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A Catalyzed Reaction of Hydrogen and Oxygen

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The catalyzed reaction of hydrogen and oxygen in the presence of nitrogen dioxide and nitric oxide has been studied at 360° and 419°C. Above a defined pressure of nitrogen dioxide, the system at the lower temperature can be described quantitatively in terms of the three reactions:

$$2NO + O_2 \rightleftarrows 2NO_2$$
$$H_2 + NO_2 \rightarrow H_2O + NO$$

At 419°C, the experimental results require the inclusion of the reactions,

$$H + O_2 + M \rightarrow HO_2 + M$$
$$HO_2 + NO \rightarrow OH + NO_2$$

and the quantitative agreement is somewhat less satisfactory than at 360°C.

I. INTRODUCTION

It is well known that hydrogen and oxygen react rapidly, in a branched chain reaction, at high temperatures and that there is a low pressure ignition region extending down to about 450°C. At temperatures about 100° below this, the addition of small proportions of nitrogen dioxide produces some remarkable effects (1). With a constant pressure of $2H_2 + O_2$ of about 100 mm and less than 0.1% of nitrogen dioxide, there is an induction period, characterized by the absence of pressure change, followed by a rapid fall of pressure. This fast reaction is replaced by ignition at a sensitizer pressure of about 0.1 mm, termed the lower limit. Further increase of the sensitizer pressure produces the reverse transition at an upper limit of about 1 mm, and above this the rate of pressure change at the end of the induction period falls off. Eventually, with further increase in the initial sensitizer pressure (P_0), the rate begins to increase again (Fig. 1).

During the induction period, nitrogen dioxide is removed by reaction with hydrogen, forming nitric oxide, and the rate of this removal increases abruptly at the end of the induction period, before ignition.

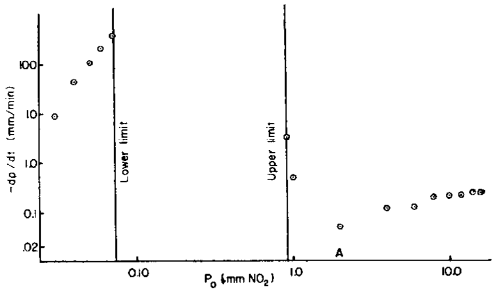

FIG. 1. Plot of $-dp/dt$ vs. P_0, 150 mm $2H_2 + O_2$, 360°C.

The phenomena connected with this removal and their effects upon the ignition limits have been described elsewhere (2,3). It has been found, however, that the slow formation of water outside the ignition limits is associated with a stationary level of nitrogen dioxide, denoted by P_s. With initial sensitizer pressures near to, but outside, the ignition limits, there is a definite induction period, and acceleration in rate of removal of nitrogen dioxide is observed before P_s is reached and the pressure change begins. With higher initial sensitizer pressures, e.g., above point *A* for the conditions illustrated in Fig. 1, the nitrogen dioxide pressure falls off smoothly to P_s. The two regions thus delineated by low and high initial sensitizer pressure are described as sensitized and catalyzed, respectively. The experimental distinction at the point they merge (at *A*, Fig. 1) is not precise. This paper describes some investigations of the rate of pressure change and the values of P_s in the region of higher sensitizer pressures where the formation of water is catalyzed by the presence of nitric oxide and nitrogen dioxide. Similar investigations of the sensitized region, where ignitions may occur, will be described elsewhere. The data given refer to the final state of a reaction mixture where P_s and the rate of pressure change alter only as the result of consumption of reactants, and no reference is made to the time taken for this condition to be reached.

There have been two previous investigations of this catalyzed region. In the first (4), only the rate of pressure change was followed, whereas in the second (2), some measurements of P_s only were made. In this work, both P_s and the rate of pressure change have been measured over a wider range of the variables than in either of the previous studies, and the temperatures chosen permit the separate studies to be correlated.

II. Experimental Procedure

The apparatus used was a conventional vacuum system and has been described in detail elsewhere (3). The reactions were carried out in plane ended, cylindrical vessels, usually 3.4 cm internal diameter, heated in an electric furnace. A quartz vessel was used in the experiments at both 360 and 419°C and also a KCl-coated Pyrex vessel at the higher temperature. Temperature measurement was by a thermocouple with the hot junction placed midway along the vessel. No part of the vessel differed by more than $0.003 \times T$°C from this measured temperature, which was measured with an absolute accuracy of ±0.7°C.

