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The chemical kinetics and thermodynamics of sodium species in oxygen-rich hydrogen flames

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Measurements of sodium and OH concentrations in ten oxygen-rich $H_2/O_2/N_2$ flames by respective saturated and low-power laser-induced fluorescence techniques have led to a much improved understanding of the complex flame chemistry of sodium in such oxygen-rich media. Previous interpretations have been shown to be largely incomplete or in error. The one-dimensional flame downstream profiles indicate that the amount of free sodium approximately tracks the decay of H atom and as the flame radicals decay sodium becomes increasingly bound in a molecular form. A detailed kinetic model indicates that the sodium is distributed between NaOH, which is dominant, and NaO_2. Concentrations of NaO are very small and NaH negligible. The actual distribution is controlled by the temperature, the oxygen concentration, and the degree of nonequilibration of the flames' basic free radicals. Na, NaO, NaO_2, and NaOH are all coupled to one another by fast reactions which can rapidly interconvert one to another as flame conditions vary. NaO_2 plays an indispensable role in providing alternate efficient channels by which NaOH can be produced. Its contribution becomes increasingly important at lower temperatures where the flux through the NaO_2 intermediate becomes dominant over that for the direct reaction between Na and H_2O. As a consequence, the ratio of NaOH to Na can become enhanced by up to two orders of magnitude at lower temperatures over what might have been expected from the $Na + H_2O$ direct reaction alone. The dissociation energy $D_0^\circ(\text{Na–O}_2)$ is established to be 39 ± 5 kcal mol^{-1} and the value of the rate constant for the $Na + O_2 + M$ reaction of $2 \times 10^{-28}\, T^{-1}$ cm^6 molecule^{-2} s^{-1} for the flame gases. The sodium distribution within the highest temperature, low-O_2 flame, in which NaOH is dominant and equilibrated, supports a value of $D_0^\circ(\text{Na–OH})$ of 78.9 ± 2 kcal mol^{-1}. The rate constants for several reactions of Na, NaOH, NaO_2, and NaO with flame species have been established approximately. An analysis of the total kinetic scheme shows that the chemical fluxes are carried predominantly by four reactions only. These considered alone, reproduce the data surprisingly well. An analysis of the implications of the corresponding large rate constants for the termolecular reaction of the other alkali metals with oxygen suggests that these will undoubtedly show to varying degrees similar behavior to sodium. Values for the bond dissociation energies of the other alkali dioxides are discussed. It appears that in practical combustion systems, even at low temperatures, the conversion of alkali metals to the corresponding hydroxide will not be kinetically constrained and its concentration will be at or in excess of the expected equilibrium value.

I. INTRODUCTION

Although it is difficult to find a flame chemist who has not studied sodium, the flame chemistry of this ubiquitous atom has not been satisfactorily characterized under many common flame conditions. This is a consequence of our continuing inability to monitor directly molecular sodium species in flames. By interpreting the laser-induced fluorescence measurements of the disappearance profiles of Na and OH in a series of atmospheric pressure, lean (oxygen-rich) $H_2/O_2/N_2$ burnt flame flows of widely varying composition and temperature, we have resolved the question as to the identity of the major sodium species involved, and unraveled the dominant chemistry.

In fuel-rich $H_2/O_2/N_2$ flames, sodium remains essentially in elemental form.[1–3] Small amounts of NaOH formation can be expected via reaction (1):

$$Na + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NaOH + H , \qquad (1)$$

which only become significant at temperatures above about 2300 K depending on the extent of suppression by excess H-atom concentrations.[2] In lean flames the decreased H-atom levels, particularly downstream, might be expected to favor increased NaOH production. However, the presence of O_2 suggests the additional possibility of NaO and NaO_2 formation and a much greater level of kinetic complexity.

Kaskan[4] monitored Na and OH profiles in absorption in a series of lean, atmospheric pressure $H_2/O_2/N_2$ flames at 1400 to 1700 K. He found reaction (1) not balanced and unable to account for the measured decays. Rather, he found the initial Na decay rates proportional to the O_2 concentration and suggested the three-body reaction (2):

$$Na + O_2 + M \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} NaO_2 + M \qquad (2)$$

as the dominant Na oxidation process in these flames. His measured decay rates correspond to a value of about 10^{-33} cm^6 molecule^{-2} s^{-1} for k_2. McEwan and Phillips,[5] in a subsequent study with temperatures ranging from 1380 to 2260 K, also monitored sodium in absorption but utilized the Li/LiOH method to measure H atom.[6] They found also that reaction (1) could not describe the observed Na decay profiles. However at temperatures above 2000 K they concluded that reaction (2) was balanced and NaO_2 was the dominant sodium oxidation product. At lower temperatures it appeared to be too slow to become balanced. From the temperature

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dependence of a plot of $[NaO_2]/[Na][O_2]$ against T^{-1} they calculated a value of 65 kcal mol^{-1} for $D_0^\circ(Na-O_2)$. This value was found to have a computational error and later revised downward[7] to 55.9 kcal mol^{-1}. From the initial Na decay rates in their flames McEwan and Phillips[5] also determined values for k_2 of about $(2-3)\times10^{-33}$ cm^6 molecule^{-2} s^{-1} in reasonable agreement with Kaskan's values.

In an extension of Kaskan's earlier effort, Carabetta and Kaskan[8] examined the sodium oxidation in a series of lean flames as a function of pressure to evaluate the third body dependence of the Na disappearance rates. Over the temperature range from 1420 to 1500 K at pressures from 100 to 1520 Torr they found the initial rates of decay of sodium to be proportional to both O_2 and M concentrations supporting reaction (2) as the dominant sodium removal process.

Recently, Husain and Plane[9] measured Na oxidation rates in a heated cell at 724 and 844 K. They generated atomic Na by flash photolysis of NaI and followed the Na decay in absorption in the presence of He, N_2, and CO_2 baths. They found the Na removal rate described by reaction (2) with a rate constant of about 1.0×10^{-30} cm^6 molecule^{-2} s^{-1} with N_2 as the third body. This is three orders of magnitude faster than the reported measurements for k_2 in the previous flame studies. The unambiguity of these static cell measurements questions the assignment of the measured sodium decay rates in flames to reaction (2). Moreover, the larger value also is supported by earlier flow reactor studies with sodium. Haber and Sachsse[10] obtained 5.5×10^{-30} (Ar), 9.0×10^{-30} (He), and 7.3×10^{-30} (N_2) at 523 K, and Bawn and Evans[11] a value of about 3.5×10^{-30} (533 K, $M=N_2$). Additional measurements on Li,[12] K,[13] and Cs[14] confirm the generality of this magnitude for k_2 among the alkali metals. Obviously some global overall process had been observed in flames that appeared to behave as reaction (2).

Very recently, Jensen and Jones[15] examined the catalysis of flame radical recombination rates by large quantities of sodium in a series of fuel-rich $H_2/O_2/N_2$ flames. They found they could explain the sodium catalzyed H-atom disappearance rates with reaction (1) along with

$$Na + OH + M \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} NaOH + M. \tag{3}$$

A computer fit to their measurements yielded 5×10^{-27} T^{-1} cm^6 molecule^{-2} s^{-1} for k_3. This corresponds to 2.5×10^{-30} cm^6 molecule^{-2} s^{-1} at 2000 K, which is several fold larger than values for k_2 and about 60-fold larger than the value for the corresponding H + OH + M reaction. Jensen[16] then noted that using reactions (1) and (3) he could account approximately for Kaskan's[4] lean flame sodium oxidation rates without recourse to the inclusion of NaO_2. Moreover, it appeared to eliminate the discrepancy existing between values for k_2 measured in flames and at lower temperatures. However, this did require using an unreasonably large value also for k_{-3} with a preexponential term that corresponds at flame temperatures to a collision cross section that is three orders of magnitude larger than expected from gas kinetic theory. This appears to be questionable for such a simple two-body dissociation process and casts doubt on the interpretation. Jensen[16] concluded that for reaction (2) to have a negligible contribution to the flame observations, but still be consistent with Husain and Plane's[9] measurements, would require a value of about 40.6 kcal mol^{-1} for $D_0^\circ(Na-O_2)$, about 15 kcal mol^{-1} below the revised value of Dougherty, McEwan, and Phillips.[7]

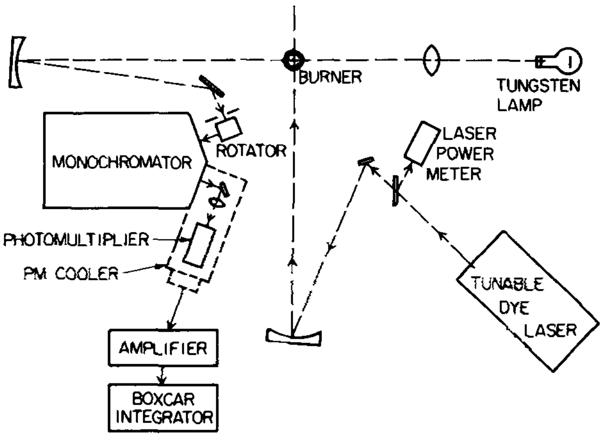

FIG. 1. Experimental arrangement for laser-induced fluorescence and line reversal temperature measurements.

Our more extensive measurements on ten different flames now permit us to resolve all these apparent difficulties. The actual nature of the flame chemistry of sodium in oxidizing stoichiometries has emerged and illustrates clearly the reasons for these discrepancies and fully explains the misinterpretations and errors of the previous flame studies.

