have similar effects in the polymorphic and stability relations of compounds with a common anion.

7. Binary crystals increase in hardness as the ionic potentials of their constituents increase.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

THE CATALYTIC ACTIVITY OF METALLIZED SILICA GELS. V. THE OXIDATION OF ETHYLENE[1]

BY L. H. REYERSON AND L. E. SWEARINGEN

RECEIVED MAY 31, 1928 PUBLISHED NOVEMBER 6, 1928

Previous investigations of the authors[2] have shown that metallized silica gels exhibit considerable activity in certain oxidation reactions. The following investigation is an extension of this work to the oxidation of ethylene. Willstätter and Bommer[3] in their quantitative study of the conditions for the formation of formaldehyde from ethylene showed that, unless dilute, both ethylene and formaldehyde are unstable at temperatures much above 300°. They found that the use of catalysts accelerated the oxidation of ethylene but no formaldehyde was detected when catalysts were used. An osmium catalyst was found to initiate the oxidation of ethylene at about 130°, while copper proved to be effective at 250°. Blair and Wheeler[4] continued these investigations and found that, with a platinum catalyst, formaldehyde was formed at 405° when the gases were streamed through the catalyst very rapidly. As a result of these investigations, it was hoped that the use of metallized silica gels as catalysts would so lower the temperature at which reaction occurred that partial oxidation of ethylene could be effected and a mechanism for its catalytic oxidation obtained.

The experimental procedure was similar to that used by the authors in the study of the oxidation of methane.[5] Samples of the same catalysts were used as in the preceding investigations. Mixtures of ethylene, oxygen and nitrogen were passed over the catalysts at temperatures ranging from about 100 to 310° at varying rates of flow. In no case did the sum of oxygen and ethylene in the mixture exceed 50% of the gas volume. Preliminary experiments showed that the products of oxidation were carbon dioxide and water, so that the gases after passing through the catalyst were analyzed for ethylene, oxygen and carbon dioxide. In no case did tests show the presence of intermediate products of oxidation.

[1] In memory of Ira Remsen.

[2] Swearingen and Reyerson, *J. Phys. Chem.*, **32**, 113, 192 (1928).

[3] Willstätter and Bommer, *Ann.*, **422**, 36 (1921).

[4] Blair and Wheeler, *J. Soc. Chem. Ind.*, **41**, 303T (1922).

[5] Ref. 2, p. 192.

Experimental Results

The results of the experiments are given in Tables I to IV and Figs. 1 and 2 graphically represent typical experiments. The symbols used in the tables have the following significance.

A = the percentage of ethylene in the original mixture
A' = the percentage of ethylene found in the exit gas
A'' = the percentage of ethylene calculated to be present
O_2 = the amount of oxygen present in the original mixture
O_2' = the amount of oxygen found in the exit gas
O_2'' = the amount of oxygen calculated to be present
f = the fraction of carbon dioxide in the final mixture
F = the percentage of carbon dioxide in the final mixtures ($F = 100f$)
x = the fraction of the ethylene oxidized
X = the percentage of ethylene oxidized ($X = 100x$)
B = temperature of bath surrounding catalyst tube
C = temperature of catalyst during reaction

TABLE I

SILVER CATALYST

Gas mixture: (A) Ethylene, 27.00%; (O_2) Oxygen, 18.00%

Temperature B C	Rate, cc. per min.	Final gas analysis A'	O_2'	F	Calcd. X	A''	O_2''
310–313	30	25.90	12.89	3.79	6.63	26.13	12.99
310–311	50	25.85	14.82	2.87	5.17	26.34	14.21
310–312	60	26.25	15.05	2.51	4.55	26.42	14.68
310–313	180	26.10	17.86	1.32	2.41	26.70	16.32
200–201	30	26.50	18.20	0.66	1.22	26.85	17.13
200–201	60	26.42	18.28	.66	1.22	26.85	17.13
200–200	180	26.85	18.62	.44	0.87	26.80	17.42
Gas mixture: (A) Ethylene, 19.00%; (O_2) Oxygen, 26.50%							
300–302	30	17.30	19.25	4.24	10.72	17.69	20.76
300–301	60	18.20	21.06	3.56	9.01	17.90	22.12
300–301	100	18.41	23.51	2.33	6.00	18.28	23.62
300–302	140	18.73	24.30	1.94	5.00	18.40	24.10
300–304	180	18.96	22.48	1.52	3.94	18.53	24.64

