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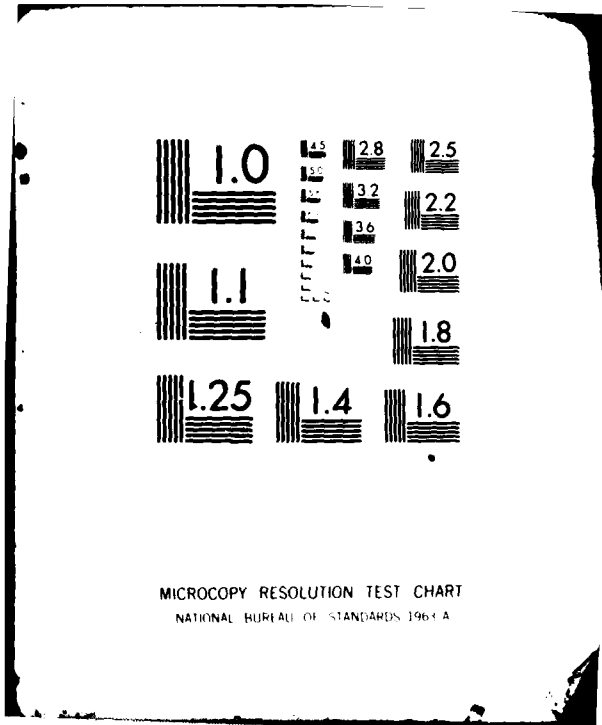
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KINETICS OF OXIDATION REACTIONS INVOLVING
B AND Al CHALCONIDES

Arthur Fontijn and the late Michael A. A. Clyne,
Department of Chemistry,
Queen Mary College,
Mile End Road,
London E1 4NS, UK

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) <p>Work on various problems in solid and air-breathing rocket development, e.g., submicron particulate formation, requires the input of kinetic data over wide temperature ranges on the oxidation reactions of refractory free radical species. Various approaches for producing these species and investigating their kinetics, using laser-induced fluorescence and high-temperature fast-flow reactors, are discussed. To demonstrate the feasibility of a new discharge-flow reactor method for producing such radicals for kinetic studies, the kinetics of $\text{BO} + \text{O}_2 \rightarrow \text{BO}_2 + \text{O}$ was investigated. A rate coefficient of $4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 295 K</p>		

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I. INTRODUCTION - SCIENTIFIC OBJECTIVES

The need for a reliable kinetic data base on reactions of refractory metal atoms, metal oxide radicals and metal halide radicals* for various aspects of solid and air breathing rocket development has frequently been expressed, e.g. Ref. 1. To provide such data for metal atoms, one of us (AF) previously developed the HTFFR (High-Temperature Fast-Flow Reactor) technique,²⁻⁴ which is uniquely useful for measuring rate coefficients and their temperature dependence within the temperature range of approximately 300 - 1900 K. Some data on a metal oxide radical, AlO, were also obtained through the convenient expedient of observing the two-step oxidation of Al atoms with the same oxidiser. However, the need for more systematic means of studying reactions of metal radicals in HTFFRs was obvious⁴. The visit, during the grant year, of AF to the laboratory of the other of us (MAAC), with its state-of-the-art equipment for laser-induced fluorescence (LIF) detection of free radicals, presented a natural opportunity for such more systematic exploration. LIF currently represents the most sensitive technique for monitoring of such radicals. Consequently, the objectives for this program were to make a kinetic study of a reaction of a refractory oxide radical ($BO + O_2 \rightarrow BO_2 + O$)

*The word "metal" is used here in its propulsion technology sense, thus specifically including B, which is not a metallic element in the usual physico-chemical sense.

and to explore means for future kinetic studies of refractory radical species of significance to Air Force development programs.

II. BIBLIOGRAPHY OF PUBLICATIONS

The present one year effort has resulted in the following publication (Appendix A of this report):

I. P. Llewellyn, A. Fontijn and M. A. A. Clyne, "Kinetics of the Reaction $\text{BO} + \text{O}_2 \rightarrow \text{BO}_2 + \text{O}$ ", Chemical Physics Letters, in press.

