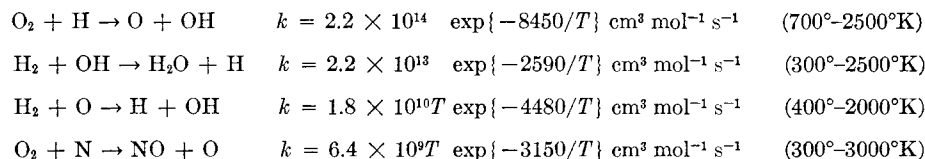


AN ASSESSMENT OF RATE DATA FOR HIGH-TEMPERATURE SYSTEMS

D. L. BAULCH, D. D. DRYSDALE, AND D. G. HORNE

Department of Physical Chemistry, The University of Leeds, Leeds, United Kingdom

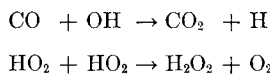
From critical evaluations of the available kinetic data for about 100 reactions of the CO/H₂/O₂ and H₂/N₂/O₂ systems (Refs. 1-3), we conclude that for only four reactions are there sufficient data for their rate constants to be defined with accuracy over a reasonable temperature range. The reactions and their rate constants are:



These four evaluations are considered briefly and the remaining uncertainties in the rate data are discussed.

Modelling of combustion systems, other than the oxidation of hydrogen, is hindered by the lack of good quality data for most of the participating elementary reactions. We consider that improved kinetic data over a range of temperatures are particularly required for rate-controlling reactions, such as the oxidation of alkyl radicals, and for reactions which determine the product distribution, for example the reactions of H, O, and OH with alkanes, alkenes, aldehydes, CO and H₂O₂. Rate data for nearly all the reactions of HO₂ are needed in order to assess the importance of this species in combustion and air pollution. Knowledge of the kinetics of radical dissociation and radical-radical reactions will be necessary as the finer details of combustion are investigated.

We consider that a promising approach to the problem of determining further kinetic data for many of the reactions discussed above would be to obtain reliable data for the rates of certain reference reactions, e.g.



By studying other elementary reactions in competition with reference reactions such as these, good kinetic data could then be obtained for most of the important combustion reactions.

Introduction

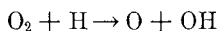
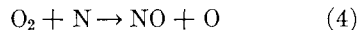
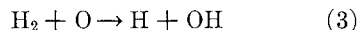
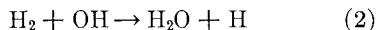
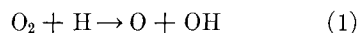
There is a growing need for reliable data on the rates of elementary chemical reactions, stemming from a variety of sources, particularly from the current interest in the modeling of complex chemical systems as encountered in combustion, air pollution, etc. To satisfy this requirement, an

evaluation project was initiated at Leeds University in 1967 and briefed to prepare tables of critically evaluated rate data for reactions of interest in high-temperature systems. To date, about 100 reactions in the CO/H₂/O₂ and H₂/N₂/O₂ systems have been evaluated,¹⁻³ including many of importance in combustion systems. In this paper, we consider the quality of the

kinetic data for these reactions and, more generally, discuss some of the data requirements for other systems, such as modeling of hydrocarbon oxidation.

Current Status of Kinetic Data

Despite the many kinetic studies of reactions in the $\text{CO}/\text{H}_2/\text{O}_2$ and $\text{H}_2/\text{N}_2/\text{O}_2$ systems, we consider that for only four reactions are sufficient reliable data available for their rate constants to be defined with any accuracy (say, $\pm 30\%$) over a reasonable temperature range. They are



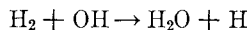
Reaction (1) (Fig. 1) is the chain-branching step in the H_2/O_2 system. The scatter on the data might appear rather large but it is possible to weight the more reliable data and obtain what we consider to be an accurate expression for k_1 in the range $700^\circ\text{--}2500^\circ\text{K}$. For example, the work of Azatyan *et al.*⁴ on the first explosion limit of the H_2/O_2 system in the temperature range $800^\circ\text{--}1000^\circ\text{K}$ utilized Semenov's treatment of the first limit, but more recently Kurzius and Boudart⁵ have shown that deviations from this treatment are important and that low values of k_1 are obtained unless they are taken into account. Consequently, Boudart's work in this temperature range is preferred.

The data are adequately described by the Arrhenius expression,

$$k_1 = 2.2 \times 10^{14} \exp \{-8450/T\} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad 700^\circ\text{--}2500^\circ\text{K}.$$

This expression is suitable only in the range $700^\circ\text{--}2500^\circ\text{K}$; extrapolation to room temperature predicts a value of k_{-1} , using $K = k_f/k_r$, which is low relative to the consensus value of k_{-1} ⁶ (Fig. 2). It is impossible to fit an Arrhenius expression for k_1 to the data on both the forward and reverse reactions without invoking an activation energy for Reaction (1) which is less than the average endothermicity between 300° and 1000°K (70.3 kJ mol^{-1}). Perhaps a non-Arrhenius expression of the form $k = AT^{-n} \times \exp(-B/T)$ could be fitted to the data for k_1 and k_{-1} , but obviously more data between 300°

and 700°K are required to resolve this discrepancy. Reaction (1) is too slow to be measurable below about 700°K , but there appears little reason (in principle at least) why measurements of k_{-1} could not be extended up to (say) 500°K to help resolve this apparent discrepancy and allow k_1 to be defined over the whole temperature range.