II. EXPERIMENTAL CONDITIONS

Most of the experimental system has been described previously[17,18] and will be discussed here only briefly. Flames were stabilized on a 2 cm diam flat-flame Padley–Sugden burner[19] constructed of bundled hypodermic tubing. The burner is manifolded such that separate metered $H_2/O_2/N_2$ flows can be fed to an inner bundle, 1 cm diam, and to the outer bundle. An aerosol of aqueous sodium chloride was added to the central burner core by passage of a few cm^3 s^{-1} of N_2 through an ultrasonic nebulizer.[20] Atomic sodium is rapidly generated in the flame reaction zone and is introduced at a rate to produce concentrations of about 10^{10} cm^{-3} in the hot flame gases. The trace of halogen so added is entirely negligible and need not be considered further.

The optical arrangement is illustrated in Fig. 1. A Nd-YAG (Quanta Ray DCR-PDL-1 with the filled-in beam option) pumped tunable dye laser was used to monitor Na and OH by their induced fluorescence. A calibrated brightness temperature tungsten ribbon lamp was used for sodium line reversal measurements of flame temperatures. The laser beam was passed through the flame and fluorescence sampled at right angles with an $f/5.3$ spherical mirror to match the monochromator aperture. The sampled beam traversed a two-mirror image rotator and the entrace slit of an 0.35 m monochromator (McPherson 218). The detection optics image a section of the horizontal laser beam into the vertical monochromator slit with unit magnification. Thus, using a 50 μm slit that is 0.5 cm high, we detect an 0.5 cm length of beam fluorescence, near flame center, with a flame height resolution on the order of 100 μm. The burner was mounted on a platform that was raised or lowered relative to the system optical axes to obtain time-dependent profiles of properties above the flame front which is positioned close to the burner.

Sodium fluorescence measurements were made by saturating the sodium 589.0 nm ($^2P_{3/2}$—$^2S_{1/2}$) transition and monitoring the closely coupled ($^2P_{1/2}$—$^2S_{1/2}$) fluorescence. By passing the unfocused laser beam through a 5 mm wide aperture, its lower intensity beam edges were removed producing an improved approximation to a "top-hat" radial distribution. This arrangement gave a high degree of saturation, indicated by the fluorescence signal becoming independent of laser power. Moreover, with the short (6 ns) laser pulse there was insufficient time for laser-induced chemistry[18] or ionization of the sodium.[21] At this wavelength multiphoton ionization also appears to be negligible. This fact is confirmed by the observation of an identical sodium downstream profile under either saturation conditions or with a very low power, short pulse laser under constant quenching conditions.[21] In this manner, the saturated relative fluorescence intensities are proportional to the atomic sodium concentrations. Relative concentrations were adequate for this study but are readily converted to absolute values by calibrating the delivery rate of the nebulizer by the curve-of-growth method.[3]

Absolute OH concentrations were measured in fluorescence using our previously established experimental conditions.[17,21,22] The OH($A\,^2\Sigma^+$–$X\,^2\Pi$) (1, 0), $R_1(6)$ transition at 281.14 nm was excited and fluorescence detected at 314.69 nm from the (1, 1) $Q_1(7)$ transition. The doubled output from the dye laser (using an R590 dye) was attenuated to produce fluorescence in the low power regime where fluorescence intensity is proportional to laser power. These relative intensity measurements were rendered quantitative by calibrating against OH fluorescence measurements in a high temperature fully equilibrated fuel-rich $H_2/O_2/N_2$ flame (4/1/2) for which the OH concentration is readily calculated for the measured temperature.

The concentrations of the other flame radicals and trace flame constituents, [H], [O], and [H_2], were calculated assuming balanced chemistry in reactions (4), (5), and (6):

$$H + O_2 \rightleftharpoons OH + O\ , \qquad (4)$$

$$O + H_2 \rightleftharpoons OH + H\ , \qquad (5)$$

$$OH + H_2 \rightleftharpoons H_2O + H\ . \qquad (6)$$

As discussed later, kinetic calculations confirmed the ability of these processes to remain balanced throughout the burnt gases of the flames employed in the study.

A flame matrix was employed to cover a wide range of compositions and temperatures. The flames studied are listed in Table I. These encompass a 750 K temperature range from about 1650 to 2400 K. Distances above the burner were converted to downstream flow times using the measured gas flow rates into the burner corrected for reaction to products, the measured flame temperatures, and the assumption of one-dimensional flow. The one-dimensional behavior of the flow above such bundled tube burners has been verified experimentally.[3] The temperature of individual flames varies but slightly in the 0.25 to 4.0 ms region due to the slight enthalpy release of recombining radicals. In the hot flame gases the two major species H_2O and O_2 have concentrations that vary over the various flames by factors of 1.2 and 24-fold, respectively. In all cases significant departures from equilibrium are apparent for the flame radicals with extensive decay occurring over the first few milliseconds of the burnt gas region. As illustrated later, although OH radical decays are not pronounced in the first 4 ms region, decaying at the most by only about an order of magnitude, those for H, H_2, and O are much more significant.

TABLE I. Experimental flame matrix and characteristics.

$H_2/O_2/N_2$	Temperature (K)	H_2O	O_2	OH
		(molecule cm^{-3})		
0.6 1 1	1906–1929	1.0 (18)	1.2 (18)	3.8 → 0.7 (16)[a]
1 1 2	2066–2100	9.9 (17)	4.8 (17)	3.8 → 1.1 (16)
1 1 3	1667–1730	9.5 (17)	4.7 (17)	3.7 → 0.3 (16)
1.4 1 3	2125–2197	9.8 (17)	2.0 (17)	3.5 → 1.4 (16)
1.4 1 4	1810–1847	9.8 (17)	2.1 (17)	3.6 → 0.5 (16)
1.4 1 5	1654–1669	9.3 (17)	2.0 (17)	3.6 → 0.3 (16)
1.8 1 3	2280–2405	1.1 (18)	5.9 (16)	4.0 → 1.9 (16)
1.8 1 4	2060–2228	9.8 (17)	5.1 (16)	3.6 → 1.4 (16)
1.8 1 5	1825–1916	1.0 (18)	5.3 (16)	3.2 → 0.7 (16)
1.8 1 6	1695–1726	9.6 (17)	5.2 (16)	3.1 → 0.4 (16)

[a] Concentrations, read as 3.8×10^{16} (0.25 ms) decaying to 0.7×10^{16} (4.0 ms).

III. MEASURED CONCENTRATION PROFILES

The concentrations of free sodium have been obtained as a function of distance (time) throughout the burnt gas regions of the ten oxygen-rich flames. The fluorescence intensities have to be corrected solely for the differing flow volumes of each flame because the same rate of addition of sodium is made to each. Resulting concentrations over the first 4 ms region are indicated in Fig. 2. These show the pronounced decays as observed previously.[4,5] The decay shapes vary from flame to flame. This behavior is markedly different from that in fuel-rich hydrogen or acetylene flames where the sodium remains almost totally in its free atomic state with only slight losses due to some NaOH formation and to diffusion. At atmospheric pressure and these temperatures, thermal ionization and diffusion are negligible for our purposes on this time scale. Molecular formation is quite evident, becoming especially pronounced for certain flame compositions. Also, there is the suggestion that each flame starts in the reaction zone region from the same level of totally free atomic sodium which is then subject to its specific rate

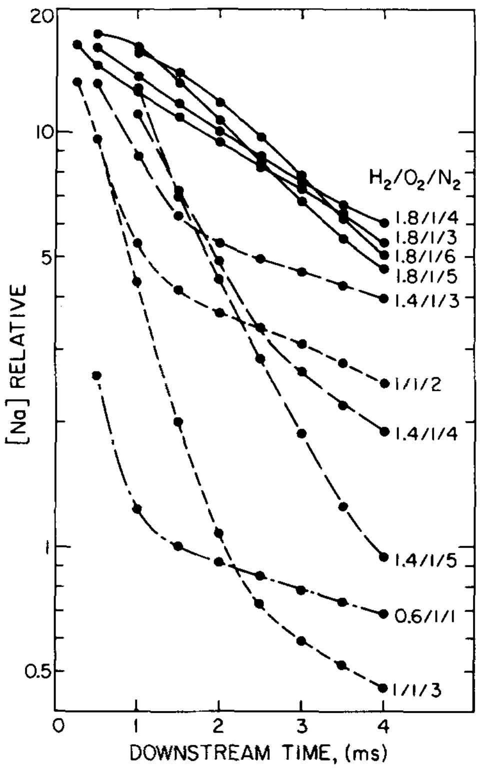

FIG. 2. Measured atomic sodium concentrations in the burnt gases of several oxygen-rich hydrogen flames. Total sodium input approximates to 10^{10} atoms cm^{-3}.

of depletion. From the initial sodium decay rates in Fig. 2, the flame properties in Table I, and assuming reaction (2) describes the system, we would also obtain values for k_2 ranging from 0.8×10^{-33} to 2×10^{-33} cm^6 $molecule^{-2}$ s^{-1} in agreement with previous flame studies.[4,5]

Corresponding OH concentrations in these flames are illustrated in Fig. 3. These are based on our earlier developed technique for quantitative low-power laser-induced fluorescence measurements,[17,21,22] which have been shown to be valid for fuel-rich flames. There appears to be no reason to question the validity of this present series of measurements.