Nitric oxide was prepared by the action of cold dilute sulfuric acid upon a saturated solution of sodium nitrite, and was purified by distillation. Nitrogen dioxide was prepared by reacting nitric oxide with an excess of oxygen, separating the nitrogen dioxide by passing the products through an acetone–dry ice cooled trap. Dried cylinder hydrogen and oxygen were used.

A modified form of a double-beam photometer (3, 5) was used to measure the nitrogen dioxide concentration, and pressure changes were recorded automatically with a recording Bourdon spoon manometer (3). The reaction mixtures, consisting of hydrogen, oxygen, and nitrogen dioxide, were premixed at room temperature.

III. Results and Discussion

a. Experiments at 360°C. With low sensitizer pressures there is little dependence of P_s on the initial sensitizer pressure (P_0) until P_0 is about 1 mm. This is illustrated in Fig. 2, for a high reactant pressure (450 mm) lying above the closed ignition region. Further increase in P_0 produces a rapid increase in P_s, initially approximating to a cubic form as shown earlier (2), but finally producing a more nearly linear dependence (see Table 1).

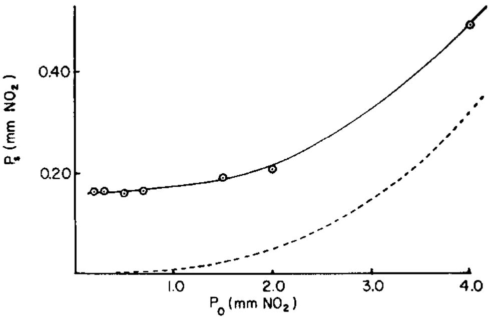

FIG. 2. Plot of P_s vs. P_0, 450 mm $2H_2 + O_2$, 360°C, 20-mm diameter quartz reaction vessel. KEY: Broken line shows value of P_s calculated on the basis of Eq. (1); (○) experimental.

This catalyzed region was investigated with 50–300 mm of a $2H_2 + O_2$ mixture and with up to 16 mm of sensitizer. The rates in the catalyzed region increase with P_0 as shown in Fig. 1.

Under conditions where the hydrogen pressure was constant and the nitric oxide pressure nearly so, both the rate and P_s rose linearly with an increase in the oxygen pressure, Fig. 3. At all the initial sensitizer pressures in the catalyzed region, the rate rose as the reactant pressure was increased, but the effect on P_s depended on the value of P_0. With $P_0 < 10$ mm, there was a small decrease in the value of P_s as $P_{2H_2+O_2}$ rose, but with P_0 above 10 mm, P_s rose slightly.

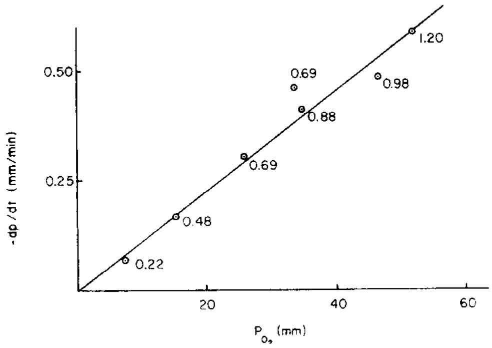

FIG. 3. Plot of $-dp/dt$ vs. P_{O_2}, 400 mm H_2, 10 mm NO_2 initially, 360°C. KEY: (○) experimental. Figures give P_s in mm NO_2 for each experiment.

