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RATE CONSTANTS FOR THE REACTION
OF PO ($v = 0$) AND PO ($v = 1$) RADICALS
WITH OXYGEN

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RESEARCH DIRECTORATE

January 1989

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SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		1b. RESTRICTIVE MARKINGS	
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION / AVAILABILITY OF REPORT Approved for public release; distribution is unlimited.	
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE			
4. PERFORMING ORGANIZATION REPORT NUMBER(S) CRDEC-TR-033		5. MONITORING ORGANIZATION REPORT NUMBER(S)	
6a. NAME OF PERFORMING ORGANIZATION CRDEC	6b. OFFICE SYMBOL (if applicable) SMCCR-RSL	7a. NAME OF MONITORING ORGANIZATION	
6c. ADDRESS (City, State, and ZIP Code) Aberdeen Proving Ground, MD 21010-5423		7b. ADDRESS (City, State, and ZIP Code)	
8a. NAME OF FUNDING / SPONSORING ORGANIZATION CRDEC	8b. OFFICE SYMBOL (if applicable) SMCCR-RSL	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER	
8c. ADDRESS (City, State, and ZIP Code) Aberdeen Proving Ground, MD 21010-5423		10. SOURCE OF FUNDING NUMBERS	
		PROGRAM ELEMENT NO	PROJECT NO 1L161102
		TASK NO. A71A	WORK UNIT ACCESSION NO
11. TITLE (Include Security Classification) Rate Constants for the Reaction of PO (v = 0) and PO (v = 1) Radicals with Oxygen			
12. PERSONAL AUTHOR(S) Long, S. Randolph, and Christesen, Steven D.			
13a. TYPE OF REPORT Technical	13b. TIME COVERED FROM 85 Jul TO 86 Mar	14. DATE OF REPORT (Year, Month, Day) 1989 January	15. PAGE COUNT 24
16. SUPPLEMENTARY NOTATION			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	Laser Photofragmentation, PO Radicals	
07	04, 05	Laser Photolysis Dimethyl Methylphosphonate	
		Laser-Induced Fluorescence → (A) (W) F	
19. ABSTRACT (Continue on reverse if necessary and identify by block number) Laser-induced fluorescence (LIF) has been used to probe vibrational state population of PO radicals generated by CO ₂ laser photolysis of dimethyl methylphosphonate. PO radicals in vibrational levels up to v = 3 have been detected. The population ratio determined for v = 0 and v = 1 is consistent with a vibrational temperature of 1000 K. LIF monitoring of the decay of PO radicals in the presence of an excess of oxygen has allowed determination of the rate constants for reaction of PO (v = 0) and PO (v = 1) with O ₂ . The measured rate constants for both these reactions are 1.5 x 10 ⁻¹¹ cm ³ /molecule/s or about 1/25 the hard-sphere collision rate. Potential laser photofragmentation/LIF detection schemes for organophosphonates should accordingly incorporate no more than 10 ns between photolysis and probing for PO radicals. Key words: ...			
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED	
22a. NAME OF RESPONSIBLE INDIVIDUAL SANDRA J. JOHNSON		22b. TELEPHONE (Include Area Code) (301) 671-2914	22c. OFFICE SYMBOL SMCCR-SPS-T

PREFACE

The work described in this report was authorized under Project No. 1L161102A71A, Research in Chemical and Biological Defense, Chemical Warfare and Smoke. This work was started in July 1985 and completed in March 1986.

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RATE CONSTANTS FOR THE REACTION OF PO ($v = 0$) AND PO ($v = 1$) RADICALS WITH OXYGEN

1. INTRODUCTION

For possible application to class identification of organophosphonates, a UV laser photofragmentation/laser-induced fluorescence (LIF) detection scheme has been studied by Long, Sausa, and Miziolek whose results have been recounted in several recent publications.¹⁻⁵ The laser photofragmentation approach uses a focused excimer laser (at 248 or 193 nm) to photodissociate the organophosphonate, and the resultant PO radicals are detected by LIF using a second (unfocused) laser beam whose wavelength is resonant with the strong PO $A^2\Sigma^+ - X^2\Pi$ transition with (0,0) bandheads near 246.3 and 247.7 nm. Many important parameters in this scheme have been determined by these authors: laser power dependence of the fragmentation process, radiative lifetime of the PO A state, rates of quenching of the A state by the atmospheric constituents nitrogen and oxygen, internal state distributions of the PO radical fragment, and pressure dependence of the photofragmentation process, as well as the rate constant for reaction of PO with oxygen.

Because the goal of the work of Long et al.^{1,2} was to evaluate this technique for application under ambient conditions, an accurate determination of the rate constant for the PO + O₂ reaction is important. However, the measurement Long et al.^{3,4} obtained contradicted two recent prior measurements. Aleksandrov, et al.⁶ first extracted a rate constant, $k = 2 \times 10^{-13}$ cm³/molecule/s, which they attributed to the PO + O₂ reaction in a discharge flow system. Using a microwave discharge in argon containing dimethyl methylphosphonate (DMMP) to generate PO, Wong et al.⁷ monitored PO via LIF in the $B^2\Sigma^+ - X$ transition near 325 nm to measure a rate constant of $k = 2 \times 10^{-13}$ cm³/molecule/s, which is in good agreement with the earlier Aleksandrov experiment.

The work of Sausa, Miziolek, and Long,^{3,4} who used a focused KrF (248 nm) laser to photodissociate DMMP and LIF in the A-X transition to monitor PO in the presence of O₂, yielded a rate constant of 1×10^{-11} cm³/molecule/s, 50 times faster than the measurements using the flow discharge systems.^{6,7} An abiding question in the excimer laser study is whether the focused 248-nm laser might generate oxygen atoms by multiphoton-induced photochemistry in O₂, thus confusing the issue of which species actually accounted for the reactive decay of PO.

