

THE THERMAL REACTION BETWEEN HYDROGEN AND NITROGEN DIOXIDE

PART 4.—THERMAL IGNITIONS OF HYDROGEN AND NITROGEN DIOXIDE

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The ignition boundary for mixtures of hydrogen and nitrogen dioxide has been determined as a function of composition at temperatures in the range 516–570° C. Analysis of the results with the aid of the Frank-Kamenetskii equation shows that the ignitions are thermal in character and that the operative rate law is quantitatively similar to that found at lower temperatures.

Parts 2 and 3 of this series ^{1,2} described a photometric investigation of the reaction between nitrogen dioxide and hydrogen at temperatures near 400° C. The effect of the reactants and nitric oxide on the early rate of the reaction were found to be described by the rate equation

$$-\frac{dp_{\text{NO}_2}}{dt} = \frac{k' p_{\text{NO}_2} p_{\text{H}_2}^{1.5}}{p_{\text{NO}} + k'' p_{\text{NO}_2}} \quad (1)$$

The results were explained by a free radical straight chain mechanism.

Ashmore observed ³ ignitions of nitrogen dioxide and hydrogen sensitized by traces of nitrosyl chloride at temperatures near 400° C. Pollard and Holbrook kindly informed us of some studies they made of unsensitized ignitions at higher temperatures. We have confirmed the general trend of their results and extended them. The ignition boundary in the range 516–570° C can now be related quantitatively to the kinetics of the fast reaction near 400° C.

EXPERIMENTAL

The experimental methods and procedure were similar to those already described,¹ except that the photometer was not used. The reactant gases were delivered by a conventional Pyrex glass vacuum system to the reaction vessel, which was heated in an electric furnace.

The lower pressure limits of ignition were determined by admitting mixtures of varying composition (x , the mole fraction of hydrogen, between 0.33 and 0.8) to the reaction vessel at temperatures in the range 516–570° C. This vessel was a quartz cylinder, of internal diameter 40 mm and length 200 mm, fitted with alternative entry tubes: one of these ran the length of the vessel close to the wall, and the gases entered the vessel through many small holes; the other was simply a tube at the end of the vessel. Rather surprisingly, the limits were slightly lower with admission through the "spray" tube. This may be due to more efficient heating of the gases before they enter the reaction vessel, or to increased initiation of reaction chains on the extra surface available.

RESULTS

In fig. 1 the lower limit of ignition (P , the total molecular concentration in mm at 800° K) is plotted against mixture composition for five temperatures in the range 516–570° C. The values of P were considerably lower than those quoted by Pollard and Holbrook, but are in reasonable agreement if allowance is made for the smaller diameter of their reaction vessel.

The curves become increasingly flat towards higher hydrogen fractions, suggesting that P becomes constant as $x \rightarrow 1$. The curvature at lower hydrogen fractions becomes very much more marked at lower temperatures.

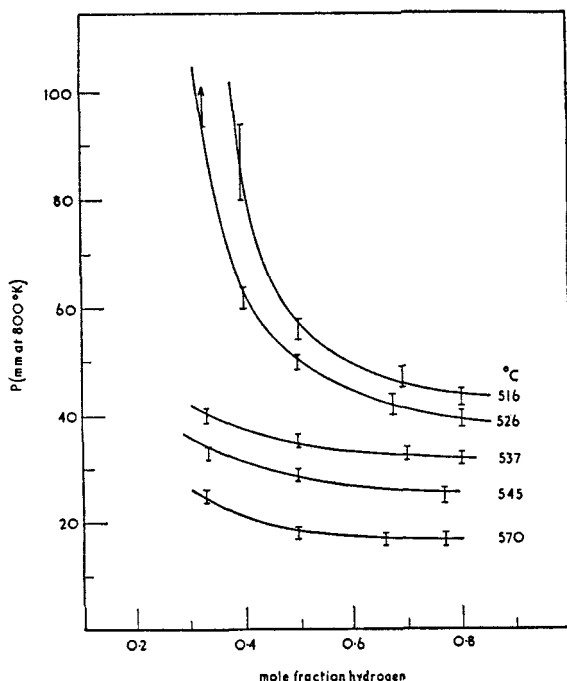


FIG. 1.