"The reaction of $\text{BCl}_3 + \text{N} + \text{O}$ was used to produce $\text{BO } X^2\Sigma^+$ radicals for study in a fast-flow reactor. Laser-induced fluorescence was used to follow the $\text{BO } X^2\Sigma^+$ radicals. The feasibility of kinetic studies on these radicals was demonstrated through a kinetic study of the $\text{BO} + \text{O}_2$ reaction, giving a rate

coefficient k_1 equal to $((4.4 \begin{smallmatrix} +4.7 \\ -3.2 \end{smallmatrix}) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 295 K."

Additionally considerable progress was made in the preparation of a book chapter which discusses the status of theory, experiments and predictive ability on the influence of temperature on rate coefficients of bimolecular reactions. The type of metal and metal radical reactions of interest to the Air Force form an important subset of the reactions discussed. This chapter and book are scheduled for publication in late 1982. The reference will be:

A. Fontijn and R. Zellner, "Influence of Temperature on Rate Coefficients of Bimolecular Reactions" in Reactions of Small Transient Species (M. A. A. Clyne and A. Fontijn, Eds.), Academic Press, London, Chap.2.

designed, constructed and tested during the course of the grant, but insufficient time was available to study the BO/O₂ reaction in this apparatus. The reaction tube and BO inlet were made from impervious mullite (Morgan Refractories Ltd.) and the three-zone furnace was made of Kanthal-A elements (Bulten-Kanthal AB) surrounded by Triton blanket and board insulating material (Morgan Refractories Ltd.). This combination of materials allows work up to about 1500 K. The observation fluorescence cell was replaced outside the heated zone. This was done to facilitate joining of the reactor to existing laser-induced fluorescence apparatus at Queen Mary College, not because of a principal advantage. A previously used^{3,4} modular HTFFR is shown in Figure 2. It is obvious that the "source section" of that reactor can be removed and the reactor section joined to a preparation line as in Figure 1, resulting in a constant high temperature zone including the observation region.

Thus there appears to be no reason in principle why the metal radical work could not be extended over the full temperature range of some previous HTFFR work (300 - 1900 K)^{3,4}. The choice of apparatus design will depend on the radical of interest, as will be discussed now.

B. Production and monitoring of further radical species

The traditional way of producing metal oxide and halide radical species is by evaporation of inorganic compounds⁵. This approach could be practised with an original^{3,4} modular HTFFR, Figure 2, in which the vaporizer contains the

inorganic parent compound. Thus, SnO can be produced by dissociative evaporation of SnO₂, or else from Sn/SnO₂ mixtures where the Sn acts as a reducing agent; these methods can be used at about 1400 K⁽⁶⁾. Such vaporization methods are in principle similar to those used in metal atom HTFFR work^{3,4}.

A number of methods for refractory radical production have been developed in recent years in the area of preparative metal-organic chemistry. These can best be utilized with a preparation line approach, Figure 1. They can be divided into two groups: gas-solid reactions and pyrolysis^{5,7}. An example of the former is the production of BF by passage of BF₃ through solid B granules at ~ 2000 K, and one of the latter is the production of BCl by passing B₂Cl₄ through a quartz tube at ~ 1300 K (also yielding BCl₃). In HTFFR studies it is of course necessary to ascertain that the other species present, BF₃ and BCl₃ in these examples, do not interfere with the reactions studied, which is in general not likely for such thermally rather stable compounds. These groups of methods can be expanded by the use of laser photolysis, a method apparently not yet used in studies of reactions of inorganic free radicals, but one for which the basic technology has reached a high degree of development in recent years^{8,9}.

It is important to note that neither the literature on evaporative, nor on the preparative, methods appears to

contain any information on the production of BO, the species investigated experimentally in the current study (Appendix A). Only B₂O₂ could be produced in metal-organic synthesis work⁷. The discharge-flow reaction method developed here for BO, i.e. reacting BCl₃ with a flow of N/O/N₂, was attempted on the basis of observations that BO emission spectra can be produced in the reaction of BCl₃ with active nitrogen containing traces of oxygen¹⁰, while the reaction of BCl₃ with O/O₂ mixtures only appears to produce BO₂.¹¹ For many radicals such emission spectroscopic observations¹⁰ could be adapted to discharge-flow methods for production of their respective ground states. Often the yields will be very low, as was found to be the case for BO. However, coupled with the extremely sensitive monitoring method, which is LIF, low radical concentrations need not be a drawback.

In the above we have emphasised the preparation and monitoring of diatomic radicals. However, triatomic radicals can be produced by similar methods and again LIF offers currently the most sensitive detection technique. For these larger species there is currently less information available from earlier work. That this situation is changing may be illustrated from the above mentioned BO₂ studies¹¹ and the recent work by Hirota¹² on BOCl.