TABLE II

COPPER CATALYST

Gas mixture: (A) Ethylene, 30.00%; (O_2) Oxygen, 18.00%

Temperature B C	Rate, cc. per min.	Final gas analysis A'	O_2'	F	Calcd. X	A''	O_2''
310–310	30	29.80	1.87	11.02	16.65	27.80	3.48
310–312	60	28.80	6.16	8.80	13.50	28.24	6.40
310–324	100	29.50	8.80	6.64	10.37	28.68	9.25
310–327	180	29.45	12.55	4.26	6.84	29.15	12.37
Gas mixture: (A) Ethylene, 24.00%; (O_2) Oxygen, 19.20%							
200–200	30	23.50	16.38	2.09	4.26	23.46	16.47
200–200	95	24.20	18.04	0.98	2.03	23.75	17.92
200–200	180	24.61	17.08	0.76	1.57	23.80	18.21

TABLE II (*Concluded*)

Gas mixture: (A) Ethylene, 19.50%; (O_2) Oxygen, 27.50%

Temperature B C	Rate, cc. per min.	Final gas analysis			Calcd.		
		A′	O_2'	F	X	A″	O_2''
300–306	30	14.45	5.58	17.76	38.70	14.09	5.75
300–317	60	15.72	6.50	14.42	32.30	15.10	9.82
300–330	140	16.88	13.68	10.62	24.65	16.26	14.48
300–320	180	17.25	16.40	8.84	20.85	16.80	16.65
200–200	30	19.00	24.65	2.13	5.36	18.85	24.89
200–200	60	19.23	25.02	1.85	4.64	18.94	25.55
200–205	180	19.43	26.10	0.96	2.45	19.20	26.32
300	30	27.80	3.87	11.02	16.65	27.80	3.48
260	30	29.55	12.25	4.52	7.19	29.10	12.08
200	30	23.50	16.38	2.09	4.26	23.46	16.47
150	30	29.20	20.18	1.18	2.00	28.75	19.78
106	30	23.75	18.73	0.54	1.14	23.86	18.49

TABLE III

PLATINUM CATALYST

Gas mixture: (A) Ethylene, 20.00%; (O_2) Oxygen, 18.00%

Temperature B C	Rate, cc. per min.	Final gas analysis			Calcd.		
		A′	O_2'	F	X	A″	O_2''
210–227	60	17.08	7.93	7.62	17.65	17.72	7.97
203–212	60	17.78	9.00	7.02	16.38	17.90	8.76
198–212	60	18.00	10.37	6.13	14.45	18.16	9.90
170–175	60	18.60	13.14	3.94	9.45	18.82	12.80
160–165	60	18.85	14.72	2.60	6.33	19.22	14.56
130–125	60	19.50	16.78	1.31	3.23	19.61	16.27
115–115	60	19.95	17.30	0.64	1.59	19.81	17.15
90– 90	60	19.85	18.07	0.22	0.55	19.95	17.71

Gas mixture: (A) Ethylene, 29.00%; (O_2) Oxygen, 21.30%

Temperature B C	Rate, cc. per min.	A′	O_2'	F	X	A″	O_2''
200–215	30	26.45	4.40	12.53	19.22	26.48	5.18
200–215	60	27.30	8.80	10.10	15.90	27.88	8.30
200–220	100	27.06	10.63	7.98	13.00	27.32	11.02
200–225	140	27.50	13.09	6.15	10.08	27.71	13.38
200–235	180	27.99	14.10	5.50	8.97	27.85	14.22
130–130	30	28.43	18.59	2.18	3.67	28.44	18.49
130–130	60	28.68	20.42	0.76	1.30	28.84	20.32
130–130	180	28.70	20.65	0.54	0.93	28.89	20.30

