90. *The Reaction of Nitric Oxide with Hydrogen and with Deuterium.*

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An earlier investigation (Hinshelwood and Green, J., 1926, 730) of the interaction of nitric oxide and hydrogen led to the conclusion that the principal reaction was homogeneous and termolecular, the rate at pressures greater than a few hundred mm. being proportional to $[NO]^2$ and to $[H_2]$. The curve of rate against hydrogen pressure was linear, but when produced did not pass through the origin, a fact which was explained by the assumption of a heterogeneous reaction independent of the hydrogen pressure, and addition of silica powder to the reaction vessel showed the existence of some surface reaction at the lower pressures. The problem has now been reinvestigated with the objects, first, of making a more detailed examination of the influence of the surface in view of the possibility of long reaction chains, as in certain other oxidation reactions, and secondly, of comparing the reaction of hydrogen with that of deuterium.

The study of the surface effect has given no evidence of the existence of chains. It has shown, however, that the original crude method of varying the surface by adding powdered silica gave an exaggerated idea of the proportion of heterogeneous reaction. The intercept made by the curves of rate against hydrogen pressure now proves to be unchanged by considerable variations of surface. Thus the complex behaviour at low pressures is part of the homogeneous reaction mechanism, which must now be reconsidered.

Measurements have been extended to lower pressures, and it is found that between 50 and 100 mm. the curve of rate against hydrogen pressure for constant [NO], instead of continuing linearly to a finite intercept, bends round and passes through the origin. We have thus to account for the following terms in the equation expressing the reaction rate: a term linearly proportional to $[H_2]$, one increasing initially with $[H_2]$ but reaching a constant limit at comparatively low pressures, and a term proportional to $[NO]^2$ at higher pressures, but including one proportional to [NO] at lower pressures. These results can be explained by the hypothesis that the reaction is essentially termolecular, but involves binary collision complexes of different lives.

Theoretical Considerations.—The shape of the lower part of the hydrogen-dependence curve is reminiscent of the behaviour of unimolecular reactions in the region where the constant falls off, and suggests the following analogy. If two molecules of nitric oxide collide and remain united long enough to be almost certain of meeting a suitably activated hydrogen molecule, the reaction rate will be independent of $[H_2]$. If, however, the hydrogen pressure is low enough, the average time elapsing before reaction will be greater than the life of the complex, and the rate will be proportional to $[H_2]$. Let [X] be the concentration of the binary collision complex. The latter is formed at a rate $c_1[NO]^2$, and dissociates spontaneously at a rate $c_2[X]$: it reacts with hydrogen at a rate $c_3[X][H_2]$. In the steady state $c_1[NO]^2 - c_2[X] - c_3[X][H_2] = 0$, whence the rate of reaction $c_3[X][H_2]$ is equal to $c_3c_1[NO]^2[H_2]/(c_2 + c_3[H_2])$, which may be written $k[NO]^2[H_2]/\{1 + b[H_2]\}$. This expression varies with $[H_2]$ in the way required.

If a binary collision complex of two nitric oxide molecules is concerned in the reaction, there is, in principle, no reason why a collision complex NO,H_2 should not also play its part, reacting with nitric oxide. The corresponding term in the rate equation will be $k[NO]^2[H_2]/\{1 + b[NO]\}$. We must take into account the limiting case of almost simultaneous ternary encounters, which adds the term $[NO]^2[H_2]$. The complete equation for the reaction rate now becomes

$$k_1[NO]^2[H_2] + \frac{k_2[NO]^2[H_2]}{1 + a[NO]} + \frac{k_3[NO]^2[H_2]}{1 + b[H_2]}$$

This will itself be only an approximation, since a whole range of lives may be expected for each type of complex, just as in the more elaborate theories of unimolecular reaction rate. Even with the form given, it is hopeless to disentangle the constants from the integrated form. Consequently, the initial rates have been measured as carefully as possible over a wide range, by drawing tangents to large-scale reaction–time curves. As well as can be expected, the results at 801° are summarised by the following formulæ :

$$\text{For hydrogen, rate (mm./100 secs.)} = 1{\cdot}0[\mathrm{NO}]^2[\mathrm{H_2}] + \frac{30[\mathrm{NO}]^2[\mathrm{H_2}]}{1 + 8{\cdot}0[\mathrm{NO}]} + \frac{11[\mathrm{NO}]^2[\mathrm{H_2}]}{1 + 3{\cdot}4[\mathrm{H_2}]}$$