Numerical kinetic calculations concerning the detailed balance among the minor flame species in oxygen-rich flames, namely for OH, H, O, and H_2, as under fuel-rich conditions, indicate that there is sufficient time for these radicals to become interrelated in the burnt gas regions. By considering reactions (4), (5), and (6) it can be shown, in the present time frame, that changes in the concentration of one radical will immediately reflect through to the others. Consequently, from measured OH concentrations it is possible to calculate the corresponding amounts of H, O, and H_2 from the appropriate equilibrium constants and concentrations of H_2O and O_2. These latter two major species are largely unperturbed from their equilibrium concentration values and so can be calculated by an equilibrium code at the measured flame temperature. In this way, the following expressions can be derived:

$$[H]=\frac{K_6[OH]^3}{K_4K_5[O_2][H_2O]}\ ,\quad \frac{K_6}{K_4K_5}=8.83\times10^{-3}\exp(16\,250/T)\ ,$$

$$[O]=\frac{K_6[OH]^2}{K_5[H_2O]}\ ,\quad \frac{K_6}{K_5}=0.105\exp(8\,400/T)\ ,$$

$$[H_2]=\frac{[OH]^2}{K_4K_5[O_2]}\ ,\quad K_4K_5=27.4\exp(-8\,840/T)\ .$$

The relationships between the radicals are markedly different from fuel-rich behavior where $[OH]\propto[H]\propto[O]^{1/2}\propto[O_2]^{1/2}$. This is apparent in the shapes and magnitudes of the [H] decays in Fig. 4 calculated from the corresponding measured OH concentrations of Fig. 3.

For oxygen-rich mixtures it is generally acceptable to assume that the H_2O and O_2 major stable flame species have concentrations much in excess of the other radicals so that their concentrations are unperturbed by the radical nonequilibrium effects. However, as may be noted in Table I, when a stoichiometric H_2/O_2 (2/1) mixture is approached, the concentration of O_2 becomes not too significantly larger than that for OH. Consequently, the question as to whether this assumption remains valid for the H_2/O_2 (1.8/1) series of flames in this study must be considered. Kinetic modeling of the H_2/O_2 flame reactions and an examination of the sensitivity of the equilibrium composition to various conditions have indicated that the assumption does in fact remain valid. It appears that the O_2 levels are in essence buffered by the larger H_2O concentration. Decays in OH concentration do not perturb O_2, which

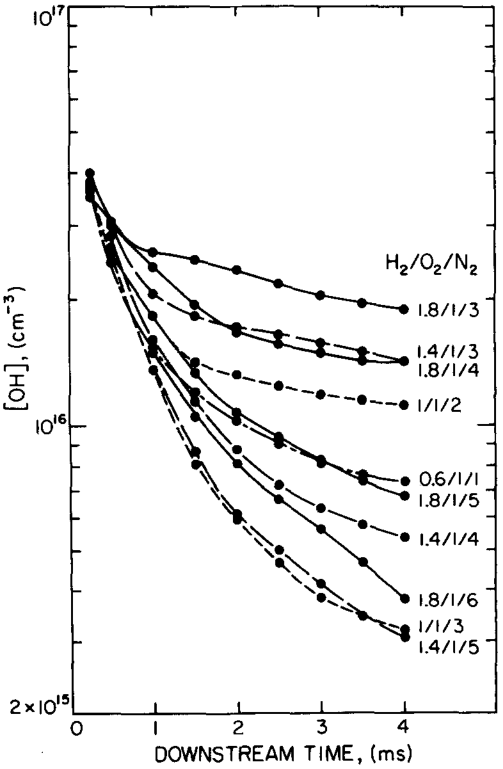

FIG. 3. Experimentally measured OH concentrations in the burnt gases of several oxygen-rich hydrogen flames.

remains close to its equilibrium value, but rather appear as very slight changes in the H_2O concentration which are too small to be noticed. Experimentally, little is to be gained by working close to the stoichiometric mixture on either the fuel-rich or lean side and at some composition these assumptions of constant equilibrium concentrations of the "major" species will break down, so making a characterization of the system much more difficult.

The pronounced decays of [H] in Fig. 4 are remarkably similar to those of sodium in Fig. 2. A comparison of the two plots indicates clearly that there is some approximate correlation between Na and H with the sodium decay tracking that of the H atom. This behavior, also observed in H_2-rich flames in a previous study of the laser-induced chemistry of sodium,[18] suggests the presence of a steady state distribution that is readjusting as the radicals decay. Moreover, this implies also that the initial rates of decay of sodium are not a measure of the progress of the three body $Na + O_2 + M$ reaction as suggested by Kaskan[4] and McEwan and Phillips,[5] and so cannot lead to a meaningful value for its rate constant. If anything, the sodium decay is more closely related to the H-atom decay, which is predominantly controlled by the three-body $H + O_2 + M \rightarrow HO_2 + M$ reaction in these lean flames. Consequently, the observed dependence on O_2 and M concentrations of these initial sodium rates of decay[8] was a consequence of this $H + O_2 + M$ reaction rather than an indication of the occurrence of the $Na + O_2 + M$ reaction. This fact signifies the care required in interpreting such flame profiles and emphasizes the need to measure as many species in as wide a range of differing flame compositions and temperatures as is possible.

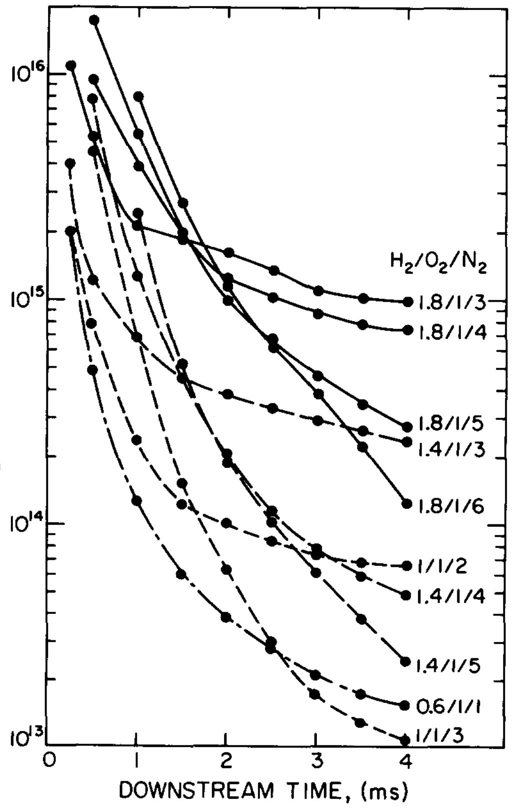

FIG. 4. H-atom concentrations calculated from the measured OH concentrations.

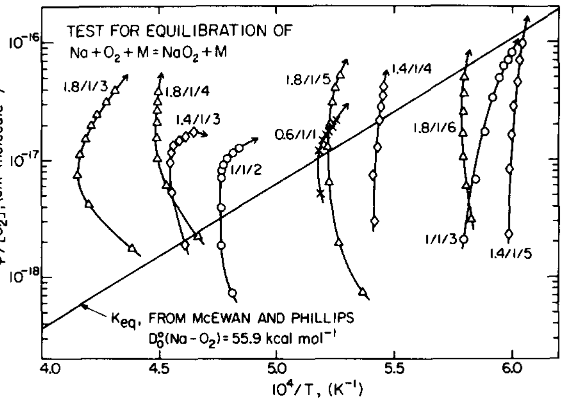

FIG. 5. Equilibrium constant plot testing for the predominant molecular formation of NaO_2 via the $Na + O_2 + M \rightleftharpoons NaO_2 + M$ reaction. For each flame, marked by its $H_2/O_2/N_2$ ratios, individual points refer to downstream times of 0.25, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0 ms, time increasing in the direction of the arrow. ϕ = [bound sodium]/[free sodium].

IV. PRELIMINARY KINETIC MODELING

McEwan and Phillips[5] assumed the predominance of NaO_2 and its equilibration via reaction (2) in their brief study of this system. Using our more extensive data base we have tested this hypothesis by calculating the equilibrium constant of this reaction at points throughout each of the flames assuming that loss of sodium is due totally to NaO_2 formation. The result is indicated in Fig. 5. ϕ represents the ratio of bound to free sodium which can be calculated from the experimental data. The expected straight line corresponding to their $D_0^\circ(Na-O_2)$ value[7] of 55.9 kcal mol^{-1} is not confirmed. Moreover, the departures in each flame clearly indicate that flame radicals are involved. A similar test of the dominance of NaOH via the balanced reaction (1) is illustrated in Fig. 6. The ordinate, $\phi[OH]^3/[H_2O]^2[O_2]$,

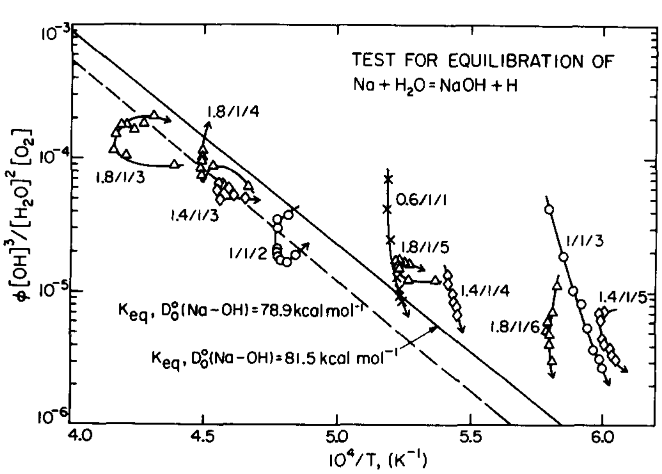

FIG. 6. Equilibrium constant plot testing for the predominant molecular formation of NaOH via the $Na + H_2O \rightleftharpoons NaOH + H$ reaction. For each flame individual points correspond to those of Fig. 5.

