

by saying that the two nitrogen atoms of the dye are linked by a chemical bond which consists of a single electron instead of a pair.

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THE REACTION BETWEEN OXYGEN AND ACETYLENE IN THE PRESENCE OF NITROGEN OXIDES

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Comparatively little work has been done on the catalyzed oxidation of the simple hydrocarbons. Study of the slow combustion of acetylene¹ led to isolation of the intermediate compounds, glyoxal, formaldehyde, and formic acid, and indicated the probable steps in the reaction. As the influence of a homogeneous catalyst is to lower the temperature at which measurable reaction begins, and thus to increase the stability of the partially oxidized products, study of the effect of gas catalysts in oxidations promised to give further information on the course of reaction.

The present investigation was a study of the effect of nitric acid vapor and its decomposition products on the slow thermal oxidation of acetylene. The oxides of nitrogen have been used repeatedly in the partial oxidation of the hydrocarbons.² It was assumed in these papers and patents that the action of the nitrogen oxides was catalytic, that is, that the nitrogen oxides were not destroyed in the reaction. This assumption was not directly tested, although Frolich, Harrington and Waitt^{2f} stated that in the oxidation of methane with nitrogen peroxide and oxygen the loss of nitrogen peroxide by complete decomposition to elementary nitrogen was of the order of 1% per pass, and Bibb and Lucas^{2g} indicated in an experiment that nitric acid was consumed in the oxidation of methane. It appears now from a recent paper by Smith and Milner³ that in the partial oxidation of methane in the presence of nitrogen oxides the nitrogen oxides are consumed in the reaction and that their action cannot be considered catalytic. The writer has found in an investigation of the oxidation of ethylene, which will be communicated shortly, that nitrogen oxides react chemically with ethylene at the temperature of the slow oxidation reaction and that their action is not one of catalysis.

¹ (a) Kistiakowsky and Lenher, *THIS JOURNAL*, **52**, 3785 (1930); (b) Spence and Kistiakowsky, *ibid.*, **52**, 4837 (1930).

² (a) Bailey, U. S. Patent 1,319,748 (1919); (b) Bibb, U. S. Patent 1,392,886 (1921), reissue 15,789 (1924); (c) Chemische Fabriken Worms A. G., British Patent 156,252 (1921); (d) Atack, British Patent 182,843 (1921); (e) Layng and Soukup, *Ind. Eng. Chem.*, **20**, 1052 (1928); (f) Frolich, Harrington and Waitt, *THIS JOURNAL*, **50**, 3216 (1928); (g) Bibb and Lucas, *Ind. Eng. Chem.*, **21**, 633 (1929); (h) Bibb, Canadian Patent 302,672 (1930).

³ Smith and Milner, *Ind. Eng. Chem.*, **23**, 357 (1931).

The catalytic action of nitrogen oxides in gaseous oxidations must be that of an active oxygen carrier which is alternately reduced in the reaction and oxidized by oxygen, or which can initiate long reaction chains from one primary reaction.

Experimental Results

The oxidation of acetylene in the presence of nitrogen oxides was studied by the flow method at atmospheric pressure. Oxygen and acetylene at a regulated rate of flow were mixed in a capillary at the entrance of the reaction vessel. Oxygen from a commercial cylinder was used without further purification. Acetylene (Prest-O-Lite) was passed through two spiral wash-bottles containing water to remove acetone and was dried with calcium chloride. Nitric acid vapor was introduced into the gas mixture by passing the oxygen through a wash-bottle containing 100 cc. of 90% nitric acid containing only 0.046% nitrogen peroxide. The concentration of nitric acid in the gas was controlled by the vapor pressure of the acid.⁴ The temperature of the acid was kept constant to $\pm 2^\circ$ with a water-bath. The cylindrical Pyrex reaction vessel, 20 mm. in diameter, was heated in an electric tube furnace. Reaction temperatures were read by means of a chromel-alumel thermocouple in a thin-walled glass tube in the center of the vessel.

