255. *The Oxidation of Chloroacetylene and Bromoacetylene.*

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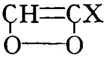
Chloroacetylene and bromoacetylene have been prepared, purified by fractionation in a vacuum, and used for precise determinations of vapour pressure. The boiling points are − 29·6° ± 0·1° and 4·7° ± 0·1°, and the latent heats of vaporisation 89 and 58 cals. per g., respectively. Both substances are shown to oxidise by a branching-chain mechanism, characterised by a lower explosion limit at pressures of the order of 0·6—2·0 mm. for chloroacetylene and 2·5—4·5 mm. for bromoacetylene. The dependence of this limit on mixture composition, on the diameter of the reaction vessel, and on temperature, has been studied in each case; and for chloroacetylene the influence of the diluent gases argon, nitrogen, and helium was also investigated. An upper explosion limit was observed in the case of chloroacetylene. Bromoacetylene and oxygen could not be mixed at higher pressures without explosion, but ignition could be inhibited by the addition of carbon disulphide, ethylene, or sulphur dioxide. The mechanism of the reactions is discussed, and the suggestion is made that the observed differences between the oxidation of acetylene and that of its halogen derivatives may be attributed to the relative stabilities of the peroxide-like intermediates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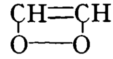

, where X is chlorine or bromine.

THE partial substitution of halogen atoms for hydrogen in an organic compound has in general the effect of rendering the molecule more reactive towards oxygen. There is little doubt that a proper understanding of the cause of this curious effect would go far towards elucidating the mechanism of certain reactions. So far, however, there has been little attempt at a quantitative approach to the problem. The choice of chloro- and bromo-acetylene for further study in this connexion was dictated by the fact that these two substances differ to a remarkable extent from acetylene in their ease of oxidation. Acetylene has an ignition point in oxygen of about 400°, depending somewhat on the experimental conditions, whereas the halogenated acetylenes, although little studied hitherto, were known to be spontaneously inflammable. As a result of the present work it is clear that, although these substances are indeed highly reactive to oxygen, yet when pure, they are stable below 100° and can be handled and kept without much difficulty.

EXPERIMENTAL.

Preparation of Chloro- and Bromo-acetylene.—These two compounds were prepared in a very pure state so that their vapour pressures could be precisely determined. For chloroacetylene Hofmann and Kirmreuther's method (*Ber.*, 1909, **42**, 4232) was modified as follows. Mercuric chloroacetylide was first prepared by shaking excess of *s.*-dichloroethylene with a solution of 50 g. of mercuric cyanide and 23 g. of potassium hydroxide in 200 c.c. of water for 48 hours. The resulting greyish sludge was filtered off, washed with a little water, dried, and extracted (Soxhlet) with hot chloroform. The salt $Hg(C{\vdots}CCl)_2$ crystallised on cooling as colourless, rectangular, strongly lustrous plates (yield of recrystallised product 15 g., m. p. 185°).

The recrystallised salt (5 g.) was placed in a flask fitted with a reflux condenser and dropping-funnel, the air in the flask was displaced with pure hydrogen, 50 c.c. of a solution containing 15 g. of potassium cyanide and 3 g. of potassium hydroxide were run in from the dropping-funnel, and the flask was heated on a water-bath. The mercuric salt slowly decomposed, and the resulting chloroacetylene, swept out of the flask by the current of hydrogen, was led through a series of calcium chloride and phosphoric oxide drying tubes into a U-bulb immersed in liquid nitrogen, where it condensed as a white solid. The U-bulb was then transferred to a vacuum line, and the chloroacetylene allowed to evaporate into a large glass reservoir, where it was freed from any dissolved hydrogen by repeated evaporation, re-condensation, and evacuation. Ordinary ground joints and stopcocks could be used, as the chloroacetylene did not attack tap grease.

The crude material, containing a small amount of liquid product, was purified by vacuum distillation with fractional condensation. It was condensed in a U-bulb, and immersed in a bath at — 115°, at which temperature, being still liquid, it was distilled slowly in vacuum through another U-tube at — 130° into a third U-tube, cooled in liquid nitrogen. A large proportion condensed at — 130°, the small head and tail fractions being rejected. The main fraction was then similarly redistilled four times with rejection of small head and tail fractions. The vapour-pressure curves of the main fractions of the third and fourth distillations were identical with each other and with those of two main fractions into which the final main fraction was split by a further distillation. Therefore it appeared that the fourth main fraction was pure.