TABLE II. Potential reactions of Na, NaO, NaO_2, and NaOH in H_2/O_2 flames.

Reaction[e]		$\Delta H^\circ_{2000\ K}$[d] (kcal mol^{-1})	Rate constants, cm^3 molecule^{-1} s^{-1} [c] Forward reaction	Reverse reaction
(1), (−1)	$Na + H_2O = NaOH + H$	$+44.4$	$3\times10^{-11}T^{1/2}\exp(-44\,400/RT)^b$	$1\times10^{-12}T^{1/2\,b}$
(2), (−2)	$Na + O_2 + M = NaO_2 + M$	$-(0.7 + D^\circ_0)$	$2\times10^{-28}T^{-1}$	$2\times10^{-11}T^{1/2}\exp[-(700+0.9D^\circ_0)/RT]^{a,b}$
(3), (−3)	$Na + OH + M = NaOH + M$	-78.7	$\leq 7\times10^{-29}T^{-1}$	$\leq 2\times10^{-11}T^{1/2}\exp(-78\,700/RT)^b$
(7), (−7)	$Na + HO_2 = NaO_2 + H$	$+(54.0 - D^\circ_0)$	...	$\simeq 2\times10^{-12}T^{1/2\,b}$
(8), (−8)	$Na + OH = NaO + H$	$+43.8$	$\leq 2\times10^{-11}T^{1/2}\exp(-43\,800/RT)^b$	$\leq 2\times10^{-12}T^{1/2\,b}$
(9), (−9)	$Na + HO_2 = NaO + OH$	$+7.6$	...	$\leq 3\times10^{-13}T^{1/2\,b}$
(10), (−10)	$Na + O_2 = NaO + O$	$+59.3$	$\leq 2\times10^{-11}T^{1/2}\exp(-59\,300/RT)^b$	$\leq 2\times10^{-13}T^{1/2\,b}$
(11), (−11)	$Na + HO_2 = NaOH + O$	-8.4	...	$\leq 4\times10^{-15}T^{1/2}\exp(-8400/RT)$
(12), (−12)	$NaO_2 + H = NaO + OH$	$-(46.5 - D^\circ_0)$	$7\times10^{-12}T^{1/2}$	$1\times10^{-12}T^{1/2}\exp[-(46\,500 - D^\circ_0)/RT]$
(13), (−13)	$NaO_2 + O = NaO + O_2$	$-(62.0 - D^\circ_0)$	$1\times10^{-13}T^{1/2}$	$2\times10^{-13}T^{1/2}\exp[-(62\,000 - D^\circ_0)/RT]$
(14), (−14)	$NaO_2 + OH = NaO + HO_2$	$+(D^\circ_0 - 10.3)$	$\leq 2\times10^{-13}T^{1/2}\exp[-(D^\circ_0 - 10\,250)/RT]$	...
(15), (−15)	$NaO_2 + H = NaOH + O$	$-(62.5 - D^\circ_0)$	$\leq 2\times10^{-13}T^{1/2}$	$\leq 8\times10^{-14}T^{1/2}\exp[-(62\,500 - D^\circ_0)/RT]$
(16), (−16)	$NaO_2 + OH = NaOH + O_2$	$-(78.0 - D^\circ_0)$	$3\times10^{-14}T^{1/2}$	$2\times10^{-13}T^{1/2}\exp[-(78\,000 - D^\circ_0)/RT]$
(17), (−17)	$NaOH + OH = NaO + H_2O$	-0.6	$\leq 1\times10^{-11}T^{1/2\,b}$	$\leq 3\times10^{-11}T^{1/2}\exp(-620/RT)^b$
(18), (−18)	$NaOH + H = NaO + H_2$	$+14.0$	$\leq 7\times10^{-11}T^{1/2}\exp(-14\,000/RT)^b$	$\leq 5\times10^{-11}T^{1/2\,b}$
(19), (−19)	$NaOH + O = NaO + OH$	$+16.0$	$\leq 2\times10^{-11}T^{1/2}\exp(-16\,000/RT)^b$	$\leq 6\times10^{-12}T^{1/2\,b}$
(20), (−20)	$NaOH + O_2 = NaO + HO_2$	$+67.8$	$\leq 2\times10^{-11}T^{1/2}\exp(-67\,800/RT)^b$	...

[a] Activation energy assumed to be $0.9\times D^\circ_0(Na-O_2)$ (see the text).

[b] Preexponential factors corresponding to a gas kinetic hard sphere collision frequency, modified where necessary for the bimolecular reactions to be compatible with the equilibrium constant.

[c] Rate constants for reactions (2) and (3) have units of cm^6 molecule^{-2} s^{-1}. D°_0 represents $D^\circ_0(Na-O_2)$: Optimum fit for 39.0 kcal mol^{-1}. $R = 1.9872$ cal deg^{-1} mol^{-1}.

[d] Reference 23. $\Delta H_f(NaOH)$ (Ref. 24), $\Delta H_f(NaO)$ (Ref. 25), $(H_{2000} - H^\circ_0)$ $NaO_2 = 25.5$ kcal mol^{-1} (calculated, see the text).

[e] Reaction number: + forward reaction, − reverse reaction.

consists of measured parameters and the easily calculated major product concentrations for H_2O and O_2. It is equivalent to the concentration ratio $[NaOH][H]/[Na][H_2O]$ and results from the substitution of ϕ for $[NaOH]/[Na]$ and $[OH]^3/[H_2O][O_2]$ for $[H]$. The expected equilibrium constant, $K_1K_4K_5/K_6$, calculated from the JANAF tables[23] and based on a $D^\circ_0(Na-OH)$ value of 81.5 kcal mol^{-1}, is drawn as the solid line in Fig. 6. A small uncertainty remains in the literature concerning the value of $D^\circ_0(Na-OH)$. The JANAF thermochemical table[23] was calculated in December 1970. A more recent experimental measure[24] obtained 78.9 ± 2.0 kcal mol^{-1}. Although this appears to be a small difference, it implies a 68% change in the NaOH/Na ratio for the equilibration of reaction (1) at 2400 K. The expected equilibrium constant based on the lower value for $D^\circ_0(Na-OH)$ is drawn as the dotted line on Fig. 6. Behavior above and below 2000 K appears to be significantly different. At the higher temperatures an approximate relationship does appear reasonable. Moreover, the agreement between the experimental data and the equilibrium expectation appears better for the lower value of the NaOH bond strength. However, below 2000 K departures are such as to suggest the participation again of supplemental chemistry that involves the radical species whose concentrations significantly vary in each flame with time. The system is obviously more complex than previously considered and a more complete kinetic modeling is necessary.

Such a model has been analyzed for all the possible reactions of Na, NaO, NaO_2, and NaOH that can occur in an H_2/O_2 flame environment. These are listed in Table II and schematically illustrated in Fig. 7. An examination of the possible reactions of NaH indicates that it will be negligible in oxygen-rich flames and need not be considered. Also, due to the very low concentrations of sodium, molecules containing more than one atom of sodium cannot form. Although $H + O_2 + M$ is the dominant radical decay process in these lean flames, HO_2 steady state levels are negligible and it was not included as a reactant in the scheme. No reliable value existed for $\Delta H_f(NaO_2)$ and the effect of this variable on the respective reaction enthalpies is indicated. At first sight, the possibility of interpreting such a large

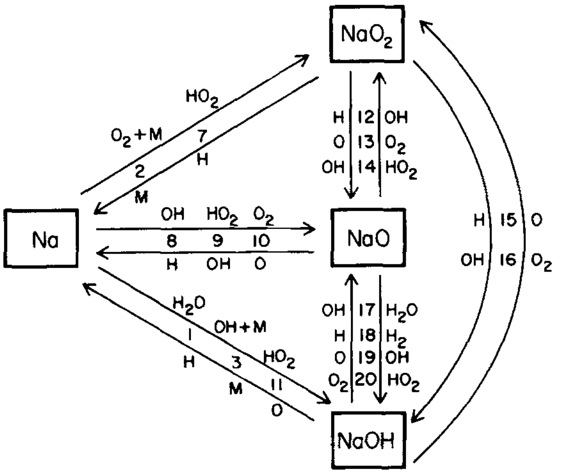

FIG. 7. Reaction scheme including all the possible reactions listed in Table II that couple Na, NaO_2, NaO, and NaOH. Specific reactants involved are indicated on the connecting arrows. Reaction number refers to Table II.

number of reactions seemed questionable, especially as rate constant values were known only for k_2[9] at about 800 K and approximately established for k_1 and k_{-1}.[18] Comparisons of the other interactions with their analogous reactions where H replaces Na showed that it was not unreasonable to expect reactions (9), (10), (12), (13), (16), and (18)–(20) to have pre-exponential rate constant factors that to a first approximation might not differ significantly from their hard sphere gas kinetic collision frequencies. Of the other reactions, numbers (1), (7), (8), (14), and (17) have no such corresponding analog comparisons due to their symmetrical atom interchanges. Reactions (11) and (15) are each analogous to the least favored branching path of the three possible channels for the $H + HO_2$ reaction. Recent branching ratio measurements for this,[26] suggest that these could have pre-exponential rate constant terms that are a factor of 4×10^{-3} below their maximum gas kinetic frequency value. Reaction (3) has been suggested by Jensen and Jones[15] as being a very efficient reaction and have estimated its rate constant.