A technique for photolytic generation of PO in the presence of O₂ without generating oxygen atoms is required to eliminate this problem. This technique is supplied in the present work by using a CO₂ transversely excited atmospheric

(TEA) laser to produce PO by IR multiphoton dissociation (IRMPD) of DMMP. The IRMPD of DMMP in a molecular beam has been studied by Chou, Sumida, and Wittig, who determined the nascent PO product state distributions by multiphoton ionization of PO.^{8,9} The effective vibrational temperature was approximately 1000 K, placing the PO ($v = 1$) population at 17% that of PO ($v = 0$).

In this report, we present the results of our measurement of the reaction rate of ground vibrational state PO with O₂ using IRMPD of DMMP to generate PO. Because this photolysis technique generates vibrationally excited PO, we have been able to measure the rate of the reaction of PO in its first excited vibrational level, PO ($v = 1$), with O₂. Prior to discussion of the reaction rate measurements, we present data on the IRMPD of DMMP.

2. EXPERIMENTATION

The experimental arrangement used in this report was similar to that used by Long et al. in the excimer laser photodissociation studies.¹⁻⁴ As depicted schematically in Figure 1, it incorporated a Tachisto 555 or Lumonics 820 CO₂ TEA laser for photolysis and a Quanta-Ray Nd:YAG-pumped dye laser system for production of the PO LIF probe laser beam. Either pure DMMP or oxygen containing less than 0.01 torr DMMP flowed through a stainless steel flow system. The approximately 1-in. i.d. stainless steel cell has four windows at right angles. The laser beams passed through opposing 2-mm thick BaF₂ windows while UV Suprasil windows on the other optical ports allowed viewing of the cell interior. PO LIF was collected by a lens system consisting of a 2-in. diameter, 75-mm focal length Suprasil lens and a 2-in. diameter, 200-mm focal length Suprasil lens onto the slit of a Spex model 1870B, 0.5-M monochromator. The dispersed fluorescence was detected either by an RCA C31034 photomultiplier (PMT) or a Tracor-Northern TN-6100 optical multichannel analyzer (OMA). The OMA was used to record spectra of the PO fluorescence while the PMT, whose output was averaged in a PAR model 162 boxcar averager, was used for the kinetics studies. The boxcar averager output was further accumulated and stored in a DEC MINC laboratory computer.

The CO₂ laser output was focused into the flow cell by a 10-cm focal input ZnSe lens; the UV probe laser beam was used unfocused. A master trigger system incorporating several delay pulse generators was employed to control the timing of the laser pulses in these two-laser experiments. A BNC model 7075 digital delay generator provided the critical time delay between the lasers. In the following discussions, "probe laser delay" always refers to the time interval between the initial CO₂ photolysis laser pulse and the UV laser pulse used to probe for the concentration of PO radicals in a given state at a given time after photolytic preparation.

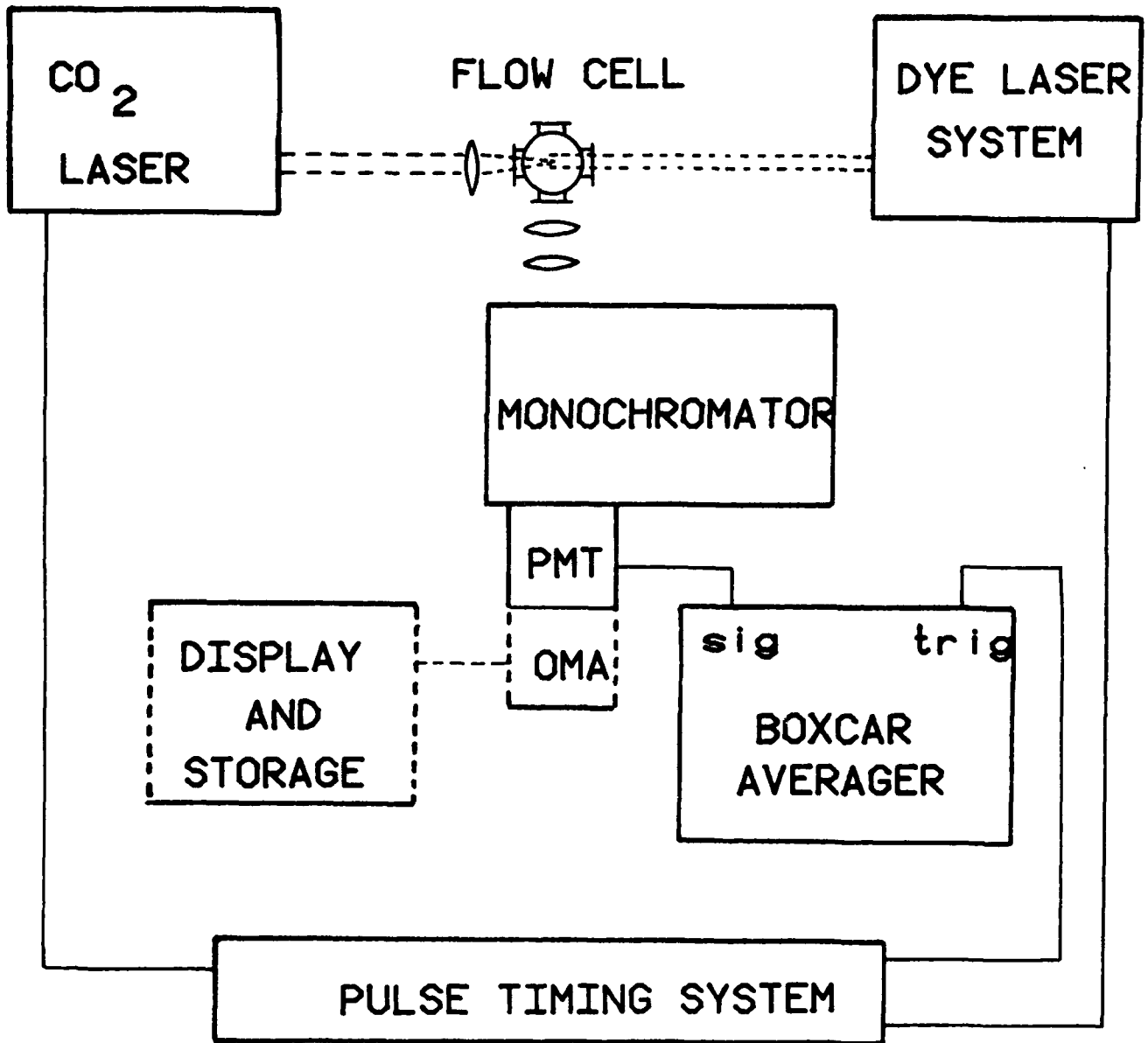


Figure 1. Experimental Schematic.

