

NASA TECHNICAL
MEMORANDUM



NASA TM X-2707

NASA TM X-2707

RATE OF REACTION
BETWEEN MOLECULAR HYDROGEN
AND MOLECULAR OXYGEN

by Richard S. Brokaw

Lewis Research Center

Cleveland, Ohio 44135

1. Report No. NASA TM X-2707	2. Government Accession No.	3. Recipient's Catalog No.	
4. Title and Subtitle RATE OF REACTION BETWEEN MOLECULAR HYDROGEN AND MOLECULAR OXYGEN		5. Report Date February 1973	6. Performing Organization Code
		8. Performing Organization Report No. E-7195	10. Work Unit No. 502-04
7. Author(s) Richard S. Brokaw		11. Contract or Grant No.	
9. Performing Organization Name and Address Lewis Research Center National Aeronautics and Space Administration Cleveland, Ohio 44135		13. Type of Report and Period Covered Technical Memorandum	
		14. Sponsoring Agency Code	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546		15. Supplementary Notes	
16. Abstract <p>The shock tube data of Jachimowski and Houghton have been rigorously analyzed to obtain rate constants for the candidate initiation reactions $H_2 + O_2 \xrightarrow{k_{01}} H + HO_2$, $k_{01} = 1.9 \times 10^{13} \exp(-24\ 100/T)$; $H_2 + O_2 \xrightarrow{k_{02}} H_2O + O$, $k_{02} = 4.1 \times 10^{13} \exp(-25\ 400/T)$; and $H_2 + O_2 \xrightarrow{k_{03}} OH + OH$, $k_{03} = 2.3 \times 10^{13} \exp(-25\ 200/T)$. (Rate constants in $cm^3 \text{ mole}^{-1} \text{ sec}^{-1}$, temperature in degrees kelvin.) Reaction (01) is probably not the initiation process because the activation energy obtained is less than the endothermicity and because the derived rates greatly exceed values inferred in the literature from the reverse of reaction (01). Reactions (02) and (03) remain as possibilities, with reaction (02) slightly favored on the basis of steric and statistical considerations. The solution of the differential equations is presented in detail to show how the kinetics of other ignition systems may be solved.</p>			
17. Key Words (Suggested by Author(s)) Reaction kinetics Ignition Combustion Initiation		18. Distribution Statement Unclassified - unlimited	
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 10	22. Price* \$3.00

RATE OF REACTION BETWEEN MOLECULAR HYDROGEN AND MOLECULAR OXYGEN

by Richard S. Brokaw

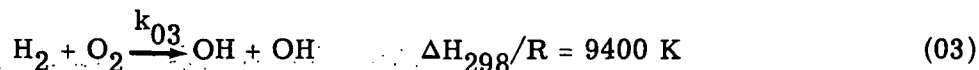
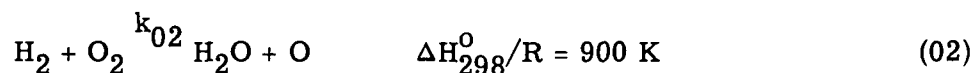
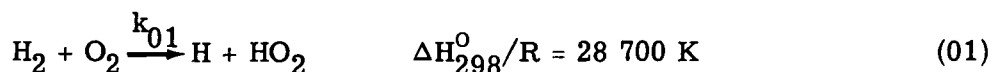
Lewis Research Center

SUMMARY

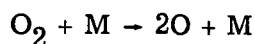
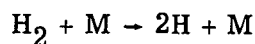
The shock tube data of Jachimowski and Houghton have been rigorously analyzed to obtain rate constants for the candidate initiation reactions $\text{H}_2 + \text{O}_2 \xrightarrow{k_{01}} \text{H} + \text{HO}_2$, $k_{01} = 1.9 \times 10^{13} \exp(-24\,100/T)$; $\text{H}_2 + \text{O}_2 \xrightarrow{k_{02}} \text{H}_2\text{O} + \text{O}$, $k_{02} = 4.1 \times 10^{13} \exp(-25\,400/T)$; and $\text{H}_2 + \text{O}_2 \xrightarrow{k_{03}} \text{OH} + \text{OH}$, $k_{03} = 2.3 \times 10^{13} \exp(-25\,200/T)$. (Rate constants in $\text{cm}^3 \text{mole}^{-1} \text{sec}^{-1}$, temperature in degrees kelvin.) Reaction (01) is probably not the initiation process because the activation energy obtained is less than the endothermicity and because the derived rates greatly exceed values inferred in the literature from the reverse of reaction (01). Reactions (02) and (03) remain as possibilities, with reaction (02) slightly favored on the basis of steric and statistical considerations. The solution of the differential equations is presented in detail to show how the kinetics of other ignition systems may be solved.

