P. concd. hydrochloric acid when using an iron-free catalyst made no difference in the activity, the data without the addition of acid being: 93% in seven minutes, linear rate 430 cc. of hydrogen per minute: with acid, 93% in eight minutes, linear rate 430 cc. of hydrogen per minute.

In the experiments with anethol the material was distilled under 2 mm. vacuum and it boiled at 79.5–80.5°; 15 cc. of this was taken, 0.05 g. iron-free catalyst, 150 cc. reagent alcohol, 8 drops of 2 *N* ferrous sulfate solution, 300 shakes per minute. The time for 92% reduction was forty-one minutes, whereas when 3 drops of glacial acetic acid were added, the time was reduced to twenty-six minutes for the same reduction.

Summary

1. It has been shown that the acid oxidation products of olefins are the impurities which offset the poisoning effect of iron on platinum catalysts used in the reduction of these olefins.

2. Benzoyl, furoyl, succinyl peroxides and benzoic, furoic, succinic, acetic, hydrochloric acids in small amounts offset this poisoning effect of iron.

3. A mechanism to explain this effect of small amounts of acids is suggested.

CAMBRIDGE, MASS. RECEIVED OCTOBER 10, 1934

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY]

The Thermal Decomposition of Organic Compounds from the Standpoint of Free Radicals. XII. The Decomposition of Methane

BY F. O. RICE AND M. DENISE DOOLEY

Recently Kassel[1] has studied the thermal decomposition of methane and has concluded that the primary step is probably represented by the equation $CH_4 \longrightarrow H_2 + CH_2$ followed by the reaction[2] $CH_2 + CH_4 \longrightarrow C_2H_6$. Furthermore, Belchetz[3] has attempted to obtain a direct experimental proof of the first step of this proposed mechanism by passing methane in a rapid stream at low pressures over a platinum filament heated in the range 877–1027°; after leaving the filament the methane and any fragments which had been formed were passed over a tellurium mirror and through a liquid air trap, the contents of which were analyzed. Similar experiments were performed using mirrors of iodine. As a result of this work Belchetz concluded that the methylene radical was formed in the decomposition of methane and that it could be identified by its products of combination with the mirrors.

These experiments, however, are not in agreement with the results obtained when diazomethane is decomposed[4] and the fragments are passed over a tellurium mirror; the compound formed by the combination of the methylene radicals thus produced with tellurium has been shown to be a polymer of telluroformaldehyde, $(HCHTe)_n$, which is so involatile that it does not pass into the liquid air trap but deposits on the walls of the tube just beyond the tellurium mirror as a red solid. We decided therefore to investigate the products formed when methane was decomposed in a quartz furnace at low pressures according to a technique previously described.[5] When the gases leaving the furnace were passed over a tellurium mirror we obtained no trace of any telluroformaldehyde on the walls of the tube; instead we obtained a red solid in the liquid air trap; this substance melted sharply at −19.5°, showing it to be dimethyl ditelluride $CH_3TeTeCH_3$. The same results were obtained when the experiment was repeated with pieces of platinum foil in the furnace. In none of the experiments did we obtain any indication of the presence of methylene radicals.

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[1] Kassel, THIS JOURNAL, **54**, 3949 (1932).

[2] The ethane thus formed undergoes dehydrogenation to yield ethylene, acetylene and finally carbon.

[3] Belchetz, *Trans. Faraday Soc.*, **34**, 170 (1934).

[4] Rice and Glasebrook, THIS JOURNAL, **56**, 2381 (1934).

[5] Rice, Johnston and Evering, *ibid.*, **54**, 3259 (1932).

We also measured the activation energy of the dissociation of methane into free radicals by measuring the time of removal of standard mirrors at different temperatures,[6] and obtained the value 100 ± 6 Cal.

Identification Experiments.—We performed several experiments in which we passed methane through a quartz tube, 1.3 cm. in diameter and fitted with a furnace 15 cm. long. The apparatus was similar to that described in a recent publication[6] except that a more powerful pumping system has to be used since methane is not condensed in the liquid-air trap and must be pumped out of the apparatus. We found either a three or four stage mercury vapor pump backed by a good oil pump quite satisfactory. It was also necessary to use a platinum wound furnace since we had to conduct some of the experiments at temperatures as high as 1200°. A heavy tellurium mirror was deposited by heating a piece of metallic tellurium about 1 cm. from the end of the furnace; the mirror was cooled by a stream of cold water.

