in their case. If the chain theory for the decomposition of aldehyde is correct, we should thus expect to be able to reduce the rate of the reaction very considerably by packing the reaction vessel with smaller tubing than Fletcher and Hinshelwood used. Probably an even better test would be to run the reaction in vessels composed of long lengths of coiled-up tubing of different sizes, which should give results more amenable to theoretical treatment.

The behavior to be expected theoretically for our reaction during a run is somewhat complicated, as the azomethane and aldehyde are decomposing at different rates. A formula can be obtained from which one should be able to calculate, from the behavior during the run, the rate at which the azomethane is going, provided the accumulation of reaction products be assumed not to affect the rate of reaction in any way. These calculations were carried through for several runs, but are not given in detail, as it was found that a slight error in the rate measured at any time produces a relatively enormous change in the calculated value of the azomethane rate constant, so that the latter can be found to a rough order of magnitude only. It was found to agree in order of magnitude with the rate obtained for pure azomethane at the same pressure and temperature; this was of course to be expected.

The chain length is the ratio of the aldehyde and azomethane decomposition rates and is given by $(K/k_0)P_{\text{ald.}}/P_{\text{az.}}^{1/2}$. As the temperature coefficient of k_0 is larger than that of K, the chain length decreases with rising temperature. At the pressures of azomethane used, we will have approximately $k_0 = 10^{15.67}\ e^{-51,200/RT}$; and $K = 10^{11.26}\ e^{-39,400/RT}$ (K is now in sec.$^{-1}$ mm.$^{-1/2}$). Then we readily find, if λ is the chain length, $\log \lambda = \log (P_{\text{ald.}}/P_{\text{az.}}^{1/2}) - 4.41 + (11,800/4.58\,T)$. Some typical values of λ are given in Table III.

The study of the reactions of methyl radicals with organic compounds is seen to be of considerable interest. It is hoped to make further studies along these lines using ethyl and possibly larger radicals as well as methyl.

Summary

The presence of decomposing azomethane induces decomposition in acetaldehyde. The kinetics of the reaction have been studied, and the results explained on the theory that the methyl radicals from the azomethane start a chain-type decomposition in the aldehyde. The temperature coefficient agrees with that expected from the theory, advanced by F. O. Rice and Herzfeld, that the pyrolysis of pure acetaldehyde is also a chain reaction.

CAMBRIDGE, MASS. RECEIVED JULY 7, 1934

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Slow Oxidation of Propane

BY ROBERT N. PEASE AND WENDELL P. MUNRO[1]

In a previous investigation of the non-explosive reaction of propane with oxygen,[2] it was concluded as a result of gas-analytical data alone that there were three main types of reaction: (1) a decomposition of the hydrocarbon to olefin, and methane or hydrogen at temperatures much below the normal, which must have been induced by the oxidation reactions, *e. g.*

$$M^* + C_3H_8 \longrightarrow C_2H_4 + CH_4 + M$$

(2) an oxidation yielding olefin and liquid oxidation products, *e. g.*

$$C_3H_8 + O_2 \longrightarrow C_2H_4 + HCHO + H_2O$$

(3) an oxidation yielding carbon monoxide and a liquid oxidation product, *e. g.*

$$C_3H_8 + 2O_2 \longrightarrow CH_3CHO + CO + H_2O$$

It was further concluded that the oxidation reactions (2) and (3) are of the chain type since—(1) the reaction is highly auto-accelerative; (2) it is suppressed by inert foreign gases in certain cases; (3) it is suppressed by a glass packing; (4) the kinetics follow no simple scheme. The purpose of the investigation here reported was to amplify the original work by determining liquid as well as gaseous products, with a view to fixing more definitely the nature of the oxidation reactions (2) and (3).

Experiments were carried out by the flow

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[1] Du Pont Fellow in Chemistry, Princeton University, 1932–1933.

[2] Pease, THIS JOURNAL, 51, 1839 (1929).

method at atmospheric pressure.[2] Liquid products were condensed in a cooled trap, while the gases were collected in a gasometer. Methods used for detection and estimation of liquid products will be presented in connection with the experiments. The method of gas analysis was the same as previously used, except that propylene was distinguished from ethylene by absorption in 90% sulfuric acid.

