the carboxyl group. Some other influence is however preponderant when the substitution is adjacent to the carboxyl group, that is to say when it is on the alpha carbon in an aliphatic acid, or in the ortho position in benzoic acid.

NEW YORK, N. Y. RECEIVED JULY 30, 1935

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

The Mechanism of the Slow Oxidation of Propane

BY ROBERT N. PEASE

In his original work[1] on the non-explosive oxidation of propane and the butanes, the writer was especially impressed with the fact that the oxidation reactions induced the dissociation of the hydrocarbons into the normal products, *e. g.*

$$C_3H_8 \longrightarrow C_3H_6 + H_2$$
$$\longrightarrow C_2H_4 + CH_4$$

This was discussed briefly in terms of what would now be called an "energy-chain." Since this work was done, F. O. Rice has brought out his "radical-chain" theory of hydrocarbon dissociation.[2] In view of the success of this theory in accounting for such experiments as those of Frey[3] on the dissociation of *n*-butane induced by decomposing dimethyl-mercury, it appeared important to attempt to account for the reactions occurring in hydrocarbon–oxygen mixtures in terms of radical-chains. For this purpose additional information about the products of the reactions was required.

In approaching this problem—the determination of liquid as well as gaseous reaction products—we were at first "side-tracked" by the discovery that substantial quantities of organic peroxides (other than per-acids) were formed.[4] However, it was eventually found that these peroxides could be largely eliminated (by coating the reaction tube with potassium chloride) without greatly affecting the reaction rate, an observation which convinced us that peroxides took no main part in the development of reaction. Had peroxides proven of greater importance, we would have been inclined toward Egerton's energy-chain theory.[5] An exhaustive search for other liquid oxidation products was then undertaken, the result of which was to show that, in the case of propane, only methanol and formaldehyde were of any importance. However, conditions were not favorable to the production of anything like stoichiometric yields of these, and the tentative conclusion was reached that the true primary products had still to be discovered.

Further investigation of this problem now indicates that methanol and formaldehyde, in addition to carbon monoxide and water, are in fact the primary products of propane oxidation, the indicated stoichiometric equation being

$$C_3H_8 + 2O_2 \longrightarrow CH_3OH + HCHO + CO + H_2O$$

How the general result is to be expressed in terms of the radical-chain theory will be discussed following presentation of the experimental data.

Experimental

The general methods of the previous investigations were employed. The gases passed at a known rate through a heated reaction tube of Pyrex glass coated with potassium chloride. Liquid products were separated at −40°, while gaseous products were separately collected over water with the trap at 0°. Methanol was determined by reaction with acetic anhydride (forty-eight hours at room temperature); formaldehyde by the potassium cyanide method; total aldehydes by the bisulfite method; esters by saponification following the alcohol determination. Carbon dioxide was absorbed in caustic; higher olefins (designated C_nH_{2n}) in concentrated sulfuric acid; ethylene in bromine water; oxygen in "Oxsorbent." Hydrogen and carbon monoxide were oxidized over copper oxide at 350°; paraffins were oxidized at 600°.

It was desirable to eliminate the olefin-producing reactions as far as possible. For this purpose, the experiments were conducted at low temperatures (300°, with one set at 260°). This necessitated the use of rather large reaction tubes. In order to minimize secondary oxidations, only mix-

---

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

[2] F. O. and K. K. Rice, "The Aliphatic Free Radicals," Johns Hopkins Press, Baltimore, Md., 1935.

[3] Frey, *Ind. Eng. Chem.*, **26**, 198 (1934).

[4] Pease and Munro, THIS JOURNAL, **56**, 2034 (1934).

[5] Egerton, *Nature*, **121**, 10 (1928); "Activation et Structure des Molecules," Société de Chimie Physique, 1928, p. 489.

TABLE I

Reaction tube					Of 400 cc. reaction mixture in								
					Used cc.		Formed, cc.						
Diam., cm.	Length, cm.	Vol., cc.	Temp., °C.	% O_2	O_2	C_3H_8[a]	CO	CH_3OH	HCHO	Higher CHO	CO_2	CH_4	C_nH_{2n}
2	30	105	300	20	77	40	28	21	14	7	15	1	5
3	22	146			79	41	38	23	12	8	10	4	6
4	12	141			78	50	37	24	11	8	12	8	5
6.5	6.5	162			76	46	38	20	13	5	11	11	7
3	22	146	300	10	39	19	14	16	9	4	4	2	4
				20	79	41	38	23	12	8	10	4	6
				30	119	47	48	27	12	11	17	5	9
6	28	762	260	10	39	17	16	12	7	4	7	5	3
				20	77	44	33	22	12	5	11	7	3
				30	116	65	47	28	14	5	19	9	2
			300	20	76	48	45	20	9	5	10	15	6

[a] "C_3H_8 used" represents the difference of two rather large numbers, and is consequently subject to a considerable error—perhaps 3 to 5 cc.

tures relatively low in oxygen (10 to 30%) were investigated.