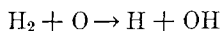


Despite the large scatter in the high-temperature results for this reaction (Fig. 3), there are sufficient good-quality data over a wide temperature range to allow a rate expression to be derived. The high-temperature scatter arises from the fact that Reaction (2) is fast and plays only a minor role in determining the over-all rate of oxidation of H_2 in flames and shock tubes from which these high-temperature data originate. Consequently, the "best fit" between calculated and experimental results is relatively insensitive to the value, or expression, selected for k_2 . On the other hand, the value of k_2 at room temperature is well defined if only those results are accepted which were obtained in simple, homogeneous systems in which it was possible to monitor directly the decay of OH in the presence of H_2 . By combining k_2 at 300°K with what we consider to be the most reliable data at high temperatures, we obtain

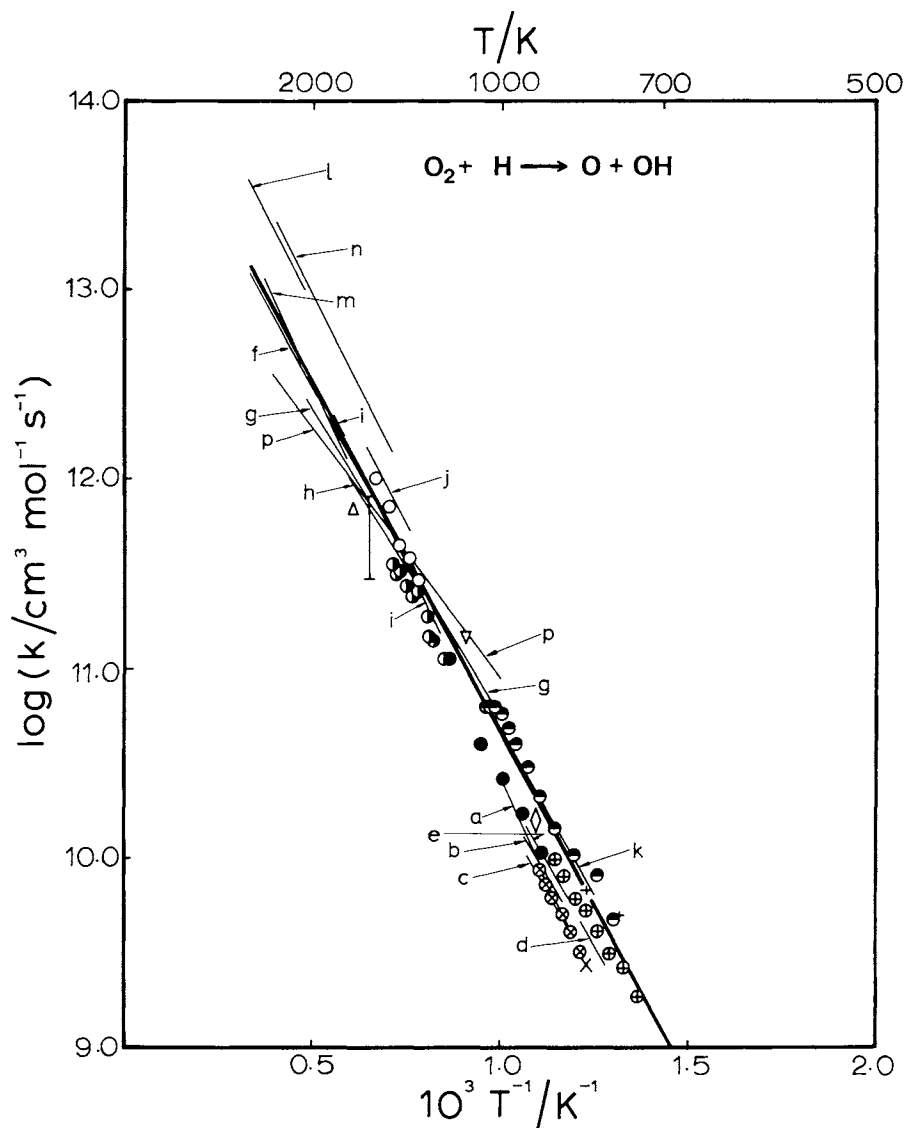
$$k_2 = 2.2 \times 10^{13} \exp \{-2590/T\} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad 300^\circ\text{--}2500^\circ\text{K}.$$

This expression predicts values of k_{-2} in good agreement with the few data available on the reverse reaction.²

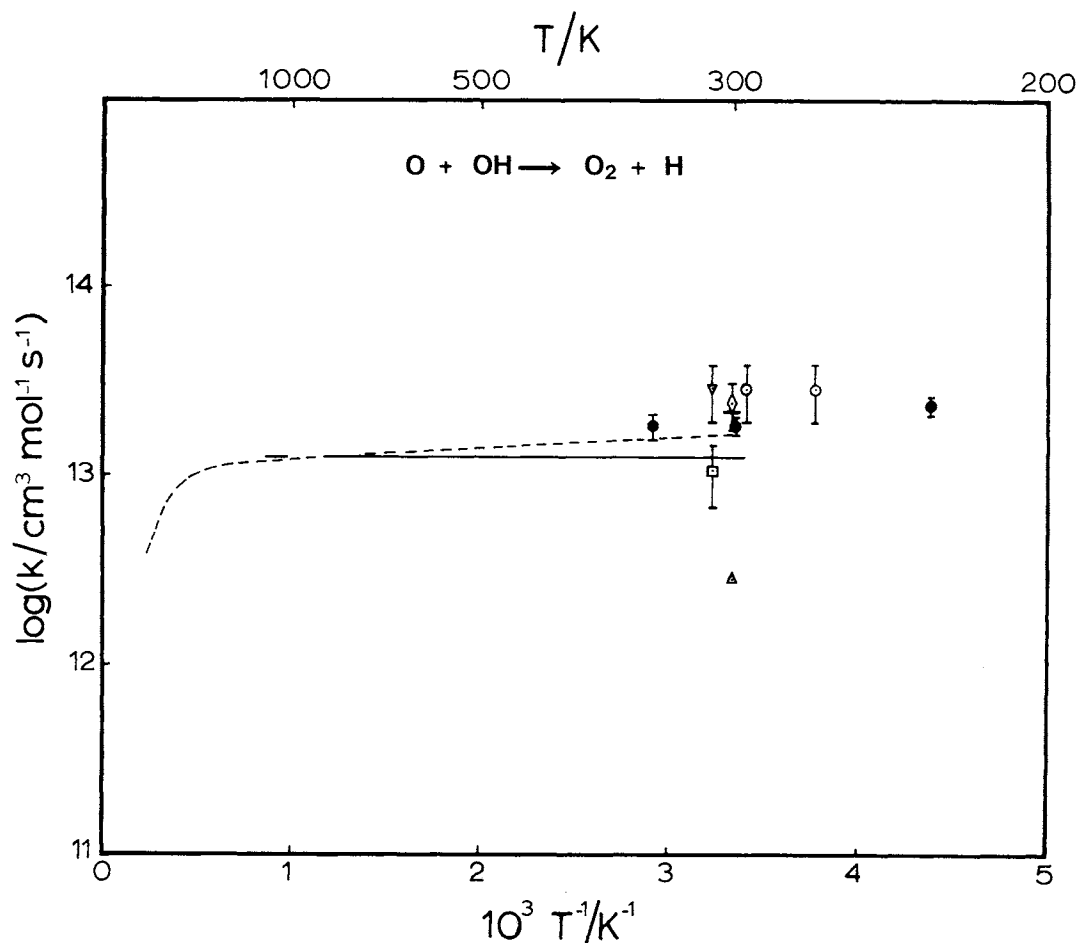
However, some recently published data are at variance with the earlier results on k_2 : the results of Eberius *et al.*⁷ lie below this rate expression by a factor of 1.5, while Greiner's data,⁸ although in agreement at 300°K , suggest a much lower activation energy (17 kJ mol^{-1}) between 300° and 500°K . These data, which appear to suggest a curved Arrhenius plot, have yet to be confirmed. This is another illustration of a temperature gap where experimental data are scarce.