Our first concern was to estimate the relative importance of peroxides and aldehydes as products, since there has been some discussion[3] of this phase of hydrocarbon oxidation. Bone[3h] has insisted on the view that all hydrocarbon oxidation proceeds via hydroxylation, the hydroxyl compound losing water to form aldehyde.

$$RCH_3 + O_2 \longrightarrow RCH(OH)_2 \longrightarrow RCHO + H_2O$$

Further oxidation could then yield the lower aldehyde and carbon monoxide

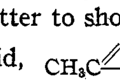
$$R'CH_2CHO + O_2 \longrightarrow R'CHO + CO + H_2O$$

or acid

$$RCHO + {}^1/_2O_2 \longrightarrow RCOOH$$

Pope, Dykstra and Edgar adopt essentially the same view, without specifying the intermediate hydroxyl compound. This is the type of our reaction (3). Bone has minimized the importance of peroxides as initial products, pointing out that aldehydes formed in the primary reaction could subsequently react with oxygen giving peracid as a secondary product. Bone and Hill show that in the oxidation of ethane, the peroxide (as determined with titanium sulfate) tends to follow aldehyde production and amounts to only about one-tenth of the latter. Others, however, leave no doubt as to the formation of true organic peroxides other than peracids. Thus, Lenher reported the formation of dioxymethyl peroxide ($OHCH_2OOCH_2OH$) from ethylene, and Mondain-Monval and Quanquin partially identified compounds of the types, ROOH, ROOR'OH, HOROOR'OH, in the oxidation of paraffins from pentane to decane.

Our results indicate that both peroxides (other than peracid) and aldehydes may be important products of propane oxidation. They further show, however, that peroxides cannot be essential to the chain-propagation of reaction since a very simple treatment of the reaction bulb (coating with potassium chloride) almost entirely eliminates these peroxides but only moderately decreases the total amount of reaction.

We analyzed for peroxides both by liberation of iodine from potassium iodide and by colorimetric determination with titanium sulfate, the two methods giving no significant differences. It was a simple matter to show that peracids (such as peracetic acid,  $CH_3C\overset{O}{\underset{OOH}{\diagup}}$) were not concerned. The reaction with potassium iodide may be written

$$ROOR + 2HCl + 2KI \longrightarrow 2ROH + 2KCl + I_2$$

If peracids (or per-esters) were present, an equivalent of acid would be formed. Direct determination of the acid consumption by subsequent alkali titration showed conclusively no acid from this source. Further, direct tests[4] showed that peracetic acid reacts instantaneously with potassium iodide, whereas the peroxides here found required twelve to twenty-four hours for completion of reaction (in a nitrogen atmosphere). We therefore eliminated peracids from consideration. However, the slowness of reaction with potassium iodide raised another question. Was our peroxide simply hydrogen peroxide, which also reacts slowly with potassium iodide? Since parallel titrations on a standard solution of hydrogen peroxide gave no definite answer to this question (the rates of iodine liberation were about the same), we required further evidence that we were dealing with an organic peroxide, and not with hydrogen peroxide simply.

This evidence was furnished by the discovery that the decomposition of the peroxide yielded an aldehyde. Total aldehydes were for the most part determined by use of the precipitant, dimethyldihydroresorcinol.[5] When this reagent was added to fresh liquid product, a precipitate whose melting point (187–189°) was that of the formaldehyde derivative was formed. The amount of formaldehyde so determined checked satisfactorily with independent determinations of formaldehyde by Romijn's potassium cyanide method.[6] Now, following the reduction of the peroxide in a fresh sample with potassium iodide, the precipitant invariably showed an increase in

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(3) (a) Bone and Hill, *Proc. Roy. Soc.* (London), **A129**, 434 (1930); (b) Callender, *Engineering*, **123**, 147 (1927); (c) Brunner and Rideal, *J. Chem. Soc.*, 1162, 2824 (1928); (d) Egerton, *Nature*, **121**, 10 (1928); (e) Mondain-Monval and Quanquin, *Ann. chim.*, **15**, 309 (1931); (f) Lenher, THIS JOURNAL, **53**, 3737, 3752 (1931); (g) Pope, Dykstra and Edgar, *ibid.*, **51**, 1875 (1929); (h) Bone and Townend, "Flame and Combustion in Gases," Macmillan and Company, 1927.

