DOE/ER/13469--T8

ANNUAL ~~PROGRESS~~ REPORT

Department of Energy

DE-FG03-86ER 13469

Project Agreement 126

RESEARCH IN CHEMICAL KINETICS

Department of Chemistry
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Progress Report on work carried out during the contract period from

January 1, 1986 - October 1, 1986

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Progress Report

Contract No. DE-FG03-86ER 13469

"Research in Chemical Kinetics"

F. S. Rowland, Principal Investigator

I. Photochemistry of Phosphine as Studied by FTIR Spectroscopy

The identification by infrared spectroscopy of PH_3 in the atmosphere of the planet Jupiter [1] has led to speculation about the role of its photochemistry in that atmosphere, and particularly to the possibility that the well known red color of Jupiter's Great Red Spot (GRS) might be caused by solid elemental red phosphorus [2]. While the GRS was first sighted from earth about three centuries ago, hypotheses about the chemical origin of its color have largely been confined to the past several decades. Among the suggestions for this reddish color are: polysulfide chains, S_n from the photolysis of H_2S [3]; the accumulation of organic materials containing C, N and S [4,5]; unsaturated nitrile polymers [6]; and solid elemental phosphorus [2]. Laboratory photolyses of pure PH_3 are known to lead directly to the formation of elemental red phosphorus [7,8]. Our initial laboratory experiments directed toward the photolysis of PH_3 in mixtures with possible H atom scavengers such as C_2H_4 or C_2H_2 appeared to prevent the formation of red phosphorus [9]. However, more recent experiments in this laboratory have indeed found red phosphorus under similar conditions, and we have therefore carried out extensive experiments with FTIR techniques.

The photolysis mechanism proposed by Melville [7] and then later by Norrish and Oldershaw [8] for the formation of red phosphorus included the five steps of reactions (1) to (5). These same reactions form the mechanistic basis for the proposal that red phosphorus can be formed by photolysis of phosphine in the Jovian atmosphere [2].

$$PH_3 + h\nu \longrightarrow PH_2 + H \qquad (1)$$

$$PH_2 + PH_2 \longrightarrow PH + PH_3 \qquad (2)$$

$$PH + PH \longrightarrow P_2 + H_2 \qquad (3)$$

$$P_2 + P_2 + M \longrightarrow P_{4\,(g)} + M \qquad (4)$$

$$P_{4\,(g)} \longrightarrow P_{4\,(s)}\ \text{(red)} \qquad (5)$$

This mechanism is now known to be incomplete because diphosphine, P_2H_4, has been identified as the initial stable photoproduct from PH_3 [10,11]. The formation of this product presumably involves reaction (6), and the mechanism may also include the attack of H atoms on phosphine by (7). If P_2H_4 is the intermediate in the Jovian atmosphere,

$$PH_2 + PH_2 + M \longrightarrow P_2H_4 + M \qquad (6)$$

$$H + PH_3 \longrightarrow H_2 + PH_2 \qquad (7)$$

then it might be expected to condense to a solid at the low atmospheric temperatures above the upper clouds in Jupiter and thus be protected against further destruction. Without further reaction of P_2H_4, the reaction mechanism would no longer lead to $P_{4\,(s)}$, and elemental red phosphorus would no longer be a satisfactory explanation for the color of the GRS.

The photochemistry of PH_3 has been considered in models of the atmosphere of Saturn and mixed with NH_3 in the atmosphere of Jupiter [12,13]. Unless P_2H_4 is removed by condensation, the models indicate that red phosphorus could be formed in potentially large quantities. These models also predict the formation of observable amounts of organophosphorus compounds. Noy et al. have pointed out [14] that the photolysis of PH_3 in the presence of H_2 does not lead to the formation of red phosphorus in the laboratory, but rather to a yellow product.