The previous investigators (2) of P_s suggested that a steady concentration of nitrogen dioxide was reached as the result of the competitive reactions,

$$H_2 + NO_2 \rightarrow H_2O + NO \qquad (I)$$

$$2NO + O_2 \rightarrow 2NO_2 \qquad (II)$$

TABLE 1

VALUES OF P_s, CALCULATED AND OBSERVED, AT 360°C, WITH 50 AND 200 MM $2H_2 + O_2$, USING $k_2 = 3.70 \times 10^{-6}$ MM^{-2} SEC^{-1}

	P_s(mm NO_2)				
	50 mm $2H_2 + O_2$		200 mm $2H_2 + O_2$		
P_0 (mm NO_2)	Obs.	Calc. from Eq. (1)	Obs.	Calc. from Eq. (1)	Calc. from $P_s \propto P_0^3$
16.0	6.80	8.1	7.85	7.83	—
12.0	4.6	5.2	4.90	4.90	—
8.0	2.40	2.88	2.05	1.94	4.46
6.0	1.30	1.72	1.01	1.00	1.88
4.0	0.53	0.72	0.40	0.44	0.56
2.0	0.07	0.11	0.10	0.07	0.07
1.0	0.014	0.016	0.057	0.009	0.009

Reaction (1) is a chain reaction of known kinetic form (6–8). From the balance of these reactions and the rate expressions for reactions (I) and (II), the relationship $P_s \propto P_0^3$ is predicted for conditions where $P_{NO} \simeq P_0$. With the more extensive data now available, it is apparent that this does not describe accurately the variation of P_s at low P_0 (Fig. 2) nor at high values of P_0 where P_s itself is high (Table 1). At high P_s it is not sufficient merely to allow for the divergence between P_{NO} and P_0, but the effect of the back reaction (III) must be considered, i.e.,

$$2NO_2 \rightarrow 2NO + O_2 \qquad (III)$$

must also be included in the scheme. The modified equation is

$$\frac{dP_{NO_2}}{dt} = k_2 \cdot P_{NO}^2 \cdot P_{O_2} - k_3 \cdot P_{NO_2}^2 - \frac{k_1 \cdot P_{NO_2} \cdot P_{H_2}^{1.4}}{P_{NO} + P_{NO_2}} \qquad (1)$$

where the last term of Eq. (1) represents the most satisfactory form (8) of the rate expression for reaction (I), k_1 having the value $10^{13.73} \exp(-44{,}000/RT)$ (cc/mole)$^{0.4}$ sec^{-1}. At $P_{NO_2} = P_s$, $dP_{NO_2}/dt = 0$, and Eq. (1) may be solved numerically for P_s for each individual value of P_0. The calculated and observed values of P_s are given for two reactant pressures in Table 1. Apart from the lowest values of P_0, there is excellent agreement of the predicted and observed values of P_s, although the rate constants for the three reactions were measured independently (3, 8) and in the absence of the other reactants.

The variation of P_s with the oxygen and the reactant pressures can also be accounted for on the basis of this scheme. The variation with P_{O_2} at constant P_{NO} was measured under conditions of low P_s, where reaction (III) can be neglected, and so from Eq. (1) a linear dependence is predicted, as is observed. The effect of increasing the reactant pressure depends on the relative magnitude of the terms 2 and 3 of Eq. (1). When the second term is dominant, P_s will increase with $P_{2H_2+O_2}$, whereas when the third term is more important, P_s will fall. This sequence corresponds with the experimental observations; the change occurs when P_0 is at about 10 mm, with P_s values at which the second term is significant.

Further tests of the theory are possible by considering the form of the predicted rate of pressure change. Since only reactions (II) and (III) involve a pressure change, then

$$dp/dt = \tfrac{1}{2}(k_3 \cdot P_{NO_2}{}^2 - k_2 \cdot P_{NO}{}^2 \cdot P_{O_2}) \quad (2)$$

Combining Eqs. (1) and (2), the expected result is obtained,

$$-dp/dt = \tfrac{1}{2} dP_{H_2O}/dt = \frac{\frac{1}{2} \cdot k_1 \cdot P_{NO_2} \cdot P_{H_2}{}^{1.4}}{P_{NO} + P_{NO_2}} \quad (3)$$

Equation (2) may be rearranged to give

$$-dp/dt + \tfrac{1}{2}k_3 \cdot P_{NO_2}{}^2 = \tfrac{1}{2}k_2 \cdot P_{NO}{}^2 \cdot P_{O_2} \quad (4)$$

A plot of the function $(-dp/dt + \frac{1}{2}k_3 \cdot P_{NO_2}{}^2)$ against $P_{NO}{}^2$ is shown in Fig. 4 for reactant pressures from 50 to 300 mm, and the predicted value, $\frac{1}{2}k_2 \cdot P_{NO}{}^2 \cdot P_{O_2}$, is also shown. The only divergence apart from that at the low sensitizer pressures, near the ignition region, is with 300 mm of reactants, where the observed values are consistently high. Further, where reaction (III) is negligible, a first-order dependence of the rate on P_{O_2} is predicted. The experimental values of the rate (Fig. 3), corrected for the small variation of P_{NO} between experiments, gave an order of 1.20 ± 0.18.