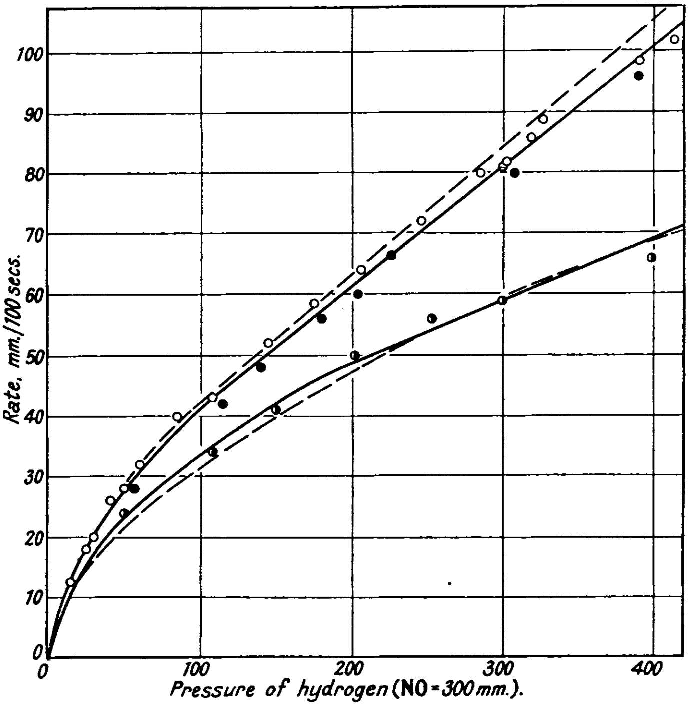
$$\text{and for deuterium, rate} = 0{\cdot}7[\mathrm{NO}]^2[\mathrm{D_2}] + \frac{12{\cdot}5[\mathrm{NO}]^2[\mathrm{D_2}]}{1 + 8{\cdot}0[\mathrm{NO}]} + \frac{7{\cdot}7[\mathrm{NO}]^2[\mathrm{D_2}]}{1 + 2{\cdot}4[\mathrm{D_2}]}$$

The concentration unit is 100 mm. at 801°.

EXPERIMENTAL.

Apparatus of the type used has been previously described : it consisted of a fused silica reaction bulb, heated in an electric furnace, and connected by capillary tubing to a manometer, to a pre-mixer, and to reservoirs of nitric oxide and hydrogen or deuterium. The capillary tubing was heated to 100° to prevent condensation of water. Electrolytic hydrogen was freed from traces of oxygen by passage over a hot tungsten filament and was dried with phosphoric oxide. Nitric oxide was prepared by the nitrometer reaction. In all the low-pressure measurements the gases were mixed outside the reaction bulb, but at higher pressures experiments with gases mixed within or without the bulb gave identical results. The temperature was measured by a platinum–platinum-rhodium thermocouple. The present results are uniformly about 30% faster than those of the earlier experiments. Since the reaction is quite reproducible, the difference is to be ascribed to a temperature error, which is understandable since, in the original series, a base-metal thermocouple had to be used and its calibration had caused difficulty. In the present series two couples and two indicators were used, and gave concordant results.

FIG. 1.



In all the figures the continuous lines represent the experimental results and the broken lines the values calculated from the formulæ. The open and the shaded circles refer to experiments with hydrogen in the unpacked bulb and tube-packed bulb respectively, the half-shaded circles to experiments with deuterium.

Influence of the Concentrations of the Reacting Gases.—All initial rates are expressed as *pressure change* (*in mm.*) *per* 100 *seconds*. The curves showing the variation of the initial rate with hydrogen pressure for constant nitric oxide pressures of 300 and 100 mm. respectively are given in

Figs. 1 and 2, and the corresponding data in Tables I and II. The variation of rate with nitric oxide pressure for constant hydrogen pressures of 100 and 300 mm. respectively is represented in Figs. 3 and 4, and the results collected in Tables III and IV.

