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THE EFFECT OF MOISTURE AND PARAFFIN SURFACE ON THE RATE OF REACTION OF NITRIC OXIDE AND OXYGEN

BY R. LEONARD HASCHE[1]

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In a previous investigation,[2] the effect of increased glass surface on the velocity of the reaction between nitric oxide and oxygen was studied. It appeared that this rapid reaction is not greatly affected by surface; that it takes place chiefly in the gas phase. When we consider that the rate of the reaction which we measure is the sum of the rates by different paths, altering the kind or amount of surface may be supplying or removing a catalyst. Accordingly, the net speed may be altered by introducing or eliminating paths through which the reaction may proceed. As possibilities of catalysts in the present case we may consider nitrogen tetroxide or moisture. Cohn and Jung[3] have recently shown in their study of the photochemical union of chlorine and hydrogen that with a pressure of water vapor under 10^{-7} mm. of mercury, no combination occurs; at a pressure of 10^{-5} mm., 88% is converted and at 10^{-3} mm. maximum catalysis results. This means that in case a film of moisture on a surface acts as a catalyst, only a very low moisture content, perhaps a monomolecular layer, is necessary to produce the maximum effect. More recently Norrish[4] has calculated from the description of the apparatus used in the experiments of Cohn and Jung that at a pressure of 10^{-3} mm. of mercury the monomolecular layer on the surface of the reaction vessel was just complete. Bodenstein and Dux[5] also found that evacuation to 10^{-3} mm.

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[1] National Research Fellow in Chemistry.

[2] Patrick and Hasche, THIS JOURNAL, **47**, 1207 (1925).

[3] Cohn and Jung, *Z. physik. Chem.*, 110, 705 (1924).

[4] Norrish, in a paper presented at the general discussion on photochemical reactions in liquids and gases, held by the Faraday Society at Oxford, October 1st and 2nd, 1925.

[5] Bodenstein and Dux, *Z. physik. Chem.*, **85**, 297 (1913).

produced no effect on the speed of photochemical union of chlorine and hydrogen. In the event of a reaction product forming an adsorbed film which acts as a catalyst, the first experiment made with a fresh surface should show a different rate or trend than do succeeding experiments, since the adsorbed film is not removed by customary pumping. Too often the first experiment is a failure or we may ascribe its non-agreement with succeeding experiments to some unknown source of error.

In the present work an attempt was made to determine the effect of a paraffin-coated reaction chamber and of moisture, sulfur dioxide and nitrogen tetroxide on the speed of reaction of nitric oxide and oxygen at 25°.

Experimental Part

The apparatus and procedure were similar to those used in the previous work with the following exceptions. A single stopcock with a double-bore key replaced the two stopcocks which connected the storage bulbs with the reaction vessel. The apparatus was made entirely of Pyrex glass. A liquid-air trap was inserted in the vacuum line and pumping was done by a mercury diffusion pump backed by a Nelson oil pump. Evacuation was carried down to a pressure of 10^{-4} mm. of mercury. The gases remained in contact with phosphorus pentoxide for two months before being used in the experiments.

A great many experiments were made and it was found that the results were easily reproducible. Therefore, only one table of experiments made under a given set of conditions is included. Table I shows the results obtained with a Pyrex glass reaction chamber which was flamed during evacuation; evacuation was carried down to the pressure stated above. It will be noted that no reaction occurred during the first ten seconds as indicated by the manometer readings. This induction period appeared in all of the experiments performed at these low pressures with the exception of those experiments made with water vapor in the reaction chamber. In the earlier work, higher pressures of the reacting gases were used and the above phenomenon was not observed. Table II shows the results of an experiment made under the same conditions that obtained with Table I

TABLE I

EXPERIMENT 25

$a = 105.2$; $b = 74.1$

T''	$\Sigma\Delta p$	α	x	dp/dt	$k \times 10^{-7}$	T''	$\Sigma\Delta p$	α	x	dp/dt	$k \times 10^{-7}$
5	0	...	...	...	..	160	12.4	0.955	11.9	0.115	4.87
10	0	...	...	...	..	200	14.4	.949	13.7	.097	4.86
25	1.8	0.997	1.8	0.236	4.59	240	16.3	.942	15.4	.076	4.70
40	3.2	.990	3.2	.218	4.66	280	17.8	.937	16.8	.067	4.62
60	5.3	.979	5.2	.189	4.66	340	19.6	.932	18.4	.058	4.80
90	7.8	.971	7.6	.160	4.72	400	21.3	.927	19.9	.047	4.68
120	10.0	.963	9.6	.130	4.51	480	23.0	.922	21.3	.038	4.54
										Av.	4.69 ± 0.08

but with initial partial pressures of the same magnitude that was used in the preceding investigation; it is seen that no induction period occurs although the velocity coefficients are identical with those of Table I. The induction period will be discussed at greater length later in the paper.