Results are presented in Table I. The data refer to runs in which 400 cc. of reaction mixture was passed through the apparatus in ten minutes. Liquid products are calculated as cc. of vapor under standard conditions (760 ± 10 mm.; 25 ± 3°). In addition to the products listed, there were found 0 to 2 cc. of ethylene, hydrogen, acid and ester, with usually traces (<1 cc.) of peroxide. These are omitted in order to simplify the table somewhat.

Tubes of various dimensions were first investigated to determine optimum conditions. Over the range of diameters from 2 to 6.5 cm. there was little choice at 300°.[6] Sets of runs were finally made with 10, 20 and 30% oxygen at 300° with the 3-cm. tube, and at 260° with a large tube 6 cm. in diameter.

It will be noted that roughly two moles of oxygen react for every mole of propane, and one mole of carbon monoxide is formed. Next to carbon monoxide, methanol is the important product; and as the oxygen input is decreased, the amount of methanol tends to approximate the amount of propane reacting (see 10% runs). Formaldehyde behaves similarly, though the agreement is poorer. Nevertheless the *total* aldehyde ("HCHO" plus "Higher CHO") follows the methanol rather closely. Losses are clearly made up by secondary formation of carbon dioxide and methane.

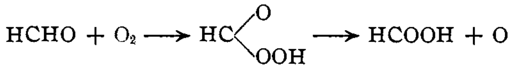
Discussion

Any consideration of the mechanism of propane oxidation must give prominence to two fundamental facts, namely, (1) the persistence of one carbon oxidation products, particularly methanol, at low temperatures and low oxygen concentrations; (2) the induced dissociation of the hydrocarbon at higher temperatures. Bone's hydroxylation theory[7] makes no provision for lower alcohols,[8] nor for induced dissociation. Norrish's development of the latter to include radical-chains propagated via oxygen atoms and alkylidene radicals[9] comes somewhat closer to what the writer is inclined to believe is the truth, but again it is not obvious how a lower alcohol could arise as a principal product. Norrish writes for the methane-oxidation chain

$$O + CH_4 \longrightarrow CH_2 + H_2O$$
$$CH_2 + O_2 \longrightarrow HCHO + O$$

The chain is started by surface reactions

$$CH_4 + O_2 \longrightarrow HCHO + H_2O$$



$$HCHO + O_2 \longrightarrow HC\begin{smallmatrix}\diagup O\\ \diagdown OOH\end{smallmatrix} \longrightarrow HCOOH + O$$

It is ended by the reactions

$$O + CH_4 + X \longrightarrow CH_3OH + X'$$
$$O + \text{surface} \longrightarrow {}^1/_2\,O_2$$

Provision is thus made for the alcohol of the same number of carbon atoms in the process of ending a chain. This type of mechanism obviously could not account for a stoichiometric yield of alcohol, especially one of fewer carbon atoms than the original hydrocarbon contained. The

---

[6] With the 2-cm. tube, reaction had to be started at 325–350° after which it would maintain itself on cooling to 300°. With a 1-cm. tube, a temperature of 400° was required for starting; and reaction would maintain itself only above 375°.

[7] Bone and Townend, "Flame and Combustion in Gases," The Macmillan Co., 60 Fifth Ave., New York City, 1927.

[8] Methanol was identified in every experiment by preparing the 3,5-dinitrobenzoate and taking its melting point. The latter was always sharp and close to the correct value for the methyl ester (108°). The alcohol from isobutane also proved to be methanol. From *n*-butane, the derivative melted from 95–102°, indicating a mixture of methyl and ethyl (m. p. 93°) esters.

[9] Norrish, *Proc. Roy. Soc.* (London), **150A**, 36 (1935).

same objection can be brought against the similar but independently developed theories of Semenoff[10] for hydrocarbon oxidation.

