THE SLOW COMBUSTION OF GASEOUS PARAFFINS, ESPECIALLY PROPANE

ROBERT N. PEASE

Frick Chemical Laboratory, Princeton University, Princeton, New Jersey

Received July 16, 1937

The non-explosive oxidation of gaseous paraffins, which occurs at about 300°C. and 1 atm., has as its outstanding characteristic a lengthy induction period. During the minutes or hours that this may take to complete itself, some infinitesimal alteration of the reaction system must be taking place. In his original work on ethane, Bone (2) limited himself to the suggestion that "the gases (or at least one of them) were merely 'getting ready' in some way." Later work on methane revealed that the reactants were not entirely inert during the induction period. Toward the end, small amounts of formaldehyde could be detected (1). This fact, coupled with the observation that the formaldehyde increases to a maximum at the maximum reaction rate and that added formaldehyde can eliminate the induction period, points inescapably to this substance as the active intermediate.

If one were to conclude that the function of the formaldehyde is to introduce active oxygen into the system either as atoms (3) or as peroxide oxygen (9), one might predict that higher aldehydes (e.g., acetaldehyde) would be even more efficient. This is, in fact, apparently just what has been observed in the case of ethane oxidation. Bone and Hill found, for example, that with 1 per cent of acetaldehyde at 316°C. explosion occurred. To be sure, this conclusion about active oxygen supplied by the aldehyde runs counter to the observation that potassium chloride largely eliminates peroxide oxygen without radically altering the rate of hydrocarbon oxidation (8). Nevertheless, the case is certainly a strong one, as von Elbe and Lewis have shown.

In view of the above, it was most surprising to find that acetaldehyde is by no means so efficient in inducing the oxidation of propane as it appears to be in the case of ethane. The experiments to be described in the following were undertaken to investigate the relation of the rate of oxidation of propane to the propane and oxygen concentrations. In order to obtain measurably low rates it was necessary to reduce the temperature somewhat below 300°C., but when this was done the induction period became excessively long. To get around this difficulty small amounts of acetaldehyde vapor were introduced into the reaction bulb before the propane–oxygen mixture. The reaction was followed by pressure measurement.

It was found that with 300 mm. each of propane and oxygen at 280°C. in the uncoated reaction bulb, the induction period ($\Delta P < 1$ mm.) was 39 min. and reaction was virtually completed in 5 min. more. When 20 mm. of acetaldehyde was first introduced into the reaction bulb a mild explosion occurred. With 2 mm. of acetaldehyde, there was a 6-min. induction period, after which reaction was again completed in 5 min.

Similar results were obtained after treating the reaction bulb with potassium chloride. At 280°C. and 300 mm. of each gas, the induction period lasted more than five hours. At 270°C. (10°C. lower) 20 mm. of acetaldehyde again caused inflammation. With 5 or 10 mm. of acetaldehyde, there was a 1- to 2-min. induction period followed by quiet reaction.

These results are evidently quite different from those obtained by Bone with formaldehyde and methane–oxygen, or acetaldehyde and ethane–oxygen. The induction period is not eliminated by aldehyde but only shortened, unless sufficient aldehyde is present to induce explosion, quite possibly as a purely thermal effect.

The writer inclines to the belief that the effect of acetaldehyde in this case is exerted on the surface. Since altering the surface (coating with potassium chloride) profoundly alters the induction period, the process of "getting-ready" (Bone) is clearly a surface process, as others have remarked. Since this process is only altered but not eliminated by acetaldehyde, this alteration should likewise be localized at the surface. The nature of the process in the presence or absence of aldehyde is by no means clear, but something in the nature of activated adsorption would seem to be indicated. Alternatively one may be dealing with the slow displacement of a catalyst poison,—water vapor, for example. In any case, there is certainly no evidence that aldehyde plays a primary rôle in the overall reaction, whatever may be the case in methane or ethane oxidation.

