[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF OREGON]

Kinetics of the Homogeneous Reaction of NO and H_2[1]

BY WENDELL M. GRAVEN

RECEIVED FEBRUARY 4, 1957

An examination of the kinetics of the reaction of NO and H_2 within the temperature interval of 850-1060° has resulted in information which may be represented by the rate expression $\frac{\Delta H_2O}{\Delta t} = \frac{2.2 \times 10^9 \exp(-41000/RT)[NO]^2[H_2]^{1/2}}{1-3.0\,[H_2]^{1/2}}$. A chain mechanism has been found to be in partial agreement with the experimental data.

Introduction

In each of the gaseous molecular reactions which have been demonstrated kinetically to be of third order nitric oxide is one of the participants.

The interaction of NO and H_2 differs from most of the other reactions in that its rate constant has a higher activation energy and a larger pre-exponential factor.[2] This fact caused Taylor and Tanford[3] to reject the mechanism proposed by Hinshelwood and Mitchell,[4] which involved ternary molecular collisions as well as collisions of molecules with "binary collision complexes." Believing the reaction mechanism to be more complex and probably to involve hydrogen atoms they undertook an investigation of the mercury-photosensitized NO–H_2 reaction. Quite understandably, a different dependence of reaction rate on H_2 and NO pressures was observed.

In view of recent interest in the high temperature behavior of NO–H_2 flames[5,6] a re-examination of the kinetics of the NO–H_2 reaction has been considered to be appropriate.

Before a comprehensive kinetic investigation was initiated an approximate dependence of the rate upon reactant concentrations was determined by a simple and rapid technique which will be described.

For a binary system, the reaction rate of which is *i*th order in reactant A and *j*th order in reactant B, the initial rate, R_N, may be expressed in terms of the mole fraction, N, of component A and a pressure-dependent rate constant, k, according to eq. 1

$$R_N = kN^i(1 - N)^j \qquad (1)$$

Elimination of k by taking the ratio of the initial rate at mole fraction N to that at some other composition, say the equi-molar mixture, enables one to define the relative rate ratio, R, by means of eq. 2.

$$R = R_N/R_{1/2} = 2^{i+j}N^i(1 - N)^j \qquad (2)$$

Equation 2 is applicable to all two-component reaction systems at constant temperature and pressure, provided that the extent of reaction is not greater than several per cent.

A plot of R against N results in a family of curves corresponding to the selected values of the exponents, i and j. Figure 1 shows such a plot in which i and j have been limited to the values of $^1/_2$, 1 and 2, and the curves have been terminated at mole fractions 0.1 and 0.9 for clarity.

Experimental measurement of R at several reactant compositions and comparison of the results with a master plot makes it possible to determine i and j, and therefore the rate law of the reaction under consideration, with relative ease.

Application of this method to the reaction

$$NO + H_2 = H_2O + {}^1/_2N_2 \qquad (3)$$

yielded results which have been plotted as individual points in Fig. 1, where N represents the mole fraction of NO. It may be observed that the