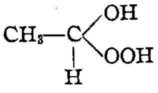
(4) Pease, THIS JOURNAL, **55**, 2753 (1933).

(5) Vorlander, *Z. anal. Chem.*, **77**, 241 (1929). This material was obtained from the Eastman Kodak Company.

(6) Romijn, *ibid.*, **36**, 18 (1897).

the amount of total aldehyde,[7] the melting point of the precipitate now being considerably lower (*ca.* 132°). Further, the increase in the amount of aldehyde so found in a number of runs averaged to the equivalent of the amount of peroxide present. We were forced to conclude, therefore, that the decomposition of the peroxide yielded aldehyde. This aldehyde is believed to be acetaldehyde because it gave the iodoform reaction and because the resin formed on heating with alkali corresponded in odor and color with that characteristic of acetaldehyde. The melting point of the precipitate (see above) also points in this direction.

Additional evidence that we were dealing with an organic peroxide which was not a peracid or perester was afforded by the fact that hydrogen was liberated on warming. Tests with hydrogen peroxide in presence of formaldehyde or acetaldehyde gave only oxygen.[8]

Although our evidence is insufficient to establish a formula for the peroxide—or to prove that only one peroxide is present—it is suggested that the compound  $CH_3-\underset{H}{C}H(OH)(OOH)$ would have the properties observed.

Data on production of peroxides and aldehydes, along with gaseous products, appear in Table I. The reaction tube for these experiments was 1.7 cm. in diameter and 14 cm. long. The volume was 31 cc. At 400° and 1 atm., the contact time when the gas inflow was 100 cc./min. (25° and 1 atm.) was eight seconds. Contact times were thus kept quite small in order to minimize secondary reactions to some extent. This tube was at first cleaned with hot nitric acid and then with distilled water. In this state it is called the "Clean Tube." Subsequently it was internally coated with potassium chloride by rinsing with an aqueous solution. In this state, it is called the "KCl Tube."

Comparison of the amounts of peroxide formed with the amounts of propane reacting shows as high as 25 moles of peroxide per 100 moles of propane. This can hardly be described as a negligible yield. Yet by the simple process of coating the reaction tube with potassium chloride, the formation of peroxide may be eliminated without seriously affecting the reaction rate. Thus, the last two experiments in the table show that 41% of the propane reacted before coating, yielding 22% peroxide. After coating, 25% of propane still reacted but there were only traces of peroxide. In view of this result it is obvious that peroxide can play no essential role in the reaction chain.[9]

Evidence that peroxide is a secondary product of reaction is also given by a comparison of amounts of peroxide formed and of propane reacting as the contact time is increased (flow rate decreased). The relative amount of peroxide passes through a maximum as reaction proceeds. Thus in the series at 400° with $1C_3H_8:3O_2$, moles of peroxide per 100 moles of propane reacting were 20, 21, 22, 25, 13 with increasing contact time; at 350° with $2C_3H_8:2O_2$, the figures are 17, 19, 25, 21; at 325° and $2C_3H_8:2O_2$, the figures are 0, 20, 19. Although the trend is not marked, it is definite and persistent. Such a trend would characterize a secondary product.

Much the same as has been said about peroxide is true of aldehyde with one important difference. Coating the reaction tube definitely increases the amount of aldehyde, whereas it decreases the amount of peroxide. Our data on aldehydes are not as numerous as on peroxide but they show the same tendency to increase with contact time. Thus in the series at 350° with $2C_3H_8:2O_2$, moles of aldehyde formed per 100 moles of propane reacting were 11, 12, 15, 23, indicating again that the aldehyde is a secondary product. This is not so surprising when it is known that the aldehyde was largely formaldehyde as determined by the melting point (187–188°) of the precipitate with dimethyldihydroresorcinol. Formaldehyde could easily be a secondary product, derived from ethylene, for example.[3f,10]

In view of our findings respecting peroxide and aldehyde, and especially because of the considerable amount of carbon unaccounted for in the products, we proceeded to look for other products of reaction. It was readily shown that acids were not formed in appreciable amounts. Ethylene and propylene oxides were tested for by the manganese chloride method.[3f] A test was also made by heating with water in a sealed tube

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(7) In some cases total aldehyde after decomposition of peroxide was checked by Ripper's bisulfite method.