The data on this reaction are good (Fig. 4). Since this reaction is slower than Reaction (2), it contributes more to the control of the over-all rate of the H_2/O_2 reaction and we can expect the high-temperature results to be more precise. The data are best described by a non-Arrhenius

FIG. 1. Rate data for the reaction $\text{O}_2 + \text{H} \rightarrow \text{O} + \text{OH}$.

- | | | | |
|---|--|---|--|
| a | Aganesyan and Nalbandyan (1965) | g | Gutman, Hardwidge, Dougherty, and Lutz (1967) |
| b | Azatyan, Nalbandyan, and Ts'ui (1962) | h | Gutman and Schott (1967) |
| c | Azatyan, Nalbandyan, and Ts'ui (1964) | i | Hirsch and Ryason (1964) |
| d | Azatyan, Romanovich, and Sysoeva (1967) | j | Jenkins, Yumlu, and Spalding (1967) |
| e | Azatyan, Voevodsky, and Nalbandyan (1961) | I | Just and Wagner (1960) |
| ● | Balakhnin, Gershenzon, Kondratiev, and Nalbandyan (1966) | ⊕ | Karmilova, Nalbandyan, and Semenov (1958) |
| × | Baldwin (1956) | k | Kurzius and Boudart (1968) |
| ○ | Brabbs, Belles, and Brokaw (1971) | l | Lovachev (1963) |
| f | Browne, White, and Smookler (1969) | m | Myerson and Watt (1968) |
| ⊗ | Buneva, Kabasheva, and Panfilov (1969) | n | Ripley and Gardiner (1966) |
| ◇ | Dixon-Lewis, Sutton, and Williams (1965) | + | Semenov (1945) |
| ● | Eberius, Hoyermann, and Wagner (1971) | p | Schott (1969) |
| ○ | Fenimore and Jones (1958) | △ | Schott and Kinsey (1958) |
| ▽ | Fenimore and Jones (1959) | — | $k = 2.2 \times 10^{14} \exp \{-8450/T\} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ |

FIG. 2. Rate data for the reaction $\text{O} + \text{OH} \rightarrow \text{O}_2 + \text{H}$.

◇ Breen and Glass (1970)

○ Clyne (1963)

▽ Kaufman (1964)

□ Kaufman and Del Greco (1963)

--- Kurzius and Boudart (1968)

△ Westenberg and de Haas (1965)

● Westenberg, de Haas, and Roscoe (1970)

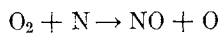
— $k = 1.3 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (based on reverse rate constant and equilibrium data)— $k = 2.3 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (Ref. 2)

expression, i.e., one containing a pre-exponential temperature dependence,

$$k_3 = 1.8 \times 10^{10} T \exp \{-4480/T\} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \\ 400^\circ\text{--}2000^\circ\text{K.}$$

