Reaction of Hydrogen Atoms With Nitrogen Dioxide

BY P. G. ASHMORE AND B. J. TYLER
Dept. of Physical Chemistry, Lensfield, Cambridge

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The ratio of the rate constants of the reactions $H+NO_2 \rightarrow OH+NO$ and $H+O_2+M \rightarrow HO_2+M$ has been measured at 360°C from a study of the hydrogen+oxygen reaction sensitized by nitrogen dioxide.

The addition of small quantities of nitrogen dioxide to mixtures of hydrogen and oxygen leads to the formation of water [1-3] at temperatures well below those at which the reaction occurs in the pure reactants.[4] With initial pressures P_0 of nitrogen dioxide between lower and upper ignition limits (for example, between about 0·1 and 1 mm, in 100 mm of $2H_2+O_2$ at 360°C) the water is formed explosively at the end of induction periods characterized by the absence of pressure change. With P_0 below the lower ignition limit, or just above the upper, similar induction periods are followed by the slow formation of water; the rate of this reaction falls as P_0 moves away from either limit. When P_0 is considerably above the upper limit, the rates increase again as P_0 is increased; an account of this region has been given elsewhere.[5]

During the induction periods, nitrogen dioxide is removed by the overall reaction $NO_2+H_2 \rightarrow H_2O+NO$, and there is an abrupt increase in the rate of removal at the end of the induction periods. With P_0 within the ignition limits, this acceleration is rapidly followed by ignition; outside the limits, the increased rate of removal is not maintained and the nitrogen dioxide pressure reaches a low, constant value P_s, although the overall pressure change continues.

This paper describes an investigation of the factors affecting P_s, and discusses critically the reactions controlling its value. The chosen mechanism leads to values of the ratios of the velocity constants of the reactions,

$$H+NO_2 \rightarrow OH+NO,$$

and

$$H+O_2+M \rightarrow HO_2+M,$$

with H_2, O_2, H_2O, N_2, He and CO_2 as M.

EXPERIMENTAL

A conventional Pyrex vacuum system was used.[3] The reactions were carried out in plane-ended, cylindrical, quartz vessels, heated in an electric furnace. Four vessels were used, all of 20 cm length and with diameters from 9 to 34 mm. The vessels were washed with concentrated nitric acid before use, followed by repeated rinsing with distilled water. Temperature measurement was by a calibrated thermocouple, accurate to ±0·7°C, placed mid-way along the vessel. The furnace temperature did not vary by more than 3·0°C along the length of the vessel.

Cylinder oxygen, hydrogen, nitrogen and carbon dioxide were used, in each case dried before admission to the vacuum line. Helium was supplied by the Mond Laboratory of this University. De-aerated, distilled water was used. Nitric oxide was prepared by the action of dilute sulphuric acid upon a saturated solution of sodium nitrite and was purified by distillation. Nitrogen dioxide was prepared by allowing nitric oxide to react with an excess of oxygen. Reaction mixtures were prepared at room temperature, and were allowed to mix for not less than 15 min before admission to the reaction vessel. Pressure measurement was by Bourdon gauge between 0 and 50 mm, and above that by mercury manometer. Sharing between known volumes was used to obtain low pressures of nitrogen dioxide.

Nitrogen dioxide pressures in the reaction vessel were measured by a recording double-beam photometer,[2, 3] calibrated directly at the operating temperature and sensitive to changes of 0·004 mm in the nitrogen dioxide pressure. Pressure changes were recorded automatically using a modified Bourdon spoon gauge.[6] All the experiments reported were carried out at 360°C.

When first using the quartz vessels, a systematic trend of results was apparent. In each case the induction period was observed to fall and the nitrogen dioxide pressure at the end of the induction period to increase slightly for perhaps the first twenty experiments. Thereafter the values were satisfactorily constant and, in one case, were reproduced when the vessel was re-used after a period of over 1 year. No observations on the values of the stationary nitrogen dioxide pressure were made during this ageing process, and the experiments reported refer to aged vessels. In the few experiments with initial sensitizer pressures close to lower limit values, the pressure of nitrogen dioxide reached at the end of the induction period did not remain constant but increased slightly as the reaction proceeded. In these cases the minimum value of the nitrogen dioxide pressure is reported. With the higher $2H_2+O_2$ pressures used, there was no noticeable acceleration in the rate of removal of nitrogen dioxide before the stationary concentration was reached.

