18. *The Interaction of Carbon Monoxide and Nitric Oxide.*

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THE decomposition of nitric oxide is not accompanied by a volume change, and cannot therefore be conveniently investigated by the usual static method. The original object of the experiments described in this paper was to find out whether the decomposition could be measured in presence of carbon monoxide, thus : $2NO = N_2 + O_2$; $2CO + O_2 = 2CO_2$. It seemed possible that the first change might govern the rate of the whole reaction, the second rapid change, which involves a decrease in pressure, merely acting as an indicator of the progress of the first.

Preliminary experiments * appeared to show that the carbon monoxide did in fact serve this purpose. The rate of reaction was measurable in the region of 900°, was proportional to the square of the pressure of nitric oxide and independent of the concentration of carbon monoxide. But it proved quite wrong to conclude from this that the carbon monoxide played no part in determining the initial change; for if nitric oxide alone was left in the reaction vessel for even longer periods than the normal time of reaction, subsequent addition of carbon monoxide caused the usual reaction to set in at nearly the usual rate. Thus the nitric oxide must have been stable in the absence of carbon monoxide.

The rate of reaction was not systematically dependent on the area/volume ratio or the dimensions of the vessel. Yet, although homogeneous, the reaction showed variations in rate which were at once recognised to be far greater than the experimental errors of the measurement. Addition of water vapour was found to increase the speed approximately in proportion to the partial pressure : the use of more thoroughly dried gases and apparatus produced slower reaction. The following hypothesis was therefore made about the mechanism :

$$(1)\ CO + H_2O = CO_2 + H_2;\quad (2)\ 2NO + 2H_2 = N_2 + 2H_2O.$$

(1) is a heterogeneous reaction, known to be fast at 900°,† while (2) is a homogeneous change which can be shown to take place at approximately the rate required to explain the results. It is termolecular,§ in accordance with the equation $-d[NO]/dt = k[NO]^2[H_2]$, and thus apparently takes place in stages such as the following : $2NO + H_2 = N_2O + H_2O$, $2N_2O = 2N_2 + O_2$. The latter decomposition is very rapid at 900°.

EXPERIMENTAL.

The apparatus and procedure have been described in previous papers. CO was prepared from $H{\cdot}CO_2Na$ and H_2SO_4 in an evacuated apparatus, and dried by simple passage over P_2O_5. NO was prepared usually by the nitrometer reaction, and stored over conc. H_2SO_4 in the vessel in which it was generated. It thus contained a small amount of H_2O, which varied somewhat in different prepns. The " dry " NO used in certain expts. was made from $FeSO_4$, HCl, and $NaNO_2$, and dried over P_2O_5.

Course of the Reaction.—The total change of press. and the amount of CO_2 formed (found by analysis) corresponded to the net equation $2NO + 2CO = N_2 + 2CO_2$. For a given set of initial conditions the reaction follows a bimolecular course.

Temp. 920°; initial [NO] = initial [CO] = 197 mm.

$a = 98{\cdot}5$; t = time in secs.; x = press. change; $k = 1/t.[1/(a - x) - 1/a]$.

t.	x.	$k \times 10^7$.	t.	x.	$k \times 10^7$.	t.	x.	$k \times 10^7$.
170	9	60·0	900	34	59·4	2400	59	63·2
290	14	57·9	1115	39	59·7	3060	64	61·6
415	19	58·5	1345	44	61·0	3950	69	60·1
550	24	59·4	1620	49	62·0	5460	74	56·2
720	29	58·9	1920	54	64·1	7320	79	56·2

Influence of Surface and Vessel Dimensions.—In each of the expts., 200 mm. of NO and 200 mm. of CO were used. The temp. was 920°. The figures recorded are initial rates of reaction expressed as rate of press. change (mm./min.).

Unpacked silica vessel	2·00	1·48	2·01	3·07
Vessel packed with silica tubes	1·75	1·30	2·72	2·37
Vessel filled with silica spheres	2·80	1·72	3·80	2·91

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* The first experiments were made by T. E. Green and one of the present authors in 1926, but the investigation was not carried to completion.

† Cf. Hadman, Thompson, and Hinshelwood, *Proc. Roy. Soc.*, 1932, *A*, **137**, 96.

§ Hinshelwood and Green, J., 1926, 730.

The various measurements made on different occasions with different prepns. of gases vary in such a way as to show the operation of an uncontrolled factor; but it is clear that the reaction is predominantly homogeneous.

Influence of Carbon Monoxide Concentration.—Temp. 920°; initial press. of NO 200 mm.; unpacked vessel.

Initial press. of CO (mm.)	99	99	100	203	198	394	397	397
Initial rate of reaction (mm./min.)	2·80	1·62	2·32	2·31	1·85	2·94	2·13	3·33

The increase in rate with increase in initial CO is but slight. A similar series of expts. made with the sphere-packed bulb gave a rate varying as $[CO]^{0\cdot13}$ between 100 and 400 mm. Below 100 mm. a more marked dependence on the CO press. becomes evident.

Influence of Nitric Oxide Concentration.

Temp. 920°; initial press. of CO 100 mm.; unpacked vessel.

Initial press. of NO	107	161	281	395	550
Initial rate	0·36	0·77	2·0	4·1	5·2
Initial rate × $10^6/[NO]^2$	31	30	25	26	17

The rate increases a little less rapidly than $[NO]^2$. Logarithmic plotting gives a dependence upon $[NO]^{1\cdot8}$ approx. In other series of expts. values of 1·9 and 1·5 were found for this power. In the packed vessels the results were similar.

Influence of Water Vapour.