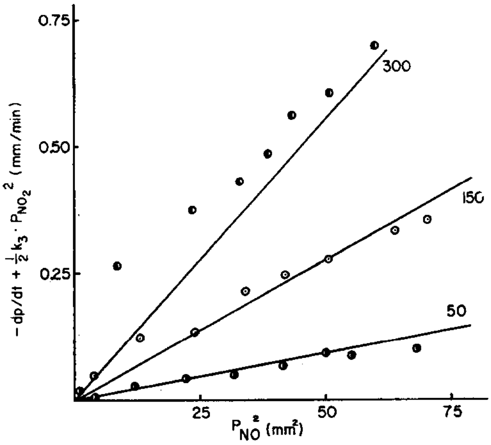

FIG. 4. Plot of $(-dp/dt + \frac{1}{2}k_3 \cdot P_{NO_2}{}^2)$ vs. $P_{NO}{}^2$, 360°C; lines show values of $\frac{1}{2}k_2 \cdot P_{NO}{}^2 \cdot P_{O_2}$ for each reactant pressure. KEY: (◐) 300 mm $2H_2 + O_2$; (○) 150 mm $2H_2 + O_2$; (◑) 50 mm $2H_2 + O_2$.

Thus it is possible at this temperature to account for the kinetics of P_s and the rate of pressure change in terms of reactions (I), (II), and (III) for initial nitrogen dioxide pressures in the catalyzed region. Further, with up to the highest reactant pressure investigated, i.e., 300 mm, both P_s and the rate of pressure change may be calculated accurately by use of rate constants measured separately for the individual homogeneous reactions.

With lower sensitizer pressures this simple system is inadequate, as indicated by the large difference between the experimental and calculated values of P_s (Fig. 2) and the large rates found in these conditions (Fig. 1). To explain these features as well as the occurrence of ignitions, it is necessary to postulate a branched chain reaction. Under these conditions the reaction resulting in the reformation of nitrogen dioxide and so controlling the value of P_s, is no longer reaction (II). Instead, it is replaced by the sequence of reactions,

$$H + O_2 + M \rightarrow HO_2 + M \quad (IV)$$

$$HO_2 + NO \rightarrow OH + NO_2 \quad (V)$$

with reaction (IV) as the rate determining step. The main reaction for removing nitrogen dioxide is still reaction (I), but the controlling step is more conveniently considered to be one of the propagation steps of the H_2—NO_2 chain reaction,

$$H + NO_2 \rightarrow OH + NO \quad (VI)$$

with the further propagation step

$$OH + H_2 \rightarrow H_2O + H \quad (VII)$$

These reactions account completely for the kinetics of P_s in the sensitized region (3) and, with the addition of certain initiation, branching, and termination reactions, form a kinetic scheme that is compatible with extensive observations on events before ignitions as well as the rates of pressure change observed outside the ignition limits (3). We intend to publish full details of the observations on P_s in this region separately.

b. Experiments at 419°C. The effect of hydrogen on the rate of pressure change and on P_s was investigated independently from that of oxygen at this temperature. The value of P_s was reduced by increasing the hydrogen pressure but it rose rapidly as P_0 rose at each hydrogen pressure (Table 2). The rates fell at the lowest values of P_0 to reach a minimum at an initial nitrogen dioxide pressure of between 6 and 12 mm, depending on the hydrogen pressure (Fig. 5). Increasing the oxygen pressure, as at the lower temperature, produced a linear increase in both P_s and the rate of pressure change.