REACTION PERIOD

As already mentioned, these experiments were originally undertaken to obtain further information about the kinetics of propane oxidation subsequent to the induction period. Previous experiments (4, 8, 6) had emphasized the "all-or-nothing" character of the reaction (due to the disparity between the lengths of the induction and reaction periods); and had stressed the formation of methanol and formaldehyde with excess of propane, the induced dissociation of the hydrocarbon at higher temperatures, and the unimportance of "active" oxygen in view of the disappearance of peroxides when the reaction bulb was treated with potassium chloride.

As to the latter, it had been indicated that the presence of the salt did not materially decrease the overall reaction rate, as had been the case in the methane–oxygen and hydrogen–oxygen reactions (7, 5). In view of the elimination of peroxide by this treatment and the repressive influence of packing, it appeared that some effect should be observed. This point was therefore especially investigated. Some suppression by coating does in fact occur, as will later appear.

EXPERIMENTS BEFORE COATING

The first experiments were conducted with a clean Pyrex bulb 2.5 cm. in diameter and 18 cm. long. This was rinsed with nitric acid and water before being sealed in place. The bulb was heated electrically, temperature being controlled manually within 1°C., and read on a mercury thermometer graduated in half-degrees. The propane and oxygen (tank gases) were measured into a mixing bulb, and thence passed to the reaction tube. The acetaldehyde was vaporized into the evacuated reaction bulb up to the desired pressure before the reactants were run in. The reaction bulb was adequately but not exhaustively evacuated after each run by means of a Langmuir pump connected to a liquid air trap and Hyvac pump. The exit tube from the reaction bulb was heated by a resistance winding to prevent condensation.

As already mentioned, with 300 mm. of each gas at 280°C. (no acetaldehyde) there was a 40-min. induction period followed by a 5-min. reaction period.

A preliminary attempt was made to cut the induction period by addition of 10 mm. of ethylene oxide to the reactants (300 mm. of each). This was ineffective. The pressure rose 5 mm. in the first 29 min., after which a further rise of 102 mm. completed the reaction in 5 min. more. In another run, 25 mm. of ethylene oxide was allowed to remain in the reaction bulb 23 min., after which the reactants were added. This was somewhat more effective. The pressure rose 4 mm. in 11 min., after which a rise of 101 mm. completed the reaction in another 5 min.

Since the induction period was more effectively eliminated with acetaldehyde, this was used in all subsequent runs.

A series of experiments with 5 mm. of acetaldehyde as "primer" was carried out at 270°C. Results appear in table 1.

There is an experiment with approximately 200 mm. of each gas; the same with 200 mm. of nitrogen added; an experiment with 200 mm. of propane and 400 mm. of oxygen; and one with 400 mm. of propane and 200 mm. of oxygen. The parallelism among the first three with the same initial propane concentration is obvious. All three accelerate to nearly the same degree up to about 60 mm. pressure increase, at which point all the oxygen in the first two is consumed. (On the basis of previous work two volumes of oxygen react with one of propane.) Evidently neither excess of oxygen nor the presence of nitrogen affects this acceleration. This indicates that the rate is really independent of oxygen concentration, and that diffusion to the walls is not a factor. The rate is, however, strongly dependent on the propane concentration.

TABLE 1

Reaction at 270°C. (5 mm. of acetaldehyde)

Uncoated bulb

	INITIAL PRESSURE IN MILLIMETERS			
C_3H_8	202	211	205	407
O_2	199	197	384	203
N_2		202		
Time	Pressure rise			
min.	*mm.*	*mm.*	*mm.*	*mm.*
1	0	0	0	1
2	0	0	0	2
3	1	1	1	6
4	2	3	2	14
5	4	5	3	28
6	7	9	6	57
7	12	15	10	63
8	19	22	17	64
9	27	30	26	
10	36	41	34	
11	45	51	45	
12	55	59	55	
13	60	60	63	
14	61		72	
15			79	
20			103	
25			118	
30			119	

EXPERIMENTS AFTER COATING WITH POTASSIUM CHLORIDE

Following the experiments just described, the reaction bulb was dismounted and filled with dilute potassium chloride solution. After standing several days, it was thoroughly drained and then slowly dried with gentle heating and suction. There was no visible coating on the bulb, but subsequent experiments showed a marked change in activity. The induction period (300 mm. of each gas at 280°C. with no acetaldehyde) rose from 40 min. to over five hours. Addition of acetaldehyde shortened the induction period, but the subsequent reaction was still slower than before coating, as shown in table 2.