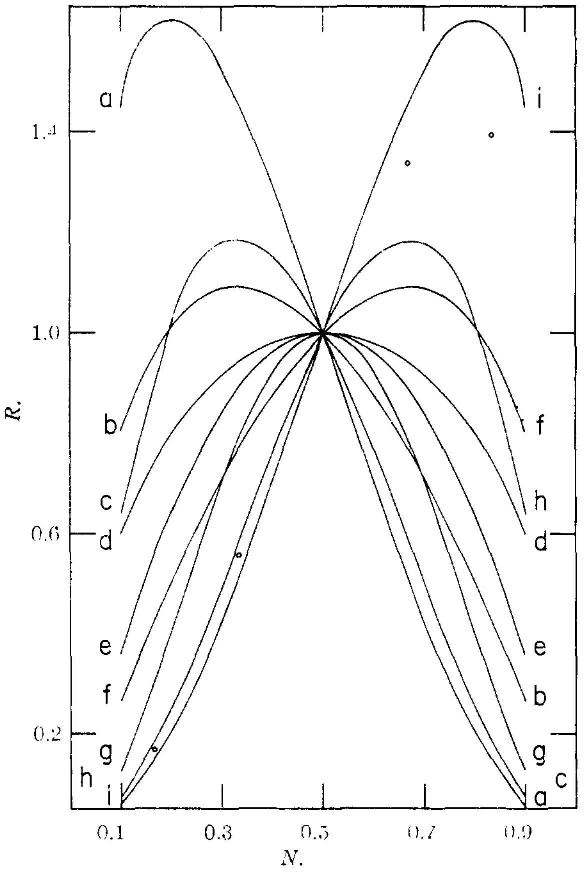

Fig. 1.—Effect of composition of binary systems on initial rate ratio: R, initial reaction rate relative to that of equimolar mixture; N, mole fraction of component with *i*th order concentration dependence; a, $i = {}^1/_2, j = 2$; b, $i = {}^1/_2, j = 1$; c, $i = 1, j = 2$; d, $i = {}^1/_2, j = {}^1/_2$; e, $i = 1, j = 1$; f, $i = 1, j = {}^1/_2$; g, $i = 2, j = 2$; h, $i = 2, j = 1$; i, $i = 2, j = {}^1/_2$; O, R (experimental) NO + H_2; T = 1025°; 0.3–3.0% reaction.

---

[1] Financial support for this research was obtained from the Graduate School of University of Oregon and Research Corporation.

[2] C. N. Hinshelwood and T. E. Green, *J. Chem. Soc.*, 730 (1926).

[3] H. A. Taylor and C. Tanford, *J. Chem. Phys.*, **12**, 47 (1944).

[4] C. N. Hinshelwood and J. W. Mitchell, *J. Chem. Soc.*, 378 (1936).

[5] G. K. Adams, W. G. Parker and H. G. Wolfhard, *Disc. Faraday Soc.*, **14**, 97 (1953).

[6] A. I. Rozlovskii, *Zhur. Fiz. Khim.*, **30**, 912 (1956).

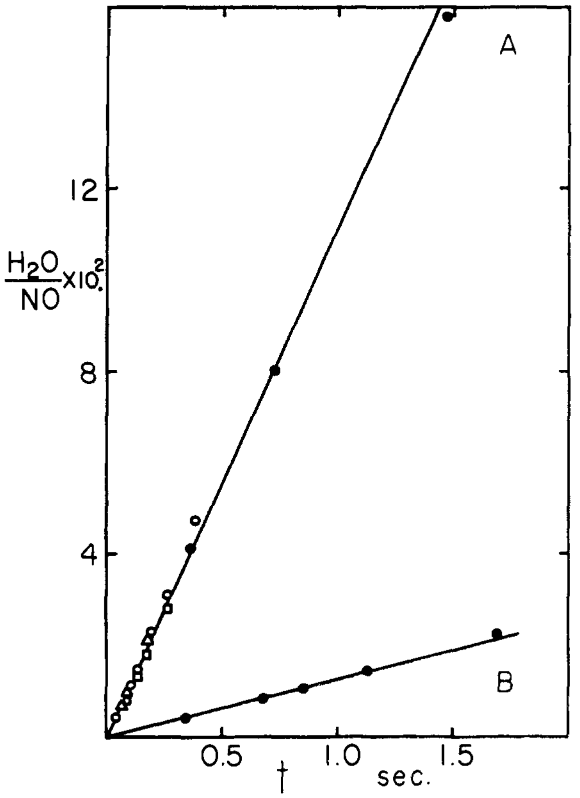

Fig. 2. Effect of reaction time on extent of reaction. A: $T = 1025°$; ●, vessel II; [NO] = [H_2]; ○, vessel I; [NO] = [H_2]; □, vessel I; [NO] = $^1/_2$[H_2]; △, vessel I; [NO] = [2H_2]; B: $T = 850°$; ●, vessel II; [NO] = [H_2]

experimental points do not coincide with any of the nine curves corresponding to integral or half-integral values of i and j. However, the data are in close agreement with the R values that would be expected if the concentration dependence of the rate were second order in NO and two-third order in H_2. Since alternative complex rate expressions might serve as well, or better, for representing the data it was thought that a more comprehensive investigation was required, particularly in view of earlier reports[2] that the reaction obeyed an over-all third-order rate law.

