Conclusions

1. Substitution of methyl groups produces very little effect on the hydrogen-ion concentration at which the indicator changes color.
2. The position of the acid group produces the greatest change in indicator properties. When in the ortho position the change takes place at the higher *P*H, when in para lower and lowest in meta.
3. The introduction of strongly negative groups such as the nitro group causes a change at a lower *P*H.

GRAND FORKS, NORTH DAKOTA

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY]

THE CHAIN CHARACTERISTICS OF THE ETHYLENE-OXYGEN REACTION

BY ROBERT SPENCE[1] AND HUGH S. TAYLOR

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It is now well known that many reactions once thought to be of the simple classical type actually occur by a chain mechanism. Generally speaking, the existence of these chains has been demonstrated in one or more of three ways, by measuring the quantum yield in photochemical experiments, by studying the unusual kinetics of gaseous reactions, or by introducing some active material or "trigger" to start the chains. In the case of hydrocarbon oxidations, the photochemical method is not very convenient experimentally. Before making a study of the kinetics of these reactions it was considered advisable to demonstrate their chain character in a direct manner by the last of the methods mentioned above. The use of ozone as a "trigger" in gaseous reactions was first developed by Semenoff and Rjabinin[2] in the combustion of sulfur. An attempt has been made to apply ozone as a "trigger" to the ethylene-oxygen system at temperatures where sufficient reaction takes place to be measurable but well below the ignition point. Under these conditions ozone has an extremely short life, so that the actual amount employed in starting chains may be very much smaller than the amounts actually introduced into the gas stream. We would therefore obtain only a lower limit of ozone efficiency and of chain length in this manner.

Ethylene and oxygen (from cylinders), at measured rates of flow, and dried over phosphorus pentoxide, were passed through a reaction vessel maintained at a definite temperature in a furnace, then through a weighed tube of phosphorus pentoxide for a given time, the increase in weight being noted. With everything else constant, the oxygen was then partially

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[1] Commonwealth Fund Fellow.

[2] Semenoff and Rjabinin, *Z. physik. Chem.*, **1B**, 193 (1928).

ozonized by passing through a Brody's ozonizer and the increase in weight of the absorption tube again noted. This increase was many times the former increase, as the appended Table I shows.

TABLE I

OXIDATION OF ETHYLENE IN PRESENCE AND ABSENCE OF OZONE

T, °C.	$C_2H_4:O_2$	Normal increase (a), g.	Using O_3 (b), g.	Ratio b/a	Time, min.
298	1:2.5	0.0020	0.1290	64.5	30
298	1:2	.0020	.0878	87.5	15
350	1:2	.0030	.1350	45.0	15
358	1:2	.0032	.0506	15.8	15
388	1:2	.0152	Exploded	..	15

Assuming that all the ozone introduced into the gas stream reacted to give water, the increase in fifteen minutes due to ozone alone would be 0.12 g.; hence these experiments do not afford conclusive proof of the existence of a chain mechanism. The explosion is significant in view of the fact that ethylene and oxygen normally do not explode until temperatures over 500° are reached. With ozone present, the system becomes very sensitive to shocks around 400° and often exploded at the turning of a stopcock.

In another series of experiments the solid and liquid products of the reaction were frozen out by a carbon dioxide–ether trap and the remaining gases analyzed. The ozonizer was calibrated so that any desired concentration could be obtained by varying the current in the 4000-volt transformer. To prevent explosions, the apparatus was made of thick-walled barometer tubing (2-mm. bore) as far as possible and, in order to prevent decomposition of the ozone before it reached the furnace, the oxygen inlet tube was cooled by water circulating through a lead coil surrounding the inlet. The reaction chamber was also considerably smaller than in the first series of experiments, having a capacity of about 8 cc. instead of 150 cc. To prevent explosions due to sudden pressure variations at the moment when a gas sample was to be collected, the gas was first allowed to stream from the furnace into the air. With the stopcock leading to the analysis buret open, the exit to the air was slowly closed by tightening a clip on a small rubber tube attached to the air exit. When the dead space of the collecting system was thoroughly swept out, a sample was collected in the gas buret in a given time, the pressure being maintained as far as possible constant throughout the procedure. The products collected in the trap appeared to be mainly formaldehyde and small amounts of a white solid, possibly a polymer. Carbon dioxide was absorbed by alkali in the gas buret, ethylene removed by bromine water and all the remaining gas except a small residue could be absorbed by pyrogallol. In order to make the two measurements under as nearly the same conditions as possible, oxygen, for the sake of rapidity, was generally obtained by difference, a few check determinations being made at intervals. Results are given in Table II. The effect of increasing temperature causes an apparent shortening of the chains but this is no doubt due to the thermal decomposition of the ozone. All the values derived for the chain length are greater than unity and hence constitute direct evidence for the existence of reaction chains in hydrocarbon combustions; a small amount of ozone reacting is able to cause additional amounts of oxygen to take part in the reaction.