(8) Lenher (Ref. 3f) reports that mixtures of hydrogen peroxide and formaldehyde liberate hydrogen after standing for some time. In our experiments the mixture was heated immediately after mixing. As to liberation of hydrogen by organic peroxides, see Rieche, "Alkylperoxide und Ozonide," Verlag T. Steinkopf, Dresden, Germany, 1931.

(9) Additional runs with a coated tube in which only traces of peroxide were formed will be found in Table II.

(10) Bone and Wheeler, *J. Chem. Soc.*, **85**, 1637 (1904).

TABLE I

PRODUCTION OF PEROXIDES AND ALDEHYDES

Methane present in small amounts (5 cc.) in some experiments

Temp., °C.	Ratio, C_3H_8/O_2	Total flow rate cc./min. 25° and 1 atm.	Per 400 cc. of reaction mixture entering: Reacted, cc. C_3H_8	O_2	Formed, cc. gas or vapor: C_3H_6	C_2H_4	H_2	CO	CO_2	Perox.	Ald.	Carbon deficiency, %[a]
					"Clean Tube"							
400	3/1	100	67	71	28	9	5	37	4	10	7	15
	1/3		41	74	13	..	..	28	5	9	1	26
400	3/1	50	85	99	28	11	5	49	5	7	14	26
	2/2		109	198	28	12	5	103	15	17	4	19
	1/3		61	141	12	5	7	67	16	15	2	12
400	3/1	250	..	..	..	..	..	..	..	10	4	..
		150	..	..	..	..	..	..	..	12	6	..
		100	67	71	28	9	5	37	4	10	7	15
		50	85	99	28	11	5	49	5	7	14	26
400	1/3	280	20	18	6	2	5	8	1	4	..	..
		167	29	45	9	2	6	15	..	6	..	..
		100	41	74	13	..	..	28	5	9	1	..
		50	61	141	12	5	7	67	16	15	2	12
		25	67	166	11	3	14	77	21	9	..	..
350	2/2	400	35	53	11	3	5	18	2	6	4	29
		200	52	85	13	5	5	33	4	10	6	28
		100	73	161	20	6	5	60	8	18	11	10
		50	87	196	20	7	7	79	10	18	20	18
325	2/2	400	13	6	1	0	4	3	0	Trace	0	(85)
		300	40	58	10	3	5	24	3	8	6	29
		200	48	77	11	4	5	25	4	9	7	34
					"KCl Tube"							
400	1/3	100	25	45	10	2	7	16	6	Trace	8	15
					Before coating							
400	1/3	100	41	74	13	..	11	28	5	9	1	..

[a] "Carbon deficiency, %" is calculated on the assumption that the peroxide contains 2 atoms of carbon. The aldehyde is taken as formaldehyde.

at 95° for several days, and then acetylating with acetic anhydride. After allowance for alcohols (see below), it was concluded that these substances were absent. A single qualitative test for propionaldehyde by means of the phenylhydrazone, and zinc chloride (formation of skatole)[11] was negative. Acetone was tested for by the method of formation of dibenzylidene acetone,[12] with negative results. Acetals were looked for by acidifying one of a pair of duplicate samples, and determining aldehydes by Ripper's bisulfite method. There was a slight balance in favor of the acidified sample, indicating small amounts of acetals.

The only additional product we could detect in appreciable amounts was alcohol, most of which was methanol, as determined by melting point of the 3,5-dinitrobenzoate (107.5°). Alcohol was determined by the acetylation method of Poznanski.[13] A number of runs were made for the determination of alcohol, using the KCl-coated tube to avoid ambiguity due to peroxides. Results appear in Table II.

