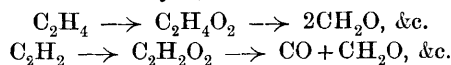


LXX.—*The Interaction of Well-dried Mixtures of Hydrocarbons and Oxygen.*

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THE experiments described in this paper were made to prove whether water vapour has an influence on the combustion of a hydrocarbon at all comparable with that which it exerts in the well-known instances of the combustion of carbon monoxide (H. B. Dixon, *Phil. Trans.*, 1884, **175**, 617) and hydrogen (H. B. Baker, *Trans.*, 1902, **81**, 400). We may here recall the fact that H. B. Dixon found that a perfectly dry mixture of carbon monoxide and oxygen was rendered explosive by the presence of even a trace of hydrocarbon, and, also, that H. B. Baker, in describing his experiments on the comparative inertness of dry electrolytic gas, emphasised the importance of obtaining it free from hydrocarbon impurity.

Most of our experiments have been made with ethylene and acetylene. In selecting these hydrocarbons for investigation, we were influenced by the fact that no steam is produced during the initial stages of their slow combustion, which has been shown to involve the early formation of formaldehyde, thus :



The experimental method consisted in comparing the amounts of change occurring in two similar tubes containing respectively thoroughly dried, and undried, equimolecular mixtures of one or other of the hydrocarbons with oxygen, when heated under similar conditions for the same length of time.

Comparative experiments were also made in similar tubes with electrolytic gas, dried and undried, in order to ensure that the degree of dryness attained in the hydrocarbon experiments was such as would practically inhibit the combustion of hydrogen. From the results of

these experiments, we have arrived at the conclusion that the rigid exclusion of moisture by means of the best-known method of desiccation has little, if any, influence on the rate of oxidation of a hydrocarbon.

Preparation of the Gases.

Electrolytic Gas.—This was prepared by the electrolysis of a solution of thrice-crystallised barium hydroxide. For the “dry” experiments, the gas as it left the electrolytic cell was passed through a system of drying tubes containing (1) solid caustic potash and (2) phosphoric anhydride,* after which it was collected in a glass holder over dry mercury. From thence it was finally transferred into the experimental tubes through another series of drying tubes containing phosphoric anhydride. Lastly, traces of moisture were removed by long standing over phosphoric anhydride in the experimental tubes, in the manner to be described later. All the glass taps used in the experiments with electrolytic gas were lubricated with glacial phosphoric acid.

Ethylene.—This was prepared by the interaction of ethyl alcohol and strong sulphuric acid at 160°. The crude gas was passed through suitable absorption vessels containing (1) ice-cold water, (2) strong sulphuric acid, (3) a strong solution of caustic potash. It was then collected over a mixture of equal volumes of glycerine and water.

The washed gas was further purified by repeated liquefaction in a bath of liquid air, followed in each case by a fractionation of the liquid, in which the first and last thirds were rejected. In the final purification, about a litre of the thrice-fractionated gas was again liquefied, and on removing the liquid air-bath the first 300 c.c. of gas were rejected. A middle fraction measuring 250 c.c. was then collected in a holder over dry mercury, where it was subsequently mixed with an equal volume of dry oxygen. The mixture was finally passed into the experimental tubes through a series of drying tubes containing redistilled phosphoric anhydride.

Acetylene.—The crude gas, prepared from commercial calcium carbide, was passed through (1) dilute sulphuric acid, (2) a mixture of bleaching powder with excess of quicklime, (3) towers containing “kieselguhr” saturated with an acid solution of cupric and ferric chlorides, and (4) a strong solution of caustic potash. The final purification was effected by repeated solidification in a small glass bulb immersed in liquid air and subsequent fractional vaporisation of the solid, much in the same way as the liquid ethylene had been fractionated. The subsequent admixture with an equal volume of oxygen,

* All the phosphoric anhydride used in the research had been redistilled in a current of dry oxygen over red-hot platinised asbestos.

and the drying of the mixture before it was filled into the experimental tube, were carried out in precisely the same manner as in the case of ethylene.

Oxygen.—This was prepared by heating recrystallised potassium permanganate. The gas was first passed through a strong solution of caustic potash, and then collected in a glass holder over pure strong sulphuric acid. Before admixture with the hydrocarbons, it was slowly passed through a long tube filled with solid caustic potash.