In all these experiments we obtained dimethyl ditelluride, which condensed as a bright red solid in the liquid air trap and was identified by its melting point. There was no trace of any red solid deposited on the walls just beyond the tellurium mirror, so that we may conclude that no methylene groups leave the furnace to come in contact with the tellurium mirror.

We repeated these experiments with a quartz tube which contained a piece of platinum foil 1 cm. × 6 cm. inside the furnace and obtained identical results.

In Belchetz' experiments methane at 0.1 mm. pressure was passed over a platinum filament heated in the range 877–1027°; the gases were then passed over a tellurium mirror 3 mm. from the filament. In our experiments we could obtain no mirror removal in this range of temperature, even with our much larger furnace, whether it contained platinum or not. We did observe, however, that evaporation of the mirror occurred if it was placed too near the end of the furnace and that the metallic tellurium was carried by the gas stream into the liquid air trap, where it appeared as a grayish-white solid.[7] It does not seem possible to reconcile our experimental results with those obtained by Belchetz.

Activation Energy Measurements.—In these measurements we used antimony instead of tellurium mirrors because the time of removal of a standard antimony mirror seems to be much less affected by the temperature of the mirror than is the case for other metals. In one series of experiments at 1150 and 1200° using a quartz tube 1.3 cm. in diameter and a furnace 15 cm. long the following data were obtained:

D, cm.	1.9	1.8	1.7	1.6	1.4	1.3	1.0
R, T_{1150}/T_{1200}	2.06	2.10	2.23	2.09	2.46	2.48	2.59

D is the distance of the standard mirror from the end of the furnace and R is the ratio of the times of disappearance of the two standard mirrors at the two furnace temperatures, respectively. The extrapolated ratio for the value of R when the two mirrors are at the end of the furnace is 3.19, which corresponds to an activation energy of 97.3 Cal. When we repeated these measurements we obtained a value of 101, but since we found that radiation from the furnace prevented any measurements nearer than 1.0 cm. we have concluded that the best value from these experiments for the activation energy is 100 ± 6 Cal.

Mechanism of the Decomposition.—The primary rupture in the decomposition of methane may be represented by

$$CH_4 \longrightarrow CH_3 + H \text{ or} \qquad (1)$$

$$CH_4 \longrightarrow CH_2 + H_2 \qquad (2)$$

Reaction (1) would probably be followed by

$$H + CH_4 \longrightarrow H_2 + CH_3 \qquad (3)$$

If reaction (3) requires an activation energy[8] of about 25 Cal., it occurs after $e^{25000/2 \times 1423} \sim 10^4$ collisions at 1150°; under our conditions a hydrogen atom formed at the entrance to the furnace would hardly undergo this many collisions before reaching the mirror.[9] Atomic hydrogen removes tellurium mirrors[10] to form presumably hydrogen telluride[11] H_2Te; however, after warming to room temperature we observed no deposit of tellurium on the walls of the liquid air trap such as must have been obtained if hydrogen telluride had been formed.[12] We have concluded, therefore, that if the primary decomposition is represented by reaction (1), the atomic hydrogen either com-

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[6] See Rice and Johnston, This Journal, **56**, 214 (1934).

[7] This reflection of metallic atoms in connection with mirror formation has been observed previously. See, for example, Paneth and Hofeditz, *Ber.*, **62**, 1340 (1934).

[8] See Rice, This Journal, **56**, 488 (1934).

[9] Since our methane was almost completely dry the hydrogen atoms might have a short life due to recombination on the wall.

[10] Pearson, Robinson and Stoddart, *Proc. Roy. Soc.* (London), **A142**, 275 (1933).

[11] Possibly such compounds as HTeTeH are formed but these are in all probability extremely unstable.

[12] Dennis and Anderson, This Journal, **36**, 882 (1914).

bines on the walls or disappears according to reaction (3) before reaching the mirror.

If on the other hand reaction (2) is the primary process it should be followed by

$$CH_2 + CH_4 \longrightarrow 2CH_3 \text{ or} \tag{4}$$
$$CH_2 + CH_4 \longrightarrow C_2H_6 \tag{5}$$

and these processes must each have an activation energy of less than 12 Cal. in order to account for the absence of methylene radicals. Since the reaction of the radicals with ether[4] has an activation energy of approximately 15 Cal., the analogous reaction with methane probably has a higher activation energy and we feel therefore that reaction (1) probably represents the first step in the thermal decomposition of methane.