Initially, all reaction rate constants other than k_2, k_3, k_{11}, k_{-11}, k_{15}, k_{-15} were set at their gas kinetic collision frequency values with appropriate exponent terms, equal to reaction endothermicity, and with the exception of the termolecular reactions (2) and (3) were modified whereever necessary to be compatible with the reaction equilibrium constants. Values for k_{-2} and k_{-3} also were set at this limit as there appears to be no justification for substantially enhancing the cross sections for such simple bimolecular collision processes. As will be discussed later, the nature of the dissociation reaction (−2) is such that its activation energy will be depressed to some extent below the reaction enthalpy. A value of 90% of $D_0^\circ(Na-O_2)$ is assumed and corrected to 2000 K. This is indicated in Table II. The activation energies for all the other endothermic reactions were assumed to equal the reaction enthalpy.

An analysis of the time constants for the reaction scheme confirmed that the ms time frame would provide a sufficient time for the establishment of a steady state distribution for such a scheme. This is compatible with the experimentally observed rapid tracking of the Na and H-atom decays as indicated in Figs. 2 and 4. Consequently, a preliminary computer analysis of the steady state model was examined to establish the feasibility of interpreting the observed sodium decay profiles in a meaningful way with such a large body of uncertain rate constant values. This model assumes that the kinetics are sufficiently rapid that a steady state distribution is maintained throughout the burnt gases. Consequently, the net reactive flux producing and removing each of the species is zero. Taking the rate equations in turn for fluxes involving either NaO_2, NaO, or NaOH together with the sodium mass balance equation

$$[Na]_{tot} = [Na] + [NaO] + [NaO_2] + [NaOH]$$

provides the necessary number of equations to solve for the concentrations of each species. In this way, using this initial set of rate constants together with the measured flame concentrations and temperatures, the predicted molecular distribution, and reactive fluxes were calculated for the various branches of Fig. 7. It was apparent immediately that exact rate constant data are irrelevant for more than half the reactions listed due to their minor roles. Also, the kinetic fluxes connecting NaO to NaOH are dominated by reaction (17) but are significant also for reactions (18) and (19). These are so large that even if some of their rate constants are degraded by one to two orders of magnitude it is clear that the concentrations of NaO and NaOH will manage to remain coupled with their concentration ratios locked very closely to that specified by the balance of either of these reactions [(17), (18), or (19)]. Actual NaO concentrations are small, falling in the range of 0.1% to 1.5% of the total bound sodium in these flames. As a result, the flux of reactions (8), (9), and (10) coupling NaO to Na is very small. Consequently, specific rate constant values for any of the reactions (8)–(10), and (17)–(20) are irrelevant for describing the observed distribution.

The implications of Husain and Plane's large value[9] for k_2 became particularly apparent in these initial calculations. It predicts a severe and very rapid depletion of Na that is too large to compensate for unless $D_0^\circ(Na-O_2)$ is drastically reduced from its previously reported value of 55.9 kcal mol^{-1}. Moreover, it is clearly incompatible with Jensen and Jones' large value[15] for k_3 which serves only to deplete sodium even more so. The depletion rates of sodium via reactions (1) and (2) alone are such as to pose severe difficulties on the system's ability to regenerate free sodium and any additional depletion must invoke unreasonable rates for regeneration steps. Due to the small concentrations of NaO, sodium regeneration depends almost entirely on the thermal dissociation of NaO_2, via reaction (−2), and by the reduction of NaOH by H-atom, reaction (−1).

Any attempt to model this system based on assuming the predominance of Na/NaO_2 or Na/NaOH chemistry alone could not reproduce the data with any degree of satisfaction. It was clear that the coupling between NaO_2 and NaOH, either directly or via NaO, plays an important role for some flame conditions and cannot be ignored.

These initial analyses suggested that kinetic parameters for only a few reactions from the initial set of 17 are important. A more detailed examination considering parametric variations of their specific rate coefficients appeared justified.

V. OPTIMUM COMPUTER FIT TO THE DATA

By adjusting the value of $D_0^\circ(Na-O_2)$ and the rate constant values for reactions (12)–(14) and (16) and to a lesser extent those for reactions (1)–(3), a least squares fit program measured the degree of fit between the model predictions and the experimental sodium decays of Fig. 2. As indicated, the model is insensitive to the specific values of the other reaction rate constants in the model.

For the single hottest flame, $H_2/O_2/N_2$ (1.8/1/3) it became apparent that the calculated distribution was independent of all these variables with the exception of reaction (1). The flame temperature was sufficiently high, and the O_2 concentration small, such that in the 1 to 4 ms burnt gas region this reaction was dominant and equilibrated. As a result, it provided a measure of the equilibrium constant for reaction (1). As was indicated earlier in Fig. 6, in the preliminary examination of the equilibration and dominance of reaction (1), an apparent closer approach to equilibrium was noted with the lower value of the NaOH bond strength. This sensitivity to bond strength was apparent in the model fits to the experimental data, particularly in the fit to the $H_2/O_2/N_2$ (1.8/1/3) flame. Although our data were not sufficiently accurate to establish an independent measure, the significant improvement that is observed using the smaller value tends to confirm that $D_0^\circ(\mathrm{Na-OH}) \leq 80$ kcal mol^{-1}.

Using the value of 78.9 kcal mol^{-1} in those rate constants affected, a systematic variation of the prescribed variables fitting the whole set of flame data indicated a particular sensitivity to the value of k_2 and $D_0^\circ(\mathrm{Na-O_2})$. The best fit value for k_2 is indicated in Table II and is probably accurate to within a factor of 2. It is four times smaller than predicted by extrapolating the 800 K measurement of Husain and Plane[9] for $M = N_2$ using a T^{-1} dependence. The activation energy for k_{-2} is about 36 ± 5 kcal mol^{-1}. Assuming that this is depressed about 10% below the reaction enthalpy, this indicates that the bond strength $D_0^\circ(\mathrm{Na-O_2})$ is about 39 ± 5 kcal mol^{-1}.

It is interesting to note that the ratio of k_2 to k_{-2} produces a value for the equilibrium constant that is about eight-fold larger than expected from that calculated theoretically. The latter is not particularly sensitive to shape and molecular frequencies. Based on a 105° bent structure with r_e (Na–O) 0.20 nm, r_e(O–O) 0.13 nm,[25] and vibrational frequencies of 1094, 391, and 333 cm^{-1},[27,28] the equilibrium constant for reaction (2) in the 1400–2400 K range is given by $1.0\times 10^{-26}\, T^{0.85} \exp(+D_0^\circ/RT)$ cm^3 molecule^{-1}. The dynamics of the termolecular reactions of the alkali metals with O_2 appear more complex than expected. Alexander[29] has indicated that NaO_2 is ionic and correlates to Na^+ and O_2^- dissociation products for which he calculates a dissociation energy of about 145 kcal mol^{-1}. By assuming that the bond dissociation energy of an ionic NaO–O is the same as that for O_2^-, a thermochemical cycle provides an approximate estimate for $D_0^\circ(\mathrm{Na-O_2})$ of 36 kcal mol^{-1}. Comparisons between the bond strength of Na–O and H–O, and Na–OH with H–OH suggest that the values for $H-O_2$ would be consistent with an estimate of about 30–34 kcal mol^{-1} for $D_0^\circ(\mathrm{Na-O_2})$.

The recombination of Na with O_2 must produce NaO_2^* initially which then converts nonadiabatically to the ground electronic state. The value of k_2 reflects a very efficient collisional interaction. Thermal dissociation reactions are characterized by activation energies that are smaller than the dissociation energy.[30,31] Similar type polyatomics such as O_3, H_2O_2, and HO_2 show thermal dissociation activation energies of 87%, 88%, and 84% of the reaction enthalpy at the highest temperatures measured.[32,33] Tabulations for other polyatomics similarly indicate depressions of up to a maximum of about 15%.[31] However, in order for the measured activation energy of k_{-2} to relate to k_2 via the calculated equilibrium constant it would be necessary for $D_0^\circ(\mathrm{Na-O_2})$ to be about 12 kcal mol^{-1} larger than the activation energy. Such a 25% depression would appear unacceptable. A more reasonable explanation appears to be that reaction (2) and (−2) are not truly represented by the equation listed in Table II. The initial intermediate products undoubtedly involve various NaO_2^* states. The complexities of these termolecular dissociation/recombination reactions are such that the use of an equilibrium constant to convert one reaction rate constant to the other should be avoided unless the relationship is known to be valid. In the present case this connection between the measured k_2 and k_{-2} values appears not to hold true.