The amounts of alcohol formed are seen to be appreciable, but they still do not make up any great part of the carbon deficiency. It is true that aldehydes were not determined in this series but previous experience would not indicate any large contribution. It will be noted also that the relative amounts of alcohol increase with the contact time, again indicating that these are secondary products.

The net result of our investigation is that organic peroxides, aldehydes and alcohols are all

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[11] Medvedev and Alexejewa, *Ber.*, **65B**, 133 (1932).

[12] Mulliken, "Identification of Organic Compounds," Vol. I, p. 148.

[13] Poznanski, THIS JOURNAL, **50**, 981 (1928). Subsequent saponification permits also a determination of esters by difference. No appreciable amounts of esters were found.

TABLE II

FORMATION OF ALCOHOLS IN "KCl TUBE"

Temp., °C.	Ratio, C_3H_8/O_2	Total flow rate cc./min. 25° and 1 atm.	Per 400 cc. of reaction mixture entering: Reacted, cc.		Formed, cc.							Carbon deficiency, %
			C_3H_8	O_2	C_3H_6	C_2H_4	H_2	CO	CO_2	Perox.	Alc.	
350	3/1	200	59	75	14	5	6	26	7	0.4	4	49
		100	70	98	18	7	5	41	11	0	8	39
350	2/2	200	58	94	14	5	6	39	11	0.2	3	40
		100	81	148	20	7	4	62	21	0	6	33
		50	95	188	20	8	5	83	27	0	16	29

present in the liquid products in appreciable amounts, while acids, ethylene oxide, acetaldehyde, propionaldehyde, acetone, acetals, and esters are unimportant. Allowance for the former (and for the gaseous products) still leaves a very considerable deficiency in the balance of carbon in the products against carbon in the propane reacting. None of the determined liquid products appears to be a primary product. There still remains undetected an important liquid product which may very well be the primary product of the chain.

Before it was determined that peroxides were eliminated by coating the tube with potassium chloride without radically altering the rate, we were strongly inclined to believe that the reaction which is of importance in chain propagation is (type 2)

$$C_3H_8 + O_2 \longrightarrow C_3H_6 + H_2O_2^*$$

This was indicated by the early appearance of propylene in quantity, as well as of peroxide. Of course, it might still be true that this is the case, and that peroxides are subsequently destroyed at the KCl-coated surface. However, the disappearance of peroxide is so nearly complete that we are now inclined to be skeptical of this view. The fact remains, however, that any reaction scheme must place propylene production, without the equivalent of hydrogen, in a primary position.

Our original scheme suggested the reaction (type 3)

$$C_3H_8 + 2O_2 \longrightarrow CH_3CHO + CO + H_2O$$

to be of considerable importance. It appears, however, that acetaldehyde is not present in detectable amounts. This follows from the fact that the melting point of the precipitate with dimethyl dihydroresorcinol corresponded to the formaldehyde compound (187–188°). Also determinations by the potassium cyanide method, which gives mainly the formaldehyde, checked with the precipitation method, which gives total aldehyde. We can only conclude from this and the other results that the important oxidation reaction has yet to be discovered.[14]

Summary

1. Liquid products of the slow combustion of propane have been examined.

2. Organic peroxides, aldehydes (mainly formaldehyde) and alcohols (mainly methanol) have been quantitatively estimated and indications noted that these are secondary products.

3. Acids, esters, acetals, acetone, propionaldehyde and ethylene oxide have been shown to be unimportant.

4. It has been found that coating the interior of the reaction bulb with potassium chloride almost completely eliminates peroxides without radically altering the reaction rate.

5. Attention is called to the early appearance of propylene in quantity without the equivalent of hydrogen, indicating its importance in the primary oxidation process.

6. Results indicate that the main reaction of hydrocarbon with oxygen has yet to be discovered.

PRINCETON, NEW JERSEY RECEIVED JULY 19, 1934

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[14] It has been suggested by Professor Taylor that our missing product is a higher olefin obtained by polymerization of propylene and ethylene in presence of oxygen. Unfortunately, our experiments give no information on this point.