TABLE II

EXPERIMENT 2

$a = 172.5;\ b = 183.0$

T''	$\Sigma\Delta_p$	α	x	dp/dt	$k\times10^{-7}$	T''	$\Sigma\Delta_p$	α	x	dp/dt	$k\times10^{-7}$
10	12.0	0.956	11.5	2.076	5.03	90	55.3	0.850	48.1	0.430	4.59
15	18.2	.936	17.1	1.750	5.09	110	60.4	.841	52.1	.350	4.68
20	22.6	.923	21.0	1.416	4.70	130	64.4	.834	55.2	.282	4.56
25	26.3	.913	24.2	1.280	4.76	150	67.8	.829	57.9	.244	4.58
35	33.0	.895	29.9	1.010	4.67	180	71.8	.822	60.9	.195	4.66
45	38.9	.882	34.8	0.830	4.69	210	75.0	.817	63.4	.156	4.53
55	43.5	.873	38.6	.700	4.67	240	77.9	.813	65.6	.130	4.53
73	51.0	.858	44.7	.513	4.60	280	80.8	.809	67.9	...	..
										Av.	4.69 ± 0.11

Expt. 7 was made with a paraffin-coated reaction chamber; it indicates that the speed of the reaction has been reduced over 20% as compared with the two preceding experiments. There is a marked trend in the velocity coefficients to lower values after the first minute and then a return to the initial value as the reaction proceeds to completion, which is slightly greater than the experimental error. In another experiment, not included in the paper, the lower value of the velocity constants was maintained to the end of the reaction. The paraffin coating used in these experiments was about 1 mm. in thickness. In other experiments, thin coatings of paraffin as well as paraffin oil coatings failed to show any difference in the speed of the reaction as compared with that in uncovered reaction vessels. The surface of the glass apparently was not covered; inspection showed that the thin coating of solid paraffin was badly cracked and crystalline, and in some places was raised from the surface of the glass, probably due to evaporation of some lighter constituents during evacuation.

TABLE III

EXPERIMENT 7

$a = 142.7;\ b = 128.0$

T''	$\Sigma\Delta_p$	α	x	dp/dt	$k\times10^{-7}$	T''	$\Sigma\Delta_p$	α	x	dp/dt	$k\times10^{-7}$
5	..	...	..	...	..	95	24.5	0.918	22.7	0.285	3.48
10	..	...	..	...	..	130	29.1	.906	26.6	.212	3.27
15	4.0	0.983	4.0	0.750	3.67	160	32.0	.898	29.0	.176	3.18
20	6.2	.975	6.1	.700	3.82	190	35.4	.890	31.9	.147	3.22
30	9.8	.963	9.5	.620	3.92	220	37.9	.885	34.0	.130	3.32
40	12.9	.953	12.3	.535	3.83	250	40.2	.880	35.9	.122	3.49
50	15.8	.943	14.9	.460	3.73	280	42.0	.876	37.4	.111	3.69
70	20.7	.930	18.9	.360	3.58	340	44.7	.870	39.6	.094	3.83
										Av.	3.58 ± 0.21

A shellac coating was also tried but apparently it was attacked by the oxides of nitrogen as the reaction followed a second-order law more closely than that of the third order. It should be pointed out that the glass surface was not completely covered with paraffin as it was impracticable to coat the connecting tubes and capillaries.

Expt. 27 (Table IV) was made in the presence of 44.0 mm. of sulfur dioxide. The velocity coefficients showed no trend and are slightly less than those of Expts. 25 and 2, but we are probably not justified in saying that sulfur dioxide has a real effect, since the difference is so small. The experiment is in accord with the idea commonly held that sulfur dioxide and the oxides of nitrogen do not react in the absence of moisture.

TABLE IV

Expt.	Conditions of experiment	Evacuation to	Speed at zero time	Initial press. of reactants		Induction period	Av. velocity constant × 10^{-7}	Av. deviation
				a(O_2)	C(NO)			
25	Glass	10^{-4}[a]	1	105.2	74.1	Present	4.69	0.08
2	Glass	10^{-4}[a]	10	172.5	183.0	None	4.69	.11
7	Paraffin	10^{-4}[a]	4	142.7	128.0	Present	3.58	.21
27	Sulfur dioxide in glass	10^{-4}[a]	2.6	102.3	122.3	Present	4.44	.08
36	Nitrogen tetroxide in glass	10^{-4}[a]	1.9	98.7	105.0	Present	4.93	.19
26	Water for 48 hours	10^{-4}[a]	1.7	115.5	91.0	None	5.16	.06
20	Glass in equilibrium with air	10^{-3}	1	78.1	86.2	Present	5.25	.04

[a] Liquid-air trap used.