Vapour-pressure measurements were carried out in the usual manner, temperatures being measured by means of an ammonia vapour-pressure thermometer. The values obtained are tabulated below :

Temp.	−35·9°	−37·5°	−39·2°	−40·3°	−41·9°	43·3°	−44·9°	−46·4°	−47·6°
V. p. (cm.).........	63·69	58·81	54·43	51·88	48·02	44·79	41·47	38·43	36·18
Temp.	−50·5°	−52·0°	−55·0°	−57·3°	−59·8°	−61·8°	−63·2°	−65·4°	−68·0°
V. p. (cm.)	31·19	28·77	24·33	21·50	18·50	16·48	15·05	13·19	11·17

The values of log p plotted against $1/T$ give a straight line, and extrapolation indicates that the b. p. of chloroacetylene is — 29·6° ± 0·1°. Its latent heat of vaporisation at the b. p., determined by Lewis and Weber's method (*J. Ind. Eng. Chem.*, 1922, **14**, 486), is 89 cals./g.

Bromoacetylene was prepared by the method of Sawitsch (*Annalen*, 1861, **119**, 182). A solution of 5 g. of sodium hydroxide in 5 c.c. of water was placed in a 50-c.c. flask fitted with a reflux condenser and dropping-funnel, and the air displaced by pure hydrogen : 15 g. of *s*.-dibromoethylene were then run in, followed by 18 c.c. of absolute alcohol. On heating the flask on a water-bath, bromoacetylene was evolved, and was carried off in the current of hydrogen. The gases were bubbled through water and dried over calcium chloride and phosphoric oxide, and the bromoacetylene was condensed out as a white solid in a U-bulb immersed in liquid nitrogen. The product was purified and tested for purity in the manner already described for chloroacetylene, except that the vacuum distillation was effected from a U-bulb cooled at — 65° through a U-bulb cooled at —105°, into a third U-bulb cooled in liquid nitrogen. A great tendency for liquid bromoacetylene to polymerise in light was at once apparent, but this could be prevented by working in yellow light. In the gaseous phase bromoacetylene had no tendency to polymerise, and did not attack tap grease. Vapour-pressure measurements were made by using a sulphur dioxide vapour-pressure thermometer in the range — 10° to — 60°, and an accurate mercury thermometer from 0° to — 10° : these are tabulated below :

Temp.	− 1·2°	− 2·2°	− 4·4°	− 6·6°	− 8·5°	−10·4°	−11·1°	−13·0°
V. p. (cm.)	61·00	58·78	53·71	48·84	45·03	41·15	40·16	36·74
Temp.	−16·5°	−23·1°	−29·2°	−35·1°	−43·6°	−48·6°	−54·8°	−58·7°
V. p. (cm.)	31·44	22·76	16·70	12·12	7·43	5·44	3·66	2·74

The b. p., extrapolated from the linear log p–$1/T$ graph, is + 4·7° ± 0·1°; and the latent heat of vaporisation, determined as for chloroacetylene, is 58 cals./g.

Oxidation of Chloroacetylene.—The study of ignition phenomena in gases has led to the view that substances having low ignition temperatures inflame through the operation of a branching-chain reaction mechanism, whereas with substances of higher ignition point degenerate branching takes place, *i.e.*, in these cases there is a much greater time lag in the multiplication of active centres. As chloro- and bromo-acetylene are both spontaneously inflammable, one would expect their oxidation to show the characteristics of branching-chain reactions, chief among which are the upper and lower explosion limit phenomena. Preliminary observations established that this was indeed the case as far as the lower-limit phenomena were concerned, and a series of measurements on these limit phenomena was therefore undertaken.

