

The Decomposition of Nitrous Oxide on the Surface of Platinum. I. The Retarding Effect of Oxygen

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The Decomposition of Nitrous Oxide on the Surface of Platinum.

I. The Retarding Effect of Oxygen

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An investigation has been made of the decomposition of nitrous oxide on the surface of spongy platinum in the temperature range 485 to 570°C. The results are in agreement with the previous work of Hinshelwood, Schwab and others using filament catalysts. Experiments have also been made on the effect of added oxygen. It is found that oxygen formed in the reaction has a much larger retarding effect

than has added oxygen. Under certain circumstances oxygen and nitrogen also retard the reaction by hindering diffusion to the more remote parts of the catalyst. It is concluded that oxygen formed in the reaction is adsorbed in the atomic condition, while added oxygen is mainly adsorbed in the form of molecules.

INTRODUCTION

ONE important phase of heterogeneous catalysis is the retardation of a reaction by its products. In general, preferential adsorption of the reaction products seems to offer a satisfactory explanation. In almost all cases, however, the retarding effect of the products has been inferred from the form of the differential equation expressing the rate of reaction and very few experiments have been performed in which the product to which the retarding effect is ascribed has been added in varying amounts and under various conditions.

One of the most thoroughly investigated reactions in this connection is the decomposition of nitrous oxide on platinum. The reaction is retarded by oxygen, but there is considerable disagreement about its action. Hinshelwood and Prichard¹ found that the rate was given by

$$-d/dt(\text{N}_2\text{O}) = K(\text{N}_2\text{O})/(1 + b(\text{O}_2)).$$

Their experiments were made with electrically heated filament catalysts at temperatures between 600° and 1200°C. They found that added oxygen had the same retarding effect as oxygen formed during the reaction. Schwab and Eberle² investigated the reaction in a similar way. They came to the conclusion, however, that added oxygen had no retarding effect on the reaction. Low pressure measurements have also been made by Cassel and Glückauf³ and by van Praagh and Topley.⁴

¹ Hinshelwood and Prichard, *J. Chem. Soc.* **127**, 327 (1925).

² Schwab and Eberle, *Zeits. f. physik. Chemie* **B19**, 102 (1932).

³ Cassel and Glückauf, *Zeits. f. physik. Chemie* **B9**, 427 (1930).

⁴ van Praagh and Topley, *Trans. Faraday Soc.* **27**, 312 (1931).

In view of the above discrepancies it seemed worth while investigating the retarding effect of oxygen in a more thorough manner. Instead of filament catalysts we have used platinum sponge.

EXPERIMENTAL

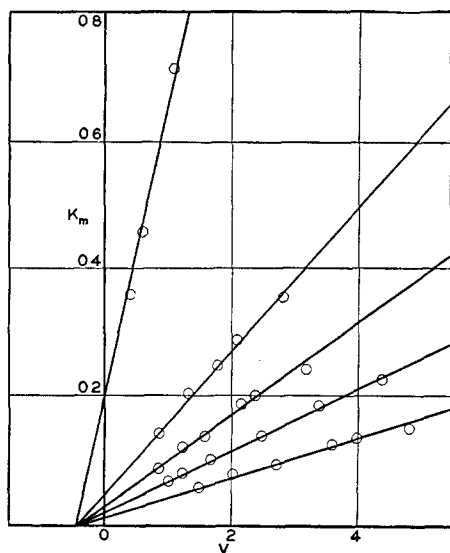
Reaction velocities were followed in the usual way by observing the rate of pressure change in a system at constant volume. The reaction vessel was of fused silica and had a capacity of about 125 cc. The apparatus was similar to one which has been used in a number of previous investigations.⁵ The required temperatures were obtained by means of an electric furnace, which could be maintained constant to within 0.5°C. Before each run the system was evacuated to about 10^{-4} mm by means of a mercury vapor pump.

The catalyst was platinum sponge prepared by the ignition of ammonium chloroplatinate. Approximately 5 grams of catalyst were used in each series of runs. Nitrous oxide was obtained in cylinders from the Ohio Chemical and Manufacturing Co. It was dried over phosphorus pentoxide. Oxygen was also obtained from cylinders and was dried in the same way. It contained 4.5 percent nitrogen.