Cleaning and Drying of the Experimental Tubes. The Final Drying of the Experimental Mixtures.

The experimental tubes were nearly all made of Jena borosilicate glass (No. 59III), which, owing to its remarkably feeble power of retaining surface moisture, is, above all other kinds, suitable for experiments with dried gases. A few experiments were made with tubes of Jena hard combustion glass, which is also admirably adapted to the purpose in view.

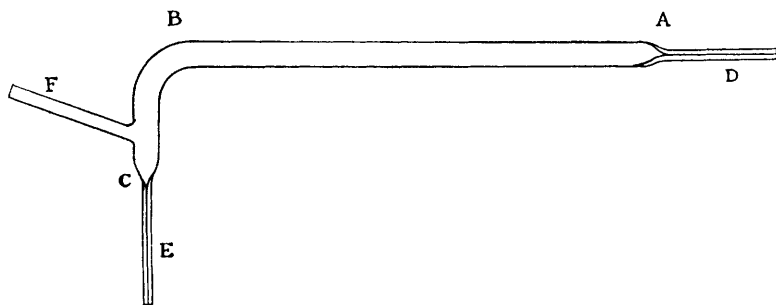
Tubes of uniform dimensions (length = 70 cm., internal diameter = 15 mm., capacity = 150 c.c.) were selected, and bent into the form shown in the accompanying figure, at a point *B*, about 15 or 20 cm. from one end.

To each end of the tube was fused a short length of capillary tubing, *D* and *E*, and the tubes to be used for the dry mixtures were also provided with a side-piece, *F*, in the vertical limb, *BC*, through which the redistilled phosphoric anhydride was subsequently introduced.

The tubes were carefully cleaned by prolonged treatment with a hot strong solution of chromic anhydride in sulphuric acid, after which they were allowed to drain. They were next thoroughly washed out with several litres of hot distilled water, after which the inside of each tube was steamed for an hour and a half. It was then dried in a current of hot air, previously dried by sulphuric acid and filtered through cotton-wool.

A quantity of redistilled phosphoric anhydride was next introduced into the tubes intended for the dried mixture through the side-piece, *F*, which was then sealed off along with the capillary tube, *D*. The operation of finally drying the tube and filling it with the dry experimental mixture was afterwards performed as follows. The horizontal portion of the tube *AB* was heated in a Lothar Meyer furnace to a temperature considerably higher than that subsequently employed in the actual experiment. The capillary tube, *E*, was connected, through an arrangement of drying tubes containing phosphoric anhydride, with an automatic Sprengel pump, and the heated tube exhausted during several hours. This, it was thought, would ensure

the removal of the film of moisture which often clings so tenaciously to a glass surface. The vacuous tube was allowed to cool slowly, and was then connected, through a drying tube containing redistilled phosphoric anhydride, with the holder containing the experimental mixture. After all the connections had been exhausted, the mixture was very slowly admitted to the tube until the pressure was about 10 mm. below the atmospheric. The capillary, *E*, was then sealed off, and the tube set aside for several weeks in a dark room, to complete the desiccation of the gases. At the end of this period, the phosphoric anhydride invariably appeared perfectly dry. Meanwhile, other similar tubes, cleaned as above, had been filled with the same experi-



mental mixture, which on its way into each tube had been slowly passed over the surface of distilled water.

Heating of the Tubes.

In an actual experiment, the horizontal portion, *AB*, of the tube was inserted into a wider tube already heated to the desired experimental temperature in a Lothar Meyer constant temperature furnace. A slow current of hot air, passed through the annular space between the two tubes, ensured the uniform heating of the inner one. The temperature was registered by a recording pyrometer, the thermojunction wires being inserted in the annular space already mentioned.

Throughout the entire duration of the experiment, the vertical limb, *BC*, containing the phosphoric anhydride, was screened from the furnace and immersed in ice-cold water. The cold portion of the tube was carefully watched for any visible signs of chemical action. After a definite time interval, the tube was withdrawn from the furnace, and, after cooling, was opened either under mercury, or in connection with a manometer of capillary bore. The gaseous products were afterwards withdrawn and analysed.

In a given experiment, one tube each of the dried and undried gases was heated under precisely similar conditions for the same length of time, and the amounts of combination in each case compared.