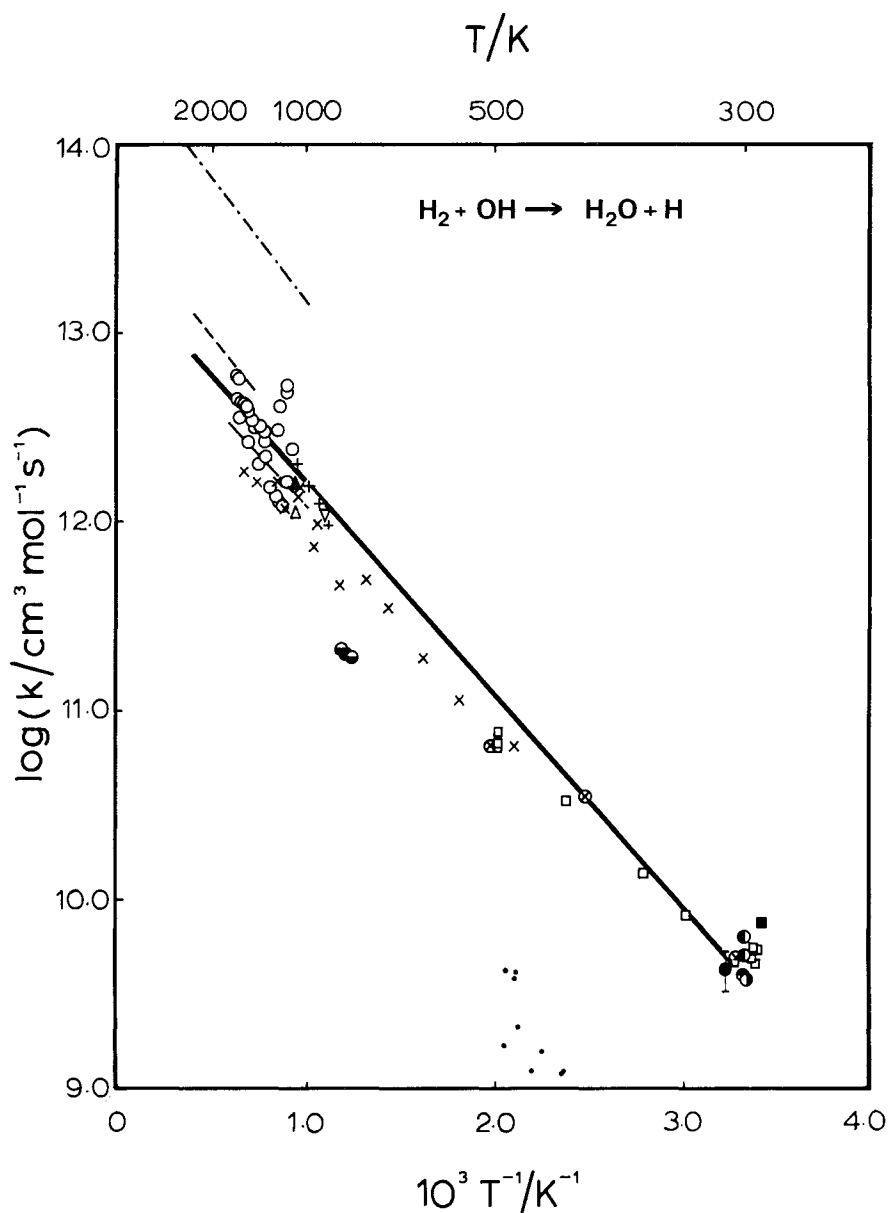
This is a reaction for which it has been possible to extend discharge-flow measurements up to 900°K and the data are continuous over the entire temperature range. One remaining problem is the behavior of k_3 at temperatures below 400°K . Here, the reaction is very slow and difficult to measure, but the existing data seem to indicate that k_3 diverges upwards from our

recommended expression in this range ($300^\circ\text{--}400^\circ\text{K}$). Accurate data are necessary to clarify the situation and establish whether quantum mechanical tunnelling is significant.

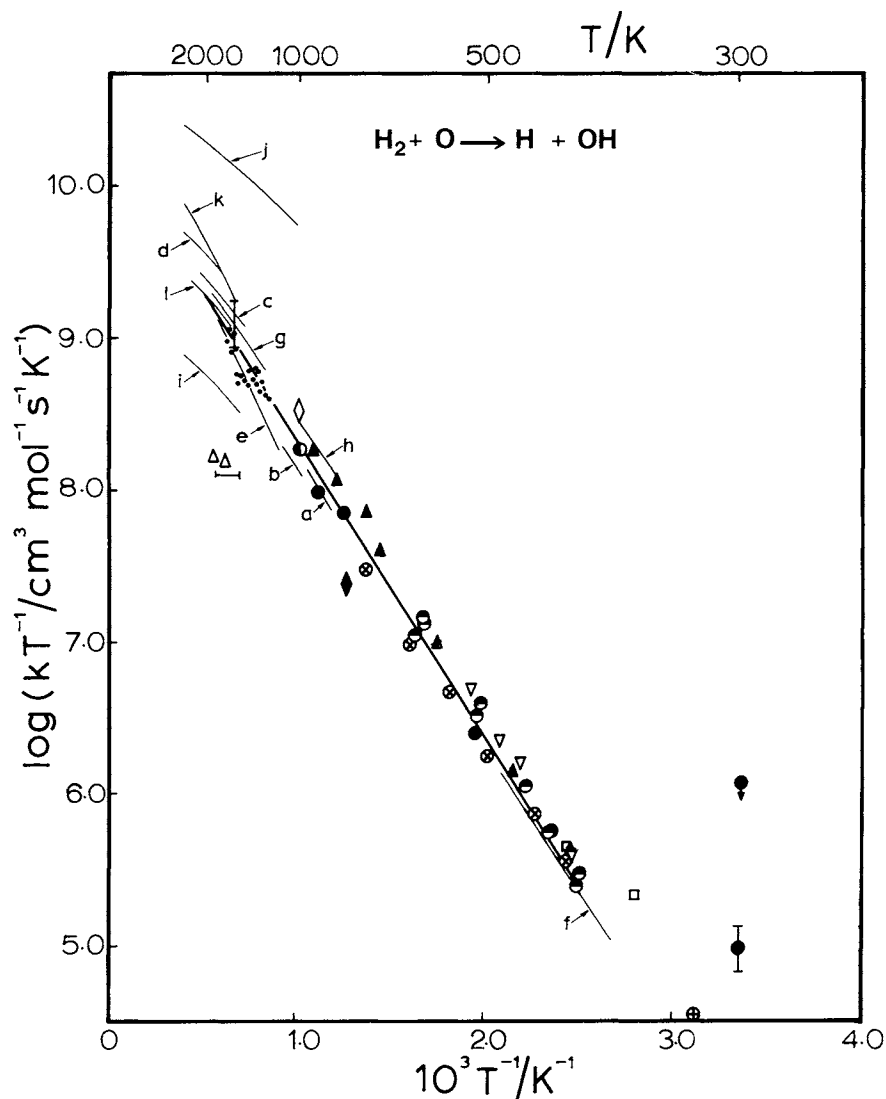


The data for this reaction are in excellent agreement up to 1000°K , and demand description by a non-Arrhenius expression (Fig. 5)