TABLE 2

VALUES OF P_s, CALCULATED AND OBSERVED, AT 419°C, WITH 90 MM O_2, 80 AND 380 MM H_2, USING $k_2 = 3.20 \times 10^{-6}$ MM^{-2} SEC^{-1}

	P_s(mm NO_2)				
	80 mm H_2		380 mm H_2		
P_0 (mm NO_2)	Obs. (quartz)	Calc.	Obs. (quartz)	Obs. (KCl-Pyrex)	Calc.
5.0	0.10	0.13	0.12	0.14	0.014
10.0	0.48	0.85	0.17	0.26	0.11
15.0	1.6	2.4	0.33	0.55	0.37
20.0	3.75	4.5	0.60	0.95	0.83
25.0	6.2	7.0	0.88	1.95	1.55

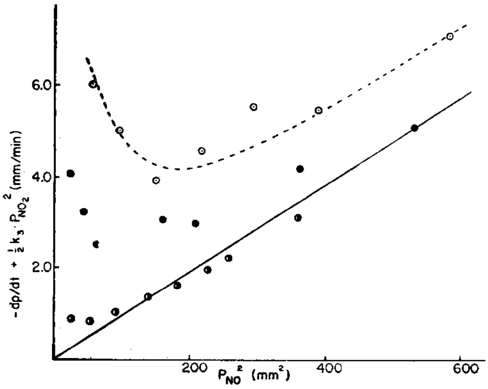

FIG. 5. Plot of $(-dp/dt + \frac{1}{2}k_3 \cdot P_{NO_2}^2)$ vs. P_{NO}^2, 90 mm O_2, 419°C. KEY: (○) 380 mm H_2, quartz vessel; (●) 380 mm H_2, KCl-Pyrex vessel; (◑) 80 mm H_2, quartz vessel; solid line shows value of $\frac{1}{2}k_2 \cdot P_{NO}^2 \cdot P_{O_2}$.

The substitution of a KCl-coated Pyrex vessel for the quartz reaction vessel lowered the rate of reaction (Fig. 5) but resulted in an increase in P_s (Table 2). The effect of water was investigated at this temperature by taking mixtures with a constant initial sensitizer pressure, but with increasing reactant pressures, and by measuring the rates and P_s after an increasing fraction of reaction so that at the point of measurement $P_{2H_2+O_2}$ was unchanged from experiment to experiment, but P_{H_2O} had increased. With 300 mm of hydrogen, 100 mm of oxygen, and an initial nitrogen dioxide pressure of 5.0 mm, P_s doubled and the rate rose by 50% as a result of the addition of 100 mm of water.

When the tests that were successful at the lower temperature are applied to the data obtained at 419°C, a considerable disparity is apparent. Thus by using from Eq. (4) the function $(-dp/dt + \frac{1}{2}k_3 \cdot P_{NO_2}^2)$ and plotting against P_{NO}^2 (Fig. 5), a linear relationship is predicted, with the function having the value, $\frac{1}{2}k_2 \cdot P_{NO}^2 \cdot P_{O_2}$. This is only approached when P_s reaches a high value, the result of a high P_0 or of a low hydrogen pressure. Similarly the calculated values of P_s are only accurate to within a factor of two (Table 2) unless P_s is large. A common feature of the results obtained at the two temperatures is that the divergences in the predicted and experimental rates are most significant at low values of P_s, and at both temperatures the values approach when P_s rises above 1–2 mm. The divergence is of greater importance at 419°C since, for the same reactant and sensitizer pressures, P_s is much lower than at 360°C, e.g., with 300 mm of reactants and 20 mm nitrogen dioxide initially, P_s was 1.25 mm at 419°C, 11.0 mm at 360°C. As the rapid rates observed at low P_0 (Fig. 5) merge with the ignition region found at still lower sensitizer pressures, an explanation for these fast rates is sought in terms of the reactions producing the ignitions.

On the basis of the kinetic scheme applied to the ignition region, the only other important reaction affecting the rate and P_s is reaction (IV), followed by reaction (V). If this is included, Eq. (1) and (2) may be rewritten

$$dP_{NO_2}/dt = k_2 \cdot P_{NO}^2 \cdot P_{O_2} - k_3 \cdot P_{NO_2}^2 - k_6 \cdot P_H \cdot P_{NO_2} + k_4 \cdot P_H \cdot P_{O_2} \cdot P_M \quad (5)$$

$$dp/dt = \tfrac{1}{2}(k_3 \cdot P_{NO_2}^2 - k_2 \cdot P_{NO}^2 \cdot P_{O_2}) - k_4 \cdot P_H \cdot P_{O_2} \cdot P_M \quad (6)$$