Gas mixture: (A) Ethylene, 21.50%; (O_2) Oxygen, 26.50%

Temperature B C	Rate, cc. per min.	A′	O_2'	F	X	A″	O_2''
300–300	30	15.50	1.18	21.00	40.40	15.50	0.55
300–308	60	16.00	2.24	20.08	38.00	15.80	1.75
300–329	120	16.40	5.18	17.06	33.95	11.64	5.45
300–335	180	17.78	7.35	15.35	31.00	17.31	7.55
200–200	30	15.53	4.23	18.35	36.10	16.26	3.80
200–217	60	16.50	5.03	18.06	35.60	16.36	4.25
200–223	180	17.75	11.41	12.80	26.40	17.85	10.68
110–110	30	21.00	25.80	0.76	1.75	21.29	25.56
95– 95	30	21.78	25.90	0.66	1.64	21.31	25.68
90– 90	30	21.00	25.95	0.55	1.36	21.34	25.82

TABLE III (*Concluded*)

Gas mixture: (A) Ethylene, 21.30%; (O_2) Oxygen, 16.85%

Temperature *B* *C*	Rate, cc. per min.	Final gas analysis			Calcd.		
		A'	O_2'	*F*	*X*	*A''*	O_2''
300–304	60	17.68	1.34	12.13	26.45	17.93	0.75
300–306	60	17.96	1.54	12.00	25.15	17.84	0.87
250–255	60	18.63	6.02	8.33	18.00	18.91	5.75
200–203	60	19.95	10.85	5.76	12.77	19.65	9.19
150–150	60	20.39	12.36	3.57	8.10	20.28	12.08
100–100	60	20.56	14.29	1.75	4.02	20.80	14.52
Gas mixture:		(A) Ethylene, 22.65%; (O_2) Oxygen, 17.50%					
310–315	60	19.20	2.07	11.65	23.08	19.46	2.07
280–285	60	19.00	4.83	10.00	20.10	19.92	4.25
260–262	60	20.25	7.67	7.80	16.00	20.51	7.17
220–222	60	20.85	11.13	5.18	10.85	21.83	10.64
134–135	60	22.50	15.70	1.53	3.33	22.23	15.47
120–120	60	22.50	16.64	1.08	2.36	22.35	16.07
95– 95	60	22.62	16.73	0.86	1.88	22.41	16.36

TABLE IV

PALLADIUM CATALYST

Gas mixture: (A) Ethylene, 24.00%; (O_2) Oxygen, 20.50%

Temperature *B* *C*	Rate, cc. per min.	Final gas analysis			Calcd.		
		A'	O_2'	*F*	*X*	*A''*	O_2''
300–304	30	20.52	2.15	14.42	26.28	20.25	1.80
300–309	60	21.60	5.17	12.12	22.54	20.85	4.81
300–312	100	21.56	7.00	10.60	20.00	21.24	6.75
300–315	140	21.95	9.08	9.11	17.40	21.63	8.70
300–330	180	22.21	10.12	8.25	15.88	21.85	9.82
200–205	30	22.58	13.75	6.49	12.73	22.31	12.09
200–205	60	23.55	14.65	4.74	9.45	22.86	13.36
200–210	100	23.60	16.40	2.86	5.80	23.26	16.80
200–210	180	24.20	19.30	0.58	1.20	23.85	19.75
250–254	30	21.80	5.80	11.02	20.70	21.13	6.20
250–255	60	21.88	9.10	9.05	17.28	21.63	8.78
250–255	100	22.06	8.96	7.98	15.40	21.92	9.15
250–259	140	22.05	10.98	7.21	14.00	22.13	11.15
250–262	180	22.40	12.06	6.71	13.10	22.25	11.80
Gas mixture:		(A) Ethylene, 21.00%; (O_2) Oxygen, 25.00%					
300–304	30	16.28	0.96	19.70	39.18	15.29	0.40
300–309	60	16.38	2.73	17.60	35.70	15.90	3.00
300–310	100	16.58	5.15	16.05	33.00	16.35	4.98
300–313	140	17.08	7.20	14.42	30.00	16.80	6.90
300–319	180	16.50	8.17	13.18	27.90	17.08	8.50
200–204	30	16.08	3.29	18.15	36.70	15.74	2.30
200–205	60	15.85	4.81	16.55	33.85	16.20	4.32
200–208	100	17.15	7.15	14.42	30.00	16.80	6.90
200–214	140	17.85	14.77	12.72	26.90	17.32	14.10
200–215	180	17.84	11.94	11.42	24.60	16.28	11.75
110–110	30	21.00	24.70	0.83	2.00	20.85	24.34
110–110	30	20.53	23.30	0.98	2.30	20.72	23.77

