ether and the ether evaporated. A brown oil remained. When this was dissolved in alcohol and poured into water, an emulsion was formed and crystallization finally took place. These crystals were purified from dilute alcohol.

The diacyls were saponified by dissolving in 10% potassium hydroxide and then acidifying with hydrochloric acid. The precipitate was purified by recrystallization from dilute alcohol. All analyses were made by the Kjeldahl method.

Summary

1. The heavier *iso*-carbopentoxy group replaces both the *n*- and the *iso*carbobutoxy from the nitrogen in diacyl derivatives of *o*-aminophenol.

2. The benzoyl group does not behave the same with the *n*-carbopropoxy and the *iso*-carbopropoxy groups in diacyl derivatives of *o*-aminophenol. In the case of the *n*-carbopropoxy derivative the benzoyl group goes to the nitrogen, but in the case of the *iso*carbopropoxy group the benzoyl group goes to oxygen.

3. New diacyl derivatives of *o*-aminophenol have been prepared and studied.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE HYDROGEN–ETHYLENE REACTION IN THE PRESENCE OF EXCITED MERCURY ATOMS

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In a former paper the authors[1] concluded from semi-quantitative evidence that ethane was formed from hydrogen and ethylene when a mixture of the latter is illuminated with ultraviolet light in the presence of mercury vapor. However, it was also known at this time that in addition to ethane other substances must be formed. The experiments about to be described were undertaken to determine the products of the reaction more definitely.

The experimental arrangement used to expose the gas to the light was the same as that described in our former paper except that the gases were kept in constant circulation.

The ethylene and hydrogen were prepared as described in our former paper. Ethane was prepared by treating an ether solution of C_2H_5MgI with dilute sulfuric acid. The ethane was dried and purified by bubbling through concentrated sulfuric acid and by means of liquid air fractionally distilled three times, the middle portion only being saved for each subsequent distillation.

In Experiment I a mixture of hydrogen at a pressure of 39 cm. and ethyl-

[1] Olson and Meyers, THIS JOURNAL, **48**, 389 (1926).

ene at a pressure of 25 cm. in the presence of mercury vapor was illuminated by ultraviolet light for thirty-nine hours, at which time the pressure drop was 24 cm. At the end of this time further illumination did not cause a further pressure decrease.

In Experiment II a mixture of hydrogen at a pressure of 40 cm. and ethylene at 2 cm. in the presence of mercury vapor was illuminated until the pressure became constant at 40 cm.

In Experiment III ethane at a pressure of 66 cm. and mercury vapor were exposed to ultraviolet light for fifty hours, at the end of which time the pressure drop was less than 2%.

In a fourth experiment pure unilluminated ethane was used.

The mixtures in these four experiments were then analyzed in the positive-ray apparatus described by Hogness and Lunn.[2] By this method the gases are ionized by electronic impact and the ions are then sent through electric and magnetic fields. It is possible to plot the number of ions of a given mass against the mass. Due to the characteristics of the apparatus, ions of a definite mass are distributed about the point corresponding to the mass of the ion, so that it is necessary to use the area under the curve as a measure of the number of ions rather than the height of the peak. This measure of the number of ions assumes that the efficiency of ionization by electronic impact of the various molecular species is the same. In the case which we are about to consider this condition is probably closely obeyed. The results of these positive-ray analyses are summarized in Table I, where the amount of ethane, for convenience, is taken as unity.

TABLE I

RESULTS OF POSITIVE-RAY ANALYSES

Expt. no.	CH_4	C_2H_6	C_3H_8	C_4H_{10}
I	0.018	1	0.64	0.42
II	0.22	1	0.04	0.0008
III	0	1	0	0
IV	0	1	0	0
Ratio I/II	0.082	1	16	525

Experiments III and IV show that under these conditions ethane undergoes no reaction large enough to be detected.