We have therefore carried out a series of laboratory photolysis experiments to clarify some of the aspects of the phosphine system. One of the first steps in this investigation has been the measurement of the FTIR spectrum of pure P_2H_4. The FTIR absorption spectrum of gaseous PH_3 is shown in Figure 1a, while that of P_2H_4 -- prepared by the reaction of H_20 with calcium phosphide [15] -- is shown in Figure 1b. The formation of P_2H_4 in substantial yield in the photolysis of PH_3 at 184.9 nm or 214 nm has been confirmed by monitoring its absorption in the region 700-900 cm^{-1}.

The variation in yield for P_2H_4 vs. exposure time to photolysis was studied to determine the time for maximum yield, with the results shown in Figure 2. The maximum in concentration has several contributory factors: The accumlation of P_4 on the cell window; the instability of P_2H_4; and the susceptibility of P_2H_4 to secondary photolysis, or to attack by free radical species such as H, PH_2, etc. The FTIR spectrum of PH_3 photolyzed for 30 sec with 184.9 nm light is shown in Figure 3a. The spectrum in Figure 3b is the difference spectrum for the same mixture, after subtraction of the spectrum of pure PH_3. A comparison on a different scale is shown in Figure 4 of the difference spectrum representing P_2H_4 (b) with the authentic material (a).

The effects of addition of C_2H_2, C_2H_4 or NH_3 during the photolysis of PH_3 have also been examined. None of these additives showed any significant scavenging effect on the formation of P_2H_4. One implication of these results is that such scavenging is unlikely in the Jovian atmosphere as well, so that the formation of P_2H_4 there must be considered further. No detectable formation was observed for N_2H_4, CH_3PH_2, or $C_2H_5PH_2$; no