The CO₂ laser pulse is approximately 100 ns wide with a low intensity tail to 1.5 μ s. The pulse was generally used at the 9P(18) line at 1049 cm⁻¹ for this work. Absorption by DMMP at this frequency is strong. The UV probe beam has a time width of about 5 ns.

3. RESULTS AND DISCUSSION

3.1 IR Multiphoton Dissociation of DMMP.

Our observations of the PO radical following its production by IRMPD of DMMP are limited to a determination of the vibrational levels of ground electronic state PO generated and their approximate relative population ratios. A full description of the nascent PO vibrational, rotational, and spin-orbit population after IRMPD of DMMP under collision-free (low pressure) conditions has been reported by Chou et al.^{8,9} who used mass spectrometric detection of PO⁺ formed by two-frequency, two-photon ionization of PO via its B² Σ^+ - X² Π transition near 325 nm. Where there is overlap between our observations and those of Chou et al.,^{8,9} the agreement between the two different studies is excellent.

Because our focus is on determining the rate of reaction of PO with O₂, we naturally operate at pressures where collisions are important. Our kinetics measurements are made under conditions of at least 0.25 torr total pressure and at least 1- μ s delay of probe laser after photolysis. Therefore, at a minimum, a PO radical would experience several collisions before detection by the probe laser (collision rate for PO on O₂ is approximately 12 μ s⁻¹ torr⁻¹), and the nascent rotational and spin-orbit populations would be substantially thermalized during this time. However, vibrational relaxation typically requires several hundred to several thousand collisions. Therefore, vibrational relaxation could occur on the timescale of the reaction between PO and O₂, and it is important to confirm the relative population of the low-lying vibrational levels of PO formed by IRMPD in order to evaluate the extent to which vibrational relaxation (e.g., v = 1 to v = 0) may affect our rate measurements (e.g., where we monitor decay of v = 0).

Figures 2-5 display a series of fluorescence spectra of PO, generated by IRMPD of DMMP, for which the probe dye laser wavelength was set to excite PO via its (0,0), (1,1), (2,2), and (3,3) bandheads in the A-X transition. The wavelengths used for fluorescence excitation and relevant experimental parameters are provided in the figure captions. The appropriate wavelengths to employ for excitation of the various vibrational levels of the A state were extracted from spectroscopic constants supplied by References.¹⁰⁻¹² Similarly, all observed fluorescence features are readily attributable to PO A-X (v',v'') bandheads by correspondence of the observed wavelengths with those calculated from the relevant spectroscopic constants.¹⁰⁻¹²

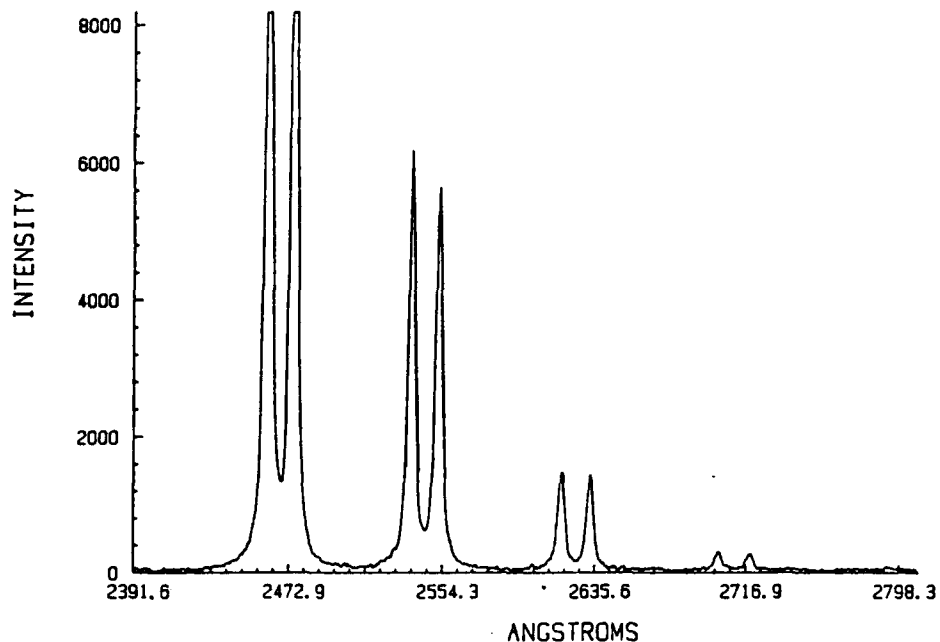


Figure 2. PO A-X LIF Excited Via the (0,0) Band.
 Excitation wavelength: 246.3 nm. CO₂ laser energy: 130 mJ.
 Probe laser delay: 4 μ s. DMMP pressure: 0.4 torr.