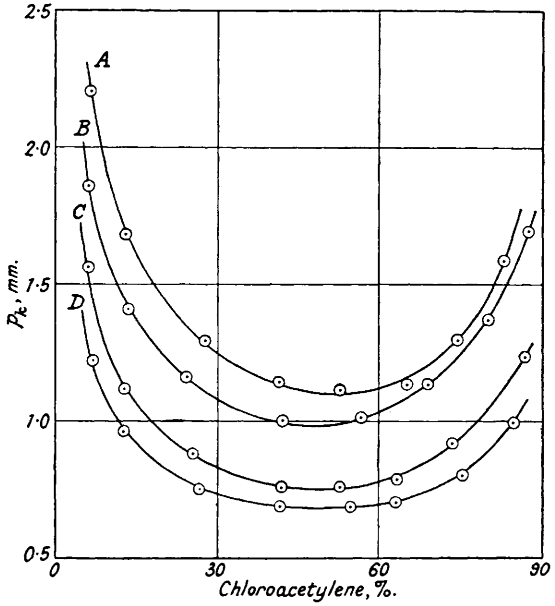
The method and apparatus used in studying the lower explosion limit of both gases was similar to that used in investigating the oxidation of the silicon hydrides (Emeléus and Stewart, J., 1936, 677). The halogenated acetylene and oxygen were allowed to leak simultaneously from containers of about 100 c.c. capacity through calibrated capillaries into an evacuated cylindrical reaction vessel. The rate of flow of each gas could be controlled by altering the pressure in its container. The time required for admission of this gas, some 10—15 minutes, was reproducible under fixed conditions within ± 15 seconds. When the composition of the mixture in the reaction vessel became that for the critical limit under the conditions employed, there was a dull flash throughout the mixture, the occurrence of which was timed. In this way the partial pressures of the two gases in the limit mixture were determined. A third capillary leak added to the system permitted the effect of a diluent gas to be studied.

Measurements on the lower explosion limit of chloroacetylene were carried out in a glass reaction vessel, the inner surface of which was rinsed first with distilled water, then with a few c.c. of 50% hydrofluoric acid, and finally again with distilled water. After a few preliminary observations with a vessel prepared in this way, results reproducible to about 0·05 mm. were obtained in 12—20 determinations. Erratic results were invariably obtained after cleaning with nitric acid–chromic acid mixtures, with nitric acid, or with water alone. Before each experiment the vessel was evacuated, heated to 300—400° with a luminous flame, and then held at 100° under vacuum for half an hour.

Effect of the diameter of the vessel on the lower explosion limit. The experiments were carried out at 100° with reaction vessels having diameters of 2·02, 2·89, 3·78, and 4·89 cm., and being each 15 cm. long. The results are shown in Fig. 1, in which p_k, the observed value of the lower limit, is plotted against the percentage of chloroacetylene in the mixture at the instant of ignition. All four curves exhibit a flat minimum at approximately 50% of chloroacetylene.

FIG. 1.

Effect of mixture composition and vessel diameter on the lower limiting explosion pressures of chloroacetylene–oxygen mixtures.



A. d = 2·02 cm. B. d = 2·89 cm. C. d = 3·78 cm. D. d = 4·89 cm.

As the diameter of the reaction vessel increases, the lower limit pressure progressively decreases. The partial pressures of oxygen in the limit mixtures plotted against the corresponding partial pressures of chloroacetylene give curves which approximate to rectangular hyperbolæ. Throughout the range of mixture composition examined (10—90%), ignition was very sharp, the intensity of the glow increasing with the chloroacetylene concentration up to 40—50% and then diminishing.

The general theory of chain reactions demands that at the lower limit the expression $p_k{}^2d^2\mathrm{f}(x)$ shall be constant, p_k being the lower critical pressure, d the diameter of the reaction vessel, and $\mathrm{f}(x)$ a function of the proportion of chloroacetylene in the mixture. Hence if x be constant the value of p_kd should be constant. The data in Table I show that this is only approximately true. The values of the product p_kd, derived from the smoothed curves in Fig. 1 for each of a series of values of x, show a definite increase with the value of d. This drift indicates an increase in p_k with increase in diameter and is due to incidence of gas-phase deactivation of active centres. In this case such a process might be connected with polymerisation of the chloroacetylene.

TABLE I.