Experimental

The measurements of reaction rates were made with a flow technique which permitted rapid heating of pre-mixed reactants and diluent and rapid quenching of effluent mixtures. A description of the design of the reaction vessel and the experimental technique has been published previously.[7,8] The use of two quartz reaction vessels, which were similar in every respect except size, permitted a test for homogeneity of the reaction as well as a hundred-fold variation of the extent of reaction. Vessel I had a free volume of 5.60 ml. and an estimated surface/volume ratio of 5.6 cm.$^{-1}$. Vessel II had a free volume of 42.6 ml. and an estimated surface/volume ratio of 2.3 cm.$^{-1}$.

Reaction rates were determined by absorption of water vapor in calcium chloride. Gravimetric measurement of the amount collected during an appropriate time interval permitted a precise estimate of the steam content of the effluent mixture.

Calibrated capillary tube flowmeters facilitated measurement and control of the flow rates of reactants and diluent. Mixing was accomplished with tangential jet mixing chambers.

Mass spectrometric analyses of the compressed N_2, H_2 and He gases showed that the principal impurity (H_2O, N_2, O_2 or CH_4) did not exceed a few tenths of a per cent. Each gas was dried and freed of O_2 by standard catalytic methods. Compressed NO gas which had been passed through ascarite absorbent showed no evidence of NO_2, an amount of N_2O which did not exceed a few tenths of a per cent., and N_2 in an amount that exceeded the maximum impurity stated by the supplier.

The temperature at the center of the reaction vessel, which was situated in an electric furnace, was maintained constant within one degree with a modified "Simplytrol" pyrometer-relay furnished by Assembly Products, Inc. Temperature measurements along the major axis of the larger vessel with a Pt, Pt-Rh thermocouple, which had been calibrated by the Bureau of Standards, indicated a temperature gradient of 11° between the entrance and the center.

The total pressure of the reactant mixture was approximately 77 or 80 cm., depending upon which vessel was being used.

With the use of helium as a diluent to maintain a constant total flow rate it was possible to vary the reactant concentrations independently of one another without changing the reaction time. A total flow rate of 1.5 l./min., which corresponded to a reaction time of about 0.05 sec. in vessel I and 0.4 sec. in vessel II, resulted in about one and 5% reaction, respectively, at the maximum temperatures. Consequently, in all runs except those in which the reaction time was increased deliberately initial rates were being measured and a differential rate law, together with initial reactant concentrations, could be employed in computing rate constants.

Results

Adjustment of the total flow rate permitted a wide variation in the residence time of the gases within the vessel. This was extended further by the use of two vessels with different volumes. Figure 2 shows the results of rate measurements in both vessels at two temperatures with three different compositions of reactants. In each case a linear relationship exists between per cent. reaction and reaction time. Curve A, in which the variation of t covers a 40-fold range, indicates that the linearity persists nearly to 15% conversion. Moreover, the close fit to a single curve of data from two vessels, one having 2.5 times the surface/volume ratio of the other, argues against any significant contribution of heterogeneous reaction.

That N_2 takes no part in that portion of the reaction mechanism which is rate-determining may be seen from the data in Fig. 3. Reaction rates were obtained from runs in which NO and H_2 concentrations remained invariant while N_2 replaced He as diluent at two temperatures with the use of both reaction vessels. The greater scatter of the points in curve A is due in part to the ten-fold magnification of error that arises from the division of product concentrations by the reaction time.

In Fig. 4 the reaction rates obtained from runs at constant H_2 concentration with varying NO concentration have been plotted against the square of the corresponding NO concentrations. Data obtained at three temperatures with both vessels give straight lines over ten-fold variations in NO concentration, thus demonstrating a second-order dependence.