In the tables under the headings A', O_2' and F are given the results of the quantitative analysis of the gases after reaction. The column headed X gives the percentage of ethylene oxidized provided the reaction proceeds according to the following reaction: $C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O$. The fraction of ethylene oxidized is given by $x = 100\,f/(2A + 2Af)$, so that $100\,x = X$. From the amount of carbon dioxide formed it is also possible to calculate the amount of ethylene and oxygen which should be present with this carbon dioxide provided the oxidation of ethylene is complete. The calculated percentage of ethylene in the products of reaction is given by $A'' = A + f\,(A - 50)$, while for oxygen we have $O_2'' = O_2 + f\,(O_2 - 150)$. The values calculated for ethylene and oxygen check the experimental values very well and probably within the limits of the experimental error in the gas analysis.

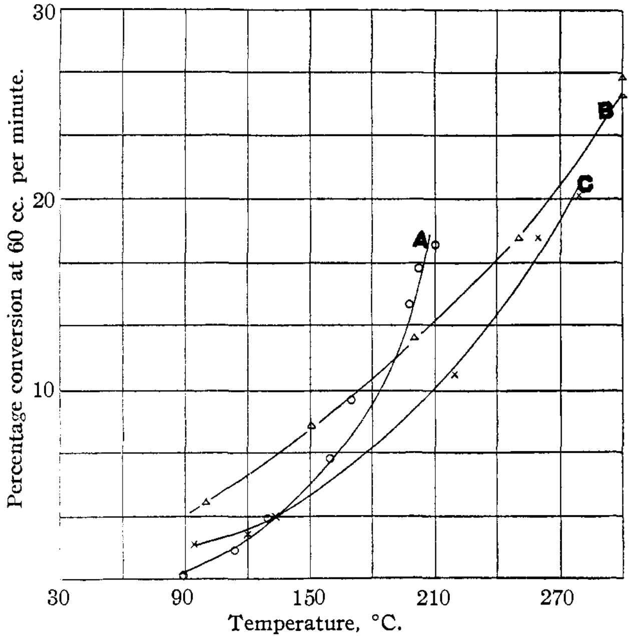

Fig. 1.—Composition of gas mixture: A = C_2H_4, 20%; O_2, 18%. B = C_2H_4, 21.3%; O_2, 16.85%. C = C_2H_4, 22.65%; O_2, 17.5%.

Discussion and Results

It is evident from these results that the catalysts used were effective in promoting the oxidation of ethylene at lower temperatures than previously reported. The copper, platinum and palladium catalysts began to be effective at about 100°. Fig. 1 shows the effect of temperature on the oxidation of ethylene for three different gas mixtures with platinized silica gel as the catalyst. The effect of increased rate of streaming on the conversion is shown graphically in Fig. 2. The silver catalyst is shown to be less effective than the other catalysts. The catalysts all speeded up the successive oxidation reactions so that no intermediate products were detected. This confirms the previous work on the oxidation of ethylene.