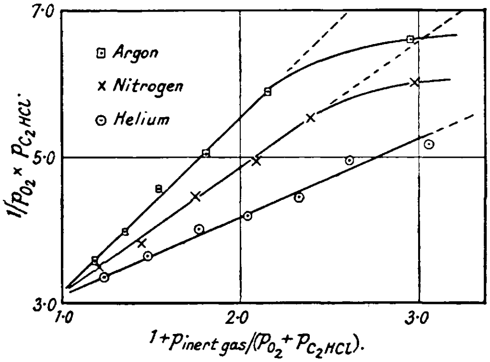
Value of the product $p_k d$ *for chloroacetylene.*

$x =$	0·10.	0·20.	0·30.	0·40.	0·50.	0·60.	0·70.	0·80.	0·90.
d.									
2·02	4·02	3·03	2·61	2·38	2·30	2·34	2·48	2·87	4·24
2·89	4·87	3·72	3·26	3·00	2·89	3·03	3·35	3·97	5·49
3·78	5·11	3·93	3·29	2·95	2·87	2·95	3·25	3·93	5·18
4·89	5·43	4·20	3·67	3·47	3·32	3·42	3·81	4·15	—

The effect of an inert gas on the lower limit of chloroacetylene was examined by allowing oxygen, chloroacetylene, and an inert gas (helium, nitrogen, or argon) to pass simultaneously through calibrated capillary leaks into a reaction vessel 2·89 cm. in diameter held at 100° throughout the series of experiments. By suitable adjustment of the reservoir pressures, the ratio of chloroacetylene to oxygen was kept constant at 1 : 3, and the variation of the limiting ignition pressure with the proportion of inert gas was observed. In all the experiments the ignition was sharply defined, even when the inert gas constituted 60—70% of the total reaction mixture. With each of the three inert gases, the addition of increasing amounts progressively lowered the lower explosion limit, *i.e.*, the sum of the partial pressures of chloroacetylene and oxygen in the limit mixture. With helium, for example, this sum, 1·25 mm. with no inert gas, was decreased to 0·95 mm. with 66% of helium present.

FIG. 2.

Effect of inert gas upon the lower limiting explosion pressure for chloroacetylene–oxygen mixtures.



The general theory of chain reactions requires constancy for the expression

$$d^2 p_X p_{O_2}[1 + p_i/(p_X + p_{O_2})],$$

where d is the diameter of the reaction vessel, p_X and p_{O_2} the partial pressures of the two reactants, and p_i the partial pressure of the inert gas added. It follows that there should be a linear relationship between $1/p_X p_{O_2}$ and $1 + p_i/(p_X + p_{O_2})$ when d is constant. The data obtained with chloroacetylene (Fig. 2) show that this linear relationship holds until the proportion of inert gas is 70% or so of the total, the divergence from linearity thereafter being most marked for argon and least for helium. The slope of the line is 0·45 for helium, 0·69 for nitrogen, and 1·0 for argon, and thus increases with the molecular weight of the inert gas. The linear relationship over the earlier part of the curves is adequately explained by considering the effect of the inert gas in hindering the diffusion of active centres to the walls, where their deactivation occurs (see, *e.g.*, Gray and Melville, *Trans. Faraday Soc.*, 1935, **31**, 452). The departure from linearity with high proportions of inert gas represents a progressive increase in the lower explosion limit, which must arise from the fact that the added gas is no longer inert at these concentrations, but is playing a part in gas-phase deactivation of active centres.

The effect of temperature on the lower limit was found to be anomalous in that the value of the limiting pressure increased with temperature. This was traced to the fact that at temperatures above 100° a slow reaction took place, the extent of which increased with rising temperature. At 100° this reaction was imperceptible, for when the flow of chloroacetylene and oxygen through the capillaries was interrupted for periods of 0·5—5·5 hrs., the observed value of the lower limit was the same (within 5%) as when no interruption occurred. Similar observations at 150° and 195° show that a substantial interruption of the flow produces an apparent increase in the value of the limiting pressure, as is illustrated by the data in Table II. The simplest and most probable explanation of this observation is, evidently, that a proportion of the reactants was removed by a slow reaction.