IV. CONCLUSIONS

In this work the practicality of producing a highly refractory free radical species, BO, by a preparation line

method has been demonstrated and kinetic data on its reaction with O_2 have been obtained. The technical possibilities for more extensive studies of rate coefficients, and their temperature dependence, for refractory radical species of Air Force interest are highly promising. A large variety of radical production methods can be combined with HTFFR methodology and laser-induced fluorescence monitoring to achieve this goal.

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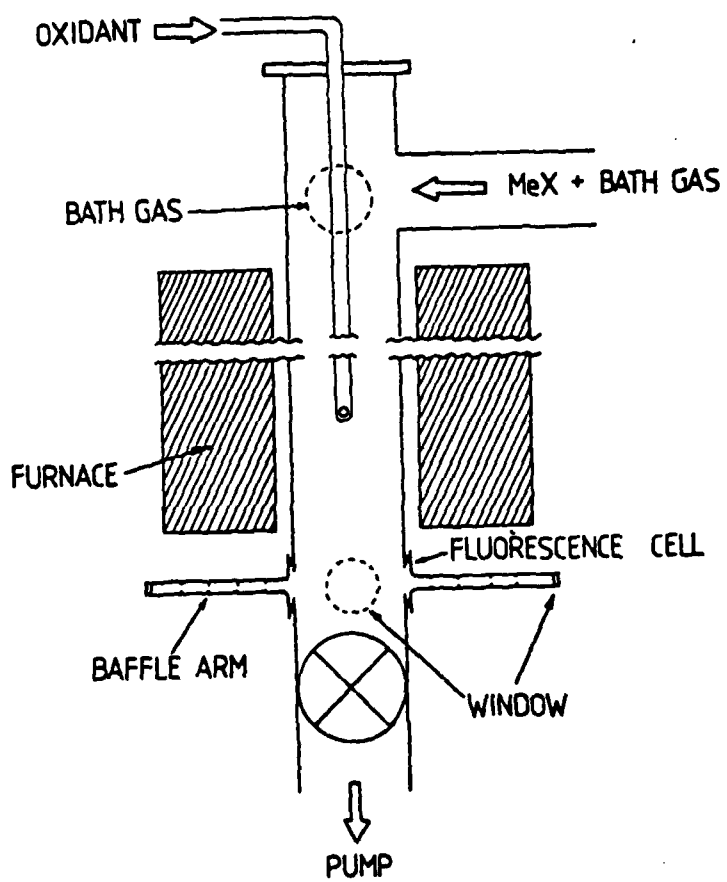


Figure 1 Schematic of a modular HTFFR with preparation line metal radical source.