Summary

When methane is decomposed thermally in a flowing system, methyl groups escape from the furnace and can be identified as dimethyl ditelluride. No telluroformaldehyde is formed, thus proving the absence of methylene radicals in the gases leaving the furnace. Furthermore, we did not detect any hydrides of tellurium in the liquid air trap, indicating the absence of atomic hydrogen among the fragments leaving the furnace.

Our experiments indicate that methane undergoes a primary dissociation into methyl groups and atomic hydrogen; the atomic hydrogen disappears before reaching the mirror, either on the walls or by reaction with methane to form methyl radicals and molecular hydrogen.

The activation energy of the primary process is 100 ± 6 Cal.

BALTIMORE, MARYLAND RECEIVED OCTOBER 13, 1934

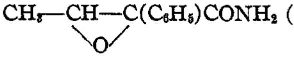
[CONTRIBUTION FROM THE WALKER CHEMICAL LABORATORY OF THE RENSSELAER POLYTECHNIC INSTITUTE]

The Formation of Glycidamides by the Action of Hydrogen Peroxide on α,β-Ethylenic Nitriles[1]

BY JAMES V. MURRAY AND JOHN B. CLOKE

In 1885, Radziszewski[2] described a method for the preparation of amides by the action of 3% hydrogen peroxide on nitriles in the presence of alkali and at a temperature of 40°. He formulated the reaction as: $RCN + 2H_2O_2 \longrightarrow R\text{—}CO\text{—}NH_2 + H_2O + O_2$. Since that time Deinert,[3] Friedländer and Weisberg,[4] Rupe and Majewski,[5] Bogert and Hand,[6] Keiser and McMaster,[7] Dubsky,[8] McMaster and Langreck,[9] Oliveri-Mandalà[10] and others have described modifications and extensions of the method.

In some work reported in 1932, Knowles and Cloke,[11] in connection with the proof of a nitrile structure, subjected α-phenylcrotononitrile, $CH_3CH{=}C(C_6H_5)CN$ (I), to the Radziszewski reaction with the expectation of obtaining α-phenylcrotonamide, $CH_3CH{=}C(C_6H_5)CONH_2$ (II). However, consistently low values for the nitrogen in the compound obtained, which were in harmony with the formula $C_{10}H_{11}O_2N$, suggested that an oxidation had taken place, and when the substance was found to give methyl benzyl ketone, $CH_3COCH_2C_6H_5$, on acid hydrolysis, it was erroneously identified as α-phenylacetoacetamide, $CH_3COCH(C_6H_5)CONH_2$ (III). Later, however, a perusal of the work of Weitz and Scheffer[12] on the formation of ketoxido compounds from unsaturated ketones cast doubt on this structure (III) and suggested that the compound $C_{10}H_{11}O_2N$ was actually the isomeric α-phenyl-β-methylglycidamide,



$CH_3\text{—}\overset{\frown O \frown}{CH\text{—}C}(C_6H_5)CONH_2$ (IV), which view was practically confirmed when it was found[13] that the compound failed to give a color with ferric chloride. Finally the phenylacetoacetamide structure (III) was excluded definitely when it was found that two forms of this compound had already been prepared by Ogata and Ito[14] by the hydrolysis of acetobenzyl cyanide,

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[1] This paper has been abstracted from the second part of a thesis presented by James Vincent Murray, Jr., to the Rensselaer Polytechnic Institute in June, 1934, in partial fulfilment of the requirements for the degree of Chemical Engineer.

[2] Radziszewski, *Ber.*, **18**, 355 (1885).

[3] Deinert, *J. prakt. Chem.*, [2] **52**, 431 (1895).

[4] Friedländer and Weisberg, *Ber.*, **28**, 1841 (1895).

[5] Rupe and Majewski, *ibid.*, **33**, 3403 (1901).

[6] Bogert and Hand, THIS JOURNAL, **24**, 1034 (1902).

[7] Keiser and McMaster, *Am. Chem. J.*, **49**, 81 (1913).

[8] Dubsky, *J. prakt. Chem.*, [2] **93**, 137 (1916).

[9] McMaster and Langreck, THIS JOURNAL, **39**, 103 (1917).

[10] Oliveri-Mandalà, *Gazz. chim. ital.*, **52**, I, 107 (1922).

[11] Knowles and Cloke, THIS JOURNAL, **54**, 2028 (1932).

[12] Weitz and Scheffer, *Ber.*, **54B**, 2327 (1921).

[13] Green, "Thesis," Rensselaer Polytechnic Institute, 1933.

[14] Ogata and Ito, *J. Pharm. Soc. Japan*, No. **409**, 209–231 (1916).