Expt. 36 (Table IV) shows that the reaction product has little effect on the speed of union of nitric oxide and oxygen under the present conditions; the velocity constants showed no trend and are only slightly increased over those of Expts. 25 and 2. Nor should we expect catalysis by $N_2O_4 \rightleftharpoons 2NO_2$, since the velocity coefficients are constant throughout, which would not be true in the case of an autocatalytic reaction. Some of the reaction product of the previous experiment supplied the equilibrium mixture of the dioxide and tetroxide for the present experiment. Since time was allowed for the reaction to have gone to completion, the fraction of the total pressure which was oxygen (all experiments were carried out with an excess of oxygen) could be calculated and this, subtracted from the total pressure as registered by the α-bromonaphthalene manometer, gave 29.1 mm. of the equilibrium mixture. This corresponds to a pressure of 15 mm. of nitrogen tetroxide calculated as undissociated.

In the calculation of this experiment, correction for the dissociation of N_2O_4 is as follows. All pressures are expressed in millimeters of α-bromonaphthalene at 25°. The decrease in pressure, $\Sigma\,\Delta_p$, is related to the pressure of nitric oxide and oxygen reacting by the expression $\Sigma\Delta_p = P(\alpha - \alpha_1) + x(\alpha - 2)$, in which P is the pressure of nitrogen tetroxide present at zero time calculated as undissociated, x is one-half the pressure of the nitric oxide that has reacted, α is the degree of dissociation of $(P + x)$ mm. of tetroxide, or the total amount present at any time interval, and α_1 is the degree of dissociation of tetroxide present at zero time. A curve was drawn showing the relation between the pressure of the tetroxide and its degree of dissociation. The values for this curve were obtained by substituting in the expression $K_p = 4P^2/(1-\alpha)$. Another curve gave the relation between $\Sigma\Delta_p$ and x for a given total pressure of tetroxide of P as given above. The value of K_p used here and in all of the experiments is 0.134; it was calculated from the work of Bodenstein and Linder[6] for a temperature of 25°. The velocity coefficients are instantaneous rate constants, the values dp/dt being read from the curve by the mirror method.

The effect of water vapor is shown in Expt. 26 (Table IV). The apparatus was evacuated as usual; water vapor was then admitted through a stopcock from a small bulb containing water. This bulb had previously been sealed into the apparatus, frozen out and evacuated. Both the storage bulbs and the reaction vessel were opened to the same pressure of water vapor. Immediately after the stopcock to the bulb containing liquid water had been closed, a reading was taken on the α-bromonaphthalene manometer which gave a pressure of 3.5 mm. The large, four-way stopcock between the storage bulbs and reaction vessel was now closed and the former were filled with a supply of the respective gases, nitric oxide and oxygen. The system, including gases in the storage chambers, now stood in contact with the water vapor for 48 hours before the experiment was performed. At the end of that time the pressure of water vapor had fallen to 1 mm. of α-bromonaphthalene. The velocity constants show no trend and no induction period; their average was about 10% greater than those of Expts. 25 and 2.

Orientation experiments were now made of which Expt. 20 (Table IV) is one. The apparatus was opened to the atmosphere for some time and then pumped down to a pressure of 10^{-3} mm. of mercury, omitting the liquid-air trap. The results check well with the preceding one showing, however, an induction period during the first ten seconds.

Discussion of Results

The results of the experiments cited are collected in Table IV. In Col. 4 the relative speeds of the reactions at zero time are calculated from the initial pressures of the reactants. It is apparent that the induction period is a function of the initial pressures and is also influenced by the moisture content of the system. We cannot be certain that there is no induction period in Expts. 2 and 26; however, if it does occur, it must be of short duration. There is an uncertainty of one second in zero time and a maximum error of 1.5–2.5 mm. of α-bromonaphthalene (depending upon the pressure) in the calculation of the initial pressures from the photographic

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[6] Bodenstein and Linder, *Z. physik. Chem.*, **100**, 87 (1922).

films. A study of Table IV reveals that the induction period cannot be of purely thermal origin, analogous to the Draper effect, nor can it be ascribed to a lag in the manometer liquid, as inspection of Expts. 7, 27, 36 and 26 will show. Two other explanations are possible: (1) the induction period may represent the time necessary to destroy an inhibitor of the reaction, such as in the case given by Burgess and Chapman,[7] where ammonia was found to inhibit the union of chlorine and hydrogen; or (2) we may assume that a primary process is taking place in this apparent halting period. We are not able, from the experimental evidence obtained in this investigation, to decide between the two possibilities. Recently, Weigert and Kellermann[8] have found some support for the occurrence of a primary process. They studied by a photographic method the early part of the reaction between chlorine and hydrogen. The study indicated the formation of a fog within the first fiftieth of a second and its disappearance after an equal period; a purely chemical reaction then followed. It appears probable that a gas reaction of this sort is composed of a chain of consecutive reactions and that water has an important part in such a mechanism.