The dependence of the reaction rate upon H_2 concentration was found by preliminary experiments, Fig. 1, to be non-integral and less than first order. By plotting a number of trial functions it

---

[7] W. M. Graven and F. J. Long, THIS JOURNAL, **76**, 2602 (1954).

[8] W. M. Graven, *ibid.*, **78**, 3297 (1956).

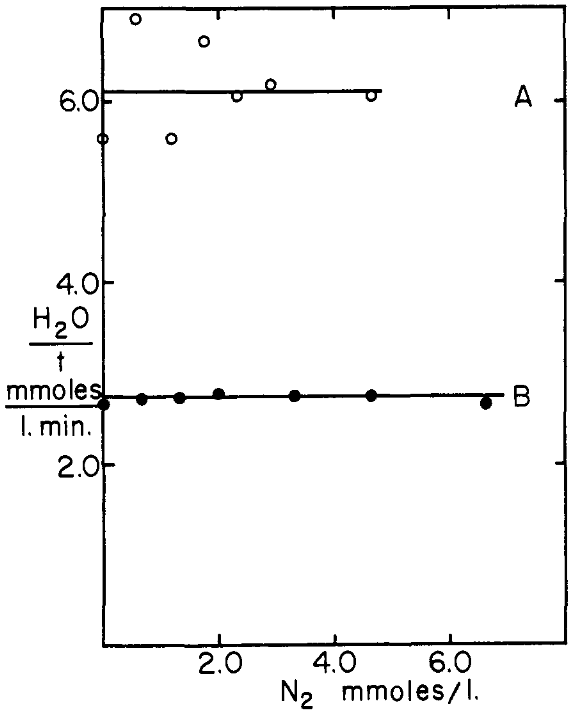

Fig. 3.—Effect of N_2 concentration on rate of reaction. A: T = 1060°; vessel I; t = 0.0469 sec.; [NO] = [H_2] = 2.33 mmoles/l.; B: T = 1025°; vessel II; t = 0.391 sec.; [NO] = 1.98, [H_2] = 1.32 mmoles/l.

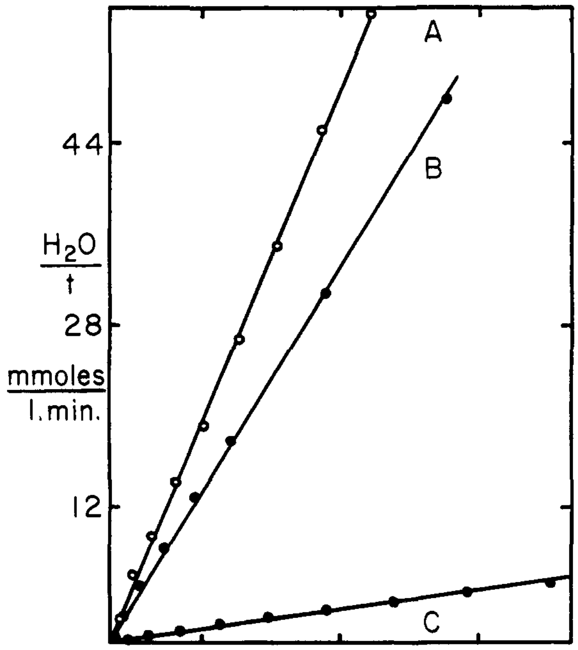

Fig. 4.—Effect of NO concentration on rate of reaction. A: T = 1060°; vessel I; t = 0.0469 sec.; [H_2] = 3.49 mmoles/l.; B: T = 1025°; vessel II; t = 0.391 sec.; [H_2] = 3.31 mmoles/l.; C: T = 850°; vessel II; t = 0.452 sec.; [H_2] = 3.79 mmoles/l.

was ascertained that for runs at constant NO and varying H_2 concentrations a plot of the reciprocals of the reaction rates against the reciprocals of the square roots of corresponding H_2 concentrations yielded a straight line. Figure 5 shows three such plots which span ten-fold variations in H_2 concentration and include data procured at three temperatures with the use of both reaction vessels.