The reacted gases passed through a U-tube cooled in solid carbon dioxide-methanol mixture, and a spiral wash-bottle containing a standardized barium hydroxide solution to absorb carbon dioxide, and were collected in a water gasometer. The gas was analyzed as described by Kistiakowsky and Lenher (Ref. 1a, p. 3786). The organic products condensed in the cooled U-tube were practically negligible as determined by oxidation with standard potassium dichromate in strong sulfuric acid and back-titration with sodium thiosulfate. The U-tube contained appreciable amounts of nitric acid and nitrogen oxides, and in many experiments drops of inky blue nitrogen trioxide (N_2O_3) were seen. The organic acid content could not be determined because of the nitric acid. Quantitative analysis of the aldehyde content was not possible because of the very small amounts of both glyoxal and formaldehyde. Accordingly, after several tests showed that less than 3% of the acetylene went to formic acid and formaldehyde, the contents of the U-tube were omitted from further quantitative analysis. A solid deposit was formed in the exit tube of the reaction vessel at the end of the furnace. The amount of this deposit was determined by weighing. This deposit showed the general physical properties of trimeric glyoxal.⁵ Monomeric glyoxal was prepared from a sample of one gram of

⁴ Taylor, *Ind. Eng. Chem.*, **17**, 633 (1925).

⁵ Beilstein, "Handbuch der organischen Chemie," Julius Springer, Berlin, **1918**, 4th ed., Vol. I, p. 759.

the deposit by heating it with phosphorus pentoxide⁶ in a small distilling flask with a condenser cooled to -78° . On warming the flask the green vapor of glyoxal which condensed in the receiver to fine yellow needles was noted.

A weighed sample of the solid glyoxal product from several experiments was dissolved in 20 cc. of warm water. Thirty cc. of 50% acetic acid solution of *p*-nitrophenylhydrazine was added and the solution was allowed to stand for thirty-six hours. The precipitate of the nitrophenylhydrazones was filtered on a small Büchner funnel, washed with warm 10% sodium carbonate solution and water, dried in powder form and weighed. The weighed precipitate was then extracted for two hours at room temperature with dry chloroform to dissolve the *p*-nitrophenylhydrazone of formaldehyde, and was then filtered, dried and weighed. The weight of phenylhydrazones in one experiment was 0.6533 g. before treatment with chloroform and 0.6319 g. after extraction, which showed that the precipitate was 96.7% the di-*p*-nitrophenylhydrazone of glyoxal, whose melting point was 302° . The precipitate gave the characteristic Bamberger test of a blue coloration with alcoholic potassium hydroxide. The weights of glyoxal given in Table I are the actual weights of the solid deposit from the reaction on the assumption that the deposit was trimeric glyoxal.

A gas mixture containing equal volumes of acetylene and oxygen was used. The rate of flow of each gas was 0.05 cc. per sec., corresponding to an average time of contact of 180 seconds for the 30-cc. vessel at an average

TABLE I
REACTION OF OXYGEN AND ACETYLENE IN THE PRESENCE OF NITRIC ACID VAPOR
Average time of contact, 180 seconds

Temp., °C.	HNO ₃ in mixture, %	Reaction products			Solid deposit (glyoxal), g.
		CO ₂ , cc.	CO, cc.	H ₂ , cc.	
180 cc. of 1 acetylene:1 oxygen mixture used					
210	1.7	0.3	5.2	0.0	0.0132
230	1.7	1.1	4.2	.2	.0130
230	1.7	1.3	1.2	.2	.0134
230	1.7	0.6	2.4	.4	.0113
240	1.7	1.2	3.5	.5	.0131
240	2.3	1.8	2.6	.0	.0183
210	4.1	3.4	18.1	.8	.0362
210	4.1	3.6	16.4	1.0	.0301
230	4.1	6.0	19.8	1.4	.0295
230	4.1	6.2	20.1	0.8	.0418
180 cc. of 1 acetylene:1 air mixture used					
210	4.1	2.7	4.9	3.4	0.0194
210	4.1	1.6	...	0.8	.0231
230	4.1	4.0	6.5	1.7	.0253

⁶ Harries and Temme, *Ber.*, **40**, 165 (1907).

temperature of 230°. One hundred and eighty cc. of acetylene-oxygen mixture was used. The nitric acid wash-bottle in the oxygen line was kept at 0° until the furnace was at the desired temperature and the gas flow was adjusted; then the acid was warmed to the temperature of the experiment. From Table I it is seen that the main products of the reaction are glyoxal and carbon monoxide with smaller amounts of carbon dioxide, hydrogen and water.