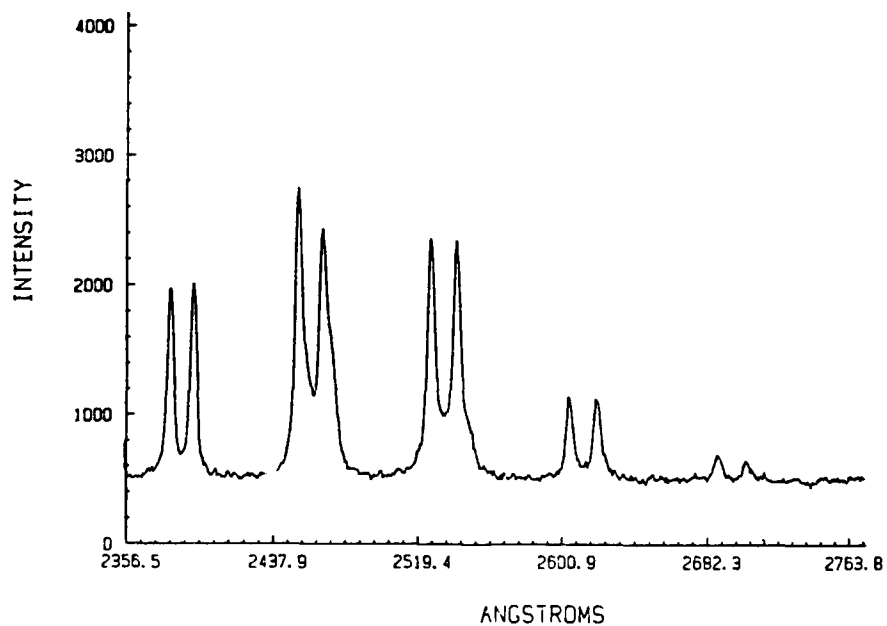


Figure 3. PO A-X LIF Excited Via the (1,1) Band.
 Excitation wavelength: 245.3 nm. CO₂ laser energy: 150 mJ.
 Probe laser delay: 2 μ s. DMMP pressure: 0.4 torr.

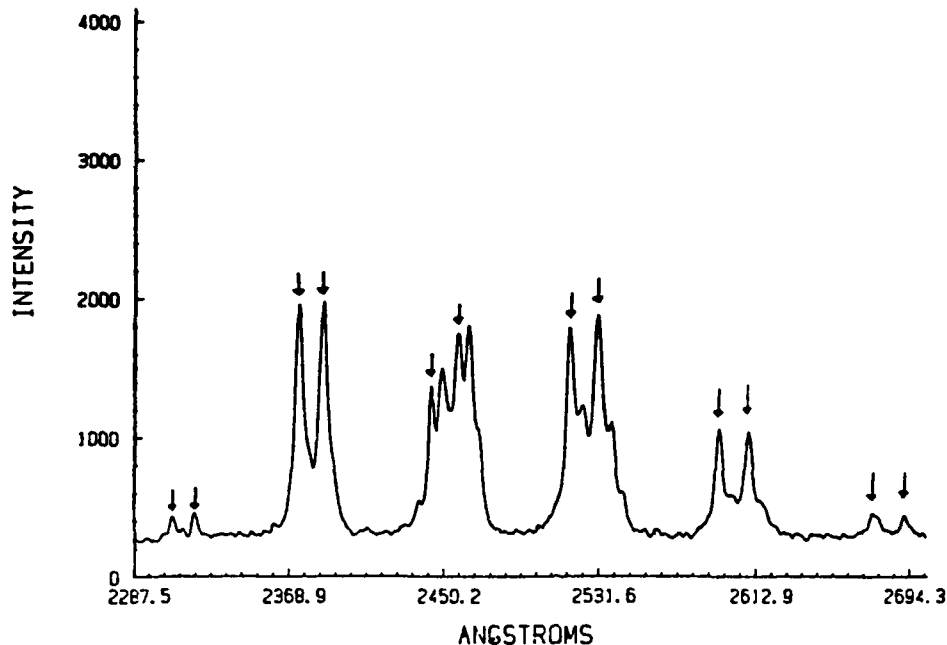


Figure 4. PO A-X LIF Excited Via the (2,2) Band. (2,v") bands are denoted by arrows. See text for explanation of additional bands. Excitation wavelength: 244.4 nm. CO₂ laser energy: 200 mJ. Probe laser delay: 2 μ s. DMMP pressure: 0.4 torr.

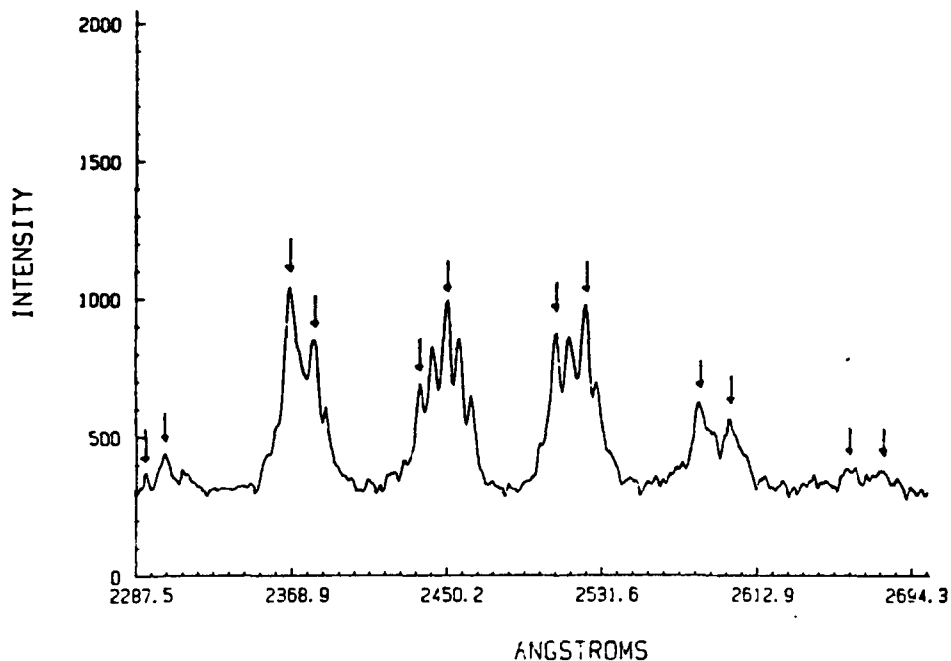


Figure 5. PO A-X LIF Excited Via the (3,3) Band. (3,v") bands are denoted by arrows. See text for explanation of additional bands. Excitation wavelength: 243.6 nm. CO₂ laser energy: 230 mJ. Probe laser delay: 4 μ s. DMMP pressure: 0.4 torr.