TABLE 2

Comparison of runs before and after coating

Temperature, 270°C.; 5 mm. of acetaldehyde added

INITIAL PRESSURE IN MILLIMETERS		TIME IN MINUTES*	
C_3H_8	O_2	Before	After
400	200	1	3
200	400	2	22

* This is the time required for the pressure to rise from 20 to 40 mm. above the initial value.

TABLE 3

Reaction at 280°C. (10 mm. of acetaldehyde) after coating with potassium chloride

	INITIAL PRESSURE IN MILLIMETERS				
C_3H_8............	195	215	213	408	295*
O_2...............	196	198	406	204	289
N_2...............		204			
Time	Pressure rise				
min.	*mm.*	*mm.*	*mm.*	*mm.*	*mm.*
1	0	1	0	1	0
2	0	4	1	4	0
3	1	5	1	12	1
4	2	6	1	26	1
5	2	8	1	49	1
6	3	10	1	56	2
7	3	13	1	57	2
8	3	15	1		3
9	4	18	2		4
10	4	22	2		5
11	5	26	2		7
12	5	30	3		10
13	5	35	3		14
14	6	40	3		19
15	6	45	4		26
16	7	50	4		36
17	7	55	4		48
18	7	59	5		63
19	8	60	5		77
20	8	60	6		87
30	14		10		87
40	20		17		
50	27		34		
60	38		63		
70	49		90		
80	56		103		
90	57		112		

* In this run with approximately 300 mm. of each gas, only 5 mm. of acetaldehyde was added.

A set of experiments corresponding to those made before coating was carried out. In order to keep the induction and reaction periods within reasonable bounds, the temperature was raised from 270° to 280°C. and it was found advisable to use 10 mm. of acetaldehyde as "primer." Results appear in table 3.

It is evident that the coating of potassium chloride has completely changed the relationships. Addition of nitrogen now very materially increases the rate, as does an excess of oxygen, once the long induction period has terminated. This rather clearly indicates the importance of diffusion in the coated bulb. The same no doubt applies in part to the marked increase in rate produced by excess of propane.

DISCUSSION

These results have materially altered the writer's conclusions about the nature of the slow oxidation of the higher paraffins. It appears that the destructive action of potassium chloride-treated walls on peroxides is more important than previously concluded (4, 8, 6). The flow experiments at 300–400°C. and 1 atm. had indicated that there was no accompanying change in rate. It is now evident that the rate does decrease rather markedly under conditions favoring destruction of peroxides at the treated wall. One may therefore conclude that peroxides do in fact play an essential rôle in the case of the higher paraffins, whatever may be the fact for methane and ethane. It is to be emphasized that the peroxides in question are not of the peracid type, as shown by the analytical evidence (4, 8, 6) and by the relative ineffectiveness of acetaldehyde as a "primer." Beyond this their nature cannot at present be specified. The writer naturally is inclined to believe that the reaction.

$$R + O_2 \rightarrow RO_2$$

is involved, as suggested by von Elbe and Lewis (9). This was previously avoided because of the supposed unimportance of peroxides. However, if one may argue from the slow but persistent increase in rate, sometimes nearly to the very end of reaction, a more stable intermediate would seem to be required. Possibly the transient compound RO_2 is stabilized by formaldehyde (which is present) to give an hydroxi-peroxide, also suggested by von Elbe and Lewis. For the rest the scheme of the latter authors seems fairly well to exhaust the possibilities.