For convenience, the initial sensitizer pressure and the stationary nitrogen dioxide pressure at the end of the induction period will subsequently be referred to as P_0 and P_s respectively.

RESULTS

The dependence of P_s upon the partial pressures of the components of the system was found in several series of experiments where only one of the variables was altered at a time. The effects observed are described separately below.

P_s AND THE SURFACE TO VOLUME RATIO

This was investigated by varying the vessel diameter between 9 and 34 mm. Within this range there was no variation of P_s outside the range of the experimental scatter. The values of P_s for two reactant pressures, 150 and 300 mm, for the four vessels are given in table 1. As it was concluded that P_s was independent of the vessel diameter the subsequent experiments were carried out in one vessel, of 15 mm internal diameter.

TABLE 1.—THE DEPENDENCE OF P_s UPON THE VESSEL DIAMETER
temp. 360°C

vessel diam.	$P_{2H_2+O_2}=150$ mm	300 mm
(mm)	P_s(mm NO_2)	P_s
9	·021-·028	·083
15	·020-·028	·075-·079
20	·022-·030	—
34	·020-·026	·078

P_s AND P_{NO}

In several studies using a constant pressure of $2H_2+O_2$, it was found that the values of P_s outside the two ignition limits were similar, although P_0 might have varied ten-fold. Since at the upper limit P_s was usually only about 10 % of P_0, this similarity suggested that P_s was not dependent upon the nitric oxide pressure. To confirm this a reactant pressure above a closed ignition region [1, 3] was chosen, and the nitric oxide pressure varied by altering P_0 in successive experiments. P_s was found to be invariant within the experimental error with P_0 between 0·20 and 0·70 mm (P_{NO} between 0·03 and 0·53 mm), and only at higher values of P_0 was P_s found to rise (fig. 1). In the experiments described below, P_0 did not exceed 0·70 mm.

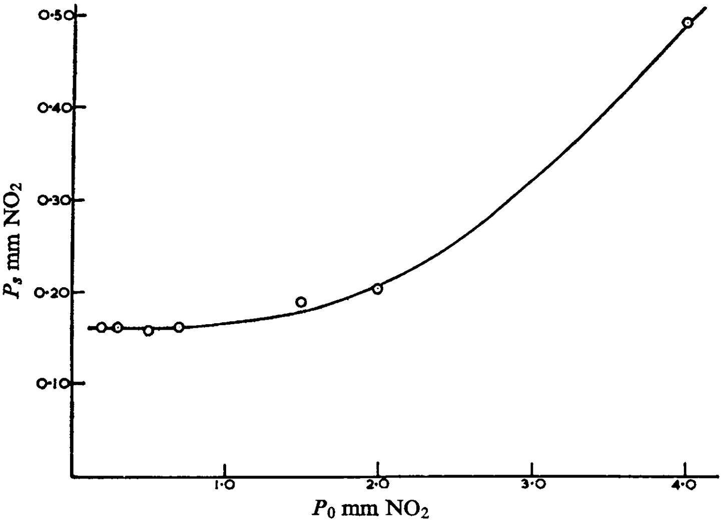

FIG. 1.—The variation of P_s with the initial sensitizer pressure, P_0.
450 mm $2H_2+O_2$; 15 mm quartz vessel; 360°C.

