[CONTRIBUTION FROM FERTILIZER AND FIXED NITROGEN INVESTIGATIONS, BUREAU OF CHEMISTRY AND SOILS]

THE IGNITION OF CARBON MONOXIDE–OXYGEN MIXTURES: THE EFFECT OF IMPURITIES

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RECEIVED JULY 16, 1930 PUBLISHED NOVEMBER 5, 1930

Introduction

In a previous communication[1] it was shown that when a $2CO–O_2$ mixture was ignited by a condensed discharge a hyperbolic relationship existed between the gas pressure and the condenser voltage, *i. e.*,

$$V = k/P \qquad (1)$$

where V is the minimum voltage necessary for flame propagation and P is the pressure of the explosive mixture. The effects of various impurities on the ease of ignition were also discussed and an attempt was made to establish a mathematical relation between the amount of impurity and the energy of ignition.

In the present paper it is proposed to extend the hyperbolic relation between voltage and pressure to other explosive mixtures and to establish a more exact mathematical relation between the quantity of impurity present and the ignitibility of the gas.

Finch and Cowen[2] have shown that the ignition current in a $2H_2–O_2$ mixture is a hyperbolic function of the pressure over an appreciable pressure range. From this they drew the conclusion that "ignition is determined solely by the attainment in some portion of the gas traversed by the discharge of a certain definite concentration of suitable ions or electrically charged particles."

The study of the effect of impurities on the ignitibility of explosive mixtures has largely been confined to that of water vapor on the $2CO–O_2$ mixtures. This problem has been investigated by W. A. Bone and his coworkers,[3] who have shown that as water vapor is progressively removed the ignitibility rapidly diminishes, the minimum spark energy for a mixture dried with calcium chloride being about thirty-fold that required to ignite the same mixture when saturated with water. They have also shown that gas dried for a year over phosphorus pentoxide is ignitible in a sufficiently powerful condensed discharge although the reaction does not go to completion.

Apparatus

The type of apparatus used in these researches was briefly described in the former article. It consisted of an explosion chamber of 56 cc. capacity which was connected

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[1] A. Keith Brewer, *Proc. Nat. Acad. Sci.*, **13**, 689 (1927).

[2] Finch and Cowen, *Proc. Roy. Soc.* (London), **116A**, 529 (1927).

[3] Bone and Weston, *ibid.*, **110**, 615 (1926).

to separate gas trains, one for the admission of the moist or dried $2CO-O_2$ mixture, and the other for the admission of the various impurities tested.

Open-end mercury manometers were used to determine the gas pressures. A McLeod gage was unsuitable since most of the impurities tested were vapors. The glass walls of these manometers can be kept clean by admitting hydrogen to the system from time to time and then passing an electric discharge from the mercury to a suitably placed auxiliary electrode. The H_2^+ ions and atoms formed in the discharge readily reduce the oxides contaminating the walls.

A Hyvac pump capable of giving a pressure of less than 0.1 mm. was used for evacuation. The explosion chamber was flushed out before admitting fresh gas.

Connection to the explosion chamber was made through ground-glass stopcocks lubricated with high vacuum stopcock grease. No effect whatsoever could be attributed to the use of the grease. Its lower vapor pressure and its greater freedom from leaks render it far more satisfactory than the sirupy phosphoric acid often used in this type of work.

The ignition was brought about by a discharge from eleven 1-mf. condensers placed in parallel. The condensers could be charged to any desired voltage by a high voltage d. c. generator placed across a suitable potentiometer. The charging voltage was read with a 750 voltmeter, which could be used with a 10^6-ohm resistance in series when necessary.

The spark gap was made from two platinum balls about 2.0 mm. in diameter; one was fastened directly to a 60-mil tungsten lead while the other was fastened to a strip of flexible platinum spot welded to a tungsten lead on one end while the other end was connected to an iron weight enclosed in glass. The discharge was caused to pass by means of an electromagnet attracting the iron weight on the flexible platinum. The electrodes were removed from time to time and the balls re-rounded with an oxy-hydrogen flame; the shape of the electrodes had little effect, however, except when they were badly burned away.

The carbon monoxide was prepared by the action of formic acid on sulfuric acid. Electrolytic oxygen was used from which the hydrogen was removed with heated copper oxide and the water with sulfuric acid. The organic vapors were all dried and purified by the usual methods.