As an example, the wavelengths we observe for PO A state $v' = 0$ fluorescence (Figure 2) are collected for comparison with those of Dixit et al.¹⁰ (observed in a discharge tube) in Table 1. The agreement is good considering the ± 0.1 nm accuracy of our measurement.

Table 1. Wavelengths of Bandheads in the A-X (0, v'') Progression.

Band	Branch	Ref. 10*	LIF, this work
(0,0)	Q ₁ , P ₁	2463.2	2462.4
	P ₂ , ^o P ₁₂	2477.0	2475.4
(0,1)	Q ₁ , P ₁	2539.4	2538.1
	P ₂ , ^o P ₁₂	2554.0	2552.7
(0,2)	Q ₁ , P ₁	2619.7	2617.8
	P ₂ , ^o P ₁₂	2635.2	2633.2
(0,3)	Q ₁ , P ₁	2705.1	2702.3
	P ₂ , ^o P ₁₂	2721.5	2719.4

*The wavelengths shown in this column represent the average wavelength of the appropriate bandheads because, with our apparatus, we do not resolve the close-lying Q₁ and P₁ or P₂ and ^oP₁₂ bandheads.

Some explanation of the structure of the fluorescence spectrum is in order. Because it is a 2π state, the lower state in the A-X transition is spin-orbit split into two components, one with $\Omega = 3/2$ lying 224 cm⁻¹ above the $\Omega = 1/2$ component. Accordingly, the vibrational bands in the fluorescence spectra appear as widely spaced doublets with the longer wavelength member of each doublet corresponding to fluorescence to X, $2\pi_{3/2}$. As Table 1 indicates, bands in the A-X system actually form heads in four branches. However, the heads associated with the Q₁ and P₁ branches (due to A-X, $2\pi_{1/2}$) and those in the P₂ and ^oP₁₂ branches (due to A-X, $2\pi_{3/2}$) are too close to be well-resolved with our resolution (0.15 nm), and the bands appear as widely spaced doublets.

It may be noted that, while the fluorescence spectra generated by exciting in the (0,0) and (1,1) bandheads (Figures 2 and 3, respectively) consist of only a single series of vibrational bands (as doublets) due to $v' = 0$ and $v' = 1$,

respectively, the spectra arising from (2,2) and (3,3) bandhead excitation (Figures 4 and 5) have features in addition to the $v' = 2$ and $v' = 3$ progressions. These additional bands are due to spectral overlap of the (2,2) and (3,3) bandheads and high K (rotational) transitions of the lower (v', v'') bands of this system. Thus, excitation in the (3,3) bandhead yields fluorescence not only from $v' = 3$ but also from $v' = 2$ and $v' = 1$ of the A state.

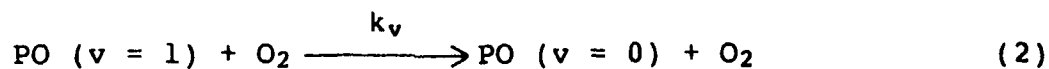
These spectra demonstrate that vibrational levels from $v'' = 0$ to at least $v'' = 3$ of the ground electronic state of PO are generated by IRMPD of DMMP. To extract an estimate of the vibrational temperature of the PO radical fragment, we measured the relative population of $v'' = 0$ and $v'' = 1$. With CO_2 laser energy of 3.5 mJ/pulse and a DMMP pressure of 0.35 torr, the fluorescence signals monitored at a (0,1) bandhead following (0,0) excitation and at a (1,2) bandhead following (1,1) excitation were ratioed. (The monochromator was set to pass the appropriate, monitored bandhead and the signals measured using the PMT/boxcar averager system. The probe laser delay was such that rotational relaxation was complete.) The observed signal ratio was scaled according to the different Franck-Condon factors for the relevant bands:¹³ (0,0), 0.696; (0,1), 0.244; (1,1), 0.280; (1,2), 0.318. This scaling yields a ratio of $v'' = 1$ population to $v'' = 0$ population of 0.17. Using this population ratio with the PO vibrational spacing of 1230 cm^{-1} yields a vibrational temperature of approximately 1000 K. This result is identical to that obtained by Chou et al.^{8,9} who detected PO by resonant two-photon ionization at low pressures in a time-of-flight mass spectrometer.

3.2 Reaction of PO with Molecular Oxygen.

Having established that IRMPD of DMMP generates PO in several low-lying vibrational states with a characteristic temperature of approximately 1000 K, we may discuss measurement of the rate constants for the reaction of PO ($v'' = 0$) and PO ($v'' = 1$) with O_2 . In these studies, we operate under conditions of excess oxygen so that the bimolecular $\text{PO} + \text{O}_2$ reaction becomes pseudo-first order. Because the LIF signal of PO is directly proportional to its concentration at the low laser intensities we employ, exponential decay of the LIF signal with increase in probe laser delay after IR photolysis is expected: I is proportional to $\exp(-k_{\text{obs}}t)$, where $I = \text{PO LIF signal}$ and the observed pseudo-first-order rate constant $k_{\text{obs}} = k_r[\text{O}_2]$, where $k_r = \text{the bimolecular reaction rate constant}$ and $[\text{O}_2]$ is the known O_2 concentration in excess. Thus, the slope of the semilogarithmic plot of LIF signal versus probe laser delay t is the observed first-order rate constant. Further plotting of k_{obs} versus the O_2 concentration over a range of O_2 pressures yields the bimolecular rate constant as the slope.