INTRODUCTION

When a mixture containing hydrogen and oxygen is subjected to a temperature and pressure pulse in a shock tube, small concentrations of atoms and free radicals are first formed from molecular hydrogen and oxygen. Reactions which have been suggested include (ref. 1)

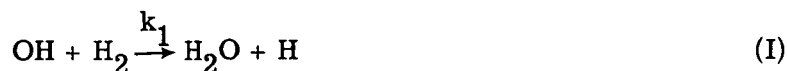


The dissociation processes



are sufficiently endothermic that they are unimportant except, possibly, at very high temperatures.

After small concentrations of H, OH, or O are formed from reactions (01), (02), or (03), the atom and radical concentrations grow exponentially via the well-known branched-chain scheme



At low temperatures and high pressures the chainbreaking reaction



must also be considered.

Recently Jachimowski and Houghton (ref. 2) studied the hydrogen-oxygen initiation process behind incident shocks. They analyzed their data to obtain rate constants assuming initiation by reaction (01) or (03). Their analysis used an approximate and intuitive formulation proposed to explain hydrogen-oxygen ignition delays (ref. 3).

In this report the data of Jachimowski and Houghton are reexamined, using a rigorous formulation of the initiation and chain-branching kinetics. Rate constants are obtained by assuming initiation by reaction (01), (02), or (03). The values of rate constants indicate the more likely initiation processes. The solution of the differential equations is presented in detail to provide a guide as to how the kinetics of other similar ignition systems may be solved.

THEORETICAL CONSIDERATIONS

The differential equations governing the growth of radical concentrations during the induction period are as follows (ref. 3):

$$\frac{d[H]}{dt} = -(\nu_2 + \nu_4)[H] + \nu_1[OH] + \nu_3[O] + i_1 \quad (1)$$

$$\frac{d[OH]}{dt} = \nu_2[H] - \nu_1[OH] + \nu_3[O] + 2i_3 \quad (2)$$

$$\frac{d[O]}{dt} = \nu_2[H] - \nu_3[O] + i_2 \quad (3)$$

Here [H], [OH], and [O] are the concentrations of hydrogen atoms, hydroxyl radicals, and oxygen atoms. Also, $\nu_1 \equiv k_1[H_2]$, $\nu_2 \equiv k_2[O_2]$, $\nu_3 \equiv k_3[H_2]$, $\nu_4 \equiv k_4[O_2][M]$, and $i_1 \equiv k_{01}[H_2][O_2]$, $i_2 \equiv k_{02}[H_2][O_2]$, $i_3 \equiv k_{03}[H_2][O_2]$, where $[H_2]$ and $[O_2]$ are the concentrations of molecular hydrogen and oxygen, $[M]$ is the total gas concentration, and the k 's are the specific reaction rate constants for reactions (01) to (03) and (I) to (IV).

During the induction period the concentrations of H, OH, and O build up rapidly, while the concentrations of H_2 and O_2 are scarcely depleted. Hence, the ν 's and i 's in equations (1) to (3) may be taken as constants.

The initiation rates i_1 , i_2 , and i_3 can be eliminated from the differential equations by introducing new variables $C_H \equiv [H] + a_H$, $C_{OH} \equiv [OH] + a_{OH}$, and $C_O \equiv [O] + a_O$, where a_O , a_{OH} , and a_H are constants. If these new variables are substituted into equations (1) to (3), the initiation rates are eliminated by equating the sums of the constant terms to zero:

$$(\nu_2 + \nu_4)a_H - \nu_1 a_{OH} - \nu_3 a_O + i_1 = 0 \quad (4)$$

$$-\nu_2 a_H + \nu_1 a_{OH} - \nu_3 a_O + 2i_3 = 0 \quad (5)$$

$$-\nu_2 a_H + \nu_3 a_O + i_2 = 0 \quad (6)$$

The new differential equations are

$$\frac{dC_H}{dt} = -(\nu_2 + \nu_4)C_H + \nu_1 C_{OH} + \nu_3 C_O \quad (7)$$

$$\frac{dC_{OH}}{dt} = \nu_2 C_H - \nu_1 C_{OH} + \nu_3 C_O \quad (8)$$

$$\frac{dC_O}{dt} = \nu_2 C_H - \nu_3 C_O \quad (9)$$

A particular solution to equations (7) to (9) is (refs. 3 and 4)