The experimental results here given indicate that the reaction is directly proportional to the oxygen concentration and inversely proportional to the ethylene concentration. For example, when the ratio of ethylene to oxygen is changed from 1.36 to 0.81, the amount of ethylene oxidized by the platinum catalyst at 200° increases from 19.22 to 36.10%. Thus the amount oxidized is nearly doubled. Similar results were obtained with the other catalysts. The simplest explanation for these results would seem to be that collisions of ethylene molecules with oxygen molecules which are adsorbed and activated by the effective catalyst centers resulted in reaction, whereas collisions of oxygen molecules with adsorbed ethylene molecules were ineffective. The adsorption studies of the authors[6] indicate specific adsorption of both ethylene and oxygen by these catalysts. Therefore, when the ethylene molecules are adsorbed by the active catalyst centers, then these centers, are no longer effective. The double bond of ethylene is no doubt directed toward the catalyst. When,

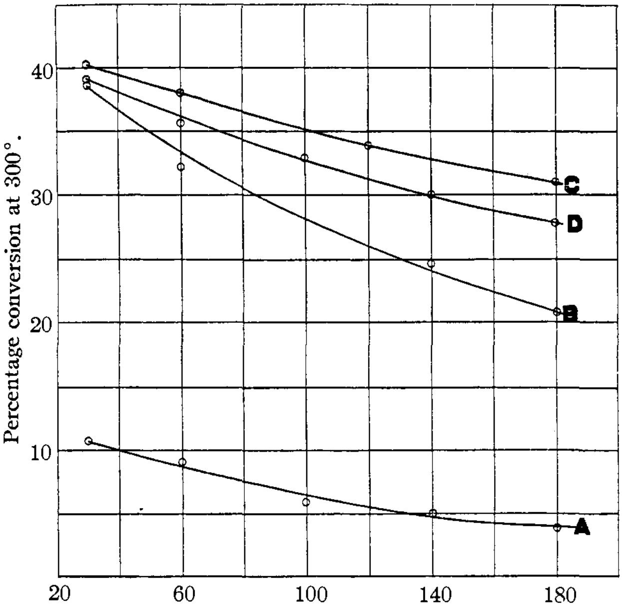

Fig. 2.—Catalysts: A, Silver; B, Copper; C, Platinum; D, Palladium.

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[6] Reyerson and Swearingen, *J. Phys. Chem.*, **31**, 88 (1927).

however, an oxygen molecule reaches an active center and is adsorbed, it is activated so that it is able to react with the ethylene which reaches it. Mere adsorption is not sufficient, otherwise the silica gel itself would be an active catalyst. Because of their higher energy content the primary products of oxidation are likely to be very reactive whether they are dihydroxyethylene or formaldehyde. Furthermore, as indicated in the tables, the temperature of the catalysts is often higher than that of the bath in which they are immersed. This indicates that the temperature at which the reaction takes place may be very much higher than that indicated, so that successive collisions with oxygen molecules result in complete oxidation. Otherwise intermediate products of oxidation should be detected when the rate of streaming through the catalyst was increased.

Conclusion

1. Metallized silica gels actively promote the oxidation of ethylene, beginning to be effective at about 100°.
2. The catalysts are so active that no intermediate products of oxidation are detected.

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THE FLUIDITY OF MERCURY[1, 2]

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RECEIVED JUNE 25, 1928 PUBLISHED NOVEMBER 6, 1928

Tammann and Hinnüber[3] have raised the question whether the viscosity of a liquid is trustworthy when it is measured in a tube that is not thoroughly wetted by the liquid. They claim to have found the viscosity of mercury in an amalgamated copper capillary to be 4.931 ± 78 *cp* at 13.5° instead of 1.609 *cp* for mercury in glass. Whether one accepts their explanation of the phenomenon based on "slippage," or not, the discrepancy of over 200% is quite beyond experimental error and demands investigation.

1. The hypothesis of slippage is, of course, not new. It has often been offered to account for results which at the time seemed inexplicable, but on further investigation it has always been found that some factor has been overlooked which has made this explanation unnecessary. On the other hand, the fair agreement among the results of different investigators using widely different forms of viscometers and shearing stresses constitutes what may be fairly regarded as proof that slippage is certainly not

[1] In memory of Ira Remsen.

[2] Part of Master's Degree "Thesis" of Theodore R. Thompson.

[3] Tammann and Hinnüber, *Z. anorg. Chem.*, 167, 230 (1927).