Results of the Experiments.

A. With Electrolytic Gas.

Altogether five experiments were made with electrolytic gas, the period of drying extending over four weeks in each case. A preliminary trial with a tube containing the undried gases indicated 525° as a suitable experimental temperature, and this was accordingly selected.

In four of the experiments, an enormous difference was observed between the rate of combination in the moist and dried gases, respectively, during ten minutes at 525°. In the case of the undried gases, water invariably appeared in the cold portion of the tube after one and a half minutes, and accumulated as the heating was continued; altogether between 40 and 50 per cent. of the gases combined during any given experiment. In the case of the dried gases, however, there was never any visible sign of combination, and on subsequently opening the cold tubes under mercury, the contractions observed never exceeded 3 per cent. of the original volume, and in two cases were negligibly small. The amounts of combination observed in the four experiments are tabulated below:

Experiment.	Undried gas.	Dried gas.
1	52 per cent.	0·5 per cent.
2	45 ,,	3·0 ,,
3	42 ,,	nil ,,
4	40 ,,	3·0 ,,

In the fifth experiment, a small quantity of the phosphoric anhydride was accidentally projected into the horizontal part of the tube during the introduction of the electrolytic gas. We were therefore not surprised to find a moderate amount of action when the tube was subsequently heated after four weeks' drying. Nevertheless, the percentage combination observed was only 14, as compared with 45 in the corresponding case of the undried gases. In this connection, the fact may be recalled that H. B. Baker had a similar experience with one out of twelve of his tubes of dried gas (*ibid.*, p. 403).

B. Experiments with an Equimolecular Mixture of Ethylene and Oxygen.

An equimolecular mixture of the two gases was selected because previous experiments (Trans., 1904, 85, 1643) had shown that the fastest rates of combination are obtained with these proportions,

1st Experiment.—For this experiment, two tubes of the dried mixture were prepared, the period of drying extending over eleven weeks. With the object of comparing the temperatures at which visible reaction commenced in the dried and undried mixtures, the furnace was lighted after the introduction of the tubes and the temperature slowly raised. The first signs of chemical action (the appearance of a white film of paraformaldehyde in the cold portion of the tube) were noticed at nearly the same temperature ($385\text{--}395^\circ$) in both the case of the dried and the undried mixtures. Moisture first appeared about five minutes later in each case. The heating was continued fifteen minutes longer (maximum temperature = $430\text{--}450^\circ$), after which the tubes were withdrawn and cooled.

The following numbers show that there was very little difference between the total amounts of change observed in the dried and undried mixtures respectively.

Mixture.	Percentage contraction (corrected) after cooling.	Percentage composition of gaseous products.					
		CO ₂ .	CO.	C ₂ H ₄ .	C ₂ H ₆ .	H ₂ .	O ₂ .
Dried	37.0	10.25	45.75	32.65	2.10	1.05	8.20
„	37.7	10.25	44.50	28.85	6.35	4.00	6.05
Undried	34.8	10.60	48.4	27.6	4.65	2.70	6.05
„	36.1	11.45	50.8	24.85	5.15	3.25	4.50

2nd Experiment.—Three tubes, one of undried and the other two of dried mixture (period of drying = twelve weeks), were introduced into the furnace and heated for fifteen minutes in each case. The first visible action was observed after about five minutes in each case. The total amount of change in the undried mixture was somewhat greater than that observed in either of the “dried” tubes.

Mixture.	Percentage contraction.	Percentage composition of gaseous products.					
		CO ₂ .	CO.	C ₂ H ₄ .	C ₂ H ₆ .	H ₂ .	O ₂ .
Undried	29.3	7.30	35.35	36.10	1.00	2.30	17.95
Dried	22.9	6.60	24.55	39.75	1.20	0.25	27.65
„	22.9	Not analysed.					

3rd Experiment.—Three tubes, one containing undried and the other two the dried gases (period of drying = twelve weeks), were introduced into the furnace at 457° . A striking difference between the dried and undried gases was observed. For, whereas the combination of the undried gases followed the normal course of slow combustion, that is, without ignition, the dried gases ignited after three minutes, a slow flame traversing the mixture and finally dying out a little distance from the cooled end of the tube. There was a slight deposit of carbon in the heated portion of the “dried” tubes, where the flame had started, but none in the case of the “undried” gases. There had, therefore, been a much faster initial rate of combination in the case of

the dried gases than with the undried mixture, the ignition following as a result of local heating. This is borne out by the ratio of the pressures in the tubes before and after the experiment (p_2/p_1), and the composition of the gaseous products.

