

structure observed. If we assume that the hydrogen atoms are placed unsymmetrically in the eight-membered ring formed by the two carboxyl groups, *i. e.*, each hydrogen being nearer to the oxygen to which it was originally attached, then there are two modes of vibration involving the stretching of the hydrogen bonds which are active in infrared absorption. Each vibration is anti-symmetric with respect to a center of symmetry but they differ in the relative motions of the oxygen atoms on either side of the hydrogen atoms. These two frequencies might be guessed to differ by the separation of the two pairs of doublets, *viz.*, 50  $\text{cm.}^{-1}$ . Because of the fact that there are alternative positions for each hydrogen and consequently, a double minimum in the potential energy curve, the doublets themselves might be expected. Their separation varies from 10 to 20  $\text{cm.}^{-1}$ . This is, of course, to say nothing of the possibility of resonance between the O-H and C-H vibrations which have nearly the same frequency. Since the C-H absorption is small this effect is probably unimportant although the C-H absorption might be considerably increased by the resonance itself.<sup>17</sup>

Some plausibility is lent to the foregoing explanations by the much simpler structure observed in the absorption peak for deuterobenzoic acid. Here the last effect is absent and because of the greater mass of the deuterium atom the

(17) In a previous note [THIS JOURNAL, 59, 176 (1937)] the authors reported on the lack of evidence for the enolization of dibenzoyl-methane. This molecule shows absorption resembling that of the carboxylic acids and it is possible to write a hydrogen bonded structure for the enolic form that resembles one-half of the dimeric ring of the acids. The matter therefore requires further investigation.

doublet separation would be too small for resolution. There would remain only the two modes of vibration differing markedly in absorption coefficients and these appear to be present.

It has been noted by various authors that formic acid in the liquid state has a dielectric constant some ten times that of liquid acetic acid. Because of the difficulty of purification no studies have been made upon formic acid but there can be little doubt that in the liquid state the dimers are transformed into higher polymers perhaps through the hydrogen attached to the carbon. In a subsequent paper this possibility will be discussed again in connection with formamide. The high dielectric constant which results from polymerization such as occurs in formamide probably offers a clue to the explanation of the greatly reduced solubility of chloroform in this solvent.

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### Summary

The general character of the infrared absorption spectra indicative of hydrogen bonding is discussed. Curves are shown for the absorption of the active or bonding hydrogen in acetic, benzoic and deuterobenzoic acids under various conditions. The generalization of Venkateswaran in regard to the shift of the hydroxyl frequency is confirmed and some suggestions are made to explain the complex absorption characteristic of association in the carboxylic acids.

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## The Negative Temperature Coefficient in the Rate of Propane Oxidation

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In the early work<sup>1</sup> on the slow combustion of propane and the butanes, it was noted that under certain conditions the rate of oxidation decreased markedly with increasing temperature, although eventually (at a higher temperature) explosion occurred. Similar observations have since been made by Beatty and Edgar<sup>2</sup> on heptane-air mixtures, by Aivazov and Neumann<sup>3</sup> on pentane-

oxygen mixtures, and by Newitt<sup>4</sup> on propane-oxygen mixtures.

The beginnings of an explanation of this anomalous behavior follow from the latter investigation. It had been found by Townend<sup>5</sup> that mixtures of air with vapors of hydrocarbons, alcohols, or aldehydes show, in addition to a "true ignition" region (higher pressures and temperatures), a region of limited explosibility giving rise to so-

(1) Pease, THIS JOURNAL, 51, 1839 (1929).

(2) Beatty and Edgar, *ibid.*, 56, 102 (1934).

(3) Aivazov and Neumann, *Acta Physicochimica* (U. R. S. S.), 4, 575 (1936).

(4) Newitt, *et al.*, *J. Chem. Soc.*, 1658, 1665, 1669 (1937).

(5) Townend, *Chem. Rev.*, 21, 259 (1937).

called "cool-flames." In a pressure-temperature plot, the latter region appears as a tongue or peninsula pointed toward lower pressures over a limited temperature range in the neighborhood of 300°.

Now it so happens that much of the work which has been done on the oxidation of hydrocarbons apparently has fallen in or near the region of cool flames. Hence the anomalies which have appeared in such work (including the negative temperature coefficient) are in effect incidental to the anomaly of the limited cool-flame region itself.

With the above in mind, Newitt investigated in some detail the characteristics of the cool-flame region for propane-oxygen mixtures. He found among other effects that at temperatures immediately above the cool-flame limit ( $\sim 350^\circ$ ), the rate of reaction dropped abruptly to a fairly flat minimum ( $\sim 425^\circ$ ) and then rose abruptly to the ignition point ( $\sim 450^\circ$ ). The negative temperature coefficient was thus identified with the crossing of the cool-flame limit on the high temperature side.

The region of negative temperature coefficient is more accurately described as a region of minimum rate, bounded at lower and higher temperatures by explosion limits. It would thus appear to be a region of transition from one to another mechanism of oxidation. One should then expect a corresponding change in the kinetics of the process, and this can in fact be observed.

The author<sup>6</sup> has reported measurements of the rate of propane oxidation at a temperature (270°) well below the lower cool-flame limit. With an uncoated<sup>7</sup> Pyrex bulb, it was found that the maximum rate was nearly independent of the oxygen concentration but varied with a power of the propane concentration between one and two, as shown in Table I.