These experiments show that the principal reaction product is glyoxal, for the glyoxal recovered corresponds to 50-60% of the acetylene oxidized.

Experiments with a different time of contact and with different gas mixtures are given in Table II.

TABLE II
EFFECT OF TIME OF CONTACT AND GAS COMPOSITION ON REACTION OF ACETYLENE WITH OXYGEN IN THE PRESENCE OF NITRIC ACID VAPOR

Temp., °C.	HNO ₃ in mixture, %	Time of contact, seconds	180 cc. of gas mixture used		Reaction products			
			Composition of gas, %		CO, cc.	CO ₂ , cc.	H ₂ , cc.	Solid deposit (glyoxal), g.
			C ₂ H ₂	O ₂				
210	4.1	180	50	50	16.4	3.6	1.0	0.0301
210	4.1	90	20	40	4.0	...	0.4	.0201
210	4.1	90	13.5	43	1.96	.0229
210	4.1	45	50	500268
230	4.1	45	50	50	...	Explosion		

The rate of reaction in the presence of nitrogen oxides appears to depend on the concentrations of acetylene, oxygen and nitrogen oxides, as shown by the experiments with air and with different amounts of nitrogen oxides in Table I and with low acetylene concentrations and the same concentration of nitrogen oxides in Table II. The rate is not dependent on the square of the acetylene concentration, as in the uncatalyzed reaction,^{1a} and the reaction is not retarded by an excess of oxygen or air.

In the above experiments with 4% of nitric acid in the gas mixture, reaction was observed below 170° by the formation of the solid deposit of glyoxal and the formation of carbon dioxide. Experiments carried out above 250° using over 2% of nitric acid vapor in the gases resulted in explosions. The sensitivity of gas containing nitric acid vapor varied with the time of contact; for example, numerous runs were made at 230° with times of contact from 90 to 180 seconds, but increasing the flow to give a time of contact of about forty-five seconds brought about explosions which shattered the reaction vessel. Dixon⁷ observed that a lower ignition temperature was obtained when a gas mixture was passed rapidly into a hot tube than when the tube was gradually heated while the gas mixture was passing through it. It may be that the phenomenon noted here is caused by a lowering of the ignition temperature as observed by Dixon.

⁷ Dixon, *Rec. trav. chim.*, **44**, 305 (1925).

A number of experiments were carried out to see if nitrogen peroxide in small amounts lowered the explosion temperature of acetylene-oxygen mixtures as it did the explosion temperatures of hydrogen-oxygen mixtures⁸ and of carbon monoxide-oxygen mixtures.⁹ A 1 acetylene-1 oxygen mixture was used containing from 0.010 to 0.45% of nitrogen peroxide. Only the slow thermal reaction was observed in the range 260-315°. As a 1 acetylene-1 oxygen mixture exploded frequently at 325° and always at 340°, it was concluded that small amounts of nitrogen oxides (below 0.5%) did not lower the explosion temperature or the temperature range of the slow oxidation reaction.

Examination of the solid reaction product and the contents of the cooled trap by the sodium fusion test gave no evidence that the nitrogen oxides had entered into chemical combination, forming organic nitrogen compounds.