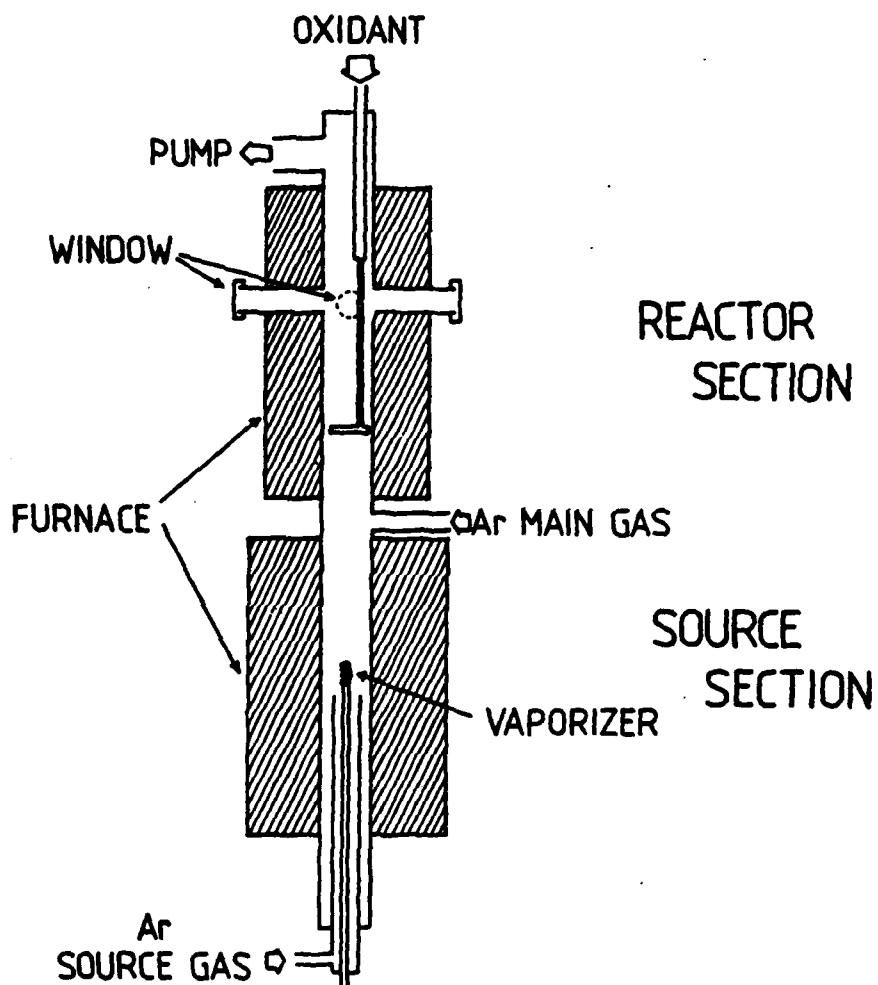


Figure 2 Schematic of a modular BTFFR with a high temperature source section for evaporative introduction of metal radicals or atoms.

1.1.8

ABSTRACT

KINETICS OF THE REACTION $BO + O_2 \rightarrow BO_2 + O$

Ian P. Llewellyn, Arthur Fontijn* and Michael A. A. Clyne

Department of Chemistry
Queen Mary College
Mile End Road
London E1 4NS, UK

The reaction of $BCl_3 + N + O$ was used to produce $BO X_2^+$ radicals for study in a fast-flow reactor. Laser-induced fluorescence was used to follow the $BO X_2^+$ radicals. The feasibility of kinetic studies on these radicals was demonstrated through a kinetic study of the $BO + O_2$ reaction, giving a rate coefficient k_1 equal to $(4.4 \pm 4.7) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 295 K.

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*Senior Visiting Fellow.
Permanent address:

Department of Chemical Engineering and Environmental Engineering,
Rensselaer Polytechnic Institute, Troy, NY 12181, USA

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1. Introduction

The development of the HFRFR (high-temperature fast-flow reactor) technique [1] has led to a number of measurements of rate coefficients $k(T)$ for reactions of refractory metal atoms over wide temperature ranges*. In that work metal atoms were produced by evaporation, and their oxidation reactions studied in a contiguous section of the flow tube. Little systematic work has been done to obtain similar $k(T)$ data for reactions of free radicals of refractory species, though the study of the $Al + O_2$ reaction has allowed rate coefficient measurements of the subsequent reaction of $AlO + O_2$ in the same flow tube [3]. An observation of the similar sequence $Al + SO_2$, $AlO + SO_2$ also has been reported [4]. Some metal oxide and halide radicals probably could be produced directly in an HFRFR by evaporative methods [5], to allow study of their reactions with various oxidisers, as in the metal atom work. An alternative approach is to produce such radicals upstream from the flow tube in a side arm by one of a number of methods (e.g. gas phase reactions, multiphase reactions, pyrolysis, photolysis). Such techniques have to be capable of producing a continuous, controllable flux of the refractory radicals over a period of several hours, to be practical for flow tube measurements. Light *et al* [6] have recently demonstrated the feasibility of such an approach for BF_2 , produced by the reaction of a BF_3/H_2 flow with boron granules at $T > 1600$ K [6].

The radical BO is a notoriously difficult species to produce with any appreciable flux; the dimer B_2O_2 is more readily obtained [5,7]. However, we now report the successful generation and detection of BO in a flow reactor, and in order to establish the feasibility of kinetic measurements

*For a review and data summary see Ref. [2], in which other observations on metal atom kinetics are also discussed.

on this radical, we present kinetic data for the reaction,



studied by laser-induced fluorescence (LIF).