Equation (6) may be rearranged to give

$$-dp/dt + \tfrac{1}{2}k_3 \cdot P_{NO_2}^2 - \tfrac{1}{2}k_2 \cdot P_{NO}^2 \cdot P_{O_2} = k_4 \cdot P_H \cdot P_{O_2} \cdot P_M \quad (7)$$

The left-hand side of Eq. (7) is termed the "additional rate" (A.R.), i.e., in excess of the rate predicted on the theory involving reactions (I), (II), and (III) only. As at P_s, $dP_{NO_2}/dt = 0$, Eqs. (5) and (7) may be solved to eliminate P_H,

$$1 + \frac{k_2 \cdot P_{NO}^2 \cdot P_{O_2} - k_3 \cdot P_{NO_2}^2}{\text{A.R.}} = \frac{k_6 \cdot P_{NO_2}}{k_4 \cdot P_{O_2} \cdot P_M} \quad (8)$$

Thus a plot of the function on the left-hand side of Eq. (8) should show a linear dependence on P_{NO_2}. An example of such a plot is shown (Fig. 6) for the data obtained with 380 mm hydrogen and 90 mm of oxygen (Fig. 5), using $k_2 = 3.20 \times 10^{-6}$ mm^{-2}sec^{-1}, a value measured at this temperature (3). The value of P_M was also incorporated into the function as there was an appreciable variation in its value between the experiments. The values of k_4/k_6 obtained from four sets of data are given in Table 3, and the constancy of the values supports this interpretation. Further, from an accurate measurement (3) of k_4/k_6 at 360°C, the value at 419°C is estimated to be $2.0 \pm 10\% \times 10^{-6}$ mm^{-1}, in good agreement with the measured values.

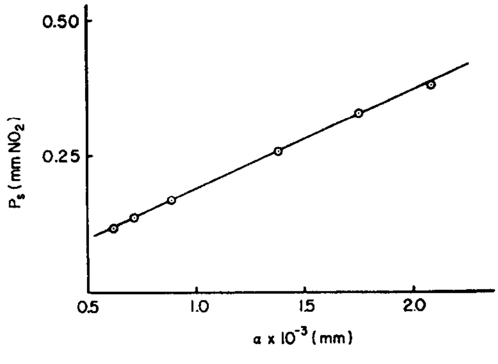

FIG. 6. Plot of $P_{NO_2}(P_s)$ vs. α, where

$$\alpha = \left(1 + \frac{k_2 \cdot P_{NO}^2 \cdot P_{O_2} - k_3 \cdot P_{NO_2}^2}{\text{A.R.}}\right) \cdot P_M$$

Quartz vessel; 380 mm H_2, 90 mm O_2; 419°C. KEY: (○) experimental.

TABLE 3
VALUES OF k_4/k_6, IN UNITS OF MM$^{-1} \times 10^6$, AT 419°C

P_{H_2}(mm)	Vessel	k_4/k_6
80	Quartz	2.00
180	Quartz	1.49
380	Quartz	1.94
380	KCl-Pyrex	1.52

However, the same explanation does not account for the inaccuracy in the calculation of P_s, since the introduction of reactions (IV) and (V) requires that the calculated values of P_s [which neglect the effect of reaction (IV)] should be lower than the observed values. It is more probable that the error is introduced by using the rate expression for reaction (I) under conditions where it no longer applies with great accuracy. It has been shown (8) that, although this expression describes accurately the initial rates of reaction of hydrogen–nitrogen dioxide mixtures, it does not necessarily apply at later stages of the reaction. Thus in certain vessels, in particular, in an aged quartz vessel, it was found (8) that the rate of reaction during a run was more nearly zero order with respect to nitrogen dioxide than first order, as predicted by the equation. Thus the rates during an experiment may be greater than predicted by the rate expression, although the initial rate was correct. This effect is favored by high hydrogen-to-nitrogen dioxide ratios. In this work the main divergences between the experimental and calculated values of P_s are found where there has been a high fraction of reaction of the initial nitrogen dioxide, typically between 85 and 98%. Thus it is feasible that the rate of the hydrogen–nitrogen dioxide reaction is proceeding at a greater rate than predicted, producing a lower value of P_s than was calculated. There is further support for this interpretation in that, if the additional rate is calculated (3) from the rate expression for reaction (I), the values obtained are between one-half and one-third of the observed values, again suggesting a greater experimental rate for reaction (I) than is predicted. At neither temperature has the effect of oxygen and water on the rate of reaction (I) been estimated, as no quantitative data are available. However, the effect of either gas is normally small (8) and, as the effects are in opposite directions in the later stages of reaction, the error introduced is likely to be small.