Mixture.	Temperature.	Duration of heating	p_2/p_1	Percentage composition of gaseous products.					
				CO ₂ .	CO.	C ₂ H ₄ .	C ₂ H ₆ and CH ₄ .	H ₂ .	O ₂ .
Undried.....	457°	15 minutes	0.708	8.0	41.5	33.1	2.5	nil	14.9
Dried.....	457	3 "	1.71	0.8	46.6	2.6	1.9	44.0	2.1
„	450	3 "	1.75	Not analysed.					

4th Experiment.—Two tubes, the one containing the undried and the other the dried gases (drying period = six weeks), were introduced into the furnace at 434°. In the case of the undried mixture, the first signs of combination were observed after four minutes, after which slow combustion continued during the remainder of the experiment. In the case of the dried gases, however, a film of paraformaldehyde appeared in the cold end of the tube after one minute, and at two and three-quarter minutes the contents of the tube ignited, as in the previous experiment.

5th Experiment.—Two tubes, containing respectively the dried and undried gases (period of drying = six weeks), were introduced into the furnace at 440°. The first signs of combination were observed at the end of five and a half minutes in the case of the dried mixture, and half a minute later with the undried mixture. There was no ignition of the gas in either case, and after fifteen minutes the tubes were withdrawn. The percentage contraction found on opening the tubes under mercury and the composition of the gaseous products in each case are given below.

Mixture.	Percentage contraction.	Percentage composition of gaseous products.					
		CO ₂ .	CO.	C ₂ H ₄ .	C ₂ H ₆ .	H ₂ .	O ₂ .
Dried	30.0	6.25	36.95	31.85	3.60	4.90	16.45
Undried	28.3	8.55	46.35	30.85	3.20	2.90	8.15

Two other experiments were made with similar results to the above. Altogether ten tubes of the "dried" mixture and ten of the undried gases were examined. Considering the results as a whole, we are inclined to think that the initial rate of oxidation, and consequently the accumulation of aldehyde, was greater in the dried than in the undried gases. It is significant, in this connection, that actual ignition never took place except with the dried gases.

C. Experiments with Acetylene.

Two experiments were made with thoroughly dried equimolecular mixtures of acetylene and oxygen, prepared as previously described.

(1) Period of drying = four weeks. Commencing with the furnace cold, the tube was heated to 415° during thirty-five minutes. A white film of paraformaldehyde appeared at 335° after twenty-seven minutes' heating, and four minutes later the formation of water was noticed.

The contraction after cooling, on opening under mercury, was 32.8 per cent., and the following analysis of the gaseous products, expressed in percentages, shows that the oxygen had completely disappeared.

CO ₂	19.65	CO	56.65	C ₂ H ₂	22.5
H ₂	0.85	C ₂ H ₆	0.35	O ₂	nil

(2) Period of drying = four weeks. The tube was placed in the furnace previously heated to 520° . Two minutes later, the gases exploded with shattering effect.

D. *Experiments with Ethane.*

The following comparative experiments were also made with tubes containing dried and undried mixtures of ethane and oxygen in equimolecular proportions.

The ethane had been prepared by the action of water on zinc ethyl and purified by repeated liquefaction and fractionation, as in the case of ethylene.

(1) Two tubes, containing respectively the dried and undried gases (period of drying = seven weeks), were placed in the furnace at 415° . The dried gas ignited after nineteen and three-quarter minutes, but after twenty minutes there was no visible sign of reaction in the tube of undried gas.

(2) Two tubes, containing respectively the undried and dried gas (period of drying = seven weeks), were placed in the furnace at 440° . In both cases, the mixture ignited, the dried gas after seven and three-quarter minutes, and the undried gas after twelve and a quarter minutes. Carbon separated and water condensed when the tubes were subsequently cooled. The ratios (p_2/p_1) were 1.503 and 1.501 respectively.

The experiments with both acetylene and ethane thus confirm the conclusions drawn from the more complete investigation in the case of oxidation of ethylene.

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