$$C_i = A_i \exp(\lambda t), \quad i = H, OH, O \quad (10)$$

Substitution of equations (10) into equations (7) to (9) yields the relations

$$-(\nu_2 + \nu_4 + \lambda)A_H + \nu_1 A_{OH} + \nu_3 A_O = 0 \quad (11)$$

$$\nu_2 A_H - (\nu_1 + \lambda)A_{OH} + \nu_3 A_O = 0 \quad (12)$$

$$\nu_2 A_H - (\nu_3 + \lambda)A_O = 0 \quad (13)$$

A nontrivial solution requires that the determinant of the coefficients of the A_i be zero, which leads to the cubic equation

$$\lambda^3 + (\nu_1 + \nu_2 + \nu_3 + \nu_4)\lambda^2 + [\nu_1\nu_3 + \nu_1\nu_4 + \nu_3\nu_4]\lambda - \nu_1\nu_3(2\nu_2 - \nu_4) = 0 \quad (14)$$

In the chain-branching region ($2\nu_2 > \nu_4$) Descartes' rule of signs indicates that, if the roots of equation (14) are real, there are one positive and two negative roots. It can be shown that the roots are always real provided $k_1 > 2k_3$, which is true for temperatures below about 2280 K, and hence true for the data of Jachimowski and Houghton (ref. 2), which are in the range 1100 to 1900 K.

The general solution to equations (7) to (9) is

$$C_i = A_{1,i} \exp(\lambda_1 t) + A_{2,i} \exp(\lambda_2 t) + A_{3,i} \exp(\lambda_3 t) \quad i = H, OH, O \quad (15)$$

where $\lambda_1, \lambda_2, \lambda_3$ are the roots of equation (14). We are specifically interested in the growth of hydroxyl concentration, which was the quantity monitored in reference 2. If we designate λ_1 as the positive root and λ_2, λ_3 as negative roots, then

$$\begin{aligned} [\text{OH}] &= A_{1,\text{OH}} \exp(\lambda_1 t) + A_{2,\text{OH}} \exp(\lambda_2 t) + A_{3,\text{OH}} \exp(\lambda_3 t) - a_{\text{OH}} \\ &\cong A_{1,\text{OH}} \exp(\lambda_1 t) \end{aligned} \quad (16)$$

The approximation shown is a good one, except very early in the reaction, because a_{OH} is small and the negative exponentials soon die out.

We will now evaluate the coefficient $A_{1,\text{OH}}$. Initially, at $t = 0$, the hydroxyl radical concentration is zero, and equation (16) gives

$$[\text{OH}]_{t=0} = 0 = A_{1,\text{OH}} + A_{2,\text{OH}} + A_{3,\text{OH}} - a_{\text{OH}} \quad (17)$$

One can write similar expressions for hydrogen and oxygen atoms and then use any two of equations (11) to (13) to eliminate the A_H and A_O in favor of A_{OH} . The same result can be obtained more easily by successive differentiation of equations (2) and (16):

$$\left(\frac{d[OH]}{dt}\right)_{t=0} = \lambda_1 A_{1,OH} + \lambda_2 A_{2,OH} + \lambda_3 A_{3,OH} = 2i_3 \quad (18)$$

and

$$\begin{aligned} \frac{d^2[OH]}{dt^2} \Big|_{t=0} &= \lambda_1^2 A_{1,OH} + \lambda_2^2 A_{2,OH} + \lambda_3^2 A_{3,OH} \\ &= \nu_2 \left(\frac{d[H]}{dt}\right)_{t=0} - \nu_1 \left(\frac{d[OH]}{dt}\right)_{t=0} + \nu_3 \left(\frac{d[O]}{dt}\right)_{t=0} \\ &= \nu_2 i_1 - 2\nu_1 i_3 + \nu_3 i_2 \end{aligned} \quad (19)$$

Equations (17) to (19) are solved to obtain

$$A_{1,OH} = \frac{\lambda_2 \lambda_3 a_{OH} - 2i_3(\lambda_2 + \lambda_3) + \nu_2 i_1 + \nu_3 i_2 - 2\nu_1 i_3}{(\lambda_2 - \lambda_1)(\lambda_3 - \lambda_1)} \quad (20)$$

where the constant

$$a_{OH} = \frac{[2\nu_2(i_1 + i_2) + \nu_4(i_2 + 2i_3)]}{\nu_1(2\nu_2 - \nu_4)} \quad (21)$$

is obtained by solving equations (4) to (6). Expressions for $A_{2,OH}$ and $A_{3,OH}$ can be obtained by permitting the indices on λ_1 , λ_2 , and λ_3 in equation (20).