The approach followed was to produce BO in a side arm of the flow tube reactor by the gas phase reaction of N -atom/ O -atom mixture with BCl_3 at room temperature. This reaction system has previously been used successfully in this laboratory for LIF observations on the spectroscopy and radiative lifetimes of the BO radical in the excited $A^2\Pi$ state [8]. The high fluorescence yield and relatively short radiative lifetime ($\tau_{rad} = 1$ to 2 μs) of BO $A^2\Pi$ combine to make LIF a sensitive probe of the relative concentrations of ground-state $X^2\Sigma^+$ BO . In addition, by accurate tuning of the laser frequency, LIF can be made completely selective for BO and completely insensitive to contaminants (e.g. BO_2). However the BO radical concentrations obtained here were low; hence, signal-to-noise ratios for the detection of BO were limited, and the resulting rate coefficient was not as accurate as would have been desired, but still adequate to allow comparison with the corresponding AlO reaction.

2. Apparatus and procedure

A schematic of the apparatus is shown in figure 1. A $N + O + N_2$ mixture, produced in the usual way from a microwave discharge in N_2 with partial NO titration, reacted in the side arm with BCl_3 to produce BO . The BCl_3 was introduced through a downstream nozzle near the junction with the reaction tube. This NO terminated the BO production by complete titration of the N atoms, as indicated by the disappearance of the intense blue BO chemiluminescence beyond this point. Additional bath gas, Ar, was introduced to the reaction tube to obtain the fast average flow velocities necessary for adequate transport of BO . O_2 was introduced through a variable position

nozzle.

The reaction tube was of 19 mm bore and was 370 mm in length from the side arm to the fluorescence cell. A single stage 240 m³ h⁻¹ vacuum pump (Edwards Model 240/30) was used. All permanent gases were standard grade. NO was purified by passage through activated alumina and KOH. BCl₃ was obtained as gas from a storage reservoir into which it was distilled from the liquid (BPH, purity > 98%) and diluted with Ar. The volume flow rates of N₂, Ar and O₂ were measured by the inverted burette method; those of BCl₃ and NO were not measured accurately. Pressure was measured after each experiment with a transducer (MKS Baratron 221) connected to a movable pressure probe [2]. During the experiment the transducer was connected to the fluorescence cell.

All kinetic measurements were made under pseudo first-order conditions, i.e., with [O₂] >> [BO], using the O₂ inlet at a number of fixed positions (times) and at which [O₂] was varied. Appreciable BO destruction on the O₂ inlet tube and reactor walls prevented the making of measurements at fixed [O₂] values with varying time (nozzle position). This BO destruction rate decreased somewhat as a thin white film of reaction products deposited on the walls in the course of the work. The relative BO concentration was monitored by pumping the (0,0) Q₁ head of the A²Π - X²Σ⁺ transition at 425 nm. The resulting fluorescence was focussed onto a slit, and detected with a photomultiplier (820 cathode, EMI 9816B, 2 ns rise time) through a filter transmitting at λ > 500 nm. The laser apparatus used has been described previously [9]. Tripled Nd-YAG output was used to produce radiation near 425 nm from an oscillator-amplifier design of dye laser, using Stilbene 420 dye. A 0.01 nm band-width and a repetition rate of 20 Hz were used, giving an average pulse energy of 300 μJ with pulse-to-pulse jitter < 5%.

Only low fluorescence intensities were obtained (indicating very low [BO]), requiring the careful minimization of cw light originating from the BO production reactions in the side arm of the flow tube. The most primitive method for measuring pulsed LIF intensities, namely, with a boxcar integrator, failed to give a reliable measurement of relative BO concentration. Instead, the pulsed fluorescence signals were digitized in real time using a fast transient recorder (Biomation 6500, 6 bit, > 2 ns channel, 1024 channels) coupled to a minicomputer (Nicolet LAB-80). This allowed data collection over many shots (typically > 1000) and reduced the laser shot-to-shot noise to a negligible level. Care was taken to use a sufficiently high PMT voltage (1900 V) to ensure proper digitisation of the signal. This was verified by subtracting the background from the decays and ascertaining that the logarithms of the resulting intensities yielded straight lines, when plotted with time.