EXPERIMENTAL RESULTS

The temperature range used was from 450 to 570°C. Even at the highest of these temperatures the homogeneous reaction is far too slow to introduce any complication. Since the reaction has been shown to be homogeneous in quartz vessels, it follows that the vessel walls have no effect in this case.

⁵ Steacie, *Can. J. Research* **6**, 265 (1932).

FIG. 1. $1/t \ln a/(a-x)$ vs. x/t .

I. The decomposition in the absence of added oxygen

The results obtained were in excellent agreement with the equation previously given by Hinshelwood and Prichard. This is shown by Fig. 1, in which $1/t \ln a/(a-x)$ is plotted against x/t . Good straight lines are obtained. The reaction is evidently retarded by the oxygen formed in the manner suggested by previous workers, in spite of the fact that previous investigations were made at high temperatures on filaments, while this work was done at comparatively low temperatures on spongy platinum.

The experimental results were quite definitely reproducible, there being no noticeable aging effects. It was also found that the vacuum treatment between runs was comparatively unimportant. Thus evacuating between runs to 1 or 2 mm pressure gave the same result as a prolonged evacuation to 10^{-4} mm. This is rather surprising in view of the fact that the reaction is retarded by the products. It was also found that it was almost immaterial whether the evacuation was carried out at the temperature of the experiments (say 532°C) or at 800°C .

A number of runs were made at various temperatures and with three different catalysts to determine the effect of the nitrous oxide concentration on the rate. The equation previ-

TABLE I.

Temp. °C	Initial pressure, cm	T_{50} mins.	Temp. °C	Initial pressure, cm	T_{50} mins.
<i>Catalyst No. 1.</i>					
529.5	2.15	0.94	485.0	7.80	(38.9)
529.5	8.10	5.4	485.0	12.85	29.0
529.5	12.90	8.3	485.0	13.45	49.0
529.5	20.00	9.6	485.0	16.30	67.4
529.5	29.90	15.7	485.0	18.30	> 75.0
485.0	4.15	17.5			
<i>Catalyst No. 2.</i>					
532.5	5.35	1.8	532.5	15.45	4.0
532.5	5.50	1.9	532.5	19.15	4.1
532.5	6.30	2.1	491.0	10.00	24.2
532.5	11.25	2.5	491.0	11.10	24.4
532.5	12.20	3.5	491.0	30.40	> 60.0
532.5	13.70	3.0	491.0	31.50	> 60.0
532.5	15.00	5.5			
<i>Catalyst No. 3.</i>					
570.0	5.50	0.85	570.0	19.40	2.0
570.0	6.20	1.6	570.0	20.85	2.7
570.0	6.80	1.1	570.0	24.00	2.4
570.0	7.15	1.2	570.0	29.35	3.1
570.0	11.15	1.9	570.0	36.00	3.5
570.0	11.40	1.6	570.0	40.00	4.0
570.0	11.60	1.5	570.0	48.40	5.5
570.0	14.45	1.7			

ously given was found to fit the results excellently for any individual run. The data are summarized in Table I.

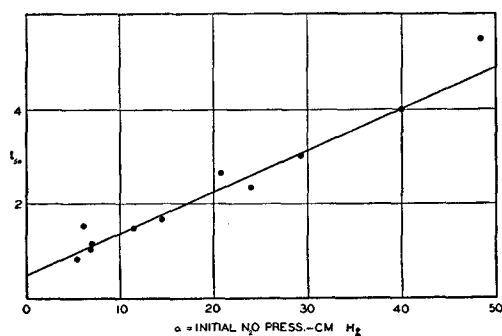
If we integrate the rate equation given previously, and solve for T_{50} , we obtain

$$T_{50} = 0.69/k + 0.19ba/k,$$

where a is the initial concentration of nitrous oxide. Hence, if the equation fits the data over the concentration range, we should obtain a straight line by plotting T_{50} against a , from the slope and intercept of which we can evaluate both b and k for any temperature or catalyst. Fig. 2 shows a typical $T_{50} a$ plot. The values of K and b obtained from curves of this type are given in Table II.

TABLE II.

Catalyst No.	Temp. °C	K	b
1	529.5	0.460	1.125
1	485.0	0.099	0.912
2	532.5	0.812	0.812
2	491.0	0.066	0.800
3	570.0	1.38	0.635

FIG. 2. Variation of T_{50} with initial pressure.