P_s AND P_{O_2}

In a series of experiments where only the oxygen pressure was varied, P_s was found to increase as the oxygen pressure was raised. Expressing the results in the form $P_s \propto P_{O_2}^x$, it was found that x lay between 1 and 2. To distinguish between the chemical and inert gas effects of oxygen, another series of runs was carried out in which there was a constant total pressure of oxygen and nitrogen, but in which oxygen and nitrogen were interchanged. Assuming that oxygen and nitrogen are equivalent in their efficiencies in any three-body reactions occurring, this method enables the oxygen pressures to be varied whilst keeping the inert gas pressure constant. With a six-fold variation of the oxygen pressure there was a direct proportionality of P_s upon P_{O_2} (fig. 2).

P_s AND INERT GAS PRESSURES

The dependence of P_s upon the partial pressures of hydrogen, oxygen, carbon dioxide, nitrogen, helium, water, and the reactant pressure, $P_R = P_{(2H_2\,+\,O_2)}$, was found. Varying the reactant pressure from 150 to 600 mm showed that P_s was proportional to P_R^2. Allowing for the first-order dependence of P_s upon the oxygen pressure, there was a linear relationship between P_s/P_{O_2} and P_R (fig. 3). The part of this effect attributable to hydrogen was found in a separate series of experiments where the hydrogen pressure was varied over a 300 mm range. In this case, as with the variation of P_s/P_{O_2} with the nitrogen, oxygen, carbon dioxide and helium pressures over similar pressure ranges, the experimental results were satisfactorily represented by a linear relationship. When varying the water pressure a smaller range was used, from 0 to 47 mm. Although there was greater scatter than with other inert gases, the results could be represented by a straight line (fig. 4). The

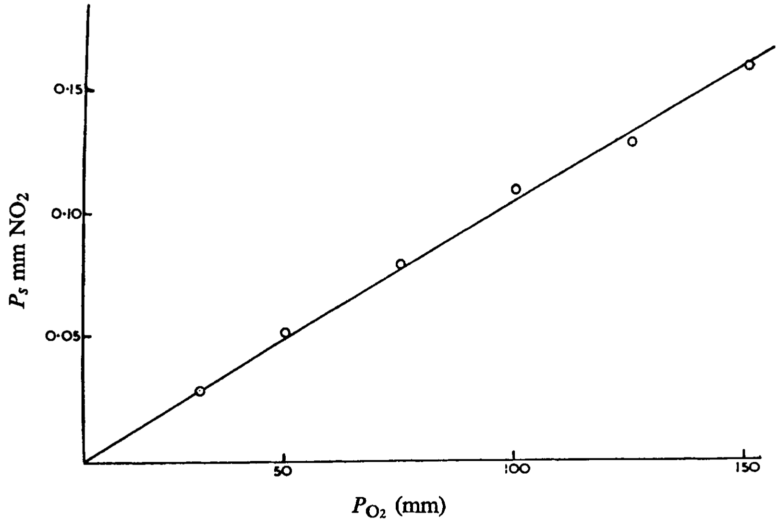

FIG. 2.—The variation of P_s with P_{O_2}. N_2 adjusted to keep $P_{O_2}+P_{N_2}$ = 150 mm; 300 mm H_2; 0·70 mm NO_2 initially; 15 mm quartz vessel; 360°C.

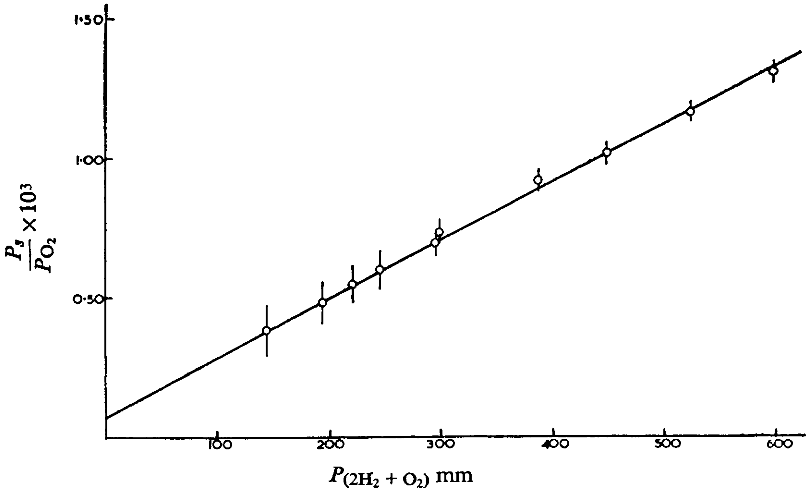

FIG. 3.—P_s/P_{O_2} (corrected) against $P_{(2H_2 + O_2)}$; 0·70 mm NO_2 initially; 15-mm quartz vessel; 360°C. Estimated errors in P_s/P_{O_2} are shown.