The data were analysed using the minicomputer. The area under each decay curve was computed by averaging a set number of time channels following the laser pulse. The average cw background was determined from a number of channels recorded before initiation of the laser pulse, and was subtracted from the integrated signal. As a check on this procedure, BO was removed by using an excess of O₂, under which conditions negligible integrated signals indeed were obtained. In addition the number of channels used in the integration was varied and were found to have negligible effect (< 10% change) on the final value of the rate coefficient. Negligible shortening of the lifetime (due to quenching) was observed upon addition of O₂ in the concentration range used. The slopes of ln(F_{BO}⁰/F_{BO}) vs [O₂] plots yielded the product kt [2]:- ln(F_{BO}⁰/F_{BO}) = -kt, noting that F_{BO}⁰ is the fluorescence intensity at a given [O₂] > 0, and F_{BO}⁰ is the intensity

in the absence of O₂. Under the conditions used (see Table I), the flow profile was intermediate between plug and parabolic flow. Exact treatment of this intermediate case was complicated by the need to have good measurements of the rate of removal of the BO on the walls of the flow tube [9]. This rate was found to be very fast, but could not be obtained accurately. Therefore a simplified method was employed by which the measured rate coefficient is multiplied by a factor equal to $1.6 \times l/l_p$, where l_p is the distance required for full parabolic flow to develop and l the distance of the O₂ inlet to the centre of the fluorescence cell. Within experimental error, this was found to be equivalent in most cases to multiplying the experimental rate coefficient values by $1.3 [2,3]$, or by applying the method due to Iannuzzi and Kaufman [10].

3. Results

The rate coefficient measurements are summarised in Table I. The results may be seen to be independent of the experimental parameters. The plots of $\ln(P_{BO}^0/P_{BO})$ against $[O_2]$ plots mostly approximated to straight lines well (correlation coefficient R in the range -0.90 to -0.99). A few experiments had $R < 0.8$ and were rejected. The mean value, and the standard deviation of the measurements is $(4.4 \pm 3.2) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Estimating systematic uncertainties to be 20%, including 10% for uncertainty in the flow profile factor, the recommended k_1 is $(4.4 \pm 3.2) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

The reaction product BO₂ of the BO + O₂ reaction, was identified using a cw laser (Coherent 599-21) and photon counting equipment. The fluorescence of the BO₂ was monitored at $\lambda > 560 \text{ nm}$, whilst exciting the

$\lambda^2 \Pi - X^2 \Pi (00^0 - 00^0)$ band at 547 nm. As O₂ was added, the BO₂ signal increased at a rate compatible only with the above magnitude of k_1 . However, no attempt was made to measure the value of k_1 of the BO + O₂ reaction in this way, since it was evident that the BO₂ so formed itself was rapidly removed.

4. Discussion and Conclusions

A rate coefficient $k_1 = (4.4 \pm 3.2) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ thus has been obtained at room temperature for the slightly exothermic ($\approx 40 \text{ kJ mol}^{-1}$) [11] reaction (1). This value for the BO + O₂ reaction may be compared to the corresponding reaction (2) of the next heavier Group IIIA element,



for which HFRFR experiments yielded $k(T) = (2.3 \pm 0.6) \times 10^{-13} \exp[(333 \pm 170)/T]$ from 300 to 1400 K [3], or $(7.2 \pm 3.6) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 300 K. Both the dioxides BO₂ and AlO₂ have in their stable ground-state form a symmetrical linear structure [11]. Reaction (1) thus appears to be considerably faster than reaction (2), notwithstanding the much higher ionization potential of the central atom (8.30 eV for B, as against 5.92 eV for Al) [12], and the expected shorter available interaction distance. The low Arrhenius A factor and small negative

temperature-dependence of reaction (2) may be attributed [3, 13] to formation of a bound intermediate complex which can with high probability redissociate to the reactants. The larger value of k_1 may thus indicate a direct reaction path (or at least a smaller probability for redissociation of a hypothetical complex), possibly related to the more covalent character of the new bond. This would suggest a more positive temperature dependence

for reaction (1) than for reaction (2).

To determine any such temperature dependence, the side-arm preparation method used here could readily be combined with an HTRFR apparatus. In general, this type of technique for production of radicals of refractory species allows for determinations of absolute rate coefficient values of reactions of the radicals with a variety of second reactants, independently of the initial radical production method; the need for such development has been discussed [2]. For several refractory radical species, methods for production, at much higher fluxes than could be achieved here for BO, are known [5, 14].