This approach assumes that the only process that affects the concentration of PO in the probed vibrational state on the time scale of the reaction is the reaction itself. Because the IRMPD generates PO in an array of vibrational states, a potential complication exists due to the possibility of collisional relaxation of vibrational states higher than those being probed. If this vibrational relaxation occurs on the same time scale as the reaction with O₂, the probed vibrational state of PO will be replenished (as well as depleted at v" > 0) as the reaction proceeds.

However, we can show that vibrational relaxation does not significantly perturb our rate constant measurement. For v = 0 PO, the pertinent processes are



Processes involving v > 1 need not be considered because the population above v = 1 is only 3% of the total (at the determined vibrational temperature of 1000 K). The time dependence of PO (v = 0) is, according to the above mechanism, given by

$$d[\text{PO(v = 0)}]/dt = k_v[\text{PO(v = 1)}][\text{O}_2] - k_o[\text{PO(v = 0)}][\text{O}_2] \quad (4)$$

The concentration of PO (v = 1) at any time t is readily obtained as

$$[\text{PO(v = 1)}] = [\text{PO(v = 1)}]_0 \exp\{-(k_1 + k_v)[\text{O}_2]t\}. \quad (5)$$

Substituting equation 5 with equation 4 yields a differential equation whose solution is

$$[\text{PO(v = 0)}] = \left(\frac{k_v[\text{PO(v = 1)}]_0 e^{K[\text{O}_2]t}}{K[\text{O}_2]} + C \right) e^{-k_o[\text{O}_2]t} \quad (6)$$

where

$$K = k_0 - k_1 - k_v \quad (6a)$$

and C is an integration constant.

We can use equation 6 to estimate the effect of vibrational relaxation of $v = 1$ PO on our measurement of the $v = 0$ PO reaction rate. We need only be concerned with relaxation rate constants k_v with values roughly similar to the reaction rate constant k_0 , since for $k_v \gg k_0$ and $k_v \ll k_0$, the observed rate constant is not affected by k_v . The slope of a plot of $\ln[PO(v = 0)]$ versus time, according to equation 6, is the observed pseudo-first-order rate constant. The slopes (observed rate constants) for several values of k_v from an order of magnitude below to an order of magnitude above the rate constant we have measured are listed in Table 2. These calculations are for an O_2 pressure of 1 torr and use for k_0 and k_1 our observed rate constant of $0.44 \mu s^{-1} \text{ torr}^{-1}$ (discussed in the following paragraphs). In addition, our observed nascent population ratio $[PO(v = 1)]_0/[PO(v = 0)]_0 = 0.17$ is incorporated.

The calculated rate constants of Table 2 are only slightly different than the assumed accurate rate constant of $0.44 \mu s^{-1}$. This demonstrates that vibrational relaxation causes a minimal perturbation in the observed rate constant. If it is a simple vibration-to-rotation, translation (V-R,T) energy transfer process, as expected, the vibrational relaxation process (reaction 2) would require several hundred to several thousand collisions. Thus, k_v would be much less than our observed reaction rate constant and vibrational relaxation would not affect the rate constant measurement.

Table 2. Dependence of Observed Reaction Rate on k_v According to Equation 6.

k_v	calculated rate constant
0.04	0.434
0.1	0.430
0.4	0.428
1.0	0.436
4.0	0.440

In measuring the reaction rate for PO ($v = 0$) with O₂, the output of the Tachisto 555 CO₂ laser [9P(1' line)] was focused (10 cm f.l. lens) into the stainless steel cell through which oxygen containing less than 0.01 torr DMMP flowed. Oxygen partial pressures ranged from 0.25 to 1.4 torr. Concentration of $v'' = 0$ PO was followed by LIF excited at the (0,0) Q₁ bandhead (formed by rotational levels K near 7.5) of the A-X system (246.3 nm). Fluorescence was monitored at the (0,1) bandhead at 255.4 nm. The probe laser pulse energy was typically 0.5 mJ/pulse and applied without focusing. The fluorescence intensity was measured using the PMT/boxcar averager system with digitization and storage of the boxcar output by the DEC MINC computer. Most of our data has been generated using CO₂ laser energies of several tens of millijoules. Data collected using from 4 to 400 mJ of CO₂ laser energies show that the PO decay rate is unaffected by change in photolysis laser energy.

As noted earlier, the loss of PO $v'' = 0$ in the presence of O₂ was monitored at O₂ pressures ranging from 0.25 to 1.4 torr. Figure 6 presents a typical semilogarithmic plot of PO LIF at 1 torr O₂ pressure versus probe laser delay and demonstrates that the decay of PO concentration is well-described as exponential and pseudo-first order. (The upper curve of Figure 6 shows the time dependence of PO $v'' = 0$ LIF with 1 torr nitrogen, a nonreactive surrogate for O₂, and illustrates that, after initial rotational equilibration, the PO $v'' = 0$ concentration does not vary on the time scale of the reaction with O₂. The line is a least-squares fit of data to 30 μ s delay.) The observed pseudo-first-order rate constants determined at each O₂ pressure studied are plotted against the O₂ pressure in Figure 7. The observed rate constant is linearly dependent on O₂ pressure.

The kinetic behavior described by the plots of Figures 6 and 7 indicates that the loss of PO results from a simple bimolecular reaction between PO and O₂. The rate constant we obtain, as determined by the slope of Figure 7, is $1.4 (\pm 0.2) \times 10^{-11}$ cm³/molecule/s or 0.44μ s⁻¹ torr⁻¹. This result agrees with that of the earlier excimer laser studies, providing confirmation of both the rate constant measurement and the absence of oxygen atom perturbation of the excimer laser result. The hard sphere collision rate for PO on O₂ is about 12μ s⁻¹ torr⁻¹; the PO + O₂ reaction is then relatively rapid as approximately 1 in 25 collisions leads to reaction.