effectiveness of the various gases used was finally determined by plotting P_s/P_{O_2} against P_M (i.e., the added gas pressure) for each series of experiments. The values of P_s/P_{O_2} were corrected for any small variation of the pressure of components apart from that of P_M, using the approximate values for the relative efficiencies of the gases found from uncorrected plots.

Thus, under the conditions of this investigation, P_s may be described by the equation,

$$P_s = P_{O_2}\Sigma k_M P_M.$$

The absolute values of the constants appearing in the above equation, and their relative value with respect to that of hydrogen, are given in table 2.

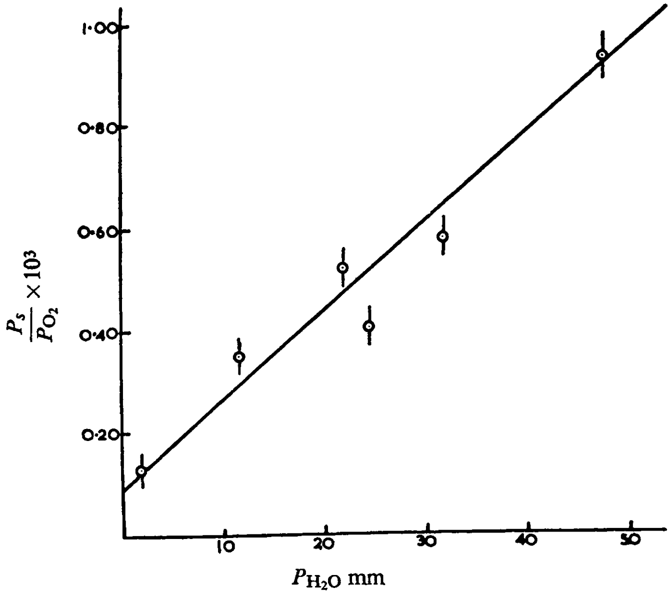

FIG. 4.—P_s/P_{O_2} (corrected) against P_{H_2O}. 150 mm H_2; 150 mm O_2; 0·70 mm NO_2 initially; 15 mm quartz vessel; 360°C. Estimated errors in P_s/P_{O_2} are shown.

TABLE 2.—EXPERIMENTAL VALUES OF k_M AT 360°C

	$k_M \times 10^6$ (mm^{-1})	estimated error of $k_M \times 10^6$ (mm^{-1})	relative value to that of hydrogen	relative third-body efficiency in $H+O_2+M$ (from ref. (4))
hydrogen	2·65	±0·28	1·00	1·00
oxygen	0·88	0·11	0·33	0·35
water	17·6	2·6	6·6	14·3
nitrogen	1·45	0·23	0·55	0·43
carbon dioxide	3·68	—	1·39	1·47
helium	1·08	0·28	0·41	0·36

DISCUSSION

As a continuing pressure change is observed at P_s, it is apparent that the stationary nitrogen dioxide concentration reached is not the result of absence of reaction in the system. A more probable explanation is that a balance of reactions forming and removing nitrogen dioxide has been reached. The ability of any added gas to participate in the reactions controlling P_s suggests that one of the reactions is a three-body process, involving stabilization by a chemically unreactive molecule. Such a reaction is likely to involve an atom or radical. On this basis the kinetics are most simply interpreted in terms of competing reactions for a radical (or atom) X, of the form,

