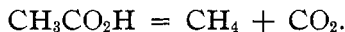


## ACTION OF PERSULPHATES ON ACETATES

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BY M. A. GORDON

When a solution containing sodium persulphate and acetic acid or sodium acetate is heated, a mixture of gases is given off, consisting of carbon dioxide and one or more hydrocarbons. The amount of carbon dioxide and the nature of the hydrocarbon may be varied by changing the conditions. One of the reactions seems to be a catalytic decomposition of acetic acid into methane and carbon dioxide,



It did not seem possible that persulphate itself could be the catalytic agent; but a process of elimination leads to this conclusion. The most plausible hypothesis was that platinum in some form, was the catalytic agent and consequently pieces of smooth platinum and of platinized platinum were immersed in the solution without any effect. In order to remove any hypothetical noble metal, including platinum, lead strips were placed in the persulphate solution so as to precipitate any unknown metal more noble than lead. This also had no effect. The addition of iron salts or of manganous salts do not increase the yield of methane. In order to show that the real catalytic agent was the persulphate itself, a solution of persulphate was heated long enough to destroy all the persulphate and was then added to the acetate solution. No decomposition into methane took place though the impurities in the persulphate were presumably still present. This last experiment seems to furnish conclusive proof that persulphate or an intermediate decomposition product of it is the catalytic agent. We may reject the hypothesis of an intermediate decomposition product being the catalytic agent because there is no relation between the amount of persulphate decomposed and the yield of methane.

Since other reaction products are usually formed besides

methane and carbon dioxide, other reactions also take place. We may have complete or partial oxidation of the acetic acid by the persulphate, the reaction products being water and carbon dioxide, ethylene, or ethane. It is not yet known whether glycollic acid, methyl alcohol and other oxidation products are formed under any conditions.

The usual form of apparatus for the evolution of the gas consisted of a bottle (the volume of which was slightly greater than that of the solution) immersed in a water bath. The bottle was fitted with a rubber stopper and a capillary tube leading to a sample gas pipette filled with mercury.

The acetate solution (about half the total volume) was placed in the bottle and brought to the temperature of the bath. The persulphate was heated to about 60° C (at a higher temperature the solution gave off gas) and then added to the acetate. About 100 cc (unless otherwise stated) of the gas were collected for analysis. The pressure was kept fairly constant during the run.

The Dennis modification of the Orsat apparatus<sup>1</sup> was used for the analysis of the gas. Friedrichs' spiral pipettes<sup>1</sup> were used for the absorbing liquid. Mercury was used as the confining liquid in a water-jacketed burette. The surface of the mercury was kept wet with a few drops of water in order that the gas might be saturated with aqueous vapor at all times. The burette was washed out after using such liquids as fuming sulphuric acid, cuprous chloride, etc.

Considerable difficulty was experienced in obtaining satisfactory results for the unsaturated hydrocarbons soluble in fuming sulphuric acid. A Friedrichs' spiral pipette, containing 25 percent sulphuric acid, was used. The absorption was quite rapid at first, but slowed up after a few passages through the reagent. Table A shows this:

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<sup>1</sup> Dennis: Jour. Ind. Eng. Chem., 4, 898 (1912).

TABLE A

The data for this table were obtained during the analysis of the gas given in Table VI

Time passed through fuming $\text{H}_2\text{SO}_4$	Volume <sup>1</sup> cc I	Volume <sup>1</sup> cc II
0	9.9	10.2
1	44.9	44.8
2	47.5	47.4
3	48.0	48.0
4	48.2	48.1
5	48.5	48.4

Methane and ethane were slowly absorbed by fuming  $\text{H}_2\text{SO}_4$ .<sup>2</sup> It may be that, with the more efficient absorption due to the Friedrichs spiral pipette, some of the saturated hydrocarbons are taken out.

Hydrogen was tested for by means of palladium black, but the results were not satisfactory, as there was an increase in volume, due to  $\text{CO}_2$  being given off. The copper oxide method<sup>3</sup> was then tried. The gas was passed through a tube containing copper oxide heated from  $250^\circ$ – $260^\circ$  C. The copper oxide was prepared by heating the commercial copper oxide in a hard glass ignition tube, in a current of air freed from  $\text{CO}_2$ .