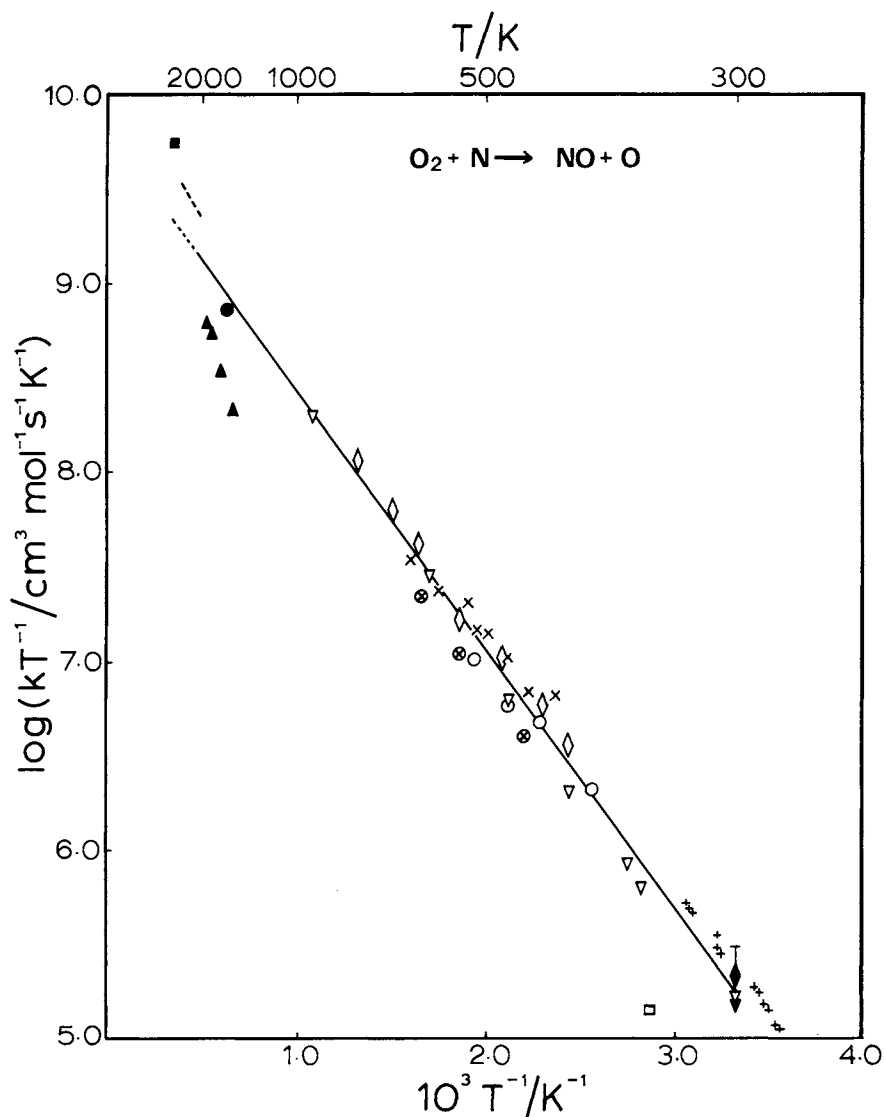
$$k_4 = 6.4 \times 10^9 T \exp \{-3150/T\} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \\ 300^\circ\text{--}3000^\circ\text{K.}$$

FIG. 3. Rate data for the reaction $H_2 + OH \rightarrow H_2O + H$.

- | | |
|--|--|
| • Avramenko and Lorenzo (1950) | ■ Dodonov, Lavrovskaya, and Tal'rose (1969) |
| ● Azatyan, Romanovich, and Sysoeva (1967) | × Eberius, Hoyer mann, and Wagner (1971) |
| + Balakhnin, Gershenzon, Kondratiev, and Nalbandyan (1966) | ● Greiner (1967) |
| ○ Brabbs, Belles, and Brokaw (1971) | □ Greiner (1967) |
| — Browne, Porter, Verlin, and Clark (1969) | ● Kaufman and Del Greco (1963) |
| ▽ Dixon-Lewis, Sutton, and Williams (1965) | --- Ripley and Gardiner (1966) |
| △ Dixon-Lewis, Sutton, and Williams (1965) | -.- Schott (1960) |
| ▲ Dixon-Lewis, Sutton, and Williams (1965) | ● Wise, Ablow, and Sancier (1964) |
| ● Dixon-Lewis, Wilson, and Westenberg (1966) | ⊗ Wong and Belles (1970) |
| | — $k = 2.2 \times 10^{13} \exp \{-2590/T\} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ |

FIG. 4. Rate data for the reaction $\text{H}_2 + \text{O} \rightarrow \text{H} + \text{OH}$.

- | | |
|---|--|
| a Azatyan, Voevodsky, and Nalbandyan (1961) | e Gutman and Schott (1967) |
| ∇ Balakhnin, Egorov, and Kondratiev (1970) | f Hoyer mann, Wagner, and Wolfrum (1967) |
| b Balakhnin, Egorov, Van Tiggelen, Azatyan, Gershenson, and Kondratiev (1968) | g Jachimowski and Houghton (1970) |
| ● Balakhnin, Gershenson, Kondratiev, and Nalbandyan (1966) | h Kaufman (1958) |
| ◆ Baldwin (1956) | i Kurzius (1968) |
| • Brabbs, Belles, and Brokaw (1971) | ◇ Mayer and Schieler (1968) |
| c Browne, White, and Smookler (1968) | i Ripley and Gardiner (1966) |
| ⊕ Campbell and Thrush (1963) | j Schott (1960) |
| ⊗ Clyne and Thrush (1963) | k Schott (1969) |
| d Dean and Kistiakowsky (1970) | ● Schumacher (1930) |
| — Fenimore and Jones (1958) | l Wakefield (1969) |
| △ Fenimore and Jones (1961) | ▲ Westenberg and de Haas (1967) |
| I Gutman, Hardwidge, Dougherty, and Lutz (1967) | □ Westenberg and de Haas (1967) |
| | ● Westenberg and de Haas (1969) |
| | ● Wong and Potter (1965) |
| | — $k = 1.8 \times 10^{10} T \exp \{-4480/T\} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ |

FIG. 5. Rate data for the reaction $\text{O}_2 + \text{N} \rightarrow \text{NO} + \text{O}$.