The writer is inclined to go back to Rice's theory of hydrocarbon dissociation[2] as a starting point for the oxidation mechanism of propane. According to this, the dissociation of propane proceeds essentially through the reactions

Chain-starting $C_3H_8 \longrightarrow CH_3 + C_2H_5$
Chain-development $(R = CH_3, (C_2H_5), H)$
(1) $C_3H_8 + R \longrightarrow RH + C_3H_7$
(2) $C_3H_7 \begin{cases} \nearrow C_3H_6 + H \\ \searrow C_2H_4 + CH_3 \end{cases}$
Chain-ending $R + R' \longrightarrow RR'$

Quite apart from the applicability of this scheme to the normal dissociation, one may grant its usefulness in interpreting induced dissociations and allied reactions. In essence, the mechanism requires a radical, R, which is capable of removing a hydrogen atom or methyl group from the propane molecule, and which is reproduced in the subsequent reactions of the residue. Our problem is to determine what reasonable sequence of reactions of this type will yield the observed products of the oxidation reactions.

The mechanism which the writer has in mind postulates the methoxyl radical (CH_3O) and the propyl radical (C_3H_7) as chain carriers

$$CH_3O + C_3H_8 \longrightarrow CH_3OH + C_3H_7$$
$$C_3H_7 + O_2 \longrightarrow C_2H_4O + CH_3O$$

These would yield methanol and the compound C_2H_4O, which is taken to be acetaldehyde. A portion of the acetaldehyde survives (higher CHO). The remainder reacts with oxygen to give formaldehyde and carbon monoxide

$$CH_3CHO + O_2 \longrightarrow HCHO + CO + H_2O$$

The addition of oxygen to acetaldehyde is measurable at 100°. It must be extremely rapid at 300°. That the low-temperature product (peracetic acid) breaks down to yield carbon monoxide at higher temperatures appears plausible from the work of Pope, Dykstra and Edgar[11] on the oxidation of *n*-butyraldehyde and *n*-heptaldehyde. The main oxidation products (CH_3OH, HCHO, CO) are thus accounted for. Further reaction of the propyl radicals will also yield the normal products of dissociation at higher temperatures by Rice's mechanism given above. The suggested scheme thus affords a straightforward explanation of the analytical data.

The starting and stopping of chains is less clear.[12] It is to be remembered that reaction is very strongly inhibited by a packing, and is at least delayed at intermediate temperatures (375–425°) by excess of foreign gases, as well as oxygen, the reaction having a negative temperature coefficient in this range. The effect of packing rather argues against a wall reaction for starting the chains. Homogeneous dissociation of propane into radicals seems to be ruled out. Likewise a homogeneous bimolecular reaction between propane and oxygen seems doubtful since the over-all reaction depends more on the propane than on the oxygen concentration. It is accordingly suggested that the starting reactions are

$$2C_3H_8 \longrightarrow C_3H_8^* + C_3H_8$$
$$C_3H_8^* + O_2 \longrightarrow C_2H_5O + CH_3O$$

the oxidation of $C_3H_8^*$ being much faster than the deactivation of $C_3H_8^*$ by collision.

The chain-stopping reactions are taken to be association of radicals by a 3-body process occurring chiefly at the walls

$$2CH_3O + M \longrightarrow X$$
$$2C_3H_7 + M \longrightarrow Y$$
$$CH_3O + C_3H_7 + M \longrightarrow Z$$

The complete mechanism would therefore be

$$(1)\quad 2C_3H_8 \overset{k_1,\, k_1'}{\rightleftarrows} C_3H_8^* + C_3H_8$$
$$(2)\quad O_2 + C_3H_8^* \xrightarrow{k_2} C_2H_5O + CH_3O$$
$$(3)\quad CH_3O + C_3H_8 \xrightarrow{k_3} CH_3OH + C_3H_7$$
$$(4)\quad C_3H_7 + O_2 \xrightarrow{k_4} C_2H_4O + CH_3O$$
$$(5)\quad C_2H_4O + O_2 \xrightarrow{k_5} HCHO + CO + H_2O$$
$$(6)\quad 2CH_3O + M \xrightarrow{k_6} X$$
$$(7)\quad 2C_3H_7 + M \xrightarrow{k_7} Y$$
$$(8)\quad CH_3O + C_3H_7 + M \xrightarrow{k_8} Z$$

Reactions (1) and (2) together are supposed to yield CH_3O at a rate proportional to $[C_3H_8]^2$. At the steady state (point of inflection of the rate curves) we have

$$d[CH_3O]/dt = k_1[C_3H_8]^2 + k_4[C_3H_7][O_2] - k_3[CH_3O][C_3H_8] - k_6[CH_3O]^2M - k_8[CH_3O][C_3H_7]M = 0$$
$$d[C_3H_7]/dt = k_3[CH_3O][C_3H_8] - k_4[C_3H_7][O_2] - k_7[C_3H_7]^2M - k_8[CH_3O][C_3H_7]M = 0$$

Solution for the steady-state concentration of $[CH_3O]$ leads to an unwieldy expression. If we

---

[10] Semenoff, "Chemical Kinetics and Chain Reactions," Oxford Press, London, England, 1935.