The $2CO-O_2$ mixture was dried by allowing the preliminary dried gases to stand over fresh sulfuric acid for about twenty-four hours, and then by passing the mixture through a deep tower filled with sulfuric acid and glass beads before entering the explosion chamber. Any sulfuric acid mist was removed with glass wool. Water was substituted for the acid when it was desired to have the mixture saturated with moisture.

Method of Procedure

In preparing the explosion chamber for a filling with a water-saturated $2CO-O_2$ mixture, no precautions were necessary after evacuation except to flush the chamber out with a small amount of gas before filling to the desired pressure. In the experiment, when the dry gas was used, the explosion chamber was baked out with a flame to remove all adhering moisture from the walls before starting the experiment. After the system was once thoroughly dried, further baking out was unnecessary during a single series of runs.

In testing for the effect of impurities it was found that a thorough mixing of the gases, as well as a more accurate pressure reading, could be obtained by admitting the impurities to the reaction chamber first. When necessary, the gases were agitated in the explosion chamber by swinging the flexible electrode with the electromagnet.

In determining the minimum ignition voltage, it was found necessary to obtain the approximate voltage first. This was done by starting at some low voltage and gradually raising the sparking voltage until the gas ignited. Since the sparking potential fluctuates statistically about a definite value for a given set of conditions, several tests had to be made at each voltage. It was found, in general, that if a gas mixture would ignite at a given voltage it would do so within three or four trials. After the approximate ignition voltage was found, the true voltage was obtained by starting the ignition tests just under the first value. Since some oxidation took place in the path of any spark the products of reaction formed before the ignition voltage was reached often caused these two values to differ by an appreciable quantity.

Results

Pure Explosive Mixtures.—The pressure ignition-voltage curve for an explosive mixture of ethyl ether and oxygen is illustrated in Fig. 1. The results obtained with explosive mixtures of oxygen with carbon disulfide, ethyl alcohol and carbon monoxide are similar. In most instances the points on a given curve checked within ±5 volts.

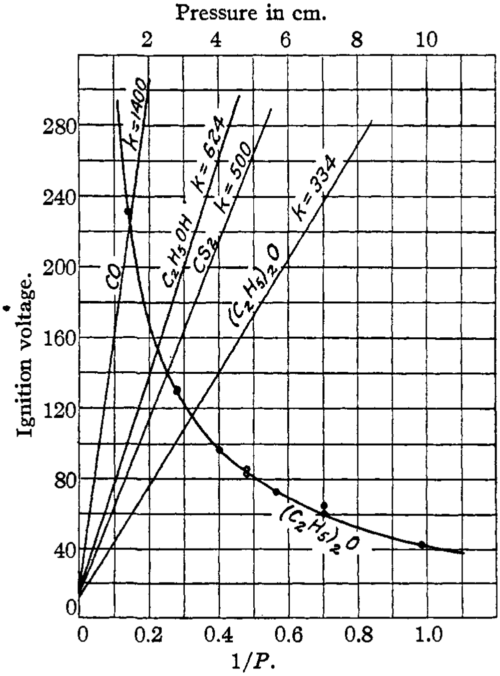

Fig. 1.

When the ignition voltage was plotted against the reciprocal of the pressure the points all fell closely on the straight lines illustrated in Fig. 1. This indicates that a hyperbolic relationship exists between ignition voltage and pressure which may be expressed as $V = k/P$. It will be noted that while the values of k differ widely for different reactions, the lines all intersect the voltage axis some place between 15 and 20 volts.

Effect of Impurities.—Impurities may be divided into two distinct classes with respect to their effect on the ignitibility of a $2CO–O_2$ mixture; namely, as *positive* and *negative* catalysts. The former are those that when added to the explosive mixture in almost any proportion lower the energy necessary for ignition, and the latter are those that raise the ignition energy.

In Fig. 2 is illustrated the effect of adding various amounts of impurities on the voltage necessary to explode a mixture containing 12 cm. 2CO + O_2 and 2 cm. water vapor.

It will be noted that ether up to 3.0 mm. and ethyl alcohol up to 6.0 mm. partial pressure lower the ignition energy, and thus behave as positive catalysts. Above these pressures the vapors of both behave as powerful negative catalysts.