Sufficient information has been provided for the formulation of a tentative rate law which may be expressed in the incremental form

$$\frac{\Delta H_2O}{\Delta t} = \frac{k_1[NO]^2[H_2]^{1/2}}{1 + k_2[H_2]^{1/2}} \qquad (4)$$

The two parameters of eq. 4, k_1 and k_2, can be evaluated from the slopes and intercepts, respectively, of the curves in Fig. 5. It may be observed that k_2 is singular by virtue of being negative and nearly independent of temperature. Thus, at 1025° it is found to be -0.095 (l./mmole)$^{1/2}$, while at 850° where the experimental uncertainty is greater a value of -0.08 is computed.

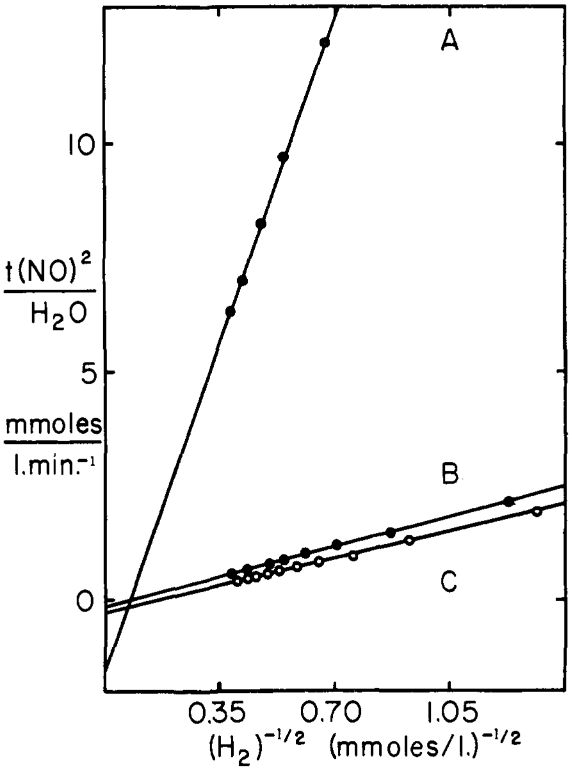

Fig. 5.—Effect of H_2 concentration on rate of reaction. A: T = 850°; vessel II; t = 0.678 sec.; [NO] = 4.45 mmoles/l.; B: T = 1025°; vessel II; t = 0.391 sec.; [NO] = 3.31 mmoles/l.; C: T = 1060°; vessel I; t = 0.0469 sec.; [NO] = 3.49 mmoles/l.

Calculations of k_1 for individual runs were made with the assumption that the value of k_2 was -3.0 (l./mole),$^{1/2}$ independent of temperature. Therefore, the observed temperature dependence of the over-all reaction rate was assigned to k_1.

Rate measurements were made with the larger vessel using an equi-molar reactant mixture and extended over a 200° temperature interval. The data appear in Fig. 6 as a plot of the logarithms of the ratios of k_1 to the square roots of corresponding temperatures against the reciprocals of the tem-