Influence of Surface on the Rate of Reaction.—In order to vary the surface and free space, three reaction vessels were used: an unpacked silica bulb of about 300-c.c. volume, a similar bulb packed with lengths of silica tubing, and a somewhat smaller bulb entirely filled with small, spherical, silica beads. In the last two bulbs the initial rates were the same as for the unpacked bulb, but the total pressure changes in 100 seconds were respectively 3% and 6% less. The effect can be explained by consideration of the ratio of the dead space to the reaction space in the different bulbs. The reaction rate depends upon a high power of the pressure, so that quite a small increase in the dead space produces an apparent diminution of the reaction rate. The experiments with the packed bulbs, therefore, point to the non-existence of long chains. But the possibility of an accidental balancing of increased heterogeneous reaction by decreased chain reaction remained. This is in the highest degree improbable for two reasons. If such a balancing occurred in one of the packed bulbs, it would not occur in the other, where the ratio of increased surface to diminished chain length would be quite different. Furthermore, the balancing of two such different effects could not leave the shapes of the complex curves in Figs. 1—4 unchanged, as they are in fact found to be. Since iodine is known to break the chains in the hydrogen–oxygen reaction, a further test for chains was made by the addition to

FIG. 2.

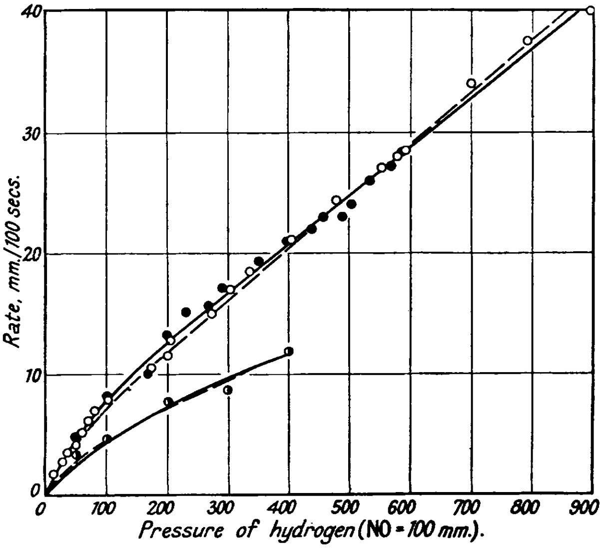
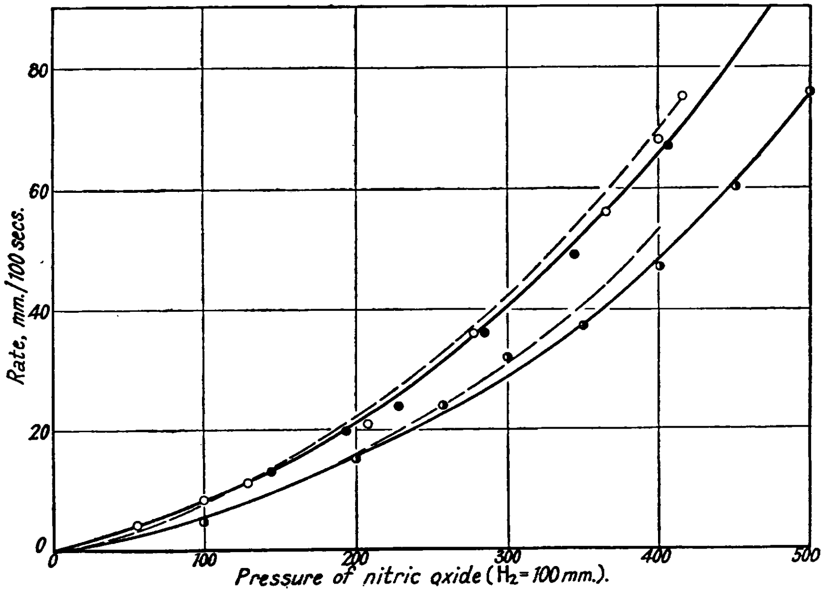


FIG. 3.