The Lower Critical Explosion Limit of Bromoacetylene.—The investigation of the lower limit for bromoacetylene was carried out precisely as for chloroacetylene, including the series of observations in tubes of different diameters at 100°. Below 100° the results were very erratic, owing possibly to a variable degree of adsorption on the walls of the vessel. The luminescence at the limiting pressures was also considerably less intense than for chloroacetylene, particularly when the proportion of bromoacetylene in the mixture exceeded 60%. Data obtained at 100°

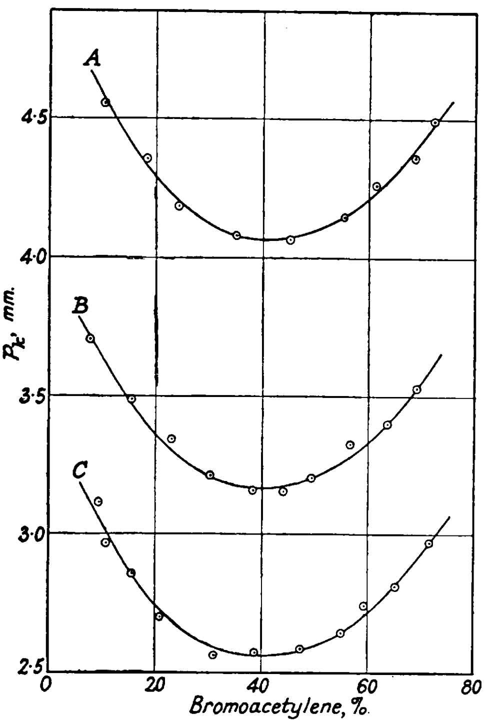
TABLE II.

Temp.	C_2HCl, %.	Fraction of reactants before interval.	Interval (mins.).	p_k, obs. (mm.) with interval.	p_k, obs. (mm.) without interval.	Increase, %.
100°	21·8	0·76	30	1·23	1·25	2
	47·6	0·83	90	1·03	1·00	3
150	25·8	0·67	30	1·57	1·42	11
	30·6	0·78	60	1·64	1·44	14
	43·5	0·81	45	1·60	1·42	13
195	20·6	0·62	30	2·04	1·65	24
	27·3	0·74	45	2·23	1·70	31
	39·6	0·84	60	2·31	1·74	33

with three reaction vessels of diameters 2·90, 3·78, and 4·89 cm. are shown in Fig. 3, in which the critical explosion pressure, p_k, is plotted against the proportion of bromoacetylene in the mixture. The absolute value of the limiting pressure for a given proportion of bromoacetylene is about three times the corresponding figure for chloroacetylene.

FIG. 3.

Effect of mixture composition and vessel diameter on the lower limiting explosion pressures of bromoacetylene–oxygen mixtures.



A, d = 2·90 cm. B, d = 3·78 cm. C, d = 4·89 cm.

Values of the product p_kd deduced for the above measurements are given in Table III. The product is roughly constant, but shows the same drift as is seen in Table I.

No measurements were made of the effect of temperature on the lower critical explosion limit of bromoacetylene, but it was verified that there was no appreciable reaction (due either to polymerisation or to oxidation) during the period of admission of the two gases to the reaction bulb at 100°. The increase in the value of p_k due to interrupting the admission of the two gases into the bulb at 100° for 15—20 minutes (Table IV) was found to be less than 5%.

The Upper Critical Explosion Limit.—Attempts to study the upper critical explosion limit in chloroacetylene- and bromoacetylene–oxygen mixtures encountered very great difficulties owing to the lack of reproducibility in the results and also to the frequent occurrence of violent explosions. The method used in studying this limit in the case of chloroacetylene was to admit the requisite amount of chloroacetylene (measured manometrically) into the reaction bulb (10 cm. long, 1·4—2·6 cm. internal diameter) and there to freeze it out in liquid nitrogen. The oxygen was then admitted, and the chloroacetylene was very slowly vaporised by allowing the liquid nitrogen to evaporate spontaneously overnight. More rapid mixing, or the admission of either gas through a capillary leak system, invariably led to explosion. Even when prepared in this way, mixtures of chloroacetylene and oxygen were very sensitive—they exploded, for example, if a small amount of additional oxygen was suddenly admitted, or if the pressure was suddenly decreased by a small amount. By very slowly reducing the pressure it was possible to obtain an explosion at a considerably lower pressure, but the magnitude of this limiting pressure was entirely erratic.

TABLE III.