The reaction of nitric oxide and acetylene was studied under the conditions of the oxidation experiments in the absence of other nitrogen oxides and oxygen. Nitric oxide, which was stored over water, was passed through the system before the run to sweep out traces of nitrogen peroxide and oxygen. The reaction was tested using a mixture of 1 nitric oxide-1 acetylene with a time of contact of thirty seconds at 260°. No reaction was observed between nitric oxide and acetylene under these conditions; the gases leaving the reaction vessel were colorless, which showed the absence of nitrogen peroxide, there was no formation of carbon oxides, and the washings from the trap cooled to -78° gave no evidence of the presence of organic oxidation products. As nitric oxide does not react with acetylene under the conditions of the reaction between acetylene and oxygen in the presence of nitric acid vapor (and its decomposition products), it was concluded that the nitrogen oxides are not reduced by acetylene beyond nitric oxide in the catalyzed oxidation.

Discussion

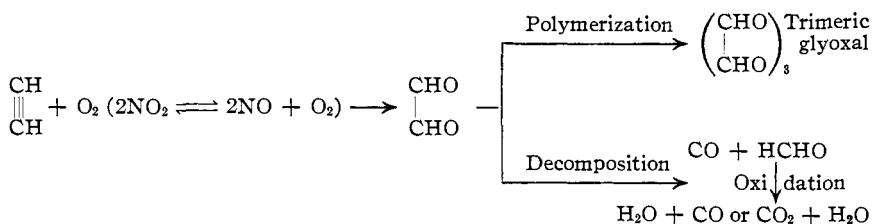
The presence of nitrogen oxides in concentrations greater than 0.5% by volume causes a marked lowering of the temperature of the slow thermal reaction between acetylene and oxygen; this lowering is as much as 80° for concentrations of 4% nitrogen oxides. As the rate of reaction is not greatly influenced by a change in the concentration of acetylene or oxygen, and as the rate of oxidation increases with increasing concentration of nitrogen oxides up to 4%, it appears that the rate-determining process is a reaction with a nitrogen oxide. At the temperature of these experiments, nitric acid vapor in the presence of oxygen is partially dissociated into water and nitrogen peroxide. The initial process is probably a reaction of

⁸ Gibson and Hinshelwood, *Trans. Faraday Soc.*, **24**, 559 (1928).

⁹ Sagulin and Semenov, *Chem. Reviews*, **6**, 350 (1929).

nitrogen peroxide with acetylene. Acetylene is oxidized with the formation of nitric oxide. This nitric oxide is oxidized by oxygen to nitrogen peroxide. Thus the action of the nitrogen peroxide is one of true catalysis, involving alternate reduction with acetylene to nitric oxide and oxidation of the nitric oxide with oxygen to nitrogen peroxide.

The predominance of glyoxal as a reaction product indicates that its formation is a principal primary reaction. In fact, the yields of glyoxal of 50% or more of the acetylene oxidized suggest that it is the primary product. The occurrence of large amounts of carbon monoxide and of only traces of formic acid, formaldehyde and hydrogen points to the thermal decomposition of glyoxal to carbon monoxide and formaldehyde, $\text{OHC-CHO} \rightarrow \text{CO} + \text{HCHO}$, as the main source of the carbon monoxide. The formaldehyde may be either oxidized to formic acid, which decomposes to water and carbon monoxide, $\text{HCOOH} \rightarrow \text{H}_2\text{O} + \text{CO}$, or may be oxidized directly to water and carbon monoxide by nitrogen peroxide, $\text{HCHO} + \text{NO}_2 \rightarrow \text{CO} + \text{H}_2\text{O} + \text{NO}$, in a reaction similar to the primary reaction of nitrogen peroxide with acetylene. The hydrogen and carbon dioxide may come from the decomposition of formic acid, $\text{HCOOH} \rightarrow \text{H}_2 + \text{CO}_2$. The course of the reaction as shown by these experiments may be given by the scheme



Summary

The reaction between acetylene and oxygen in the presence of nitrogen oxides proceeds between 170 and 250° as a homogeneous reaction catalyzed by nitrogen peroxide. The main product is trimeric glyoxal; the other products are formaldehyde, formic acid, carbon oxides, hydrogen and water.

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