The linear effect of oxygen upon the additional rate is as predicted by this scheme (3), taking into account the simultaneous variation of P_s. Also the lower rates and higher values of P_s found in the KCl-coated vessel are as expected if there is additional chain termination on this more effective surface coating. The effect of water was determined under conditions where the rate cannot be calculated with great accuracy (3), so no precise test is possible with respect to this variable, but the observed trend is not incompatible with the predictions of the kinetic scheme.

Thus at this higher temperature, P_s and the rates of pressure change can only be calculated with reasonable accuracy when P_s is greater than 2 mm, and is also an appreciable fraction of P_0, preferably greater than 25%. With a low value of P_s, an allowance must be made in calculating the rate for the occurence of reaction (IV). Under these circumstances the rate may be calculated from Eq. (8) if P_s is known. However, P_s cannot be calculated with the necessary accuracy from Eq. (1), even allowing for reaction (IV), because of the uncertainty in the accuracy of the rate equation for reaction (I) at high percentage reaction.

In the light of this investigation it is possible to reconsider the data and the conclusion of Crist and Wertz (4). Working in a temperature range from 384 to 444°C and with high hydrogen-to-nitrogen dioxide ratios, they found the rate of reaction to show a first-order dependence on the nitric oxide pressure and on the oxygen pressure from 15 to 25 mm of nitric oxide in the presence of 25 mm of oxygen and 500 mm of hydrogen. The order with respect to oxygen was demonstrated by examination of the variation of the rate within each run. The data were interpreted as resulting from a rate determining step,

$$NO + O_2 \rightarrow NO_3$$

with a rapid reaction of the NO_3 so formed with hydrogen to give water. It is possible to reproduce both of these experimental findings. A first-order dependence of the rate upon the oxygen pressure has been found at both temperatures used in this work (Fig. 3). Also if the data for the highest hydrogen pressure used at 419°C are replotted against P_{NO} rather than $P_{NO}{}^2$ as was done in Fig. 5, then the experimental points lie on a reasonably straight line for the nitric oxide pressure range investigated by Crist and Wertz. More directly, repeating experiments using their method of analysis gave a first-order dependence on P_{O_2} within a run, and within the considerable experimental error, a first-order dependence on P_{NO} between runs, again, with 15–25 mm of nitric oxide. However, it would appear to be fortuitous that this simple order with respect to nitric oxide was found, mainly the result of the limited range of sensitizer pressure investigated and the high hydrogen pressure. As has been shown, with lower hydrogen pressures, and more particularly, at lower temperatures, there is a linear dependence of the rate on $P_{NO}{}^2$, taking into account the contribution to the pressure change from reaction (III). As the reaction scheme of Crist and Wertz cannot account for the more extensive data of this work and is not easily modified, it is to be rejected as an explanation of the reactions occurring here.

IV. SUMMARY

For the reactant pressures investigated at 360°C, the values of P_s and the rate of pressure change are accurately described by the combination of reactions (I), (II), and (III) provided P_s is in excess of about 1.5 mm. Under these conditions P_s and the rate of pressure change can be calculated from the individually measured rate constants of the three reactions. At 419°C, reactions (IV) and (V) significantly affect the rate of pressure change over much of the region investigated. However, Eqs. (1) and (2) are still valid provided P_s is greater than 2 mm, and so both P_s and the rate of pressure change can be calculated under these conditions. At lower values of P_s the rate of pressure change may be calculated from Eq. (8) if P_s is known. The calculated values of P_s below 2 mm are in error because of the uncertainty in the rate constant of reaction (I) at these high percentage conversions of the nitrogen dioxide to nitric oxide.

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