Thus, equations (16), (20), and (21) describe the growth of hydroxyl concentration until such time as the effects of depletion of molecular hydrogen and oxygen are important or until the temperature rises due to atom and radical recombination processes.

ANALYSIS OF EXPERIMENTAL INDUCTION TIMES

The induction times reported by Jachimowski and Houghton (ref. 2) correspond to the time at which the hydroxyl concentration has risen to 10^{-10} mole per cubic centimeter. They also report experimental values of the growth constant. Thus, one can

obtain experimental values of $A_{1,OH}$ from equation (16)

$$A_{1,OH} = 10^{-10} \exp(-\lambda\tau) \quad (22)$$

where λ is the experimental growth constant and τ is the induction time. Rate constants for initiation by reactions (01), (02), and (03) were obtained from equation (20), assuming that only one of the initiation reactions was occurring:

$$k_{01} = \frac{A_{1,OH}}{[H_2][O_2]} (\lambda_2 - \lambda_1)(\lambda_3 - \lambda_1) \left[\frac{2\nu_2\lambda_2\lambda_3}{\nu_1(2\nu_2 - \nu_4)} + \nu_2 \right]^{-1} \quad (23)$$

$$k_{02} = \frac{A_{1,OH}}{[H_2][O_2]} (\lambda_2 - \lambda_1)(\lambda_3 - \lambda_1) \left[\frac{(2\nu_2 + \nu_4)\lambda_2\lambda_3}{\nu_1(2\nu_2 - \nu_4)} + \nu_3 \right]^{-1} \quad (24)$$

$$k_{03} = \frac{2A_{1,OH}}{[H_2][O_2]} (\lambda_2 - \lambda_1)(\lambda_3 - \lambda_1) \left[\frac{\nu_4\lambda_2\lambda_3}{\nu_1(2\nu_2 - \nu_4)} - \lambda_2 - \lambda_3 - \nu_1 \right]^{-1} \quad (25)$$

In these calculations the rate constants for reactions I, II, and III were taken from reference 5. The rate constants for reaction IV was taken from reference 6. And λ_1 , λ_2 , and λ_3 were obtained by solution of equation (14).

These rate constants were least-squares fitted to the Arrhenius equation

$$k = A \exp\left(\frac{-E}{RT}\right) \quad (26)$$

Results are summarized in table I, where the Arrhenius equation parameters and their standard deviations are presented.

DISCUSSION OF RESULTS

In this section the three candidate initiation reactions will be discussed in turn, with an indication as to which are the most likely initiation processes.

The reaction



is a simple abstraction or two center reaction involving the breaking and formation of

one bond. Hence it is the most likely candidate based on steric considerations. However, as Jachimowski and Houghton (ref. 2) have already observed, the activation energy, 24 100 K, is substantially less than the endothermicity of 28 700 K. This amounts to more than three standard deviations in the activation energy and would seem to eliminate reaction (01), barring a temperature dependent systematic error in the experimental data.

Further, in reference 7 the rate of reaction (01) is reported to be

$$k_{01} = 5.5 \times 10^{13} \exp(-29\,100/T) \quad (27)$$

in the range 290 to 800 K, with an uncertainty of a factor of 2.5. Equation (27) predicts a rate at 1100 K which is less than one-thirtieth of the rate at that temperature given by the constants in table I. Thus it is very unlikely that reaction (01) is the initiation process in these mixtures.

The reaction



might be termed a three center reaction inasmuch as new bonds are formed among three atoms. This would seem sterically more probable than the four center reaction



In addition, reaction (02) is less endothermic than reaction (03), although in either case the endothermicities are substantially smaller than the activation energies. Finally, the standard deviations in $\ln k$, $\ln A$, and E/R are slightly smaller for reaction (02) than for either reaction (01) or reaction (03). Initiation in these mixtures may be due to either reaction (02) or reaction (03) (or both), with reaction (02) the slightly more probable candidate.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, November 10, 1972,
502-04.