It may therefore be concluded that the rate of decomposition of nitrous oxide in the absence of added gases is satisfactorily given by

$$-(d/dt)(\text{N}_2\text{O}) = K(\text{N}_2\text{O})/(1+b(\text{O}_2)).$$

II. The effect of added oxygen

(a). *Gases mixed prior to admission to the reaction vessel.* An investigation was made of the effect of added oxygen on the rate of reaction over a wide range of oxygen concentrations. There is found to be a definite diminution in rate in the presence of added oxygen. If the added oxygen has the same effect as the oxygen formed during the reaction, then the equation previously given should hold as before. If we let y be the concentration of added oxygen, and use the other symbols as before, we obtain

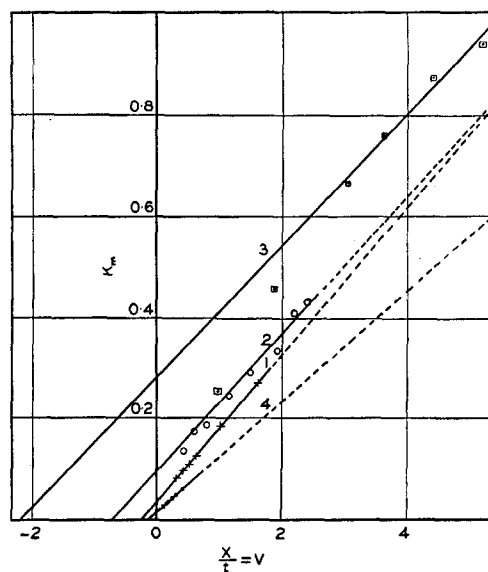
$$(1+by+ab)/t \ln a/(a-x) - bx/t = K.$$

Following Hinshelwood and Prichard's procedure and putting $1/t \ln a/(a-x) = K_m$, and $x/t = V$, we have

$$V = (a+y+1/b)K_m - K/b.$$

Hence V should be a linear function of K_m , the intercept being $-K/b$ as before. The slope, however, is now $(a+y+1/b)$ instead of $(a+1/b)$.

It follows that plotting K_m against V we should obtain straight lines as before. This is actually the case, as is shown by Fig. 3, curves 1 and 2. Curve 3 shows the same plot for a run with no added oxygen. All three curves are for runs with a constant initial pressure of nitrous oxide (6 cm). Hence the slopes should vary greatly in virtue of the y term. Actually the slopes are identical within the experimental error, as is also the case in some 30 similar runs. We must therefore conclude that $y=0$ or, in other words,

FIG. 3. K_m-V curves: 1 and 2, oxygen mixed with nitrous oxide; 3, no added oxygen; 4, oxygen followed by nitrous oxide.

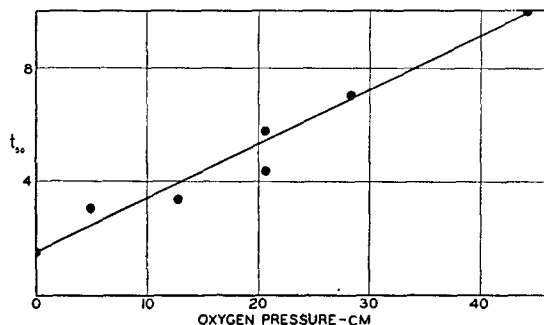
that the oxygen formed during the reaction exerts its customary effect without interference from the oxygen added. This is confirmed by the fact that the values of b obtained from the slopes of the lines in Fig. 3 are in excellent agreement with the value given in Table II for the same temperature and catalyst in the absence of added oxygen. We have therefore adopted this value of b for the calculation of K for these runs. The summarized data for runs of this kind are given in Table III.

The variation of T_{50} with added oxygen for a constant nitrous oxide pressure of 6 cm is shown by Fig. 4. It will be seen that T_{50} is proportional to the amount of oxygen added. It follows that added oxygen must exert an initial blocking effect on the surface which persists throughout, and is independent of the retarding effect of the oxygen formed during the reaction.

(b). *Oxygen admitted first.* The results described in this section were obtained by admitting oxygen to the reaction vessel, letting it stand for 5 minutes and then adding N_2O . (It was found that the time of standing in contact with oxygen had no effect within the limits 2 minutes to 12 hours.) The previous equation again fitted the results, the value of b being the same as that for runs in the absence of added oxygen. Hence any retarding effect due to the added oxygen is

TABLE III. Oxygen-nitrous oxide mixtures. 570.0°C. Catalyst No. 3.