Temp. 920°; initial press. of NO 200 mm.; initial press. of CO 200 mm.

Press. of H_2O vapour	2	2	5	9	14
Time for 25% reaction	7′ 35″	7′ 48″	4′ 24″	3′ 11″	2′ 31″
Initial rate (mm./min.)	5·0	5·3	8·0	11·5	14·0

In the absence of any added H_2O vapour the time required for 25% change was about 16 min. With the specially prepared NO this time lengthened to about 40 min.

In all the vessels, packed and unpacked, H_2O had a similar effect. The increase in rate on addition of H_2O is almost linearly proportional to the H_2O concn.

Order of Reaction in Presence of Considerable Amounts of Water.—The rate of the rapid reaction taking place in presence of 10 mm. of H_2O vapour is still nearly independent of the CO press.:

Temp. 920°; [NO] = 200 mm.; $[H_2O]$ = 10 mm.

Initial press. of CO	100	170	311	403
Initial rate (mm./min.)	8·0	7·75	8·5	8·4

and proportional to a power of the NO press. approaching the second; *e.g.*, the following results give a rate which varies approx. as $[NO]^{1\cdot7}$.

Temp. 920°; [CO] = 200 mm.; $[H_2O]$ = 10 mm.

Initial press. of NO	421	320	286	211	161	105	68
Initial rate (mm./min.)	32·1	24·6	19·2	10·8	7·9	3·9	1·4

DISCUSSION.

The nitric oxide does not decompose in the absence of carbon monoxide. Further, careful drying reduces the speed of the reaction to an extent which proves that at least a considerable proportion of the ordinary change is dependent on the presence of water. At 920° small quantities of water will be converted almost completely into hydrogen by the action of an excess of carbon monoxide. Hydrogen is known to react with nitric oxide at a rate proportional to the square of the nitric oxide pressure. If there is enough carbon monoxide to convert all the water, the rate will be independent of the carbon monoxide concentration, as required.

At 826° the value of k in the equation $-d[NO]/dt = k[NO]^2[H_2]$ is $1\cdot3 \times 10^{-7}$ when the concentrations are expressed in mm. of mercury and the time in seconds. The heat of activation is 44,000 cals. Hence, at 920°, k should be *ca.* $6\cdot5 \times 10^{-7}$. In an experiment with 295 mm. of nitric oxide, an equivalent of carbon monoxide, and 10 mm. of water, the initial rate was 20·3 mm./min. pressure change, *i.e.*, 40·6/60 mm. of nitric oxide changed per second. Thus $[H_2]$ in the equation $295^2 . [H_2] . 6\cdot5 \times 10^{-7} = 40\cdot6/60$ is 12 mm. Thus 12 mm. of hydrogen in the hypothetical reaction correspond to 10 mm. of water in the actual reaction. It can at least be said, therefore, that the hypothesis predicts a reaction rate of the right order of magnitude. Too much importance cannot be attached to the numerical agreement since it is doubtful whether the termolecular formula for the interaction of nitric oxide and hydrogen is valid when extrapolated to hydrogen pressures as low as those appearing in the present calculation.

The hypothesis that the reaction proceeds by way of the hydrogen formed in the water-gas reaction is supported by the fact that bromine exerts a strong retarding action. Bromine converts hydrogen into hydrogen bromide which at the experimental temperature is very little dissociated.

One point only remains difficult to explain. From the method of preparation of the nitric oxide, it would have been expected that most of the water would be introduced with this gas. Thus, when the nitric oxide concentration is varied the concentration of water vapour should be varied in the same proportion. If the rate, as well as being proportional to $[NO]^2$ is proportional to the pressure of water (*i.e.*, hydrogen), we should expect proportionality to the cube of the concentration of the undried nitric oxide. It will not do to suppose that the rate is really proportional to [NO] and that the $[NO]^2$ found means [NO] [H_2O contained in it], because the order of reaction is unchanged in presence of considerable amounts of added water, compared with which the amounts in the nitric oxide are negligible. Therefore we must conclude that for quite small pressures of water vapour there is much less than direct proportionality between rate and amount added. No complete explanation of this can be given, but the following causes, or a combination of them, are possible. First, although the water may be converted into its equivalent of hydrogen by the carbon monoxide, the rate of the reaction between the nitric oxide and the hydrogen may not be directly proportional to the hydrogen pressure at such low concentrations. (Hinshelwood and Green found deviations as the pressure of hydrogen was reduced, but attributed them to the concurrence of a surface reaction.) Secondly, the pressure of water prevailing in the reaction vessel may be determined much less by the small amounts added with the nitric oxide than by the amount retained by the walls after a normal evacuation. The adsorption relations between a mass of hot silica and minute amounts of water can hardly be predicted, but there is nothing inherently improbable in supposing that, with a constant technique of working, the surface might provide through a series of experiments something simulating a constant vapour pressure of water. Thirdly, by some complex process the silica surface might " buffer " the system against variations, over a moderate range, in the minute quantities of hydrogen produced from the water. Since the further elucidation of the matter would be very laborious, it was not pursued, because there seems to be little doubt about the essential parts of the reaction mechanism, even if this detail remains obscure.

SUMMARY.

The reaction between nitric oxide and carbon monoxide at 920° is sensitive to the presence of small quantities of water vapour. The mechanism of the change appears to be $CO + H_2O = CO_2 + H_2$; $2NO + 2H_2 = N_2 + 2H_2O$. The latter reaction, which is termolecular, has already been studied.

Most of the results relating to the kinetics of the reaction between nitric oxide and carbon monoxide can be satisfactorily explained by the hypothesis.

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