For the reactions coupling NaO_2 to NaOH, less sensitivity was shown in the fitting to their exact rate constant values. However, it was necessary to reduce their magnitudes from the gas kinetic collision frequency estimates used initially otherwise the flux towards NaOH production was too large and eliminated the importance of the thermal dissociation of NaO_2. Moreover, it appeared necessary to reduce k_{13}, k_{14}, and k_{16} to a point where reaction (12) became dominant. k_{12} at this point had a value corresponding to a ten-fold reduction from the initial gas kinetic collision frequency estimate. k_{13}, k_{14}, and k_{16} values reflect a 100-fold reduction. These are indicated in Table II as reduced preexponential factors. The attenuations might result in part also from the presence of activation energies. A factor of 10 alternatively might reflect the presence of a 9 kcal mol^{-1} activation term and a factor of 100, an 18 kcal mol^{-1} added exponent. There was insufficient sensitivity to isolate any temperature dependence on these rate constants. They must be regarded as approximate estimates of the rate constants at temperatures about 2000 K. The final set of values are listed in Table II. Upper limit values refer to those reactions to which the model is insensitive due to their noncontrolling roles. Reaction (−1) is critical for regenerating sodium and its rate constant reflects a normal gas kinetic cross section. As indicated already, reaction (3), the three body recombination of Na + OH + M must make a negligible contribution. For this to be the case its rate constant must be similar in magnitude to that for H + OH + M rather than have the enhanced value that has been suggested.[15]

The degree with which the set of rate constants can reproduce the data is indicated in Fig. 8. The chemical behavior in the ten flames is sufficiently varied that to reproduce the data in all cases with this level of agreement is a severe test of our understanding of the system. A picture emerges of a very flexible kinetic scheme in which NaO_2 plays a pivotal role in providing an alternate route for the formation of NaOH. However, the large production and destruction fluxes of NaO_2 are such that its steady state concentration lies in the range of 0.4% to 12% of the total bound sodium. Likewise, NaO which has an even smaller concentration of about 0.1% to 1.5% of the total bound sodium appears to act as the important intermediate between NaO_2 and NaOH in preference to the direct reaction channel. Consequently, as indicated in Fig. 9 for two flames, the in-

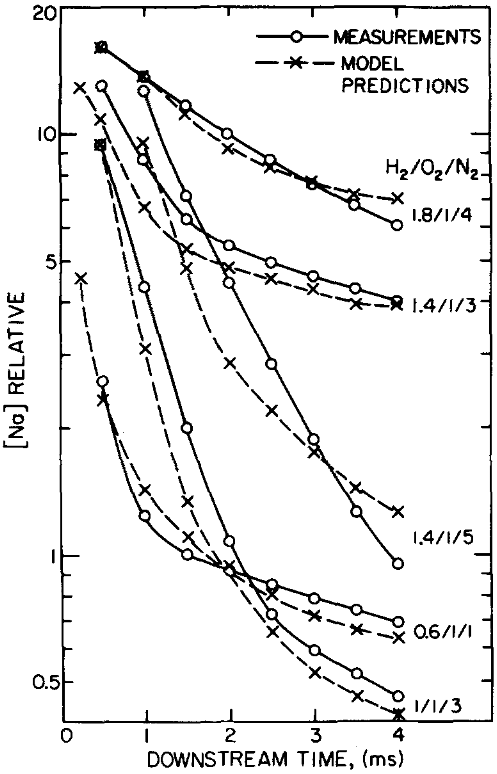

FIG. 8. Comparison of the experimental sodium concentrations with those predicted by a complete kinetic model based on the rate constants of Table II and $D_0^0(\text{Na—O}_2) = 39$ kcal mol^{-1}.

teresting conclusion is that NaOH is always the dominant molecular form as suggested by Jensen[16] and constitutes between 86.5% and 98.8% of the total bound sodium in the burnt gases of these ten lean flames. The participation of NaO_2 and NaO provides a more efficient method of producing NaOH. As a consequence the levels of NaOH observed can exceed what would have been expected considering the reaction of $Na + H_2O$ alone. The additional kinetics enhance the NaOH concentration to the point where the return flux due to reaction with H atoms is sufficient to maintain the steady state distribution. This apparent enhancement factor of the NaOH/Na ratio over what might otherwise have been expected from a consideration of the equilibration of reaction (1) alone is indicated in Fig. 10. It explains the discrepancies that were apparent in Fig. 6 which tested the equilibration of reaction (1). By chance, we see that downstream in the hottest (1.8/1/3) flame due to the temperature and low O_2 levels, reaction (1) does in fact become equilibrated and dominant. This is why the better fit of the lower dissociation energy of NaOH to the high temperature data of Fig. 6 is meaningful. At all temperatures below about 2350 K the amount of NaOH is increasingly larger than would have been expected from the equilibration of reaction (1) and begins, at early times in the coolest flame studied, to exhibit two orders of magnitude overshoots.

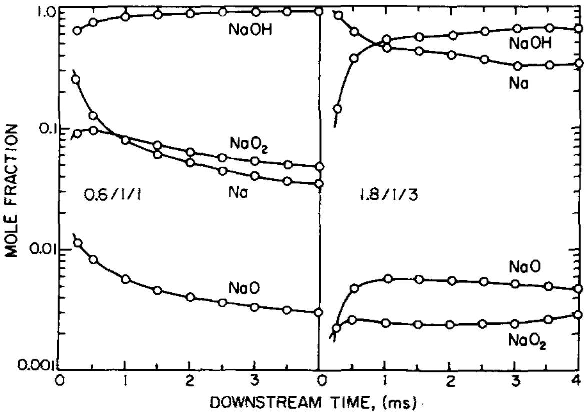

FIG. 9. The distribution of sodium among its molecular forms for the hottest 1.8/1/3 flame (2400 K) and for the oxygen-rich, 0.6/1/1 flame (1925 K).

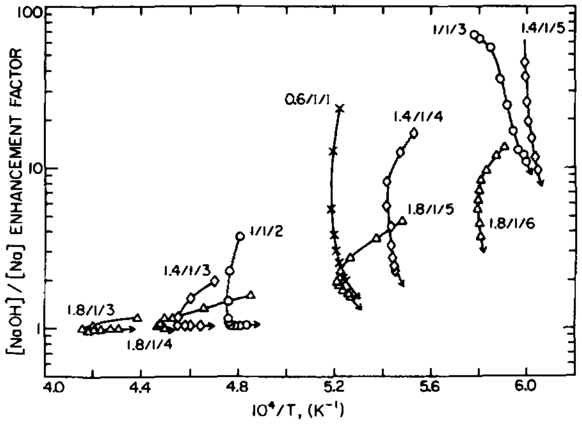

FIG. 10. The flame dependence of the factor by which the NaOH/Na ratio is increased due to NaO_2 participation over that expected from the equilibration of reaction (1). Flames are labeled as in Fig. 6.

VI. SIMPLIFIED MODEL

Close examination of the fluxes of all the reactions at each point in the flames indicates that the distribution is largely controlled by only several of the reactions in the scheme, namely,

$$Na + H_2O \rightleftharpoons NaOH + H\ , \qquad (1), (-1)$$

$$Na + O_2 + M \rightleftharpoons NaO_2 + M\ , \qquad (2), (-2)$$

$$NaO_2 + H \rightarrow NaO + OH\ , \qquad (12)$$

$$NaOH + OH \rightleftharpoons NaO + H_2O\ . \qquad (17), (-17)$$

By comparison, the contributions of the other reactions is very small in most cases. At temperatures above about 2350 K reaction (1) is equilibrated and if O_2 levels are small, as is the present case, only small fluxes produce and dissociate NaO_2. However, as temperatures decrease or more O_2-rich flames are used, the importance of NaO_2 increases and the predominant depletion of sodium is via reaction (2). Depending on the H-atom concentration, the sodium is then regenerated either by the thermal dissociation of NaO_2 or by reduction of NaOH which is produced mainly via NaO_2. Ultimately the chemistry becomes described by the cycle $Na \rightarrow NaO_2 \rightarrow NaO \rightarrow NaOH \rightarrow Na$. The efficient kinetics of reaction

(2) and its subsequent chemistry are favored due to the adverse enthalpy of reaction (1). Although NaO_2 is converted to NaO and NaOH efficiently, the reverse step is negligible and it is not necessary to consider reaction (−12) in a simplified scheme.

These four equations are sufficiently dominant that considered alone they reproduce the fit indicated in Fig. 8 to almost the same exactness. The differences are slight and within the general levels of uncertainty. Consequently, these four reactions alone can be used to adequately calculate the molecular distributions.

VII. A REANALYSIS OF THE PREVIOUS FLAME STUDIES

As outlined in the Introduction, the limited studies of Carabetta and Kaskan[4,8] and of Dougherty, McEwan, and Phillips[5,7] led them to erroneously associate the observed sodium decay rates with reaction (2), particularly as the decays also showed a linear dependence on O_2 and the third body concentrations. As noted already, this is a rather interesting consequence of the relationship between Na and H atoms. Because the predominant radical decay process in fuel-lean hydrogen flames is via

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

the sodium decay is a reflection of this reaction, so explaining the dependences and also the too small value quoted, in these earlier studies, for what was thought to be k_2.

Kaskan[4] measured Na and OH concentrations in two very similar $H_2/O_2/N_2$ flames of temperatures 1705 and 1715 K. Using his OH, H_2O, and O_2 concentrations and temperatures, the present kinetic model reproduces almost exactly the shape and decay rate of his experimental Na curves. The absolute magnitude is too low, suggesting that the OH measurements were about 60%–70% underestimated. This fact has been noted before[16,34] and considered to result from using too large an $OH(A-X)$, (0, 0) oscillator strength of 1.1×10^{-3}. Although the correct value for this was considered for many years to be about 35% smaller,[35] its presently accepted value[36] has returned in fact to that used by Kaskan. Consequently, the required correction may lie rather with the assumed experimental line shape factors which remain unspecified.