P_{O_2} cm	T_{50} min.	K	P_{O_2} cm	T_{50} min.	K
<i>Initial nitrous oxide pressure = 6 cm</i>					
0.00	1.56	1.395	20.64	4.24	0.279
5.05	3.08	0.584	28.10	7.00	0.229
12.72	3.47	0.501	44.60	10.00	0.121
20.60	5.82	0.222			
<i>Initial nitrous oxide pressure = 12 cm</i>					
0.00	1.88	1.208	22.60	8.10	0.241
5.30	5.16	0.451	33.35	9.60	0.159
11.17	5.20	0.381	48.38	14.40	0.127
<i>Initial nitrous oxide pressure = 18 cm</i>					
0.00	2.87	1.194	27.88	8.04	0.216
9.30	4.55	0.552	39.25	10.58	0.171
17.05	5.44	0.375			

FIG. 4. Oxygen-nitrous oxide mixtures. Variation of T_{50} with added oxygen. $P_{N_2O} = 6$ cm.

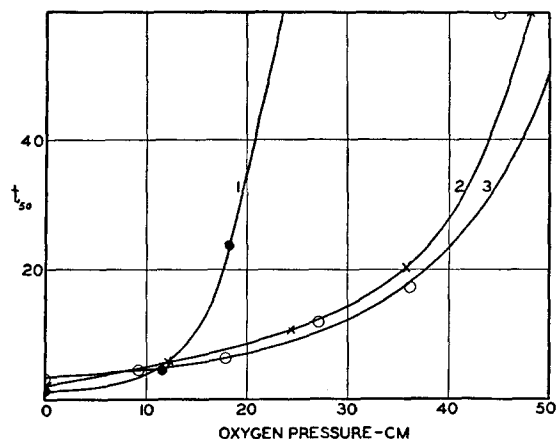
again entirely independent of the retarding effect of the oxygen formed during the reaction. The data are given in Table IV.

The variation of T_{50} with added oxygen for constant nitrous oxide pressures of 6, 12 and 18 cm is shown by Fig. 5. It will be seen that for oxygen pressures below 10 cm the order of admission of oxygen and nitrous oxide has little effect. At higher pressures, however, oxygen added first has a much more pronounced effect than oxygen added mixed with the reactant.

It is evident that the effect of oxygen is of three kinds, depending on whether it is formed in the reaction, mixed previously or added first. The effect of the three types of oxygen is illustrated by Fig. 6. The "addition" of oxygen formed in the reaction is accomplished by starting with a high pressure of nitrous oxide, letting it decompose until the partial pressure has fallen to 12 cm and calling this point zero

TABLE IV. Oxygen followed by nitrous oxide. 570.0°C. Catalyst No. 3.

P_{O_2} cm	T_{50} min.	K	P_{O_2} cm	T_{50} min.	K
<i>Initial nitrous oxide pressure = 6 cm</i>					
0.00	1.56	1.395	23.95	> 60	0.056
11.85	4.51	0.302	49.05	> 24 hrs.	0.015
18.30	23.8	0.089			
<i>Initial nitrous oxide pressure = 12 cm</i>					
0.00	1.88	1.208	36.05	20.0	0.121
12.10	6.00	0.235	48.45	> 60	0.054
24.25	11.10	0.178			
<i>Initial nitrous oxide pressure = 18 cm</i>					
0.00	2.87	1.194	27.15	12.50	0.248
9.00	4.32	0.635	36.00	17.70	0.102
17.90	6.46	0.318	44.95	> 60	0.076

FIG. 5. Oxygen followed by nitrous oxide. Variation of T_{50} with oxygen concentration. 1, $P_{N_2O} = 6$ cm; 2, $P_{N_2O} = 12$ cm; 3, $P_{N_2O} = 18$ cm.

time. In this way a certain amount of oxygen formed in the reaction is present at the start.

A number of experiments were carried out in which oxygen was left in contact with the catalyst for various lengths of time, pumped off partially or wholly, either quickly or slowly, and a new run made immediately. These showed conclusively that the adsorption and desorption of oxygen is complete within one or two minutes.