TABLE II

OXIDATION OF ETHYLENE IN PRESENCE AND ABSENCE OF OZONE

		Residual gas in given time interval						
		Without O_3		With O_3				
T, °C.	Time, sec.	O_2	C_2H_4	O_2	C_2H_4	O_2 used due to O_3, cc.	O_2 supplied as O_3, cc.	Ratio
260	30	41.5 cc.	27.5 cc.	37 cc.	25 cc.	4.5	0.630	7.1
274	30	36	29	32	26	4	.630	6.35
283	30	34	28	32	24.5	2	.630	3.2
323	15	52.5	13.5	49	12.5	3.5	.960	3.64
342	60	63	56	59	52.5	4	1.344	3.0
351	60	62	58	60	54	2	0.840	2.4
356	15	49	18	47.5	16	1.5	.936	1.6
401	15	48.5	16.5	47	15	1.5	.936	1.6
410	15	48.5	17	47.5	15.5	1.0	.924	1.1
430	30	57.5	12.5	54.5	11.0	3.0	.920	3.26
430	30	57.5	13.5	56.5	12.5	1.0	.920	1.1
430	60	104.5	25.5	101	22	3.5	1.84	1.9
438	15	48.5	14.5	46	13	2.5	0.906	2.75

Since this work was completed, a study of the oxidation of ethylene from the standpoint of reaction kinetics has been published by Thompson and Hinshelwood.[3] They conclude that "between 400 and 500° the oxidation is probably a chain reaction." They suggest that "the first stage in the reaction is the formation of an unstable peroxide; if this reacts with more oxygen the chain ends, but if it reacts with ethylene, unstable hydroxylated molecules are formed which continue the chain." They conclude "that from a consideration of the temperature coefficient and the influence of foreign gases on the rate of reaction that the chains are probably not of great length." The present experiments therefore constitute an important line of auxiliary evidence with respect to the chain characteristics of this hydrocarbon oxidation and supplement the data already supplied by Pease[4] with respect to the chain nature of the oxidation of the saturated hydrocarbons.

We desire to acknowledge our indebtedness to the Commonwealth Fund which provided one of us (R. S.) with the Fellowship with the aid of which this work became possible.

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[3] Thompson and Hinshelwood, *Proc. Roy. Soc.* (London), **125A,** 277 (1929).

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

Summary

The use of ozone as an initiator of reaction between ethylene and oxygen at temperatures below the normal reaction temperature in absence of ozone has been studied.

The results are consistent with the hypothesis that the oxidation process is a chain reaction.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN]

SOLUBILITY OF LEAD SULFATE, CHROMATE AND MOLYBDATE IN NITRIC AND IN PERCHLORIC ACID

BY H. H. WILLARD AND J. L. KASSNER[1]

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It has been shown by Thiel and Stoll[2] that the difference in potential between lead electrodes in 0.05 molar solutions of lead perchlorate and nitrate is 0.016 volt. From this they calculated the ratio of the concentrations of Pb^{++} in the two solutions to be 1:0.28. In connection with other work the present authors had noticed that lead sulfate, chromate and molybdate were less soluble in perchloric acid than in nitric acid of the same concentration. In order to investigate this matter more thoroughly, with the possibility of utilizing the results in analytical separations, the solubilities of these salts were determined in perchloric and in nitric acids of different concentrations, both with and without the addition of a common ion.

Experimental

Preparation of Lead Sulfate.—Lead sulfate was prepared by adding simultaneously from two burets dilute solutions of sulfuric acid and lead perchlorate to 800 cc. of slightly acidified water, with vigorous stirring. This gave a fairly coarse precipitate. It was washed with water five times by decantation, centrifuged in platinum cups and washed four times on the centrifuge.

Preparation of Lead Chromate.—Lead chromate was prepared in the same manner as lead sulfate, using lead perchlorate and potassium dichromate. The lead chromate was washed with water eight times by decantation, four times on the centrifuge, dried in a vacuum over phosphorus pentoxide and analyzed by electrometric titration with ferrous sulfate. The average of two closely agreeing analyses gave 16.09% chromium, compared to a theoretical value of 16.08%.

Preparation of Lead Molybdate.—Lead molybdate was prepared in a similar manner by adding lead perchlorate and ammonium molybdate to hot water acidified with perchloric acid. After boiling the solution for a few minutes, the precipitate was washed eight times by decantation with hot 2% ammonium nitrate solution, centrifuged, and

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[1] From a dissertation submitted by J. L. Kassner to the Graduate School of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry.

[2] Thiel and Stoll, *Z. anorg. allgem. Chem.*, **139**, 317 (1924).