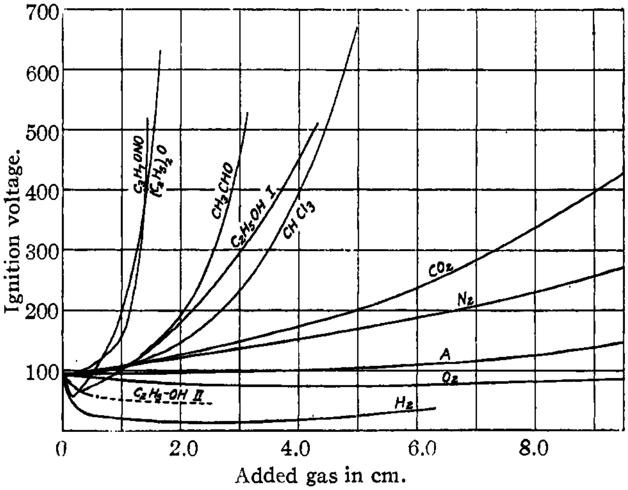

Fig. 2.

The ethyl alcohol curve is divided into two sections: Part I represents the addition of alcohol vapor alone, while Part II represents the effect produced when sufficient oxygen to burn the alcohol is also added. The effect of ether with additional oxygen is the same. Hydrogen also behaves, in this respect, like alcohol and ether, but the effect is not so pronounced. The reason is probably that the hydrogen burns even without additional oxygen because it ignites more readily than the carbon monoxide and requires much less oxygen per volume than alcohol or ether. Thus it will be seen that whether these vapors are to be considered as positive or negative catalysts depends entirely on whether or not they burn in the explosion; if they burn, they are positive catalysts, while if oxygen is insufficient for their combustion, they are negative catalysts.

The data in Fig. 1 show that gases differ widely in their negative catalytic properties. To illustrate, the amount of impurities in centimeters of mercury that must be added to a given explosive mixture to raise the ignition voltage from 95 volts to 150 volts is as follows.

Impurity	Cm. of Hg	Impurity	Cm. of Hg
A	9.75	C_2H_5OH	1.7
N_2	4.0	CH_3CHO	1.6
CO_2	3.0	C_3H_7ONO	0.95
$CHCl_3$	2.2	$(C_2H_5)_2O$	.80

It will be seen from the foregoing that the ability of an impurity to inhibit ignition is a function of the complexity of the molecule; indeed it is almost directly proportional to the number of atoms in the molecule. An exact mathematical relationship between the number of atoms and the ignition voltage is difficult to establish, since many of the impurities such as hydrogen and alcohol behave both as positive and negative catalysts, depending on the amount present.

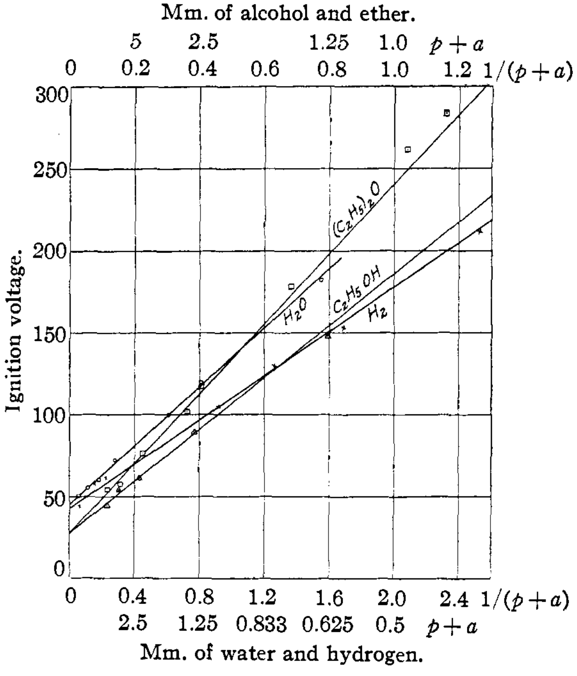

Fig. 3.

Quantitative Effects of Four Positive Catalysts.—The effect of adding explosive mixtures of oxygen with hydrogen, water, alcohol and ether vapors as impurities to the dry $2CO–O_2$ explosive mixture at 14 cm. pressure is exhibited in Fig. 3. The abscissas are $1/(p + a)$, where p mm. is the observed pressure of gas added, and a is a constant that differs from one gas to another. The ordinates are the voltages necessary to ignite the mixture when the p mm. of gas have been added; p and V seem to satisfy the relation

$$V = \frac{c}{p + a} + b \qquad (2)$$

This is the equation of the lines drawn in the figure. The values of a, b, c are tabulated below.