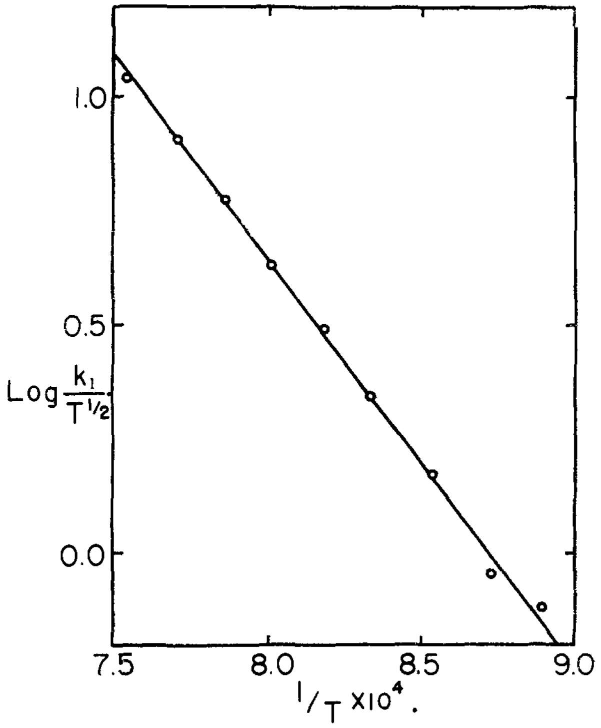

Fig. 6.—Effect of temperature on rate of reaction. T = 850–1053°; vessel II; t = 0.383-0.452 sec.; [NO] = $[H_2]$ = 3.23–3.79 mmoles/l.; 0.33–3.3% reaction.

peratures. From the slope of the straight line which results an activation energy of 41 kcal. has been computed.

A comparison of k_1 computed from data obtained with each of the reaction vessels shows excellent agreement. The averages of 27 measurements with vessel I and 28 measurements with vessel II at 1025° were 268 and 279 $(l./mole)^{3/2}$, respectively. Twenty-three measurements at 850° with vessel II yielded an average of 23.2 $(l./mole)^{3/2}$.

The mean values of k_1 at each of the two temperatures were combined with the observed activation energy to obtain eq. 5.

$$k_1 = 2.2 \times 10^9 \exp(-41000/RT)\ (l./mole)^{3/2} \quad (5)$$

Discussion

It is unusual to find a rate expression in which the denominator consists of the difference between two terms, associated with a non-detonating reaction. However, if use is made of the experimental values of k_2 it may be seen that the alternative series form of eq. 4 effectively terminates with the third term within the range of H_2 concentrations used in its formulation and eq. 6 serves as well to represent the experimental results.

$$\frac{\Delta H_2O}{\Delta t} = k_1[NO]^2[H_2]^{1/2}(1 + 0.095[H_2]^{1/2} + 0.0090\,[H_2]) \quad (6)$$

It is evident that the termolecular mechanism,[2] which was proposed on the basis of kinetic data obtained at temperatures well below those employed in this investigation, will not satisfactorily account for the observed rate expression.

A homogeneous chain mechanism, which has been suggested for the reaction in NO–H_2 flames,[9] is in approximate, although incomplete, agreement with the data.

$$2NO + H_2 \longrightarrow N_2 + 2OH \quad (7)$$

$$OH + H_2 \longrightarrow H_2O + H \quad (8)$$

$$H + NO \longrightarrow NOH \quad (9)$$

$$NOH + NO \longrightarrow N_2 + O_2H \quad (10)$$

$$O_2H + H_2 \longrightarrow H_2O + OH \quad (11)$$

$$2H + M \longrightarrow H_2 + M \quad (12)$$

With the customary steady-state assumptions this mechanism leads to a rate expression corresponding in form to the first two terms of eq. 6, which, it may be observed, account for 95% of the experimental rate of reaction at the highest H_2 concentration employed in this investigation.

Although it has been demonstrated that the reaction is predominantly homogeneous no unambiguous test for a chain mechanism, which would be suitable under the experimental conditions, was devised. Consideration of the form of the rate law, the low observed activation energy and large pre-exponential factor makes plausible such a mechanistic postulation.

The lack of complete concordance between the observed rate law and the expression which results from the proffered mechanism tends to vitiate a detailed examination of the energetics of the individual steps in the reaction mechanism. However, it may be noted that as the chain length diminishes the mechanism predicts an approach to the third-order rate law which has been observed at lower temperatures. A concurrent increase of the experimental activation energy to the reported value of 47 kcal.[4] is not implausible.

EUGENE, OREGON

---

[9] A. I. Rozlovskiĭ, *Zhur. Fiz. Khim.*, **30**, 1411 (1956).