A mechanism for the role of water in this reaction might be the formation of $NO\text{-}H_2O$ and of $(NO)_2\text{-}H_2O$. The latter aggregate on collision with an oxygen molecule could form the product according to the scheme:

$$\begin{aligned} NO + H_2O &= NO\text{-}H_2O \\ NO\text{-}H_2O + NO &= (NO)_2\text{-}H_2O \\ (NO)_2\text{-}H_2O + O_2 &= N_2O_4 \rightleftharpoons NO_2 + H_2O \end{aligned}$$

The present work furnishes evidence that there is a chemical catalysis produced by moisture. Baker has shown that the "super-dried" gases nitric oxide and oxygen do not react. The paraffin surface and other conditions imposed in the present experiments would then serve only to alter the moisture content. In the ordinary evacuation a film of moisture several molecules deep occurs and maximum catalysis has undoubtedly been reached. The experiments of d'Huart[9] show that after the usual evacuation in the presence of phosphorus pentoxide 0.009 mg. of water per sq. cm. of glass surface remains adsorbed. The number of molecular layers, Θ, may be calculated from the formula $\Theta = gN\sigma^2/M$, in which g is the weight of water adsorbed per sq. cm. of glass surface, N is the Avogadro number, M is the molecular weight of water and σ the diameter of the molecules calculated from the kinetic theory. If we take the value of 2.6×10^{-8} for σ,[10] then $\Theta = 20.5$. This we may compare with the value $\Theta = 51.8$ given by McHaffie and Lenher[11] for the moisture film in equi-

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[7] Burgess and Chapman, *J. Chem. Soc.*, **89**, 1399 (1906).

[8] Weigert and Kellermann, *Z. physik. Chem.*, **107**, 1 (1923).

[9] d'Huart, *Compt. rend.*, **180**, 1594 (1925).

[10] See Landolt-Börnstein-Scheele-Roth, "Tabellen," 5th edition.

[11] McHaffie and Lenher, *J. Chem. Soc.*, **127**, 1559 (1925).

librium with liquid at 25°. At about 40°, according to the same authors, the water film is less than one molecule deep, so it is safe to assume in the experiments made under the conditions of Expts. 25, 2, 7, 27 and 36, that there was a very small moisture content, less than a monomolecular layer. The above considerations emphasize our meager knowledge of the mechanism of gaseous reactions. The study of the oxidation of nitric oxide at lower pressures will be continued by means of a motion-picture camera in order to gain some insight in regard to the induction period.

Summary

1. Moisture catalyzes the reaction between nitric oxide and oxygen. The decrease in velocity with a paraffin surface has been interpreted as due to a decreased amount of moisture. Water vapor produces a maximum increase of speed of 50% over that in a paraffin-lined vessel.

2. Sulfur dioxide and the reaction product have practically no effect on the speed of reaction.

3. An induction period with a duration of ten seconds has been noted at initial partial pressures of the gases below about 14 mm. of mercury.

Berkeley, California

[Contribution from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology, No. 181]

THE UNIMOLECULARITY OF THE INVERSION PROCESS

By George Scatchard

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If the rate of a reaction be defined as that fraction of a reactant present in the system which reacts in unit time, this definition may be expressed mathematically as

$$R = \frac{-\mathrm{d}y/y}{\mathrm{d}t} = \frac{-\mathrm{d}\,ln\,y}{\mathrm{d}t} \tag{1}$$

in which R is the rate, t is the time and y is the quantity of the reactant in the system at the time t. Since y occurs in a ratio or in a logarithm, it may be expressed in any units—as mass, as moles or, corresponding to the quantity actually measured in most inversion experiments, as $\lambda - \lambda_\infty$, where λ is the optical rotation in a tube of any definite length, and the subscript ∞ refers to complete inversion. It is somewhat more convenient to work with another quantity, r, defined by the equation

$$r = 0.4343\ R = \frac{-\mathrm{d}\log y}{\mathrm{d}t} \tag{2}$$

It is customary, for unimolecular reactions, to assume that the rate as defined above is constant and to integrate Equations 1 or 2 to determine the numerical value of the rate. However, the very accurate measure-