Gas	a (mm.)	b (volts)	c (mm. volts)
Water	−0.35	45.4	90.2
Hydrogen	.10	42.7	67.6
Alcohol	.67	27.3	158.9
Ether	.46	27.4	213.8

These values were worked out by least squares, throwing all the errors of observation on to p, and giving the higher values of p several times as much weight as the lower values.

It is interesting to observe that the points satisfy this relation as closely as they do, that the V intercepts for hydrogen and water are nearly equal, and that those for alcohol and ether are equal. These curves, if extended, would not be straight lines throughout their entire course; at their upper ends they must all become asymptotic to the ignition voltage for the pure $2CO-O_2$ mixture at 14-cm. pressure. At the lower ends beyond the last experimental points, their shapes cannot be predicted with certainty, but the curve for water will turn up and become asymptotic to the V axis. Over the range of these experiments the data are well represented by the relation (2).

An explanation of the constant a that enters the above relation can be found from the following reasoning. The impurity was always admitted to the explosion chamber and its pressure p read before the explosive mixture was turned in. The pressure of the impurity was in most cases comparatively small—from 0.2 mm. to 20 mm.—and if a few tenths of a millimeter of the gas condensed on the walls after it was read, or if some that had already condensed before its pressure was read was displaced by the carbon monoxide or oxygen, then the pressure of the impurity actually in the gas phase at the moment of explosion would differ from the value recorded for p. It seems plausible to consider that a represents the average discrepancy between p and the actual pressure $p + a$ of the impurity at the moment of explosion. $1/(p+a)$ could then be considered the specific volume (in arbitrary units); and since the curves are straight lines it appears that the change in ignition voltage is proportional to the change in the specific volume of the impurity present at the moment of ignition.

Discussion

A consideration of the ignition process is helpful to an understanding of the mechanism. A critical voltage exists for each explosive mixture, and propagation never takes place at lower voltages. Chemical action does take place, however, directly in the path of the spark at a voltage far below that necessary for propagation. The amount of gas burned in the non-propagating sparks was measured by the change in pressure following the spark; when low voltages were used it was found necessary to measure the pressure after several sparks had been sent through the gas. In gases with a low ignition voltage, the amount that can be burned in a non-propagating discharge is small, but for a dried $2CO–O_2$ mixture, which has a high ignition voltage, a discharge wherein slightly over one cubic centimeter of gas, at the pressures used, is burned in the spark can be sent through the gas without propagation. For the moist mixture the gas that could be burned in a non-propagating spark was of the order of 1 to 5 cubic millimeters; the size of the ball of gas burning in the path of the spark increases with the decrease in percentage of moisture. It appears, therefore, that a certain amount of the mixture must be burned in the spark before the combustion will go to completion; the higher the ignition voltage the more must be burned in the spark.

In the case of the added impurities, it will be seen in Fig. 2 that both alcohol and ether in themselves are strong negative catalysts in the oxidation of carbon monoxide, while in Fig. 3 both of these vapors, in the presence of sufficient oxygen for their combustion, appear as powerful positive catalysts. From this it appears that ether and alcohol molecules, as such, are negative catalysts and that the burned product is the positive catalyst. Since carbon dioxide, as will be seen in Fig. 2, shows only negative catalytic properties, it follows that the positive action of both alcohol and ether as well as hydrogen is largely due to their ability to furnish water to the reaction. No doubt the heat liberated in this oxidation is also a contributing factor, but is of minor importance compared to the formation of water.

A comparison of the slopes of the lines in Fig. 3 shows that per total water molecules formed there is a decreasing efficiency per molecule in the order water, hydrogen, alcohol and ether, probably because the effective water concentration is materially less than the total number formed in the explosion, since the rate of burning of carbon monoxide is appreciable compared with that of the hydrogen, alcohol or ether. In the two latter cases the apparent efficiency of the water is also impaired by the presence of carbon dioxide.

These observations confirm the relation that has been shown to exist between ignition voltage and pressure. The equation $V = k/P$ shows that the ignition voltage is inversely proportional to the pressure and hence to the number of molecules in the path of the spark. Thus for propagation it appears that a definite number of molecules must be burned in the path of the spark, the exact number being specific for each reaction. While the number of molecules that must be burned for propagation cannot be told, the relative number for different mixtures may be obtained from the values of k; since the slopes of the lines of V *vs.* $1/P$ are 1400 and 334 for carbon monoxide and ether, respectively, we can say that the number of molecules that must be burned for propagation in the two mixtures are in the ratio 1400:334. This statement assumes that density is proportional to pressure, and that the lines all have the same intercept on the V axis, both of which are not strictly true but introduce only small corrections. k can therefore be used as a measure of the ease of ignition in various explosive mixtures and may be termed the *ignitibility constant.*

In a condensed discharge, such as was used in this work, the quantity of electricity passing across the spark is proportional to the voltage, since $Q = CV$, where Q is expressed in coulombs, C is the condenser capacity, which was kept constant, and V is the voltage. The word *quantity*, therefore, can be substituted in the place of *voltage*, in these discussions.