Carbon dioxide was given off as in the case of the palladium black. Apparently, this was due to  $\text{CO}_2$ , which had been occluded by the copper oxide and not due to the burning of the hydrocarbon, for, on passing the gas through  $\text{KOH}$ , it was brought back to its original volume. No hydrogen was present.

Trouble was experienced in completely burning the gases in the combustion pipette. It was not discovered until a number of experiments had been made that the combustion was not complete even with an excess of oxygen. A second combustion was necessary, after passing the gas through  $\text{KOH}$  to remove the  $\text{CO}_2$ .

<sup>1</sup> Gas not passed through  $\text{KOH}$  before volume is read.

<sup>2</sup> Worsatt: Jour. Am. Chem. Soc., **21**, 245 (1899).

<sup>3</sup> Dennis: "Gas Analysis," 198 (1913).

Confirmation of this is found in some work by Hempel.<sup>1</sup>

"Numerous experiments with the Winkler-Dennis combustion pipette, show that it is extremely difficult to completely burn mixtures of methane and nitrogen, as part of the methane easily escapes combustion. Where one employs a combustion pipette filled with mercury and heats the mixture of oxygen, nitrogen and methane with the platinum spiral for a long time, in order to obtain complete combustion, the surface of the mercury becomes covered with a film of mercuric oxide. One naturally obtains a too high contraction due to the formation of this oxide of mercury."

Under "contraction ratio" in the tables is given the ratio of the volume contraction on combustion to the volume of the carbon dioxide formed. This ratio is 2.00 in the case of methane and 1.25 for ethane.

Under some conditions the hydrocarbon gas is pretty nearly pure methane. In Table I incomplete combustion probably accounts for the contraction ratio being 2.03 instead of 2.00. No free hydrogen is formed:

TABLE I

Sodium persulphate (70 percent)	6.3 grams
Sodium acetate (cryst.)	23 grams
Acetic acid (glacial)	100 cc
Water	100 cc
Temperature	75°-80°
About 500 cc of gas collected after passing through KOH solution.	
Analysis of gas (freed from CO <sub>2</sub> )	

Olefines cc	Combustion			Volume hydrocarbon cc	Contraction ratio
	O <sub>2</sub> added cc	Contraction cc	CO <sub>2</sub> cc		
1.4	72.7	71.5	35.2	34.8	2.03
1.6	77.4	76.4	37.6	37.4	2.03

The favorable conditions for the formation of methane seem to be a relatively low concentration of sodium persulphate

<sup>1</sup> Hempel: Zeit. anorg. Chem., 25, 1841 (1912).

and a high concentration of sodium acetate and acetic acid. A dilute solution of persulphate is more stable than a concentrated one and consequently there is less decomposition in the unit time and less oxidation of the acetic acid. It seems not unreasonable that a high concentration of acetic acid should be favorable to the methane dissociation. The part played by the sodium acetate is not entirely clear. It is, of course, a simple matter to say that undissociated acetic acid is the active mass and that sodium acetate forces back the dissociation; but acetic acid is dissociated so slightly that one would hardly expect the change in the degree of dissociation to be very important. It is also possible that the dissociation of sodium persulphate is forced back by another sodium salt. This would account for the beneficial effect of sodium sulphate.

The data in Table II illustrate the effect of varying the amount of sodium acetate, the concentration ratio increasing from 1.94 to 2.00.