- | | |
|--|---|
| + Becker, Groth, and Kley (1969) | × Mavroyannis and Winkler (1961) |
| .. Bowman (1971) | I Miyazaki and Takahashi (1968) |
| ◆ Clark and Wayne (1970) | --- Newhall and Shahed (1971) |
| ◇ Clyne and Thrush (1961) | ▲ Vetter (1949) |
| ● Kaufman and Decker (1959) | ⊗ Vlastaras and Winkler (1967) |
| ○ Kistiakowsky and Volpi (1957) | ▼ Westenberg, Roscoe, and de Haas (1970) |
| □ Kretschmer and Petersen (1963) | ▽ Wilson (1967) |
| ■ Livesey, Roberts, and Williams (1971). | — $k = 6.4 \times 10^9 T \exp \{-3150/T\} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ |

The results at $T > 1000^\circ\text{K}$ are scattered, and additional data are required to confirm our evaluation. The choice of expression takes into account data on the reverse reaction at temperatures above 1500°K .

These four reactions illustrate some of the

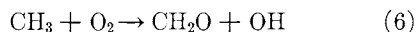
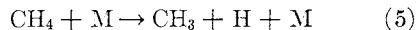
difficulties encountered in evaluating reaction rate data. For example, it is rare for results to be available over the entire range of interest, because each experimental technique usually provides data in only a limited temperature range. Further data are required at intermediate temperatures,

even for such well studied reactions as (1) and (2). It is interesting to note that, in the two cases where results are available over a continuous wide range of temperatures, namely Reactions (3) and (4), the data are inadequately described by simple Arrhenius expressions. As more extensive and better quality data become available, it should be possible to derive non-Arrhenius rate constant expressions for other reactions.

The available results on the other elementary reactions in the $\text{CO}/\text{H}_2/\text{O}_2$ and $\text{H}_2/\text{N}_2/\text{O}_2$ systems are inferior in quality and quantity to those for Reactions (1)–(4). From this point of view, most of these reactions merit further study but some are of greater importance because of their role in systems of practical significance, for example, as rate-determining reactions in complex systems and as reference reactions which are used to determine rate constants by competitive methods.

Modeling of Combustion Systems

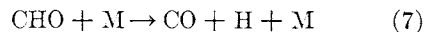
In modeling combustion systems, rate constants are required in order to predict the rates of reactant consumption and the product distribution. At present, only the H_2/O_2 reaction can be modeled with any accuracy⁹; attempts to model the oxidation of even the simplest hydrocarbons are restricted by the lack of data. For example, in investigating the early stages of the CH_4/O_2 reaction, Cooke and Williams¹⁰ found it necessary to consider 34 elementary reactions to predict ignition delays over a range of equivalence ratios. But, of those 34 reactions, reliable rate data are available for only eight or nine, of which five are reactions from the H_2/O_2 system. Of the remainder, some are more important than others, e.g., in controlling the over-all reaction rate. Without rate data for all the reactions, it is difficult to decide their relative importance with certainty. However, a number of authors have shown that both the initiation reaction and the subsequent alkyl radical oxidation step are important in determining the ignition delays.



Accurate rate data are available for Reaction (5) and for analogous reactions which occur in many other oxidation systems. On the other hand, data for Reaction (6) are virtually nonexistent, and there is even doubt about the detailed course of the reaction. For more complex alkyl radicals,

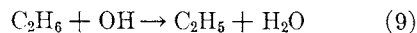
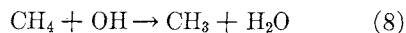
oxidation leads predominantly to olefin formation; the absence of good rate data for these very common and important alkyl radical oxidations is general.

Once data on reactions such as (6) are available, it should be possible to assess the importance of radical decomposition and radical-radical reactions in influencing the over-all oxidation rate. Seery and Bowman¹¹ have suggested that the decomposition Reaction (7) is important in the CH_4/O_2 system, but reliable rate data for this reaction and others like it are lacking.



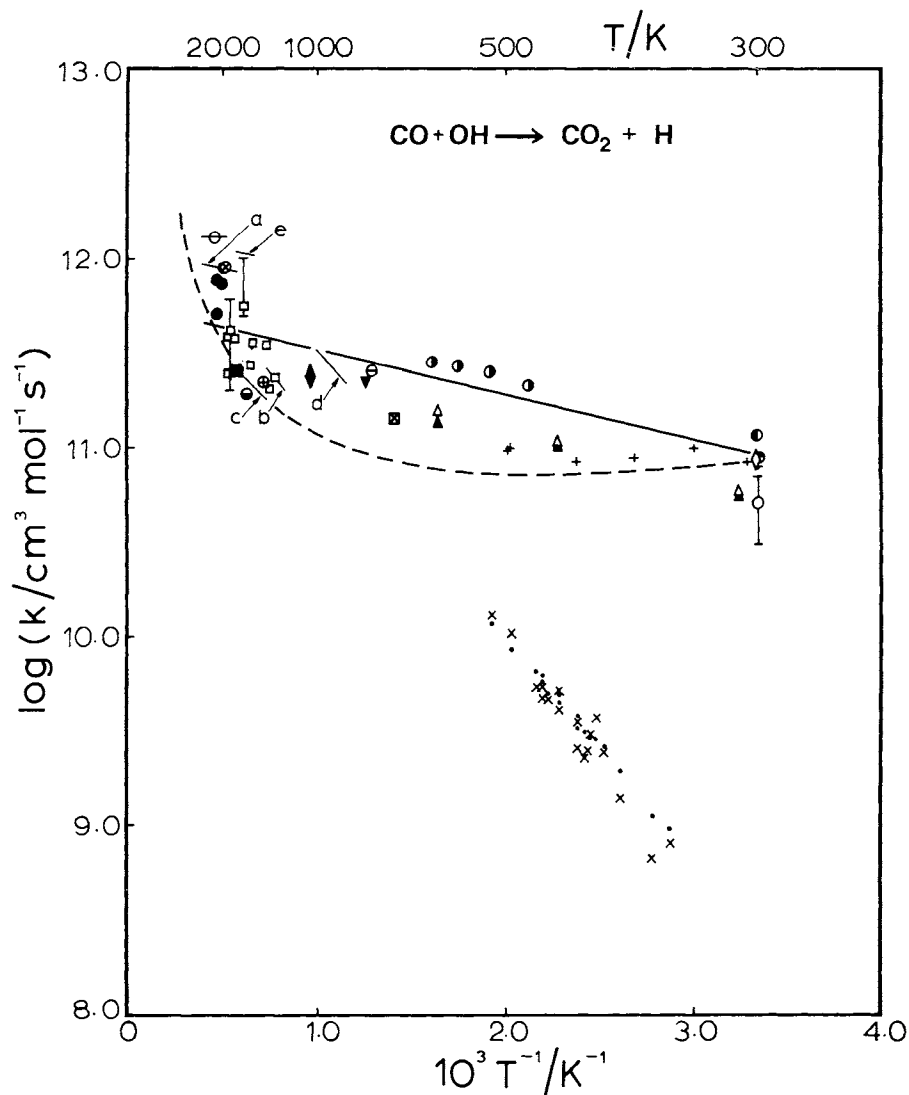
Clearly, radical-radical reactions involving CHO must also be considered in models of this system (e.g., Ref. 10). This type of reaction is very difficult to study experimentally and virtually no data are available. Even in the H_2/O_2 reaction, the data on the important radical-radical reactions (e.g., $\text{H} + \text{OH} + \text{M}$, $\text{HO}_2 + \text{H}$, $\text{HO}_2 + \text{OH}$, etc.) are very poor.