Eqn. (1) shows that the rate of the reaction is reduced by the addition of nitric oxide; this suggests that the limit should then be raised. Table 1 shows that this occurs for 1:1 mixtures at 550° C. The nitric oxide was mixed with the reactants before admission.

TABLE 1

	$P = p_{\text{NO}_2} + p_{\text{H}_2} = 2p_{\text{NO}_2}$				
p_{NO}/P	0	0.01	0.02	0.05	0.07
P (mm)	27 ± 1	30 ± 1	35 ± 2	44 ± 3	49 ± 3

DISCUSSION

The rate eqn. (1) observed near 400° C has been interpreted² in terms of a non-branching chain mechanism. If this still holds above 500° C, the onset of ignition will be controlled by thermal rather than isothermal conditions. Frank-Kamenetskii predicted⁴ that the limiting rate of a reaction for thermal ignition to occur in a long cylindrical vessel is given by

$$\text{rate} = 2\lambda_m RT^2 / QEr^2, \quad (2)$$

where λ_m is the thermal conductivity of the mixture, R the gas constant, T the absolute temperature, Q the heat of reaction, E the energy of activation of the reaction, and r the radius of the vessel. The correction for a cylinder of finite length can be neglected (< 2 %).

Combining (1) and (2) with the initial conditions $p_{\text{H}_2} = xP$, $p_{\text{NO}} = 0$, the total molecular concentration P for the boundary of ignition is given by

$$\frac{k'}{k''} (xP)^{1.5} = \frac{2\lambda_m RT^2}{QEr^2}. \quad (3)$$

In these experiments $r = 2$ cm, $R = 2$ cal/mole deg., $Q = 44,000$ cal and E has been taken as the activation energy found at 400°C (43,000 cal). The latter choice is justified below. k' can be computed from the expression ²

$$k' = 10^{14.0} e^{-43,000/RT} \text{ cm}^{3/2} \text{ mole}^{-1/2} \text{ sec}^{-1}.$$

k'' was found ² to lie between 0.7 and 0.8 near 400°C ; as the results showed that it declines slightly at higher temperatures, a value of 0.6 has been adopted for 510 – 570°C . The computed values of k'/k'' in this range are accurate to about $\pm 20\%$.

Measurements of the thermal conductivity of nitrogen dioxide have been made ⁵ at temperatures below 100°C , but these cannot be extrapolated to higher temperatures because no allowance was made for the equilibrium $2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$. The best assumption that can be made is that the thermal conductivity of nitrogen dioxide will be the same as that of carbon dioxide. λ_{CO_2} is known ⁶ up to 600°K , and λ_{H_2} up to 700°K ; as both vary almost directly as T , the values can be extrapolated with some confidence to the temperature range required (790 – 850°K). Lindsay and Bromley have shown ⁷ that the thermal conductivity λ_m of mixtures of CO_2 and H_2 at room temperature can be expressed accurately by

$$\lambda_m = \frac{\lambda_{\text{CO}_2}}{1 + A_1 x/(1 - x)} + \frac{\lambda_{\text{H}_2}}{1 + A_2(1 - x)/x},$$

where $A_1 = 0.6$, $A_2 = 2.6$. Theoretical expressions for A_1 and A_2 suggest that they vary only slightly with temperature; λ_m can thus be computed at 800°K .

x	1.0	0.7	0.5	0.0
$10^4 \lambda_m$	9.7	5.2	3.6	1.52 cal/sec cm deg.

Eqn. (3) can now be tested both for variation of P with temperature and also by calculation of absolute values of P for different compositions at each temperature.

The activation energy E of the reaction is given by $k' = k \exp(-E/RT)$, since k'' varies only slowly with temperature. If $\lambda_m \propto T$, eqn. (3) leads to

$$E = R \frac{d \ln((xP)^{1.5}/T^3)}{d(1/T)}.$$

Fig. 2 shows $\log_{10} 10^8 (xP)^{1.5}/T^3$ plotted against $1/T$ for $x = 0.5$, 0.7 and 1.0 . The set of points for $x = 1.0$ were obtained by extrapolation (see below). The points are a good fit to straight lines of slope corresponding to $E = 43 \pm 3$ kcal; this is in excellent agreement with the value 43 ± 3 kcal found ² at lower temperatures and used in the absolute calculations below.