$$X+NO_2 \rightarrow OX+NO, \tag{1}$$

$$X+O_2+M \rightarrow XO_2+M, \tag{2}$$

with a subsequent reaction of XO_2 leading to the reformation of NO_2; this may be represented by the reaction,

$$XO_2 \rightarrow \alpha\, NO_2. \tag{3}$$

Provided that α is constant, this sequence of reactions gives the required kinetics. Thus, with stationary-state concentrations for XO_2 and NO_2,

$$\mathrm{d}P_{XO_2}/\mathrm{d}t = \Sigma k_{2,M}P_XP_{O_2}P_M - k_3P_{XO_2} = 0, \tag{I}$$

$$\mathrm{d}P_{NO_2}/\mathrm{d}t = \alpha k_3P_{XO_2} - k_1P_XP_{NO_2} = 0. \tag{II}$$

Combining (I) and (II) gives the equation,

$$\alpha\Sigma k_{2,M}P_{O_2}P_M = k_1P_{NO_2}, \text{ where } P_{NO_2} = P_s.$$

Of the species present in a reacting $H_2+O_2+NO_2+NO$ system, including O, H, HO_2 and OH, only hydrogen and oxygen atoms as X lead to feasible reaction schemes of the type described above.

Although there is no simple decisive test between these possibilities, there are a number of reasons for preferring hydrogen atoms. There can be little doubt that the reaction responsible for the removal of nitrogen dioxide during the induction period is

$$H+NO_2 \rightarrow OH+NO \tag{4}$$

as the observed rate closely parallels the rate of the H_2+NO_2 reaction under similar conditions.[2] Further, with the apparent exception of water, the third-body efficiencies measured for reaction (2) are in excellent agreement with those for the reaction,

$$H+O_2+M \rightarrow HO_2+M \tag{5}$$

measured independently [4] (table 2). The anomaly in the case of water is removed by recent work of Baldwin.[7] From a review of the previous experimental work, it was concluded [7] that the relative efficiency of water was considerably less than the value of 14·3 found by Lewis and von Elbe.[4] Further, an extensive reinvestigation [7] of the effect of water on the second ignition limit of the hydrogen+oxygen ignition system led to a value of $6{\cdot}4 \pm 0{\cdot}7$. Thus the measured relative efficiency of water found in this work is not merely compatible with X being a hydrogen atom, but provides strong evidence for this identification. In contrast to these arguments favouring the choice of hydrogen atoms, there are several difficulties in any reaction scheme involving oxygen atoms. Apart from the difficulty of proposing a reaction forming oxygen atoms, it is necessary to consider the kinetic consequences of reactions (6) and (7),

$$O+NO+M \rightarrow NO_2+M, \tag{6}$$

$$O+NO_2+M \rightarrow NO_3+M. \tag{7}$$

It would be expected that reaction (7) would be followed by the fast reaction of NO_3 and NO to form nitrogen dioxide,[8] and so both reactions (6) and (7) can be considered to form NO_2, in addition to reaction (3). If $\alpha = 1$, and neglecting any other possible reaction of oxygen atoms, the resulting kinetic equation is

$$k_1P_{NO_2} = \Sigma k_{2,M}P_{O_2}P_M + \Sigma k_{6,M}P_{NO}P_M + \Sigma k_{7,M}P_{NO_2}P_M. \tag{III}$$

The rate constants of reaction (2),[9] with oxygen atoms as X, and of reactions (6) [10] and (7) [11] have been measured at room temperature. Their values relative to that of reaction (1) are [11] $k_{2,N_2}/k_1 = 1{\cdot}75\times10^{-6}$, $k_{6,N_2}/k_1 = 4{\cdot}70\times10^{-4}$, and $k_{7,N_2}/k_1 = 2{\cdot}5\times10^{-3}$ (all in mm^{-1} at 300°K). Assuming (*a*) that these ratios are unchanged at 633°K, and (*b*) that the relative efficiencies of hydrogen, oxygen and nitrogen are the same for reactions (2), (6) and (7) and are equal to those determined experimentally (table 2), then the values of P_s can be calculated from eqn. (III) for various concentrations of reactants. Thus, when $P_{H_2} = 300$ mm, and $P_{O_2} =$ 150 mm, P_s would be 0·47 mm for $P_0 = 0{\cdot}70$ mm, and 0·28 mm for $P_0 = 0{\cdot}20$ mm. These figures are far greater than the experimental values.