The rates of the propagating steps in the oxidation of hydrocarbons in part determine the relative distribution of products. Generally speaking, such rates are less well characterized than those of the rate-determining reactions, especially at high temperatures. The rate of the main propagating reactions, even for methane and ethane oxidation [Reactions (8) and (9)] are uncertain.¹²



However it seems likely that this situation will improve in the near future, since many of the reactions of H, O, and OH can be studied with existing techniques. Although much room-temperature data already exist for the reactions of these three species with alkanes, alkenes, aldehydes, CO, and H_2O_2 , reliable data are particularly required over a range of temperatures.

Similar data are also required for reactions of HO_2 , but so far the lack of a satisfactory source of this radical has hindered experimental work. The reactions of this species are important in combustion systems and it is also possible that it plays an important role in air pollution. In some circumstances, the atmospheric HO_2 concentration is likely to be relatively high, but until rate data are available it cannot be established whether its reactions, particularly with hydrocarbons, are important.¹³ The disproportionation of HO_2 is discussed later in another context and other

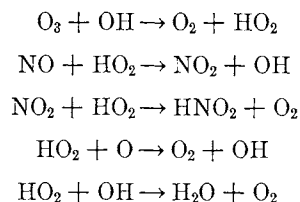
FIG. 6. Rate data for the reaction $\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$.

- | | |
|--|---|
| • Avramenko (1947) | ⊕ Hottel, Williams, Nerheim and Schneider (1965) |
| × Avramenko and Lorenzo (1950) | c Jost, Schecker and Wagner (1965) |
| ⊖ Baldwin and Cowe (1962) | d Kijewski and Troe (1971) |
| ⊖ Baldwin, Jackson, Walker, and Webster (1965) | ● Porter, Clark, Kaskan and Browne (1967) |
| ⊗ Baldwin, Walker, and Webster (1970) | e Singh and Sawyer (1971) |
| □ Brabbs, Belles, and Brokaw (1971) | ● Ung and Back (1964) |
| a Dean and Kistiakowsky (1971) | ■ Wagner (1965) |
| ◆ Dixon-Lewis (1972) | ⊗ Westenberg and Fristrom (1961) |
| ● Dixon-Lewis, Wilson, and Westenberg (1966) | I Westenberg and Fristrom (1965) |
| --- Dryer, Naegeli, and Glassman (1971) | ● Wilson and O'Donovan (1967) |
| b Fenimore and Jones (1963) | ● Wilson, O'Donovan, and Fristrom (1969) |
| ◇ Greiner (1967) | ▲ Wong and Belles (1970) |
| + Greiner (1969) | △ Wong, Potter, and Belles (1967) |
| ▼ Haskell and Read (1969) | — $k = 5.6 \times 10^{11} \exp \{-540/T\} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ |
| ⊗ Heath and Pearson (1967) | |
| ○ Herron (1966) | |

TABLE I
Rate-constant ratios involving k_{14}

$\text{CO} + \text{HO}_2 \rightarrow \text{CO}_2 + \text{OH}$	(16)
$\text{H}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{H}$	(17)
$\text{C}_2\text{H}_6 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{C}_2\text{H}_5$	(18)
$\text{C}_2\text{H}_5 \cdot \text{CHO} + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{C}_2\text{H}_5 \cdot \text{CO}$	(19)
$\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	(14)
Measured: $k_{16}/k_{14}^{1/2}(773^\circ\text{K})$, $k_{17}/k_{14}^{1/2}(773^\circ\text{K})$, $k_{18}/k_{14}^{1/2}(773^\circ\text{K})$, $k_{19}/k_{14}^{1/2}(713^\circ\text{K})$.	
Known: $k_{14} = 2 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 300°K .	

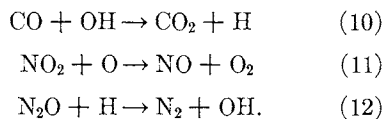
reactions which are of particular interest are¹⁴



for which few kinetic measurements are available.