[11] Pope, Dykstra and Edgar, THIS JOURNAL, **51**, 1875 (1929).

[12] This analysis of the starting and stopping of chains is recognized to be incomplete. In particular, the occurrence of long induction periods, the negative temperature coefficient, and the rôle played by aldehyde oxidation require further consideration.

assume chains are ended only by reaction (6), we find

$$[CH_3O] = \sqrt{k_1/k_6M}\ [C_3H_8]$$

If only reaction (7) is effective

$$[CH_3O] = \frac{1}{k_3}\left(k_1[C_3H_8] + k_4\sqrt{\frac{k_1}{k_7M}}\,[O_2]\right)$$

If only reaction (8) is effective

$$[CH_3O] \cong (k_1/2k_3)\ [C_3H_8]$$

or

$$[CH_3O] \cong \frac{k_1}{4k_3}\,[C_3H_8] \pm \sqrt{\frac{k_1k_4[C_3H_8][O_2]}{2k_3k_8M}}$$

depending upon the approximation which is made. The rate of disappearance of propane will be determined principally by the rate of reaction (3) if chains are long.

$$-d[C_3H_3]/dt \cong k_3[C_3H_8][CH_3O]$$

Substituting the above values of $[CH_3O]$ shows that the rate will depend on a power of $[C_3H_8]$ between 1 and 2, and will be relatively independent of oxygen concentration no matter which reaction is effective in terminating chains.

Mechanisms similar to the above may be written for methane and ethane in terms of hydroxy- instead of methoxyl radicals, yielding water in place of methanol. Such mechanisms are to be considered as an alternative to the Semenoff–Norrish mechanism.

Summary

1. Investigation of the slowoxidation of propane at lower temperatures and oxygen concentrations than heretofore employed indicates that methanol, formaldehyde, carbon monoxide and water are the primary products.

2. Results are interpreted in terms of Rice's radical-chain theory, on the assumption that methoxyl (CH_3O) and propyl (C_3H_7) are the chain carriers.

3. It is pointed out that similar mechanisms involving hydroxyl in place of methoxyl, and producing water in place of methanol, may apply to the oxidation of methane and ethane.

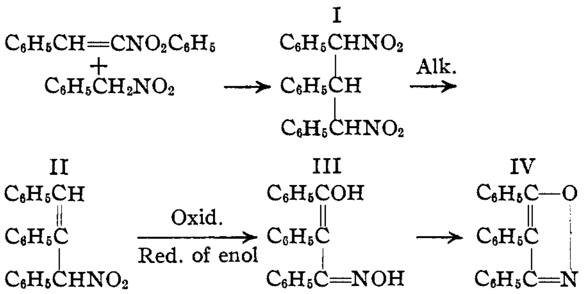
PRINCETON, N. J. RECEIVED JULY 31, 1935

[CONTRIBUTION FROM THE PEARSON MEMORIAL LABORATORY OF TUFTS COLLEGE]

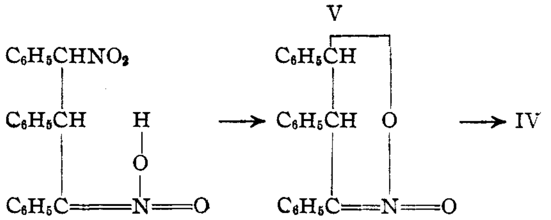
Alcoholic Ammonia as a Reagent in the Nitrostilbene Series

BY DAVID E. WORRALL

Heim[1] assumed the following transformations to account for the presence of triphenylisoxazole as a by-product in the Knoevenagel reaction



He succeeded in isolating the dinitro compound I, likewise an unsaturated nitro compound isomeric with II, but not the monoxime III. Later Kohler and Barrett[2] proved that triphenylisoxazoline oxide (V) is an intermediate between I and IV, using sodium methylate. Consequently they postulate this sequence of events.



It has now been found possible, using a milder reagent, to isolate III and while this does not necessarily mean that the oxime is the sole or even principal precursor of IV, it does fit in with the scheme of Heim.

Ammonia in the absence of water does not react by addition or otherwise with nitrostilbene. A trace of water is sufficient to induce hydrolysis, the starting point of a chain that continues until sufficient phenylnitromethane is liberated to react with unchanged nitrostilbene thereby forming I. It is not improbable that this substance loses nitrous acid so as to form II, which for the most part rearranges into the isoxazoline oxide (V).

---

[1] Heim, *Ber.*, **44**, 2021 (1911).

[2] Kohler and Barrett, THIS JOURNAL, **46**, 2106 (1924).