A value of P_s in better agreement with the observed value for $P_0 = 0{\cdot}20$ mm ($P_s = 0{\cdot}16$ mm) can be obtained if it is assumed that k_1 has a small activation energy (about 300 kcal/mole). However, the value of P_s would then rise from 0·16 mm at $P_0 = 0{\cdot}20$ mm to 0·27 mm at $P_0 = 0{\cdot}70$ mm, which is incompatible with observation (fig. 1); moreover, the line in fig. 2 would intercept the axis $P_{O_2} = 0$ at about 0·18 mm NO_2 instead of passing through the origin.

The oxygen-atom scheme predicts a very small intercept in fig. 2 if a larger activation energy is attributed to reaction (1). This reaction has been shown [12] to occur at not less than 1 in 100 collisions at 300°K, suggesting a maximum possible activation energy of 2·8 kcal/mole. However, this activation energy leads to an intercept of 0·010 mm, which would be still detectable. It also leads to values of P_s which are absurdly low for the conditions of fig. 1 unless it is also assumed that reaction (2) has an activation energy of several kcal/mole. An activation energy of 4·3 kcal/mole has been reported [13] for this reaction from work on the glow limits of phosphorus. However, this is so unusual for a recombination reaction, where a negative temperature coefficient is usually observed, as to require confirmation by methods which do not depend upon the mechanism assumed for the glow limits.

Thus, the oxygen-atom scheme can only explain the results if unlikely activation energies are assumed for both of the reactions (1) and (2). In view of this and of the positive evidence in favour of hydrogen atoms, the choice of the latter can be made with some confidence.

Identifying XO_2 as the radical HO_2, there are at least two possible paths by which reactions of HO_2 could lead to the reformation of nitrogen dioxide, giving different values of α. The simplest path is by the reaction,

$$HO_2+NO\rightarrow OH+NO_2, \tag{8}$$

but a possible alternative is the sequence,

$$2HO_2\rightarrow H_2O_2+O_2, \tag{9}$$

$$H_2O_2+NO\rightarrow HNO_2+OH, \tag{10}$$

$$2HNO_2\rightarrow H_2O+NO+NO_2. \tag{11}$$

With reaction (8), $\alpha = 1$, and with the sequence (9) to (11), $\alpha = \frac{1}{4}$. Reaction (9) and the overall reverse process of reaction (11) have been used to account for kinetic observations in other systems.[14, 15]

Although with the present knowledge of the rate constants of these reactions an unambiguous decision between the alternative paths is not possible, there are several reasons for preferring reaction (8), apart from its simplicity. As the experimental data require the absence of wall reactions, it is necessary to postulate that there is no appreciable heterogeneous decomposition of hydrogen peroxide if the sequence (9) to (11) is to be adopted. This is only conceivable if reaction (10) is fast, as hydrogen peroxide decomposes by a predominantly heterogeneous process at this temperature.[14] Also, since there is a loss of radicals in this sequence, the overall reaction and the related ignitions can only be explained by short, frequently-branched chains. This requires that a relatively fast branching process should occur compared with the normal branching reaction of the hydrogen+oxygen system,

$$H+O_2 \rightarrow OH+O. \qquad (12)$$

Apart from the difficulty of suggesting a suitable reaction, it has been shown [3] that a simpler long-chain process can explain the ignitions, although this does not imply that a short-chain process is necessarily incompatible with the experimental data. A more direct reason for preferring reaction (8) is that a preliminary investigation [3] of the reaction of hydrogen peroxide and nitric oxide at 300°C has yielded a kinetic form suggesting that reaction (8) is more important than reaction (9) with as little as 3 mm of nitric oxide. It is possible that direct evidence about the relative rate constants of reactions (8) and (9) will be obtained from the investigation of the hydrogen peroxide+nitric oxide system; this study is being continued. On the basis of these arguments, reaction (8) is preferred to reactions (9)-(11).