TABLE I  
RATE OF PROPANE OXIDATION AT 270° (5 MM. CH<sub>3</sub>CHO ADDED)

Initial pressure, mm.			Total pressure change, mm.	[dP/dt] <sub>(max.)</sub> mm./min.
C <sub>3</sub> H <sub>8</sub>	O <sub>2</sub>	N <sub>2</sub>		
199	202	.	61	9.93
212	197	202	61	11.03
205	384	.	119	10.62
300	301	.	92	23.5
408	202	.	65	34.8

On the other hand, Newitt found that above the cool-flame limit (but below the ignition point),

(6) Pease, *Chem. Rev.*, **21**, 279 (1937).

(7) That is, not treated with potassium chloride solution.

the equimolecular mixture is the most reactive (total pressure constant at 360 mm.; temp. 408°) *i. e.*, the rate is roughly proportional to the product of propane and oxygen concentrations.

In order to make sure that this difference is real, the author has repeated Newitt's experiments under somewhat different conditions as follows.

A reaction bulb like that used for the low temperature experiments was prepared, and washed out with nitric acid and then with distilled water. This was mounted in an electric heater and connected with sources of tank gases, with a manometer, and with vacuum pumps. A series of runs was then carried out at 400° with results as shown in Table II.

It is clear from these results that the rate now depends on *both* propane and oxygen concentrations, the powers being rather higher than the first. There is thus excellent evidence from the kinetics of the reaction that there are two mecha-

TABLE II  
RATE OF PROPANE OXIDATION AT 400°

Initial pressure, mm.			Total pressure change, mm.	[dP/dt] <sub>max.</sub> mm./min.
C <sub>3</sub> H <sub>8</sub>	O <sub>2</sub>	N <sub>2</sub>		
105	103	.	59	15.9
101	103	104	60	15.6
207	101	.	67	42.
102	203	.	115	51.
102	103	.	59	14.2

nisms of oxidation, one predominating at low temperatures (and leading to cool-flames under optimum conditions), and the other predominating above the cool-flame region and leading to true ignition.

In order the better to visualize these two alternative reactions, a series of runs was made at 10° intervals between 300 and 430° (Fig. 1). These runs were made with 100 mm. each of propane and oxygen. With such a mixture, one would (according to Newitt's results) just cut the tip of the cool-flame peninsula at about 290-320°. As, however, Newitt worked with a reaction vessel 5.5. cm. in diameter, whereas the one here used was 2.0 cm. in diameter, it is probable that the experiments were outside the cool-flame region entirely. Certainly there was nothing in the pressure records to indicate the occurrence of cool-flames.

The procedure was to measure rates at 20° intervals from 300 to 420°, then to return to 310° and again proceed upward (to 430°) by 20° intervals. The second set of measurements are lower

than the first but the general form of the curve is evident (Fig. 1.).

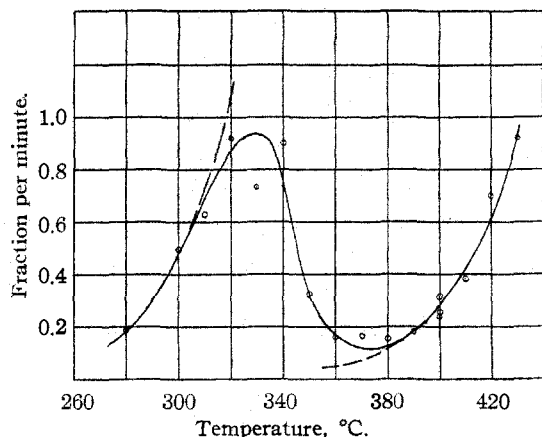


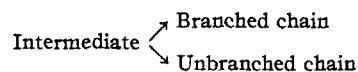
Fig. 1.—Variation of rate of oxidation of propane with temperature for 1:1 mixture at 200 mm. The rates are maximum rates corresponding to the inflection points of the pressure-time curves.

Individual rate curves were of the familiar S-shaped type, with an induction period which decreased regularly with increasing temperature. The values of the rate given are the maximum rates as read from the curves.

This maximum rate rises to an upper level at about 340°, and then drops to a fairly flat minimum. Subsequently, it rises again, and would terminate in true ignition.

Two curves have been sketched in Fig. 1 to emphasize the existence of two mechanisms of oxidation. These curves were drawn on the basis of points read from a log rate-reciprocal temperature plot. The one for lower temperatures corresponds to an activation energy of 29,000 cal.; that for the higher temperature range corresponds to an activation energy of 38,000 cal.

Between these two curves lies the transition region within which the rate passes through a minimum as the temperature increases. If we assume with von Elbe and Lewis<sup>8</sup> that the low-temperature reaction at least is of the branched-chain type, the rather sharp suppression of reaction as temperature rises may be attributed to suppression of branching. The subsequent development of reaction at higher temperatures would then represent the same or a new reaction proceeding by an unbranched chain. In bare outline, one might write



the balance between the two alternatives being determined by the temperature, other things being equal. The experimental work here reported appears to be in general accord with the speculations of von Elbe and Lewis.

### Summary

A further study of the negative temperature coefficient in the rate of oxidation of propane has been carried out. It is shown that the rate passes through a minimum at 360–380° (100 mm. of each gas). At low temperatures, the steady-state rate is independent of oxygen concentration (uncoated reaction bulb), whereas at higher temperatures it depends upon the concentrations of both gases, the powers being between one and two.

It is suggested that a low-temperature branched-chain reaction is suppressed in the transition region and gives place to an unbranched chain.

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(8) Von Elbe and Lewis, *THIS JOURNAL*, **59**, 976 (1937).