TABLE II

Sodium persulphate (56.7 percent)	1.68 grams
Sodium acetate (cryst.)	$x$ gram
Acetic acid (glacial)	20 cc
Water	20 cc
Temperature	98°-99°

## Analysis of hydrocarbon gas

Sodium acetate g	Combustion			Volume hydrocarbon cc	Concentration ratio
	O <sub>2</sub> added cc	Contraction cc	CO <sub>2</sub> cc		
0.00	41.1	39.9	20.2	19.0	1.94
0.66	68.9	68.4	34.2	33.7	1.98
0.66	70.8	69.8	34.7	33.7	1.99
2.3	78.0	78.9	38.2	37.8	2.01
2.3	68.9	66.6	33.3	31.8	2.00

The data in Table III show the effect of varying the concentration of another sodium salt, sodium sulphate. With increasing concentration of sodium sulphate, the concentration ratio increases from about 1.70 to 1.90. The lower concen-

tration of acetic acid causes a drop in the concentration ratio from 1.94 (Table II) to 1.72 (Table III).

TABLE III

Sodium persulphate (70 percent)	1.28 grams
Sodium sulphate (anhydrous)	$x$ gram
Acetic acid (glacial)	1 cc
Water	20 cc
Temperature	98°-99°

## Analysis of hydrocarbon gas

Sodium sulphate g	Combustion			Volume hydro- carbon cc	Concen- tration ratio
	O <sub>2</sub> added cc	Contraction cc	CO <sub>2</sub> cc		
0.0	31.7	30.2	17.4	16.3	1.74
0.0	36.5	33.7	20.0	17.7	1.69
2.0	41.9	39.9	21.1	19.5	1.90

In Table IV are given special data to illustrate the effect of changing the concentration of acetic acid. One cubic

TABLE IV

Sodium persulphate (56.7 percent)	1.68 grams
Volume of solution	40 cc
Temperature	98°-99°

No.	Acetic acid cc	Sodium acetate g	Water cc
1	20	2.3	20
2	20	2.3	20
3	1	—	39
4	1	—	39
5	—	2.3	40
6	—	2.3	40

No.	Combustion			Volume hydro- carbon cc	Concen- tration ratio
	O <sub>2</sub> added cc	Contraction cc	CO <sub>2</sub> cc		
1	78.0	76.9	38.2	37.8	2.01
2	68.9	66.6	33.3	31.8	2.00
3	37.3	35.3	18.3	16.9	1.93
4	31.4	30.0	15.5	14.3	1.93
5	50.1	43.4	25.6	19.7	1.69
6	56.0	46.9	27.9	19.6	1.68

centimeter glacial acetic acid is equivalent to 2.3 grams  $\text{CH}_3\text{CO}_2\text{Na} \cdot 3\text{H}_2\text{O}$ .

In the following experiments, Table V, the concentration of sodium persulphate was kept relatively high, with a corresponding decrease in the concentration ratio, which drops to 1.45. The gas contained considerable quantities of olefines soluble in fuming sulphuric acid:

TABLE V

Sodium persulphate (70 percent)	1.92 grams
Sodium acetate (cryst.)	0.14 gram
Acetic acid (glacial)	0.1 cc
Water	20 cc
Temperature	98°-99°

## Analysis of hydrocarbon gas

Combustion		CO <sub>2</sub> cc	Volume hydrocarbon cc	Contraction ratio
O <sub>2</sub> added cc	Contraction cc			
23.8	19.7	13.2	10.5	1.49
23.7	19.7	13.6	10.0	1.45
29.1	23.8	16.4	11.5	1.45
28.7	24.8	16.3	13.2	1.52

Another run was made at a lower temperature, Table VI, in which the olefines were removed by means of fuming sulphuric acid before the hydrocarbon gas was analyzed:

TABLE VI

Sodium persulphate (70 percent)	96 grams
Sodium acetate (cryst.)	7 grams
Acetic acid (glacial)	5 cc
Water	1000 cc
Temperature	75-78°

About 500 cc gas collected after passing through KOH solution.

## Analysis of hydrocarbon gas (freed from olefines)

Olefines cc	Combustion		CO <sub>2</sub> cc	Volume hydro- carbon cc	Contraction ratio
	O <sub>2</sub> added cc	Contraction cc			
38.8	32.8	30.7	16.6	15.0	1.85
38.4	33.0	30.7	16.8	14.8	1.85

The hydrocarbon gas left after the removal of the olefines appears to consist of a mixture of methane and ethane. Calculations based on the combustion, oxygen consumed, and volume of hydrocarbon, check quite closely with the theoretical. The hydrocarbon gas, therefore, consists approximately of 72 percent olefines, 22.4 percent methane, and 5.6 percent ethane. The composition of the olefines has not been determined satisfactorily as yet, but we are evidently dealing with a mixture.