REFERENCES

1. Ripley, Dennis L.; and Gardiner, W. C., Jr.: Shock-Tube Study of the Hydrogen-Oxygen Reaction. II. Role of Exchange Initiation. *J. Chem. Phys.*, vol. 44, no. 6, Mar. 15, 1966, pp. 2285-2296.
2. Jachimowski, Casimir J.; and Houghton, William M.: Shock-Tube Study of the Initiation Process in the Hydrogen-Oxygen Reaction. *Combustion and Flame*, vol. 17, no. 1, Aug. 1971, pp. 25-30.
3. Brokaw, Richard S.: Analytic Solutions to the Ignition Kinetics of the Hydrogen-Oxygen Reaction. Tenth Symposium (International) on Combustion. Combustion Institute, 1965, pp. 269-277.
4. Brokaw, Richard S.: Ignition Kinetics of the Carbon Monoxide-Oxygen Reaction. Eleventh Symposium (International) on Combustion. Combustion Institute, 1967, pp. 1063-1072.
5. Brabbs, T. A.; Belles, F. E.; and Brokaw, R. S.: Shock Tube Measurements of Specific Reaction Rates in the Branched-Chain H_2 -CO- O_2 System. Thirteenth Symposium (International) on Combustion. Combustion Institute, 1971, pp. 129-135.
6. Baulch, D. L.; Drysdale, D. D.; and Lloyd, A. C.: Critical Evaluation of Rate Data for Homogeneous, Gas-Phase Reactions of Interest in High-Temperature Systems. Rep. 3, Leeds Univ., Apr. 1969, pp. 18-27.
7. Baulch, D. L.; Drysdale, D. D.; Horne, D. G.; and Lloyd, A. C.: Evaluated Kinetic Data for High Temperature Reactions. Vol. 1. Homogeneous Gas Phase Reactions of the H_2 - O_2 System. CRC Press, 1972.

TABLE I. - RATE CONSTANTS OF POSSIBLE HYDROGEN-OXYGEN
INITIATION REACTIONS

	Reaction		
	$\text{H}_2 + \text{O}_2 \xrightarrow{k_{01}} \text{H} + \text{HO}_2$	$\text{H}_2 + \text{O}_2 \xrightarrow{k_{02}} \text{H}_2\text{O} + \text{O}$	$\text{H}_2 + \text{O}_2 \xrightarrow{k_{03}} \text{OH} + \text{OH}$
A, $\text{cm}^3 \text{mole}^{-1} \text{sec}^{-1}$	1.9×10^{13}	4.1×10^{13}	2.3×10^{13}
Activation energy, E/R, K	24 100	25 400	25 200
Standard deviations of -			
ln k	1.22	1.15	1.21
ln A	0.95	0.90	0.94
E/R, K	1310	1250	1310



POSTMASTER: If Undeliverable (Section 158 Postal Manual) Do Not Return

"The aeronautical and space activities of the United States shall be conducted so as to contribute . . . to the expansion of human knowledge of phenomena in the atmosphere and space. The Administration shall provide for the widest practicable and appropriate dissemination of information concerning its activities and the results thereof."

—NATIONAL AERONAUTICS AND SPACE ACT OF 1958

NASA SCIENTIFIC AND TECHNICAL PUBLICATIONS

TECHNICAL REPORTS: Scientific and technical information considered important, complete, and a lasting contribution to existing knowledge.

TECHNICAL NOTES: Information less broad in scope but nevertheless of importance as a contribution to existing knowledge.

TECHNICAL MEMORANDUMS: Information receiving limited distribution because of preliminary data, security classification, or other reasons. Also includes conference proceedings with either limited or unlimited distribution.

CONTRACTOR REPORTS: Scientific and technical information generated under a NASA contract or grant and considered an important contribution to existing knowledge.

TECHNICAL TRANSLATIONS: Information published in a foreign language considered to merit NASA distribution in English.

SPECIAL PUBLICATIONS: Information derived from or of value to NASA activities. Publications include final reports of major projects, monographs, data compilations, handbooks, sourcebooks, and special bibliographies.

TECHNOLOGY UTILIZATION PUBLICATIONS: Information on technology used by NASA that may be of particular interest in commercial and other non-aerospace applications. Publications include Tech Briefs, Technology Utilization Reports and Technology Surveys.

Details on the availability of these publications may be obtained from:

SCIENTIFIC AND TECHNICAL INFORMATION OFFICE

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Washington, D.C. 20546