More recently, Jensen[16] realized the significance of Husain and Plane's[9] measure of k_2 and endeavored to reinterpret this limited data of Kaskan. Postulating that NaO_2 played a negligible role he suggested that the sodium decay could be modeled solely by reactions (1) and (3). The very large rate constants used for reaction (3) previously had appeared to explain the catalytic recombination of excess radicals in fuel-rich flames containing large quantities of sodium ($\simeq 1-6\times10^{14}$ cm^{-3}).[15] Testing Jensen's hypothesis on our larger data set shows a poor fit both in shape and magnitude of the sodium profiles. It is apparent that its limited success with Kaskan's data resulted from reaction (3) acting as a reasonable global rate constant for the NaO_2 production and loss kinetics. In fact the algebraic addition of reactions (2), (12), and (17) together with the H_2/O_2 reactions (4), (5), and (6) reduces down to the equation representing reaction (3). Consequently, this reaction is a very approximate and unacceptable replacement for these actual reactions. As outlined already, it was not possible to include it in the full kinetic analysis unless its rate constant was drastically reduced. This suggests that the interpretation of sodium's role in catalyzing radical recombination requires reexamining. That study[15] posed severe experimental difficulties in utilizing large concentrations of sodium and required measurements of H-atom concentrations using Na/Li emission intensities in optically thick flames. Reaction (3) similarly appears to be a global simplification of more complex kinetic behavior and the exact description of the catalytic behavior of sodium[15] and also of potassium[37] on the radical concentrations appears to require further studies.

VIII. IMPLICATIONS FOR THE OTHER ALKALI METALS

A theoretical analysis of the reactive surfaces of the $Na + O_2$ and $Li + O_2$ interactions by Alexander[29] is noteworthy particularly for its predictions of $D_0^\circ(Na-O_2)$ 36 kcal mol^{-1} and $D_0^\circ(Li-O_2)$ 53 kcal mol^{-1}. The agreement with our values for NaO_2 lends credence to their estimate for lithium. The only measure of $D_0^\circ(Li-O_2)$, by Dougherty, McEwan, and Phillips,[7] yielded 53.1 kcal mol^{-1} and was intended as an approximate upper limit. However, their estimate was based on assuming the extent of the role played by the $Li + O_2 + M$ reaction in dry $CO/O_2/N_2$ flames and that this interaction also was equilibrated. Based on our present understanding of these systems a reanalysis of the data indicates that the value is totally unfounded and can be given no weight. It is of the correct magnitude purely by chance.

As noted in Fig. 11, the pattern of bond strengths for the hydroxide, oxide, and dioxides appears to vary in a

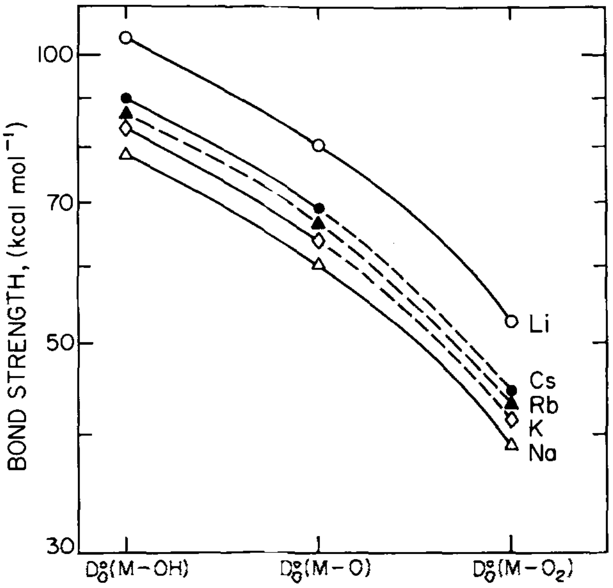

FIG. 11. Bond strength patterns for the alkali metal hydroxides, oxides, and dioxides. Broken lines indicate extrapolated estimates.

TABLE III. Bond strengths for the alkali metal hydroxides, oxides, and dioxides (kcal mol^{-1}).

	D_0°(M–OH)	D_0°(M–O)	D_0°(M–O$_2$)	
Li	104.5±1[c]	80.5±1.5[e]	52.6[i]	(52±5)[b]
Na	78.9±2[d]	60.3±4[f]	<44[j]	39±5[a]
K	84±3[d]	64±3[g]	45[j]	(41.5±5)[b]
Rb	86.5±3[d]	(66±3)[b]	46[j]	(43±5)[b]
Cs	90±3[d]	70±6[h] (69±3)[b]	48[j]	(44.5±5)[b]

[a] This work.
[b] Estimated values.
[c] Reference 38.
[d] Reference 24.
[e] Reference 39.
[f] Reference 25.
[g] References 40 and 41.
[h] Reference 42.
[i] Reference 29.
[j] Reference 43.

uniform manner. On this basis it is reasonable to estimate the uncertain dissociation energies of KO_2, RbO, RbO_2, and CsO_2. These are listed in Table III. Also included are the most recent estimates by Figger *et al.*[43] for NaO_2, KO_2, RbO_2, and CsO_2. They observed a weak chemiluminescence from the interaction region of an alkali metal and O_2 crossed beam experiment at low pressure. This was attributed to MO_2^* electronic emission resulting from the reaction

$$M_2 + O_2 = MO_2^* + M \ .$$

From the shortest wavelength chemiluminescent cutoff they derive the approximate values quoted in Table III for the bond strengths of the dioxides. No emission was observed for sodium and only an upper limit could be assessed from the experimental recording limit. The error bars associated with their estimates are difficult to assess. Besides the problem of actually fixing the exact cutoff wavelength due to experimental insensitivity, which implies that the quoted values are lower limit estimates, an additional difficulty centers on relating the cutoff wavelength to the bond strength. This requires assumptions concerning the location of the radiating electronic levels relative to the reactant energies. Depending on whether the radiation at the cutoff results from a level above or below that of the reactants this will raise or lower, respectively, the implied bond strength. Nevertheless, in spite of these interpretative uncertainties their values are in substantial agreement with our measurements and estimates.

It may be noted that those species included in the JANAF Thermochemical Tables,[23] namely LiOH, NaOH, KOH, CsOH, LiO, NaO, KO, and CsO, each need updating to various extents to reflect the more reliable dissociation energies presently available.

The more recent reliable experimental rate constant measurements of the three-body reaction of the alkali metals with molecular oxygen are listed in Table IV. They are seen to be consistently large and increase only slightly with increasing atomic weight. The third-body efficiencies from the studies of Husain and Plane[9,13] for Na and K are of the order of He : N_2 : CO_2 = 1 : 1.6–1.7 : 3.3–4.1. These are comparable to the corresponding values of 1 : 1.3 : 5 for the $H + O_2 + M$ reaction.[32] However, the latter's rate constant is about two orders of magnitude smaller [$4.1\times10^{-33}\exp(500/T)$, He, Ar; 5.3×10^{-33} cm^6 molecule^{-2} s^{-1} at 2000 K]. The large third-body efficiency evident with $H + O_2 + H_2O$ ($k_{H_2O} : k_{N_2} = 16 : 1$)[32] appears to be a unique feature suggesting it arises due to the similar nature of the reactants and the third body. For the corresponding sodium reaction such an enhancement would predict a flame value in our case of about four times larger than the extrapolated value of Husain and Plane,[9] whereas only a value of about four times less is compatible with the data.

The large rate constants for these three-body reactions have significant and similar implications for all the alkali metals. In all cases there will be large production fluxes of the dioxide in oxygen-rich flames. The exothermic reactions coupling MO_2 to MO and MOH are energetically similar, suggesting that enhanced concentrations of MOH are probable particularly at lower flame temperatures. It appears that concentrations of MO will be ≤1% of the bound alkali in the presence of flame H_2O and that concentrations of MO_2 will only be significant if all the depletion reactions are inefficient. The case of lithium differs only in the greater stability of LiO_2. This will be less prone to thermal dissociation and as a re-

TABLE IV. Measured rate constants for the three-body reaction of alkali metals with oxygen.

Alkali metal	$k(\mathrm{Alk} + O_2 + M)$ (cm^6 molecule^{-2} s^{-1})	M	Experimental temperature (K)	$k = AT^{-1}$	$k_{2000\,\mathrm{K}}$, $\times10^{-31}$ Extrapolated	Reference
Li	3.1(−30)[a]	Ar	393	$1.2(-27)\,T^{-1}$ [b]	6.1	12
	7.4(−31)	He	463	$3.4(-28)\,T^{-1}$ [b]	1.7	12
Na		0.2–0.4 H_2O 0.4–0.8 N_2 0.01–0.3 O_2	1650–2400	$1.8(-28)\,T^{-1}$ [b]	0.9	This work
	6(−31)	He	724, 844	$4.7(-28)\,T^{-1}$ [b]	2.4	9
	1.0(−30)	N_2		$7.8(-28)\,T^{-1}$ [b]	3.9	9
	2(−30)	CO_2		$1.6(-27)\,T^{-1}$ [b]	7.8	9
K		He	753, 873	$9.8(-28)\,T^{-1}$	4.9	13
		N_2		$1.7(-27)\,T^{-1}$	8.5	13
		CO_2		$4(-27)\,T^{-1}$	20.0	13
Cs	4.4(−30)	Ar	325	$1.4(-27)\,T^{-1}$ [b]	7.2	14

[a] 3.1(−30) read as 3.1×10^{-30}.