In suggesting the form of eqn. (I) and (II), an implicit assumption was made that the only reactions involving NO_2 or XO_2 are (1), (2) and (3). It is unlikely that there are alternative reactions to (5) that form HO_2, and only wall or mutual termination, i.e., reaction (9), are probable reactions that could remove it. The arguments suggesting that reaction (8) is in fact faster than (9) under these conditions are presented above and it is conceivable that reaction (8) should predominate over wall removal of HO_2. In considering further reactions of NO_2, it is possible to neglect the initiation and termination reactions that might be expected to effect the nitrogen dioxide concentration, as previous studies of the hydrogen+nitrogen dioxide reaction in this temperature region suggest [16] that long chains will occur unless there is termination by HO_2, a possibility dismissed above. The molecular reactions of nitrogen dioxide, nitric oxide and oxygen are unimportant, as indicated by a comparison of their calculated rates and the observed rates of pressure change at P_s. The only other reaction of NO_2 is

$$O+NO_2 \rightarrow NO+O_2 \qquad (13)$$

and the only certain source of oxygen atoms is by reaction (12). As the rate of reaction (12) never exceeded 2 % of the rate of reaction (5) under the conditions of this investigation, the rate of (13) cannot be more than 2 % of the alternative reaction removing NO_2, i.e., reaction (4).

The formation and subsequent reaction of HNO is neglected as the rate constant [17] of its formation is approximately one-tenth of that of reaction (5), and as the ratio P_{O_2}/P_{NO} was always greater than 25, and was usually greater than 100. It appears, therefore, that the assumptions required in the derivation of eqn. (I) and (II) are correct.

It is now possible, subject to the acceptance of the arguments above, to identify the experimental constant k_M with the ratio of rate constants, $k_{5,M}/k_4$. Further, this ratio has the value $1{\cdot}01 \times 10^2 \pm 10$ % cm^3 mole^{-1} at 360°C with $M = H_2$. As the rate constant of reaction (5) has been determined, it is possible to estimate k_4. Hoare and Walsh [18] using experimental values of $k_{5,M}$ at 20° and 520°C suggest that reaction (5) has a negative activation energy of 3 to 4 kcal/mole. On the basis of their data, k_{5,H_2} at 360°C is interpolated as $2{\cdot}2 \times 10^{16}$ cm^6 mole^{-2} sec^{-1}. However, in a recent review of the available data on this reaction, Voevodsky and

Kondratiev[19] prefer a value of $5{\cdot}5 \times 10^{15}$ cm^6 mole^{-2} sec^{-1} for the temperature range from 450 to 650°C with little, if any, variation with temperature. On the basis of these values, k_4 is calculated to be $2{\cdot}2 \times 10^{14}$ or $5{\cdot}5 \times 10^{13}$ cm^3 mole^{-1} sec^{-1} respectively. The error in these values is 10 % from the experimental ratio of $k_{5,M}/k_4$, a maximum possible of 2 % from neglecting reaction (13), and the error involved in the determination of $k_{5,M}$.

There has been only one previous estimate of k_4. From the relative rates of removal of NO_2 and Cl_2 in the system $H_2+Cl_2+NO_2$, Rosser and Wise[20] found the rate constant of reaction (4) relative to that of the step,

$$H+Cl_2 \rightarrow HCl+Cl. \tag{14}$$

Using independently measured values of k_{14}, their results gave a value for k_4 of $3{\cdot}2 \times 10^{13}$ cm^3 mole^{-1} sec^{-1} between 227 and 267°C. No critical estimate was made of the possible error in this determination. The different values of k_4 cannot be attributed to an activation energy for the reaction, as the high value of k_4 implies that E_4 is small or negligible. The most probable source of error lies in the uncertainties of the absolute values of the rate constants $k_{5,M}$ and k_{14}.

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