Value of the product p_kd *for bromoacetylene.*

x = d.	0·10.	0·20.	0·30.	0·40.	0·50.	0·60.	0·70.
2·90	13·4	12·5	12·0	11·6	11·6	12·3	12·9
3·78	13·9	12·7	12·2	12·0	12·1	12·8	13·5
4·89	15·0	13·3	12·7	12·5	12·8	13·4	14·7

TABLE IV.

C_2HBr, %.	Fraction of reactants admitted before interval.	Interval, mins.	p_t, obs. (mm.) with interval.	p_t, obs. (mm.) without interval.	Increase, %.
19·8	0·36	15	3·45	3·39	2
25·4	0·67	15	3·35	3·27	2
30·7	0·41	20	3·34	3·22	3

In all, 14 experiments were carried out in which the gases were successfully mixed and exploded by pressure reduction, and the " upper critical pressure " varied from 2·4 cm. for a mixture containing 20·7% of chloroacetylene to 38·5 cm. for a 17·5% mixture. The experiments prove the existence of an upper critical explosion pressure in the oxidation of chloroacetylene, but there is every indication that its quantitative study is impossible. In the course of these experiments it was ascertained that the products of the explosive reaction were carbon monoxide, carbon dioxide, chlorine, hydrogen chloride, and in some cases, a considerable amount of carbonaceous material.

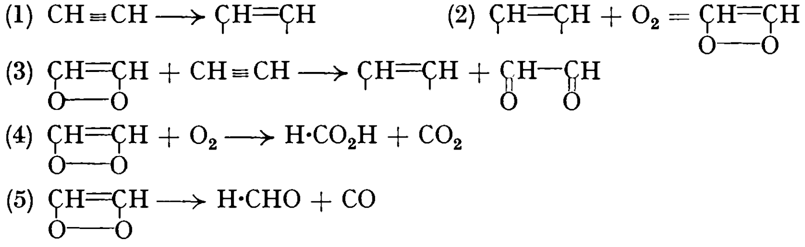
For bromoacetylene it was quite impossible to obtain a mixture with oxygen even with the precautions which were successful in the case of chloroacetylene. When the attempt was made to mix the gases slowly by evaporating bromoacetylene into oxygen, part of the liquid polymerised to a brown material, and the mixture became non-explosive. Rapid mixing always resulted, as before, in explosion.

It seemed of interest to determine how far the addition of typical inhibitors of oxidation reactions would prevent inflammation during the mixing process, and the effects of ethylene, sulphur dioxide, and carbon disulphide were investigated. Trial experiments with these substances gave no indication of any direct reaction with bromoacetylene. In each case a constant ratio of 24 mm. of bromoacetylene to 360 mm. of oxygen was employed. The bromoacetylene and the inhibitor were separately admitted and measured, and then condensed out in liquid nitrogen. The oxygen was then introduced, and the whole allowed to warm to room temperature, and so, by repeated trials, the amounts of the various inhibitors necessary just to prevent inflammation on mixing were found. The requisite pressures for inhibition of the ignition of the above mixture (with rather ill-defined conditions of mixing) were as follows : CS_2, 8 ; C_2H_4, 39 ; SO_2, 49 mm. These observations show quite clearly that the reactions can be inhibited, and so support the other evidence that these oxidations are chain reactions.

DISCUSSION.

The experiments described leave little doubt that the oxidation of both chloro- and bromo-acetylene proceeds by a branching chain reaction. This is shown by the existence in each case of lower explosion limits (without an induction period), by the effect of diluent gases on the lower limit for chloroacetylene, by the existence of an upper limit in the case of chloroacetylene, and by the effect of inhibitors upon the oxidation of bromoacetylene. The mechanism of such a chain reaction is necessarily speculative, but some guidance may be expected from investigations on the slow oxidation of acetylene, in which definite intermediates have been isolated. For instance, it is known that at 1 atm. and 250—315°, glyoxal, formaldehyde, and formic acid may be isolated as intermediates (Kistiakowsky and Lenher, *J. Amer. Chem. Soc.*, 1930, **52**, 3785), carbon monoxide, carbon dioxide, and hydrogen being also formed. The reaction has the general characteristics of a chain reaction in which degenerate branching takes place, and further studies by Spence and Kistiakowsky (*ibid.*, p. 4837), and, later, by Spence (J., 1932, 686) have established this view of its nature.