[b] Value assuming a T^{-1} dependence.

sult will significantly perturb the Li/LiOH balance even though the reaction of $Li + H_2O$ has the smallest energy barrier of all the alkalis of only 15 kcal mol^{-1}.

Controlled by the coupling kinetics, it is quite possible that MOH will be the dominant molecular species for all the alkalis under oxygen-rich conditions. However, only at higher temperatures and/or low O_2 concentrations may the M/MOH distribution become equilibrated. Consequently, the use of the Li/LiOH method as a measure of H-atom concentrations[6] in lean flames must be subject to varying degrees of error and should not be used until the system is better characterized.

One interesting study by Dougherty *et al.*[44] noted that about 60% of the lithium remains as free atoms in their dry $CO/N_2/O_2$ flames. In such a case, molecular formation is limited to either LiO or LiO_2. A reanalysis of the data considering the large production flux of LiO_2 indicates that the system is more complex than originally considered. Li and LiO will not be equilibrated as was assumed. The fact that a seemingly correct value for $D_0^\circ(\text{Li–O})$ was derived now appears to have been fortuitous. It was based on the assumption of CO and O concentrations being at their equilibrium values in these flames. However, the reanalysis indicates in fact, that these must be at least three times larger, irrespective of the exact rate constant values for the appropriate reactions. Overshoots of the LiO/Li ratio can be expected over that calculated assuming only the reactions directly coupling Li to LiO. Although the actual distribution between LiO_2 and LiO cannot be derived from this limited flame data it appears that LiO_2 will only be significant if the exothermic reactions coupling it to LiO all have rate constants that are at least two orders of magnitude lower than the gas kinetic collision frequency equivalent.

IX. CONCLUSIONS

Generally in flames, termolecular reactions are not kinetically competitive with bimolecular processes. However, with the alkali metals in oxygen-rich flames, due to the large rate constants and the involvement of molecular oxygen as a reactant, the production fluxes of the MO_2 species can be so large that this species can play a controlling role. For sodium, and probably also for the other alkali metals, this is in spite of their generally weak chemical bonding and, as noted, low steady state concentrations. The differing extent to which NaO_2 contributes to the total molecular formation has become evident by studying a matrix of ten flames in which the behavior is quite varied. Because the fluxes connecting the various species can drastically alter the importance of specific reactions from one flame condition to another, it is imperative that flame chemistries be studied for several differing flame temperatures and compositions. The analysis of a single flame can easily give a very limited and possibly incorrect or certainly incomplete insight into the real nature of the kinetic relationships and flexibilities of the system. This could easily have been the situation in the present case.

This study has led to the correction of previous misconceptions over the relative importance and kinetics of NaO_2. Its rapid conversion to NaO and NaOH is such that it can severely perturb the NaOH/Na ratio and produce significant concentration overshoots over that predicted from the balance of the reaction of Na with H_2O. This becomes increasingly so in flames of large O_2 concentrations and temperatures below 2500 K. The corresponding large rate constants for the termolecular formation of the other alkali peroxides imply that similar considerations will be necessary for them. Depending on the rate constants for the exothermic conversions of MO_2 to MO or MOH the steady state concentrations of MO_2 could be more or less significant than for sodium. In the latter's case these have an efficiency that is at least tenfold less than the hard sphere gas kinetic collision frequency. Due to the numerous reactions which can produce these conversions it would appear that the MOH species will most probably be the dominant species in all cases in oxygen-rich hydrogen or hydrocarbon flames, with MO concentrations at $\leq 1\%$ of the bound metal.

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[1] C. G. James and T. M. Sugden, Proc. R. Soc. London Ser. A 227, 312 (1955).
[2] D. E. Jensen and P. J. Padley, Trans. Faraday Soc. 62, 2132 (1966).
[3] C. Th. J. Alkemade, Tj. Hollander, W. Snelleman, and P. J. Th. Zeegers, *Metal Vapors in Flames* (Pergamon, Oxford, 1982).
[4] W. E. Kaskan, Symp. (Int.) on Combustion 10, 41 (1965).
[5] M. J. McEwan and L. F. Phillips, Trans. Faraday Soc. 62, 1717 (1966).
[6] M. J. McEwan and L. F. Phillips, Combust. Flame 9, 420 (1965); 11, 63 (1967).
[7] G. J. Dougherty, M. J. McEwan, and L. F. Phillips, Combust. Flame 21, 253 (1973).
[8] R. Carabetta and W. E. Kaskan, J. Phys. Chem. 72, 2483 (1968).
[9] D. Husain and J. M. C. Plane, J. Chem. Soc. Faraday Trans. 2 78, 163 (1982).
[10] F. Haber and H. Sachsse, Z. Phys. Chem., Bodenstein Festband 831 (1931).
[11] C. E. H. Bawn and A. G. Evans, Trans. Faraday Soc. 33, 1580 (1937).
[12] S. D. Kramer, B. E. Lehmann, G. S. Hurst, M. G. Payne, and J. P. Young, J. Chem. Phys. 76, 3614 (1982).
[13] D. Husain and J. M. C. Plane, J. Chem. Soc. Faraday Trans. 2 78, 1175 (1982).
[14] L. W. Grossman, G. S. Hurst, S. D. Kramer, M. G. Payne, and J. P. Young, Chem. Phys. Lett. 50, 207 (1977).
[15] D. E. Jensen and G. A. Jones, J. Chem. Soc. Faraday Trans. 1 78, 2843 (1982).
[16] D. E. Jensen, J. Chem. Soc. Faraday Trans. 1 78, 2835 (1982).
[17] C. H. Muller III, K. Schofield, M. Steinberg, and H. P. Broida, Symp. (Int.) on Combustion 17, 867 (1979).
[18] C. H. Muller III, K. Schofield, and M. Steinberg, J. Chem. Phys. 72, 6620 (1980).
[19] P. J. Padley and T. M. Sugden, Proc. R. Soc. London Ser. A 248, 248 (1958).

[20] M. B. Denton and D. B. Swartz, Rev. Sci. Instrum. 45, 81 (1974).

[21] K. Schofield and M. Steinberg, Opt. Eng. 20, 501 (1981).

[22] C. H. Muller III, K. Schofield, and M. Steinberg, Am. Chem. Soc. Symp. Ser. 134, 103 (1980).

[23] D. R. Stull and H. Prophet, JANAF Thermochemical Tables, 2nd ed., Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. (U.S.) 37 (1971); 1974, 1975, 1978, 1982 supplements, J. Phys. Chem. Ref. Data 3, 311 (1974), 4, 1 (1975), 7, 793 (1978), 11, 695 (1982).

[24] R. Kelly and P. J. Padley, Trans. Faraday Soc. 67, 740 (1971).

[25] D. L. Hildenbrand and E. Murad, J. Chem. Phys. 53, 3403 (1970).

[26] U. C. Sridharan, L. X. Qiu, and F. Kaufman, J. Phys. Chem. 86, 4569 (1982).

[27] L. Andrews, J. Phys. Chem. 73, 3922 (1969).

[28] R. R. Smardzewski and L. Andrews, J. Chem. Phys. 57, 1327 (1972).

[29] M. H. Alexander, J. Chem. Phys. 69, 3502 (1978).

[30] H. Johnston and J. Birks, Acc. Chem. Res. 5, 327 (1972).

[31] J. Troe and H. Gg. Wagner, in *Physical Chemistry of Fast Reactions*, edited by B. P. Levitt (Plenum, New York, 1973), Vol. 1, Chap. 1, pp. 1–80.

[32] D. L. Baulch, D. D. Drysdale, D. G. Horne, and A. C. Lloyd, *Evaluated Kinetic Data for High Temperature Reactions. Volume* 1. *Homogeneous Gas Phase Reactions of the H_2–O_2 System* (Butterworths, London, 1972).

[33] D. L. Baulch, D. D. Drysdale, J. Duxbury, and S. J. Grant, *Evaluated Kinetic Data for High Temperature Reactions. Volume* 3. *Homogeneous Gas Phase Reactions of the O_2–O_3 System, the CO–O_2–H_2 System, and of Sulfur-Containing Species* (Butterworths, London, 1976).

[34] G. Dixon-Lewis, Philos. Trans. R. Soc. London Sect. A 292, 45 (1979).

[35] D. M. Golden, F. P. Del Greco, and F. Kaufman, J. Chem. Phys. 39, 3034 (1963).

[36] C. C. Wang and C. M. Huang, Phys. Rev. A 21, 1235 (1980).

[37] D. E. Jensen, G. A. Jones, and A. C. H. Mace, J. Chem. Soc. Faraday Trans. 1 75, 2377 (1979).

[38] P. J. Th. Zeegers and C. Th. J. Alkemade, Combust. Flame 15, 193 (1970).

[39] D. L. Hildenbrand, J. Chem. Phys. 57, 4556 (1972).

[40] T. C. Ehlert, High Temp. Sci. 9, 237 (1977).

[41] H. J. Byker, I. Eliezer, R. C. Howald, and T. C. Ehlert, High Temp. Sci. 11, 153 (1979).

[42] A. V. Gusarov, L. N. Gorokhov, and A. G. Efimova, High Temp. USSR 5, 524 (1967).

[43] H. Figger, W. Schrepp, and X. Zhu, J. Chem. Phys. 79, 1320 (1983).

[44] G. J. Dougherty, M. R. Dunn, M. J. McEwan, and L. F. Phillips, Chem. Phys. Lett. 11, 124 (1971).