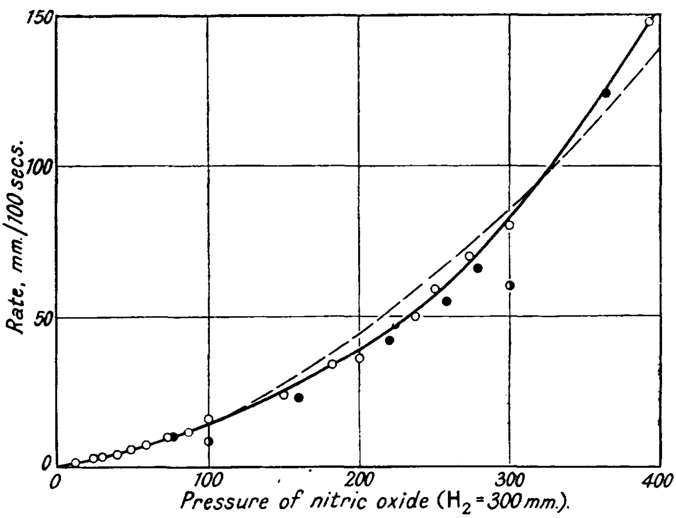
the reaction system of 0·2 mm. of *iso*propyl iodide, which decomposes to give an iodine concentration of about 0·04 mm. The initial rate was increased, and under no conditions could an inhibition be observed. This suggests the absence of a chain mechanism involving atomic hydrogen.

DISCUSSION.

An equation has already been deduced which might be expected to account for the experimental results. It is now necessary to test this and to determine the constants. The constants k_3 and b can be determined separately from the low-pressure part of the curve for variable hydrogen pressures as follows. The terms in k_1 and k_2 contribute to the rate an increment, proportional to the hydrogen pressure, which can be found by producing the linear part of the curves in Figs. 1 and 2 to meet the axis, and then subtracting the intercept. From the total rate, R, we subtract the contribution r from the linear terms; $R - r$ thus represents the contribution to the rate of the term $k_3[\mathrm{NO}]^2[\mathrm{H_2}]/(1 + b[\mathrm{H_2}])$, or $1/(R - r) = 1/(k_3[\mathrm{NO}]^2[\mathrm{H_2}]) + b/(k_3[\mathrm{NO}]^2)$.

For the curve for 300 mm. of nitric oxide, the concentration unit of 100 mm. being used, $1/(R - r) = 1/(9k_3[\mathrm{H_2}]) + b/(9k_3)$. If this equation is applicable, $1/(R - r)$ plotted against $1/[\mathrm{H_2}]$ should give a straight line of slope $1/9k_3$ making an intercept on the axis of $b/9k_3$. This was confirmed, and from the curve, k_3 was found to be 11·0 and b to be 3·4. The remaining constants were determined largely by trial and error, being finally adjusted so as to make the mean differences between calculated and observed values as small as possible for all four curves. The calculated values are given in Tables I—IV and are also shown by curves in the corresponding figures. No adjustment of the other constants allows the term reducing to a linear function of [NO] to be dispensed with.

FIG. 4.



The Reaction with Deuterium.—Deuterium was prepared by the decomposition of 99·2% deuterium oxide (*d* 1·1079) by passage over activated iron at 560°. Control experiments with hydrogen were made at intervals and gave results concordant with those previously obtained. The results with deuterium are shown in Table V. The investigation was not made in great detail, it being assumed that the rate would follow an equation of the same form as that established for hydrogen. A set of constants was found which would reproduce the experimental curves within the limitations imposed by the use of initial rates.