The mechanism of the reaction was discussed by Bodenstein (*Z. physikal. Chem.*, 1931, *B*, **12**, 151), who regarded the first stage in the oxidation as the formation of a peroxide which was capable of reacting as follows :



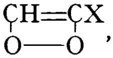
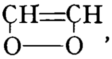
$$(1)\ \mathrm{CH{\equiv}CH} \longrightarrow \underset{|}{\mathrm{C}}\mathrm{H{=}}\underset{|}{\mathrm{C}}\mathrm{H} \qquad (2)\ \underset{|}{\mathrm{C}}\mathrm{H{=}}\underset{|}{\mathrm{C}}\mathrm{H} + \mathrm{O_2} = \begin{array}{c}\mathrm{CH{=}CH}\\ |\qquad|\\ \mathrm{O{-\!-}O}\end{array}$$

$$(3)\ \begin{array}{c}\mathrm{CH{=}CH}\\ |\qquad|\\ \mathrm{O{-\!-}O}\end{array} + \mathrm{CH{\equiv}CH} \longrightarrow \underset{|}{\mathrm{C}}\mathrm{H{=}}\underset{|}{\mathrm{C}}\mathrm{H} + \begin{array}{c}\mathrm{CH{-}CH}\\ \|\qquad\|\\ \mathrm{O}\qquad\mathrm{O}\end{array}$$

$$(4)\ \begin{array}{c}\mathrm{CH{=}CH}\\ |\qquad|\\ \mathrm{O{-\!-}O}\end{array} + \mathrm{O_2} \longrightarrow \mathrm{H{\cdot}CO_2H} + \mathrm{CO_2}$$

$$(5)\ \begin{array}{c}\mathrm{CH{=}CH}\\ |\qquad|\\ \mathrm{O{-\!-}O}\end{array} \longrightarrow \mathrm{H{\cdot}CHO} + \mathrm{CO}$$

Spence (*loc. cit.*) postulated a mechanism, in better agreement with the analytical and kinetic data, whereby an intermediate product, CH_2O_2, capable of existing in two energy-rich forms, was responsible for carrying on the chain reaction. Steacie and Macdonald (*J. Chem. Physics*, 1936, **4**, 75) have shown, however, that addition of glyoxal to an acetylene–oxygen mixture does not increase the rate of reaction; whereas a marked acceleration might have been expected had the glyoxal been one of the species responsible for carrying on the chain. These authors favour a mechanism similar to that proposed by Bodenstein (*loc. cit.*).

The Bodenstein mechanism gives a definite, though rather slight clue as to the possible mechanism of oxidation of the halogenated acetylenes. If we assume that the initial product in these oxidations is also a peroxidic compound  $\begin{array}{c}\text{CH}=\text{CX}\\ \vert \qquad \vert\\ \text{O}-\text{O}\end{array}$, it seems very probable that this intermediate would be much less stable than Bodenstein's  $\begin{array}{c}\text{CH}=\text{CH}\\ \vert \qquad \vert\\ \text{O}-\text{O}\end{array}$, as regards both spontaneous decomposition and ease of oxidation. The latter intermediate might, for example, isomerise to give the relatively stable glyoxal, and only occasionally react further to carry on the chain and produce branching. The halogenated glyoxal, however, would be a much more reactive substance, and we believe that this fact will serve to explain the branching chain oxidation mechanism, and the consequent ready inflammability of the halogenated acetylenes. No thermochemical data exist for the halogenated acetylenes, but they are probably, like acetylene, highly endothermic compounds. The observations on chloro- and bromo-acetylene, here described, are in general agreement with other observations upon the enhanced ease of oxidation of halogenated hydrocarbons. Remarkable instances of this sort were pointed out recently by Swarts (*Inst. Intern. Chim. Solvay*, 5ème Conseil de Chimie, 1934, p. 79). Thus, *as.*-dibromoethylene is oxidised at room temperature by molecular oxygen, and the halogenated hydrocarbons C_2BrF_3 and C_2ClF_3 will react explosively with oxygen. In these cases there is evidence of the intermediate formation of a peroxide, which must, however, be highly unstable in those cases where explosive reactions occur. Further work is projected on the mechanism of certain of these remarkable reactions.

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