Reference Reactions

Much information on the rates of elementary reactions has been obtained in the form of rate-constant ratios involving a relatively small number of reference reactions. Examples of such reference reactions for the species OH, O, and H are



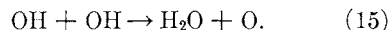
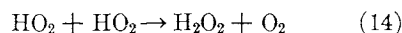
In each reaction, a characteristic product is formed and can be monitored. By using competitive methods, it is possible to deduce relative rate constants which, in turn, allow absolute values of unknown rate constants to be calculated. It is important that the rate constants of these reference reactions be known over a wide temperature range, so that reactions studied in competition can be accurately characterized. Reaction (10), between CO and OH, has been

used both to determine relative rates (e.g., Ref. 15) and to monitor hydroxyl radical concentrations in flames (e.g., Ref. 16). In view of what has already been said about OH radical reactions, it is potentially an extremely valuable reference reaction, but the available data are not sufficiently precise to allow the rate expression to be defined accurately (Fig. 6). It has recently been suggested that k_{10} may show a large deviation from simple Arrhenius behavior.¹⁷ At present, the experimental results are inadequate and further work is needed to resolve this point. Most of the data for Reaction (11) refer to temperatures below 550°K , and Reaction (12) has been the subject of only a few experimental studies. Additional data are required to fully characterize the rates of these reactions over a wide temperature range.

The reference Reactions (10)–(12) are radical-molecule reactions; another class of reference reaction involves radical–radical interactions. The best known of these is the recombination of methyl radicals,



which plays an important role in kinetic studies of methyl radical abstraction reactions. Two other similarly important reactions, but for which the data are sparse, are



The only information available on the reactions of HO_2 is in the form of rate-constant ratios, derived from analyses of complex systems, each ratio containing k_{14} (Table I). These ratios have been obtained in the temperature range 713° – 773°K , but k_{14} is known only at 300°K . No information is available on the activation energy E_{14} , although it is likely to be of the order of 4.2 kJ mol^{-1} (Ref. 2). Reaction (15) is often significant in OH-containing systems. It is important to know its rate constant accurately, both when it is used as a reference reaction, in the same sense as Reactions (13) and (14), and when analyzing OH consumption. At present, its rate constant is known only at room temperature to within about 60%.

The importance of reference reactions, as they are defined above, is obvious. If a group of such reactions could be studied in great detail to determine accurate values of their rate constants, then an extensive research program could be developed to measure the rate constants of many of the reactions occurring in combustion systems.

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COMMENTS

R. W. Walker, University of Hull, England. The authors have suggested, quite correctly, that Reaction (12) is an important reference reaction in gas kinetics. By measuring the relative yield of N_2 and loss of H_2 , when 5%-10% of N_2O is added to slowly reacting mixtures of $H_2 + O_2$, we have determined k_{12}/k_1 as 0.64 ± 0.07 at 500°C. Using the Leeds value of $k_1 = 2.24 \times 10^{11} \exp(-16,800/RT)$ in kcal, liter $mol^{-1} s^{-1}$ units, then $k_{12} = 2.6 \times 10^6$ l $mole^{-1} s^{-1}$, with an accuracy of 30%-40%, due mainly to the uncertainty in the value of k_1 . Combination with independent data on k_{12} gives $A_{12} = 7.6 \times 10^{10}$ l $mol^{-1} s^{-1}$ and $E_{12} = 15.1 \pm 1.0$ kcal mol^{-1} .

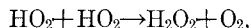
Authors' Reply. We have evaluated Reaction (12), in preparation for a forthcoming publication.¹ Until recently, the expression deduced by Dixon-Lewis *et al.*² [$k_{12} = 3.8 \times 10^{10} \exp(-12,600/RT)$ l $mol^{-1} s^{-1}$] adequately described the existing data in the temperature range 900°-

2500°K. Dr. Walker's new value for k_{12} at 773°K lies a factor of 4 below an extrapolation of this expression, but is in good agreement with data in the range 700°-1100°K, reported at this Symposium by Gehring *et al.*³ Furthermore, Dr. Walker's suggested expression [$k_{12} = 7.6 \times 10^{10} \exp(-15,100/RT)$ l $mol^{-1} s^{-1}$] describes all the available data over the significantly wider range 700°-2500°K, and seems to us to be the most satisfactory one available at the present time.

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J. Troe, Institut de Chimie-Physique de l'EPF-Lausanne, Lausanne, Switzerland. I would like to mention that we have recently¹ determined the value of the rate constant of your reference Reaction (14),



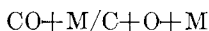
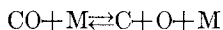
at about 1200°K. We obtained $k_9 = 10^{12.3 \pm 0.3} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, in good agreement with the room-temperature value.

REFERENCE

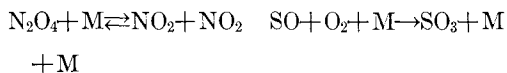
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K. Schofield, General Motors Corp., Goleta, Cal. On the premise that rate-data evaluations are useful, and those of us in the business sincerely hope we are meeting a definite need, I have just completed a critical evaluation of an additional list of gas-phase reactions, under contract from the National Bureau of Standards for their National Standard Reference Data System Program. The following reactions have been included:



(over all)



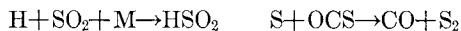
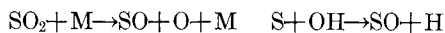
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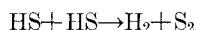
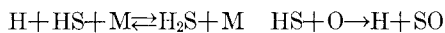
+ M



+ M



+ M



The left-hand column lists reactions which have been thoroughly evaluated in a style very similar to that used by the Leeds group. For completeness, the reactions in the right-hand column also have been included, although very little information is available for most of them. As can be seen, the emphasis is on reactions of sulfur, but several additional reactions were included to round off the coverage now available in other recent critical evaluations.

This report is soon to be printed in the new Journal of Physical and Chemical Reference Data, which is published jointly by the American Chemical Society and the American Institute of Physics for the National Bureau of Standards. Evaluations by Wilson (OH reactions), Lloyd (HO₂ reactions), and future programs of the National Bureau of Standards Kinetics Group also will appear in this journal.