The constants for deuterium bear to those for hydrogen a ratio of 0·7 : 1·0 in those terms which are concerned with collisions between nitric oxide and hydrogen or deuterium. Most of the difference can be accounted for by the different molecular speeds. The second term of the expression for the rate needs further consideration. If [X] is the concentration of the binary collision complex $\mathrm{NO,H_2}$ or $\mathrm{NO,D_2}$, then in the steady state

$$\gamma_1[\mathrm{NO}]\{[\mathrm{D_2}] \text{ or } [\mathrm{H_2}]\} - \gamma_2[\mathrm{X}] - \gamma_3[\mathrm{X}][\mathrm{NO}] = 0$$

and the reaction rate is

$$\gamma_3[\mathrm{NO}][\mathrm{X}] = \frac{\gamma_3\gamma_1[\mathrm{NO}]^2\{[\mathrm{H_2}] \text{ or } [\mathrm{D_2}]\}/\gamma_2}{1 + \gamma_3[\mathrm{NO}]/\gamma_2}$$

TABLE I.

Unpacked bulb; 801°. Constant initial press. of NO = 100 mm.

H_2, mm.	Rate.		H_2, mm.	Rate.	
	Obs.	Calc.		Obs.	Calc.
13	1·8	—	(300)	16·6	15·9
27·8	2·8	—	304	17	—
35	3·5	—	335	18·5	—
(50)	4·8	4·2	(400)	20·8	20·3
60	5·2	—	401	21	—
70	6·2	—	478	24·4	—
80	7·0	—	533·5	27	—
(100)	8·0	6·8	578	28	—
100	8·2	—	591	28·5	—
173	10·5	—	(600)	29·2	29·1
(200)	12·5	11·5	700	34	33·6
204·5	12·8	—	794	37·5	—
273	15	—	896	40	42·0

Packed bulb; 801°. NO = 100 mm.

H_2, mm.	Rate.	H_2, mm.	Rate.
48·5	4·8	438	22
101	7·9	457	23
166	10·0	487	23
200	13·2	504	24
230	15·2	532	26
266	15·6	568	27·2
290	17·2	585	28·4
350	19·4		
397	21		

Results in parenthesis are taken from the smoothed curve.

TABLE II.

Unpacked bulb; 801°. Constant initial press. of NO = 300 mm.

H_2, mm.	Rate.		H_2, mm.	Rate.		H_2, mm.	Rate.		H_2, mm.	Rate.	
	Obs.	Calc.		Obs.	Calc.		Obs.	Calc.		Obs.	Calc.
15	12·5	—	60	32	—	(200)	62	65·0	303	82	—
25	18·0	—	85	40	—	206	64	—	319	86	—
30	20·0	—	(100)	42	42·4	246	72	—	327	88	—
41	26·0	—	108	43	—	285	80	—	391	98·5	—
(50)	29·0	28·3	145	52	—	(300)	82	85·9	(400)	102	106·3
50	28	—	175	58·5	—	300	81	—	414	102	—

The results for the packed bulb are similar. They are shown in the figure but not tabulated in detail.

TABLE III.

Unpacked bulb. Constant initial press. of H_2 = 100 mm.

NO, mm.	Rate.		NO, mm.	Rate.		NO, mm.	Rate.		NO, mm.	Rate.	
	Obs.	Calc.		Obs.	Calc.		Obs.	Calc.		Obs.	Calc.
56	4·4	—	(200)	20·6	21·1	(300)	40	42·4	(400)	68	70·5
(100)	8·4	6·8	208	21	—	300	42	—	400	68	—
129	11·2	—	279	36	—	365	56	—	416	75	—

The experiments in the packed bulbs are shown in the figure, the data not being tabulated.

TABLE IV.

Unpacked bulb. Constant initial press. of H_2 = 300 mm.

NO, mm.	Rate.		NO, mm.	Rate.		NO, mm.	Rate.		NO, mm.	Rate.	
	Obs.	Calc.		Obs.	Calc.		Obs.	Calc.		Obs.	Calc.
12	1·5	—	59	7·2	—	150	24	—	250	59	—
24	3·0	—	73	10	—	182	34	—	273	70	—
30	3·4	—	87	11·6	—	200	36	—	300	81	85·9
40	4·0	—	(100)	14	15·9	(200)	38	44·9	393	148	—
49	6·0	—	100	16·6	—	237	50	—	(400)	153	140

Packed bulb. Hydrogen = 300 mm.