To measure the decay of $v'' = 1$ PO in the presence of O₂, we have used the same procedures as discussed for $v'' = 0$ PO except that excitation by the probe occurred at the (1,1) Q₁ bandhead at 245.3 nm and fluorescence was monitored at the (1,0) bandhead at 239.4 nm. In addition, the total pressure of the system was maintained at 1 torr by adding N₂ buffer to minimize decay of PO LIF with time due to diffusion of PO out of the detection region of the cell. Figure 8 provides a sample

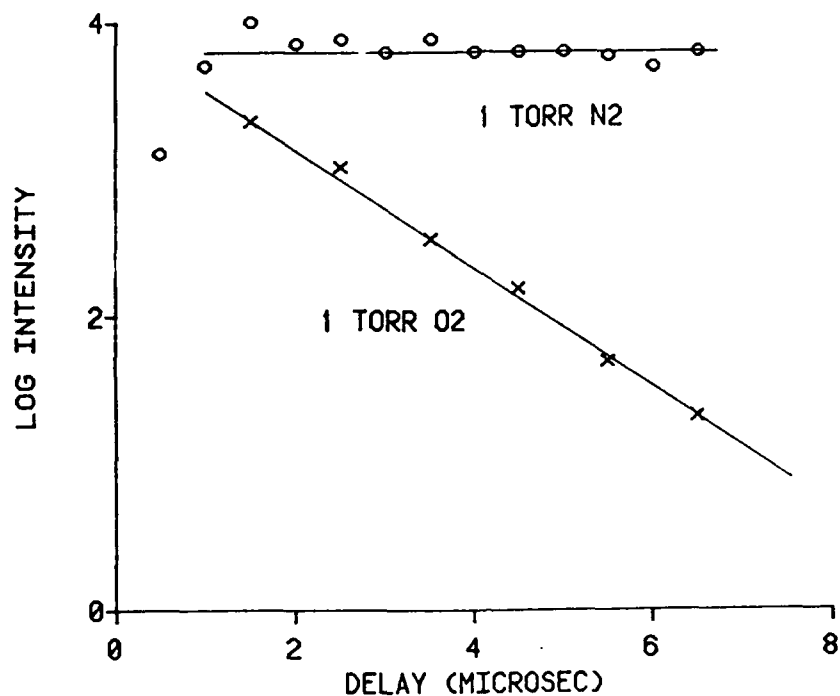


Figure 6. Plot of PO $v = 0$ LIF Intensity Versus Probe Laser Delay at 1 torr O₂.

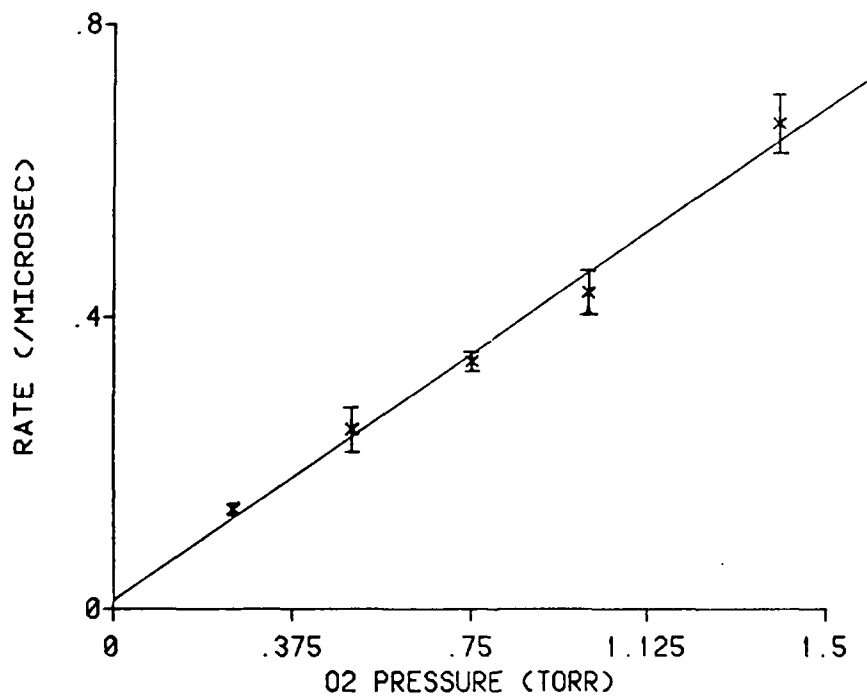


Figure 7. Plot of First-Order Rate Constants Versus O₂ Pressure for $v = 0$ PO.

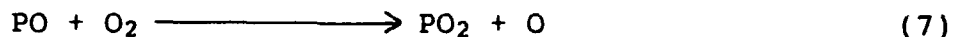
semilogarithmic plot of PO ($v'' = 1$) LIF as a function of probe laser delay with N₂ buffer only and with O₂ at 0.45 torr. The data for three pressures of O₂ (0.25, 0.45, 0.75 torr) as a plot of the observed pseudo-first-order decay rate versus O₂ pressure are presented in Figure 9. These plots are very similar to those for $v'' = 0$ PO. In fact, the measured bimolecular rate constant for PO ($v'' = 1$) + O₂ is $1.5 (\pm 0.2) \times 10^{-11}$ cm³/molecule/s or identical to the result for PO ($v'' = 0$).

It is not surprising that the additional internal (vibrational) energy of PO ($v'' = 1$) does not enhance the PO + O₂ reaction rate. Significant enhancements in bimolecular reaction rates by increasing vibrational energy may be expected when the vibrationally excited mode is along the reaction coordinate in the collision complex (i.e., in the bond which breaks). Quite small reaction rate enhancements are likely when the vibrational excitation is in a bond that does not break in the reaction. Our observations show quite simply that the PO + O₂ reaction follows this expectation.