Table 2 shows the computed and observed values of P for $x = 0.5$, 0.7 and 1.0 . The latter set of points represent the limiting value of P as $x \rightarrow 1$. Here λ_m becomes λ_{H_2} ; this can be calculated without ambiguity. The limiting values were obtained by short extrapolations of plots of P against $(1/x)$ to $(P, 1)$. These plots are linear within experimental error for $x > 1/2$.

TABLE 2

	$T (^\circ\text{C})$	516	526	537	545	570
$x = 0.5$	computed	64	52	44	38	24
	obs.	56	50	38	30	20
	computed	55	46	37	32	21
$x = 0.7$	obs.	46	42	32	26	17
	computed	47	38	32	28	18
	obs.	39	35	31	24	15

The general agreement is extremely good: this is somewhat fortuitous since the observed values are only accurate to $\pm 10\%$, and the computed to about $\pm 25\%$ together with any error due to the assumption that $\lambda_{\text{NO}_2} = \lambda_{\text{CO}_2}$. This latter error does not apply to the limiting values of P ($x = 1$).

At lower values of x the values of P become steadily greater than those expected from calculation. The striking change in the shape of the plots of P against x (fig. 1) over a range of temperature too small for the transport properties to be affected markedly suggests that at lower temperatures and lower values of x the actual rate of reaction is lower than that predicted by the rate eqn. (1). This phenomenon had already been observed during the photometric studies² near 400°C , where nitrogen dioxide inhibits the hydrogen + nitrogen dioxide reaction strongly at low hydrogen to nitrogen dioxide ratios ($x < 0.7$).

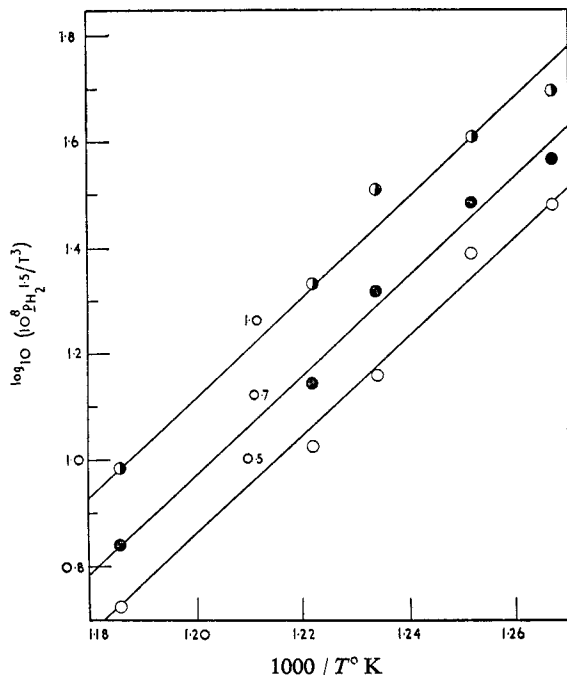


FIG. 2.

When nitric oxide is mixed with the reactants, the ignition limit is raised as shown in table 1. This is in qualitative agreement with the inhibiting effect of nitric oxide on the reaction. However, calculations show that the nitric oxide is somewhat more effective in raising the limit than would be predicted from eqn. (1).

Ignitions of hydrogen and nitrogen dioxide where hydrogen is in excess can thus be explained quantitatively as chain thermal in origin. They are controlled by the same rate law as that found for the fast reaction at temperatures well below the ignition boundary. This implies that the mechanism of the reaction before ignition at temperatures up to 570°C is the same as that proposed² for the fast reaction at 400°C .

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¹ Ashmore and Levitt, *Trans. Faraday Soc.*, 1956, **52**, 835.

² Ashmore and Levitt, *Trans. Faraday Soc.*, 1957, **53**, 945.

³ Ashmore, *Research* (corr.), 1954, **7**, S35.

⁴ Frank-Kamenetskii, *Diffusion and Heat Exchange in Chemical Kinetics* (Princeton University Press, Princeton), 1955.

⁵ Todd, *Proc. Roy. Soc. A*, 1910, **83**, 19.

⁶ Hilsenrath *et al.*, *Transport Data of Gases* (National Bureau of Standards, Washington, circ. 564), 1955.

⁷ Lindsay and Bromley, *Ind. Eng. Chem.*, 1950, **42**, 1508.