In this connection it is of interst to recall that in a former article[1] it was shown that when the capacity was varied a 600% increase in C resulted in only an 18% decrease in Q. From this it will be seen that the ignition is actually established by the quantity of electricity flowing and is at most only slightly related to the voltage. The slight increase in Q with increased V and decreased C is probably because the ionizing efficiency of an electron is slightly less than proportional to the voltage. From these considerations it seems very probable, as was pointed out by Finch and Cowen,[2] that ignition results from the attainment of a definite ion density as determined by Q at some point in the gas.

The fact that the lines for the various gases listed in Fig. 1 intersect the voltage axis at a point that is very close to the ionization potential for the gases used indicates that ionization is necessary for ignition. In this respect the results are very similar to those obtained in the glow discharge, for the oxidation of hydrogen[4] and the oxidation of carbon monoxide,[5] wherein it was possible to trace the oxidation from a simple ionic reaction through chain reactions to the ignition point.

Laws of Ignition.—These observations, when interpreted in the light of the hyperbolic relation between pressure and ignition voltage, may be summed up in the following rules for ignition.

Equation 1 may be interpreted as: (*I*) *the voltage necessary to ignite a given explosive mixture is inversely proportional to the number of molecules in the path of the spark.* Similarly, Equation 2 may be interpreted: (*II*) *the ability of a positive catalyst to lower the voltage necessary to ignite a given explosive mixture is, over a wide range, proportional to the number of its molecules in the path of the discharge.* The data tabulated in Fig. 1 may be interpreted as: (*III*) *the ability of a negative catalyst to raise the ignition voltage is a direct function of the complexity of its molecule.*

Summary

The hyperbolic relation $VP = k$ between ignition voltage and pressure of the mixture, noted by Brewer in 1927, working with a $2CO-O_2$ mixture,

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[4] Brewer and Westhaver, *J. Phys. Chem.*, **34**, 2343 (1930).

[5] Brewer and Kueck, *ibid.* (in press).

is shown to hold also for explosive mixtures of oxygen with ethyl alcohol, ether and carbon disulfide. Arguments are advanced to prove that this is a general law of ignition. k is different for each mixture.

Impurities in the explosive mixture are divided into two classes, positive and negative catalysts; the former lower the ignition voltage and the latter raise it. Vapors that burn to form water as one product of combustion will be positive catalysts when present in a small amount and negative catalysts when present in a greater amount. The positive action of a catalyst probably comes from the water formed in its combustion, which precedes the ignition of the main mixture. All impurities that form water seem to act as positive catalysts when present in *any* amount provided there is sufficient extra oxygen to burn the catalyst.

A quantitative relation, also hyperbolic, is worked out for impurities that act as positive catalysts. It is

$$(V - b)(p + a) = c$$

$p + a$ is the pressure of the explosive mixture added as impurity, V the ignition voltage, and b and c are constants for each catalyst.

The two hyperbolic relations explained can be restated thus: (*I*) *the voltage necessary to ignite a given explosive mixture is inversely proportional to the number of molecules in the path of the spark.* (*II*) *the ability of a positive catalyst to lower the voltage necessary to ignite a given explosive mixture is, over a wide range, proportional to the number of its molecules in the path of the discharge.*

A study of curves for several catalysts shows that, (*III*), *the ability of a negative catalyst to raise the ignition voltage is a direct function of the complexity of its molecule.*

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THE ANHYDROUS LOWER BROMIDES OF TITANIUM

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Received July 18, 1930 Published November 5, 1930

Considerable work has been done on the anhydrous trichloride and dichloride of titanium, and the di-iodide and trifluoride have been prepared, but we have been unable to find any data concerning the anhydrous lower bromides. The present work had for its purpose the preparation of these latter compounds and a study of some of their properties.

Three methods of preparation were considered and tried: (1) reduction of the tetrabromide by hydrogen; (2) the action of hydrogen bromide on titanium; (3) reduction of the tetrabromide by metals with and without a solvent.