In Tables I-VI the important point has been the composition of the hydrocarbons and no data have been given for the carbon dioxide set free during the reaction. If no acetic acid is oxidized completely to carbon dioxide and water and if there is no lower, non-gaseous, carbon compound formed, such as methyl alcohol for instance, the amount of carbon dioxide set free during the reaction should be equal to that produced by combustion of the hydrocarbon gases. A ratio greater than unity indicates some oxidation of acetic acid to carbon dioxide and water. Conditions which favor the decomposition of the persulphate, such as acidity, rise of temperature, etc., should increase the oxidation as shown by the  $\text{CO}_2$  ratio or the ratio of  $\text{CO}_2$  produced during the reaction to the  $\text{CO}_2$  produced by the combustion of the saturated hydrocarbons. In Table VII are given data for the effect of temperature under condition such that the hydrocarbon is practically pure methane, the contraction ratio being approximately 2.00:

TABLE VII

Sodium persulphate (56.7 percent)	1.68 grams
Sodium acetate (cryst.)	4.6 grams
Acetic acid (glacial)	20 cc
Water	20 cc

Temp.	Reaction $\text{CO}_2$ cc	Combustion $\text{CO}_2$ cc	Contraction ratio	$\text{CO}_2$ ratio
98°-99°	41.1	34.5	2.02	1.19
98°-99°	22.0	18.4	2.01	1.20
98°-99°	34.1	34.8	1.99	1.24
78°-79°	33.8	31.1	2.00	1.09
78°-79°	33.0	31.4	1.97	1.05
64°-65°	31.9	30.0	1.99	1.06



Even at the highest temperature, the amount of acetic acid oxidized is only one-fifth that decomposed catalytically, and the value drops nearly to one-twentieth at the lower temperatures:

In Table VIII are similar data for cases in which relatively large amounts of ethane and unsaturated hydrocarbons are formed, the contraction ratio being distinctly less than two:

TABLE VIII

Sodium persulphate (70 percent)	1.92 grams
Sodium acetate (cryst.)	0.14 gram
Acetic acid (glacial)	0.1 cc
Water	20 cc

Temp.	Reaction CO <sub>2</sub> cc	Combustion CO <sub>2</sub> cc	Contraction ratio	CO <sub>2</sub> ratio
98°-99°	42.1	16.2	1.45	2.55
98°-99°	43.3	16.3	1.52	2.66
78°-79°	64.5	33.8	1.51	1.91

Tables VII and VIII indicate that temperature has little or no effect on the composition of the hydrocarbon as the contraction ratio does not change with change of temperature.

Even at the lower temperature nearly twice as much acetic acid is burned to carbonic dioxide and water as is converted into methane and ethane. If the solution is made distinctly acid with sulphuric acid, the decomposition of the persulphate takes place so rapidly that large amounts of oxygen are set free. This is shown in Table IX, the persulphate concentration being extremely high:

TABLE IX

Sodium persulphate (70 percent)	1.28 grams
Acetic acid (glacial)	1 cc
H <sub>2</sub> SO <sub>4</sub> (sp. gr. 1.84)	5 cc
Water	9 cc
Temperature	98°-99°

Reaction CO <sub>2</sub> cc	Combustion CO <sub>2</sub> cc	CO <sub>2</sub> ratio	O <sub>2</sub> set free cc
5.2	0.8	4.5	42.0

If the persulphate concentration be kept down and if sodium sulphate be added, a small amount of sulphuric acid can be added without causing evolution of oxygen. The oxidation ratio is high under these circumstances.