From the total amount of ethylene used and the relative amounts of

TABLE II

FINAL PRESSURES IN CM. OF MERCURY

Expt. no.	CH_4	C_2H_6	C_3H_8	C_4H_{10}	H_2	C_2H_4
I	0.16	8.9	5.8	3.75	21	0
II	0.376	1.71	0.068	0.0013	38	0
Ratio I/II	0.425	5.2	85	2880		

[2] Hogness and Lunn, *Phys. Rev.*, **26**, 44 (1925).

substances formed, we can calculate the final pressures in cm. of mercury of all the gases. The results of these calculations are collected in Table II.

From the experiments already reported in our former paper, as well as from the results of other investigators, it is shown that at least two primary processes occur

$$H_2 + Hg^* = 2H + Hg \quad (1)$$

where Hg* stands for the excited state, and

a splitting off of hydrogen from ethylene (2)

In the present set of experiments the formation of methane and propane demonstrate that a third primary process occurs by the breaking of the ethylene bond

$$C_2H_4 \longrightarrow 2CH_2 \quad (3)$$

It seems reasonable to assume that the amount of CH_2 formed is proportional to the amount of ethylene present.

We must now consider the reactions between the products of these primary reactions and the original substances to form the final products. It is clear at the outset that the chance of CH_2 adding molecular hydrogen must be very low, for otherwise the concentration of methane would be much higher or the concentration of propane much lower than was found. There remain, then, the following reactions to be considered

$$C_2H_4 + 2H = C_2H_6 \quad (4)$$
$$CH_2 + 2H = CH_4 \quad (5)$$
$$CH_2 + C_2H_4 + 2H = C_3H_8 \quad (6)$$
$$2CH_2 + C_2H_4 + 2H = C_4H_{10} \quad (7)$$
$$C_2H_4 + C_2H_x^* + yH = C_4H_{10} \quad (8)$$

where $C_2H_x^*$ is a molecule of ethylene which has been activated probably by loss of hydrogen.

From the postulated reactions and the final pressures of the products, we can calculate the amount of ethylene (measured in cm. of mercury) of the reaction

$$C_2H_4 + Hg^* = 2CH_2 + Hg$$

which is required to produce the calculated amounts of the above products. The results of these calculations are collected in Table III.

TABLE III

CALCULATED AMOUNTS OF ETHYLENE (CM. OF MERCURY)

Expt. no.	By reactions (5), (6) and (7)	By reactions (5), (6) and (8)
I	6.74	2.99
II	0.222	0.222
Ratio I/II	30.4	13.5

We have already assumed the amount of CH_2 formed to be proportional to the ethylene pressure, or 12.5 times as much in Experiment I as in

Experiment II. If we compare this ratio with the required amount of CH_2 in Table III, we see that it agrees very closely if we assume mechanisms (5), (6) and (8), but it is less than half of that required for mechanisms (5), (6) and (7). We conclude, therefore, that Reaction (7) does not take place to an appreciable extent under these conditions. The tremendous decrease of butane with decrease of ethylene must be accounted for by an increased rate of hydrogenation of the activated ethylene molecules.

The fact that Reaction (7) does not take place is in agreement with the fact that the higher hydrocarbons are absent, for these would all involve reactions between three or more ethylene molecules or radicals formed from ethylene before complete hydrogenation took place.

At high pressures of ethylene, the chance of reaction between CH_2 and ethylene is large compared with the chance of CH_2 being completely hydrogenated, whereas at low pressures of ethylene almost all of the CH_2 is removed as methane. This is clearly shown by reference to Table I. The average pressure of ethylene in Experiment I is 12.5 times as high as in Experiment II. The amount of methane formed in Experiment II per unit amount of ethane is 12.2 times as high as that found in Experiment I, while the amount of propane decreases at the same time 16-fold.

We take pleasure in acknowledging our indebtedness to Mr. Hamline M. Kvalnes of this Laboratory for making the positive-ray analyses.

Summary

Mixtures of hydrogen and ethylene react when subjected to the action of excited mercury atoms. By positive-ray analysis it is shown that the products of reaction are methane, ethane, propane and butane. Mechanisms for the formation of these substances are proposed. It is demonstrated that the carbon-hydrogen bond in ethylene and the ethylene bond itself require less than 4.9 volts of energy for rupture.

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