SUMMARY

In the slow oxidation of propane at 270–280°C. it has been found that treating the Pyrex reaction bulb with potassium chloride greatly lengthens the induction period, thus indicating that the preliminary reaction occurs

on the surface. Addition of small amounts of acetaldehyde shortens but does not eliminate the induction period, a fact which confirms previous conclusions that peracids (formed from aldehyde) are unimportant in the reaction scheme. Experiments after the potassium chloride treatment show that conditions favoring access to the walls diminish the rate of reaction markedly. This, together with the previously observed destructive action of the treated wall on peroxides, indicates that the latter play an essential rôle in the slow oxidation of the higher paraffins, whatever may be the case for methane and ethane.

REFERENCES

(1) Bone and Gardner: Proc. Roy. Soc. (London) **A154,** 297 (1936).
(2) Bone and Hill: Proc. Roy. Soc. (London) **A129,** 434 (1930).
(3) Norrish: Proc. Roy. Soc. (London) **A150,** 36 (1935).
(4) Pease: J. Am. Chem. Soc. **51,** 1839 (1929).
(5) Pease: J. Am. Chem. Soc. **52,** 5106 (1930).
(6) Pease: J. Am. Chem. Soc. **57,** 2296 (1935).
(7) Pease and Chesebro: Proc. Natl. Acad. Sci. U. S. **14,** 472 (1928).
(8) Pease and Munro: J. Am. Chem. Soc. **56,** 2034 (1934).
(9) von Elbe and Lewis: J. Am. Chem. Soc. **59,** 976 (1937).

DISCUSSION[1, 2]

Bernard Lewis and Guenther von Elbe: Dr. Pease has brought out some rather striking new facts. At 270°C. in an uncoated vessel the reaction rate of propane oxidation was found to be very little accelerated by the addition of nitrogen. After coating the wall with potassium chloride the reaction rate dropped sharply, and in order not to make the experiments unduly tedious the temperature had to be raised to 280°C. and a larger amount of acetaldehyde added. Now the rate proved to be strongly accelerated by nitrogen. The substitution of nitrogen by oxygen showed no comparable effect. It is possible to advance an explanation consistent with a branched-chain mechanism such as has been proposed by the writers (J. Am. Chem. Soc. **59,** 976 (1937)) in conjunction with the diffusion theory of chain reactions (von Elbe and Lewis: J. Am. Chem. Soc. **59,** 970 (1937)) for the case of chain breaking at the wall.

For low chain-breaking efficiency of the wall, the diffusion theory demands that the reaction be independent of the presence of inert gas. For high chain-breaking efficiency, such as may be supposed to exist in potassium chloride-coated vessels, the reaction rate will be much smaller and it will be accelerated by inert gas.

The fact that oxygen does not produce an effect comparable to that of

---

[1] Published by permission of the Director, U. S. Bureau of Mines, and the Director, Coal Research Laboratory, Carnegie Institute of Technology.

[2] Received September 25, 1937.

nitrogen suggests that it should not be regarded only as an inert gas. It may be possible to connect this effect with the inhibition by oxygen of the methyl alcohol-forming chain reaction discovered by Pease (J. Am. Chem. Soc. **57**, 2296 (1935)). We proposed this inhibition (J. Am. Chem. Soc. **59**, 976 (1937)) to consist of the oxidation of the chain carrier CH_3O to CO, H_2O, and OH. There are now two principal chain carriers, namely, CH_3O and OH, the former being predominant at high percentages of hydrocarbon and the latter at high percentages of oxygen. It is possible that CH_3O is a more efficient promoter of the reaction than OH, either because it is destroyed at the wall at a smaller rate or because of its greater reactivity in the gas phase, or both.

We have expressed the view that the wall plays the dual rôle of initiating and destroying chains, the chain-initiating reaction to consist of the dissociation of peracids formed heterogeneously from aldehydes. Such a view would appear to be consistent with experimental facts concerning aldehyde oxidation brought out by Pease and others. It would imply that potassium chloride not only increases the chain-breaking efficiency of the wall but also decreases the rate of chain initiation by the destruction of peracids. The peracids formed in the chain-initiating process are of necessity short-lived at the high temperatures in question, as is also shown by the analytical results in studies of the high-temperature oxidation of aldehydes; in any case they would be present in very small concentrations.