NO, mm.	76·5	161	220	258	279	364
Rate	10	22·4	42	55	66	124

γ_1 will depend upon the molecular velocity of deuterium or hydrogen, but γ_3 will not. The activation energies of NO,H_2 and NO,D_2, depending upon different zero-point energies, may well be different. But the influence of the zero-point energy on γ_2 and γ_3 might easily be nearly the same, so that the ratio γ_3/γ_2 remains constant, as appears in the formula

TABLE V.

Unpacked bulb; 801°.

NO, mm.	D_2, mm.	Rate. Obs.	Rate. Calc.	NO, mm.	D_2, mm.	Rate. Obs.	Rate. Calc.	NO, mm.	D_2, mm.	Rate. Obs.	Rate. Calc.
100	50	3·4	—	300	50	24	21·2	200	100	15	14·8
100	(50)	3·4	2·8	300	108	34	—	257	100	24	—
100	100	4·6	4·4	300	(100)	33	31·2	350	100	37	—
100	200	7·6	6·9	300	150	41	—	400	100	47	54
100	300	8·6	—	300	(200)	47	45·6	450	100	60	—
100	(300)	9·1	9·1	300	202	50	—	500	100	76	81·7
100	400	11·8	—	300	253	56	—				
100	(400)	11·3	11·3	300	(300)	60	57·8				
				300	304	60	—				
				300	398	66	—				
				300	400	72	69·5				

used to represent the experimental results. γ_1 being affected both by speed and by zero-point energy, k_2 may differ considerably for the two isotopes, as is in fact found. A more detailed discussion of the various ratios observed would be too speculative to be profitable.

The Influence of Temperature.—The temperature coefficient of the rate was determined for 400 mm. of nitric oxide and 200 mm. of hydrogen, the results being shown in Table VI. In principle, it should be possible to measure the temperature coefficients of all the constants in the equation, but as these constants themselves could not individually be fixed to within less than about 10%, the detailed analysis was considered impracticable. The activation energy found is a complex quantity, but it would be well-nigh impossible to separate the individual values. The Arrhenius equation is obeyed, and gives $E = 47{,}000$ cals. This is a better value than the older one of 44,000, which was probably rendered inaccurate by an undetected drift in the base-metal thermocouple. The three types of process into which we now analyse the reaction differ only in their time relations, and all involve a direct interaction of two molecules of nitric oxide and one of hydrogen. Thus it is quite possible that the various activation energies are all nearly the same: 47,000 cals. will then be nearly the true value. It is quite evident, in any case, that the reaction of nitric oxide and hydrogen has an activation energy of a different order of magnitude from that of the reaction of nitric oxide and oxygen. The qualitative remarks at the end of the earlier paper hold good.

TABLE VI.

Temp.	700°	725°	740°	750°	760°	775°	800°	825°
k	46	84	122	158	193	271	467	776

The velocity constants are calculated from the time of half change by means of the simplified formula

$$k = \frac{1}{t_{\frac{1}{2}}}\left\{\frac{1}{(a-b)^2}\log\left(\frac{2a-b}{a}\right) + \frac{1}{(b-a)}\cdot\frac{b}{a(2a-b)}\right\}$$

where a is the initial concentration of nitric oxide and b that of hydrogen, *i.e.*, that for a third-order reaction. This is nearly true at the pressures used, *viz.*, 400 mm. of nitric oxide and 200 mm. of hydrogen.

The constants are expressed in g.-mol./l./sec.

SUMMARY.

The reaction between nitric oxide and hydrogen has been reinvestigated. No evidence of long reaction chains has been found. The proportion of surface reaction is much smaller than was previously assumed, and the complex behaviour at lower pressures has now proved to depend upon the homogeneous reaction mechanism.

The results can be explained by the hypothesis that the reaction, though essentially termolecular, involves binary collision complexes of different lives.

On this basis an equation was obtained to describe the curves obtained for initial rates with various pressures of nitric oxide and hydrogen.

The reaction of nitric oxide and deuterium at 801° is represented by an analogous equation with different constants.

The temperature coefficient of the reaction with hydrogen has been redetermined.

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