(c). *Diffusion*. A few experiments were performed in which oxygen was admitted to the catalyst first, followed by a mixture of oxygen and nitrous oxide. It was found that the reaction proceeded *faster* under these circumstances than would have been the case if the initial oxygen had been followed by the nitrous oxide alone. This immediately suggests that when oxygen is

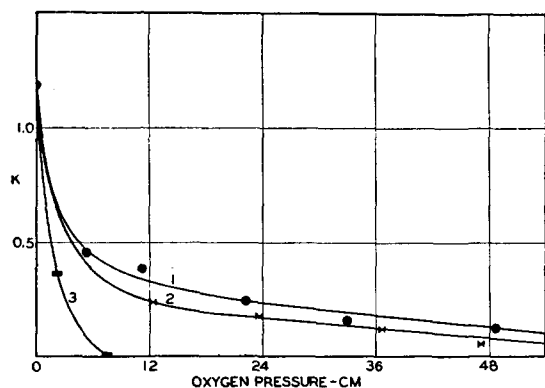


FIG. 6. Variation T_{50} with added oxygen. $P_{N_2O} = 12$ cm. 1, oxygen mixed with nitrous oxide; 2, oxygen followed by nitrous oxide; 3, oxygen formed in reaction.

admitted to the catalyst first its enhanced retarding effect is due to hindering the diffusion of the reactant into the pores of the catalyst. If more oxygen is added mixed with the nitrous oxide, a small additional retarding effect results, as has been shown in Table III. This effect, however, is more than offset by the compression of the gases into the pores of the catalyst, thus partially overcoming the slowing down of the reaction due to hindered diffusion. That this explanation is correct is proved by experiments with added nitrogen, the results of which are given in Table V.

The following conclusions may be drawn from Table V: (a). Mixing nitrogen with nitrous oxide in the absence of oxygen causes a very small retardation of the reaction. This may obviously be explained on the basis of hindered diffusion. (b). If nitrogen is admitted to the reaction vessel before nitrous oxide, the retarding effect due to hindered diffusion is considerably greater, as would be expected. The effect, however, is small compared to that of a similar amount of oxygen. (c). If oxygen is admitted first, followed by nitrogen mixed with nitrous oxide, there is an accelerating effect. This effect is greater than when the initial oxygen is followed by oxygen mixed with nitrous oxide. Hence oxygen under these circumstances has two effects, (i) acceleration due to aided diffusion, (ii) retardation due to an increase in the total oxygen concentration. The latter effect is absent with nitrogen, and hence the net acceleration is greater than with oxygen.

TABLE V. The effect of nitrogen. 570.0°C. Catalyst No. 3. Initial nitrous oxide pressure = 6.00 cm.

Nitrogen added first, cm	Oxygen added first, cm	Nitrogen added with N_2O , cm	K
		20.00	1.395
39.85			1.240
	39.70		0.508
	39.90	5.65	0.015
	39.90	12.77	0.079
	39.90	15.02	0.078
16.95	22.90		0.087
27.60	12.35		0.025
34.05	5.95		0.035
			0.069

DISCUSSION

The results of this investigation may be qualitatively explained as follows. In agreement with Schwab and Eberle it may be assumed that the oxygen formed in the reaction is adsorbed in the atomic condition and that the rate of desorption is comparatively slow (but not excessively slow, since the gas can be removed by evacuation in one or two minutes). Added oxygen may be assumed to be adsorbed as molecules. It is less effective than oxygen formed in the reaction either because it is only adsorbed to a comparatively small extent or because it can be displaced more easily by nitrous oxide. The form of the rate equation indicates fairly strong adsorption of oxygen but, as we have seen, this equation holds only for the oxygen formed in the reaction. We have therefore no definite indications as to the extent to which added oxygen is adsorbed.*

Added gases also retard the reaction by hindering the diffusion of the reactant to the catalyst. The order of admission of the gases is therefore of importance. If oxygen is admitted to the reaction vessel first it thus has a larger total retarding effect than when it is admitted mixed with nitrous oxide. Other effects due to hindered diffusion have already been discussed.

* We can obviously substitute 'activated' and 'van der Waals' adsorption for atomic and molecular adsorption without in any way affecting the argument. Since, however, the decomposition of the nitrous oxide molecule leads to the formation of atomic oxygen (the reaction being first order with respect to nitrous oxide), atomic adsorption seems to be the simpler and more plausible explanation.