Acknowledgement

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T A B L E 1

Summary of $\text{BO} + \text{O}_2 \rightarrow \text{BO}_2 + \text{O}$ Rate Coefficient Measurements

P (Torr) ^{a)}	N ₂ flow (cm ³ (STP)s ⁻¹)	Ar flow (cm ³ (STP)s ⁻¹)	\bar{v} (b) (m s ⁻¹)	t (ms)	[O ₂] (10 ¹² cm ⁻³)	I_{BO}^0 (c) (arbitrary units)	k (10 ⁻¹² cm ³ molecule ⁻¹ s ⁻¹)	R
2.8	16	67	89	2.2	0.6 - 20	0.18	3.9	-0.96
2.7	16	67	90	3.1	3 - 34	0.20	9.6	-0.99
2.3	16	33	50	5.5	1 - 14	0.23	1.1	-0.99
2.9	16	67	87	2.9	8 - 21	0.23	3.7	-0.90
2.8	16	33	53	5.5	7 - 13	0.40	0.7	-0.97
2.8	16	33	53	5.9	5 - 22	0.43	4.3	-0.98
2.8	16	33	53	6.1	3 - 40	0.54	1.8	-0.94
2.8	16	33	53	4.8	2 - 40	0.62	1.5	-0.98
2.7	15	18	37	7.0	3 - 40	0.46	0.7	-0.86
2.8	15	18	35	9.1	2 - 50	1.0	1.5	-0.98
2.6	27	18	51	6.0	4 - 50	1.0	7.4	-0.81
2.6	27	18	52	5.2	4 - 25	0.30	7.5	-0.98
2.6	27	18	52	4.8	2 - 23	0.41	3.7	-0.99
2.5	27	18	53	4.3	2 - 30	0.39	10.6	-0.96
2.7	28	35	69	3.5	0.7 - 4	0.12	9.3	-0.95
1.9	22	18	65	3.7	2 - 20	0.20	7.7	-0.99
2.0	22	18	60	5.3	0.7 - 4	0.14	8.6	-0.93
4.1	22	18	30	9.3	2 - 12	0.23	1.9	-0.91
4.0	22	18	30	7.9	2 - 20	0.12	5.0	-0.94
4.1	22	18	30	6.7	4 - 40	0.13	5.6	-0.90
5.5	22	96	64	1.2	1 - 20	0.29	2.2	-0.96
5.5	22	96	64	3.6	2 - 13	0.64	2.0	-0.99
5.5	22	96	65	2.9	1 - 17	0.89	1.0	-0.89

a) 1 Torr = 133.3 Pa

b) mean plug flow velocity

c) initial BO^+ fluorescence intensity

GXUAAJ

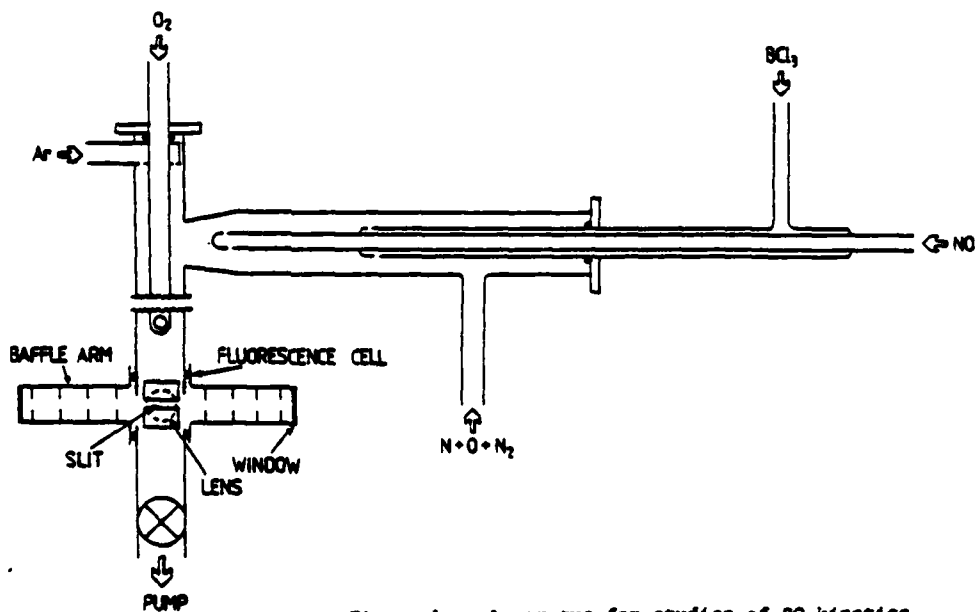


Figure 1 Apparatus for studies of BO kinetics.

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