TABLE X

Sodium persulphate (56.7 percent)	1.68 grams
Acetic acid (glacial)	1 cc
Sodium sulphate (hydrated)	3.2 grams
Sulphuric acid (sp. gr. 1.84)	1.0 gram
Water	39 cc
Temperature	98°-99°

Reaction CO <sub>2</sub> cc	Combustion CO <sub>2</sub> cc	Contraction ratio	CO <sub>2</sub> ratio
46.1	10.3	1.94	4.48
45.4	10.6	1.90	4.28

Addition of 1 cc molar manganous sulphate to a solution containing 1.68 grams sodium persulphate (56.7 percent), 1 cc glacial acetic acid and 39 cc water caused an increase in the carbon dioxide ratio to 7.05, a manganese oxide precipitating. A piece of platinum foil with a surface of 200 cm<sup>2</sup> also acted as a catalytic agent increasing the carbon dioxide ratio from about 3.0 to about 4.0.

It seemed desirable to determine, if possible, the relation between persulphate decomposed and carbon dioxide set free during the reaction. Preliminary experiments indicated that persulphate could be determined in presence of acetate by adding an excess of ferrous sulphate to the solution acidified with sulphuric acid. The analysis for persulphate was made by adding, to the mixed persulphate and acetate solution, 100 cc of ferrous ammonium sulphate solution (30 grams per liter), 10 cc H<sub>2</sub>SO<sub>4</sub> (1 : 4), and 100 cc boiling water. The solution was then heated to 50°-70° C and titrated rapidly with *N*/5 KMnO<sub>4</sub>. The results have been calculated on the assumption that part of the CO<sub>2</sub> comes from the catalytic decomposition of the acetic acid. Only the excess of CO<sub>2</sub> over that

equivalent to the methane is considered as due to oxidation by persulphate. On this basis only half the active oxygen of the persulphate seems to be accounted for and there must be some other product which has not yet been isolated. It is possible that this may be glycollic acid since Professor Orndorff tells me that he has obtained glycollic acid by slow oxidation of acetic acid with permanganate. This would be the first oxidation product in case the oxidation takes place in stages, as it probably does. The data are given in Table XI:

TABLE XI

Sodium persulphate (56.7 percent)	0.84 gram
Sodium acetate (cryst.)	2.3 grams
Acetic acid	10 cc
Water	10 cc
Temperature	98°-99°

## Analysis of hydrocarbon gas

No.	Combustion			Volume hydrocarbon cc	Contraction ratio
	O <sub>2</sub> added cc	Contraction cc	CO <sub>2</sub> cc		
1	38.2	36.9	18.4	17.6	2.01
2	69.8	68.1	34.3	33.2	1.99
3	71.0	69.1	34.8	33.6	1.99

No.	CO <sub>2</sub> cc	CO <sub>2</sub> ratio	O <sub>2</sub> lost Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub> Grams	O <sub>2</sub> found CO <sub>2</sub> Grams
1	22.0	1.20	0.0135	0.0056
2	42.0	1.23	0.0225	0.0111
3	43.1	1.24	0.0239	0.0119

The general results of this paper are:

(1) Persulphates decompose acetic acid catalytically into methane and carbon dioxide.

(2) Persulphates oxidize acetic acid, some of the products being ethane, olefines, carbon dioxide and water.

(3) The catalytic decomposition is favored by high concentration of acetic acid, low acidity, and low concentration of persulphate.

(4) Low acidity together with high concentration of acetic acid can be obtained by adding sodium acetate to force back the dissociation.

(5) Conditions favoring the decomposition of persulphate increase the oxidation of acetic acid if not carried to an excess.

(6) High concentration of persulphate, high temperature, moderate acidity, presence of manganous sulphate or platinum foil, increase the oxidation of acetic acid.

(7) Addition of too much sulphuric acid makes persulphuric acid so instable at high temperatures that oxygen is set free and the oxidation of acetic acid is cut down correspondingly.

(8) Temperature has no effect on the composition of the hydrocarbon gas.

(9) Impurities in the persulphate are apparently not the catalytic agents because no probable impurity acts in this way and because the catalytic action ceases when the persulphate is destroyed.

This research was suggested by Professor Bancroft and has been carried on under his supervision.

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