4. CONCLUSION

The purpose of the work described herein was to determine, by independent observation using CO₂ laser IRMPD, whether the rate constant for the PO + O₂ reaction measured using excimer laser photolysis² was an accurate determination. The rate constant we find, 1.4×10^{-11} cm³/molecule/s, is in good agreement with the prior excimer laser-based measurement of 1.2×10^{-11} cm³/molecule/s. There remains the discrepancy of these measurements with the flow discharge system measurements^{6,7} that derive a rate constant 50 times slower.

Again, the reaction we observe is presumed to be



with $\Delta H \approx 1.6 (\pm 4.0)$ kcal/mole.^{14,15} Although presently undetermined complications in the reaction mechanism may cause the discrepant measurements of this rate, the near thermoneutrality of the reaction coupled with our measured high rate constant implies the possible establishment of equilibrium between the forward and reverse reactions in experiments (e.g., the flow discharge experiments)^{6,7} that incorporate a long contact time between reactants. This problem is compounded by the probable presence of oxygen atoms (appearing on the product side of the above equilibrium) in both flow discharge studies. Oxygen atoms are produced in reference 6 by the PO generation technique, whereas the microwave discharge in Ar carrier in reference 7 may act as a windowless Ar lamp generating radiation ~ 105 nm that could dissociate some fraction of the reactant O₂. Whether these or other considerations are responsible for the discrepancy would

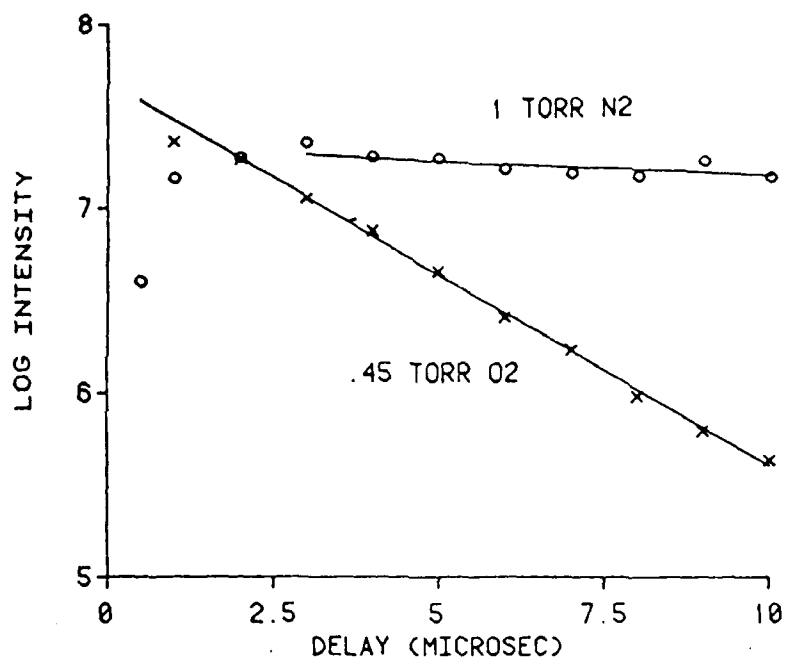


Figure 8. Plot of PO $v = 1$ LIF Intensity Versus Probe Laser Delay at 0.45 torr O_2 . Total pressure, buffered by N_2 , is 1 torr. Upper plot is for 1 torr N_2 .

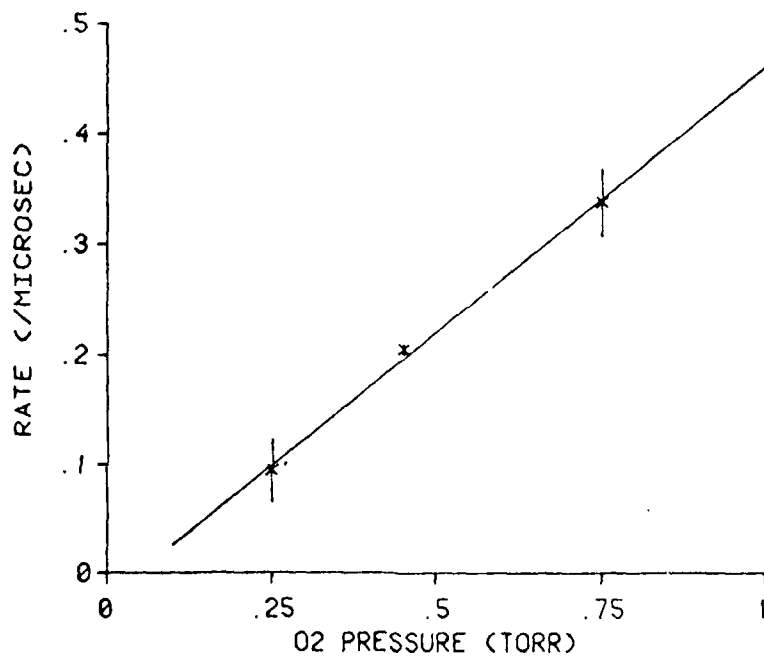


Figure 9. Plot of First-Order Rate Constants Versus O_2 Pressure for $v = 1$ PO.

require more detailed study of the interactions of various reactive species in the flow discharge experiments.

With respect to detection schemes based on laser photolysis, the measured reaction rate constants impose a limit on the length of delay between generation of PO radicals and their detection by LIF or laser ionization at atmospheric pressure under ambient conditions. In the ambient atmosphere, a PO radical would undergo about two collisions/nanosecond with O₂. Because the PO + O₂ reaction occurs at about 1/25th the hard sphere collision rate, the PO concentration would be at its 1/e value in about 10 ns. Therefore, the PO probe laser pulse should interrogate the detection region within 10 ns of the photolysis laser pulse. Clearly, it would be most advantageous if a single laser pulse were used to perform photolysis and detection where possible.

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