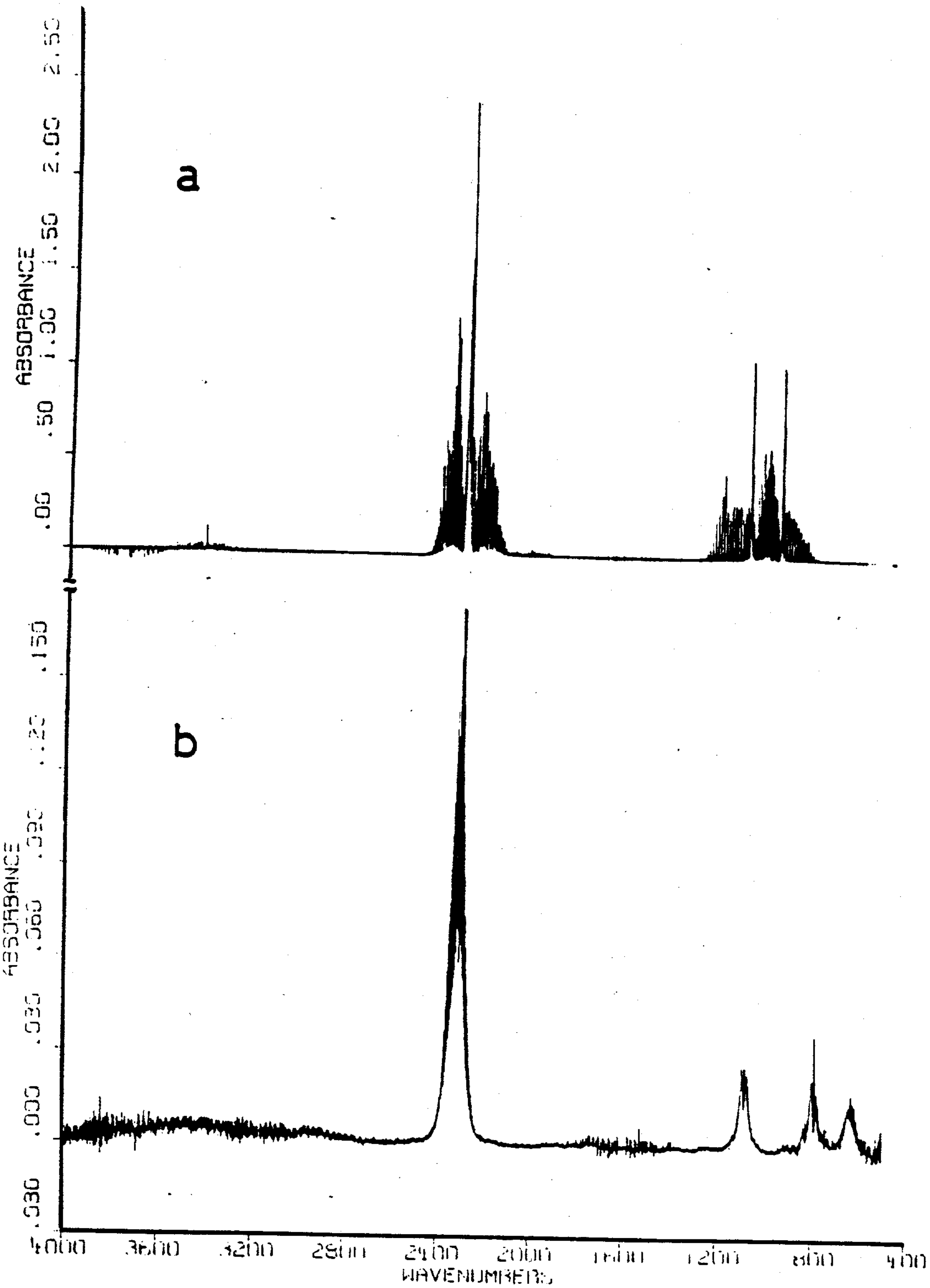

Fig. 1 (a) the FT-IR absorption spectrum of gaseous PH_3 (50 torr) and
(b) the FT-IR absorption spectrum of an authentic P_2H_4 (1.66 torr) which was prepared by the reaction of water on calcium phosphide (light path length of the cell for IR is 145.7 mm)

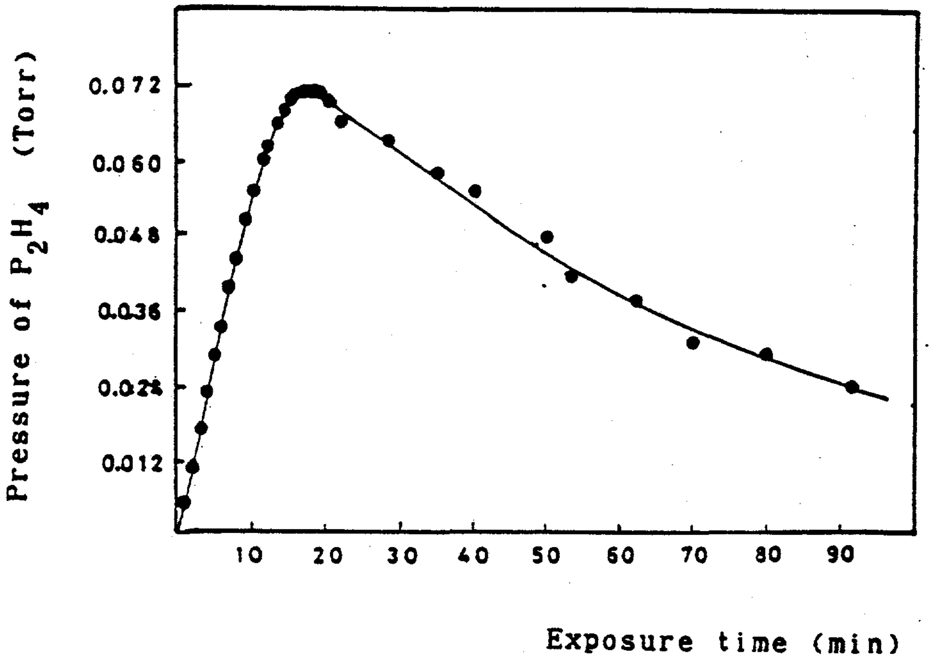

Figure 2. The effect of variation in exposure time on the yield of P_2H_4 from the photolysis of PH_3 (50 torr) at 214 nm by using the cross-shaped cylindrical cell. One direction used for photo-irradiation, the other for measurements of UV-Vis absorption.

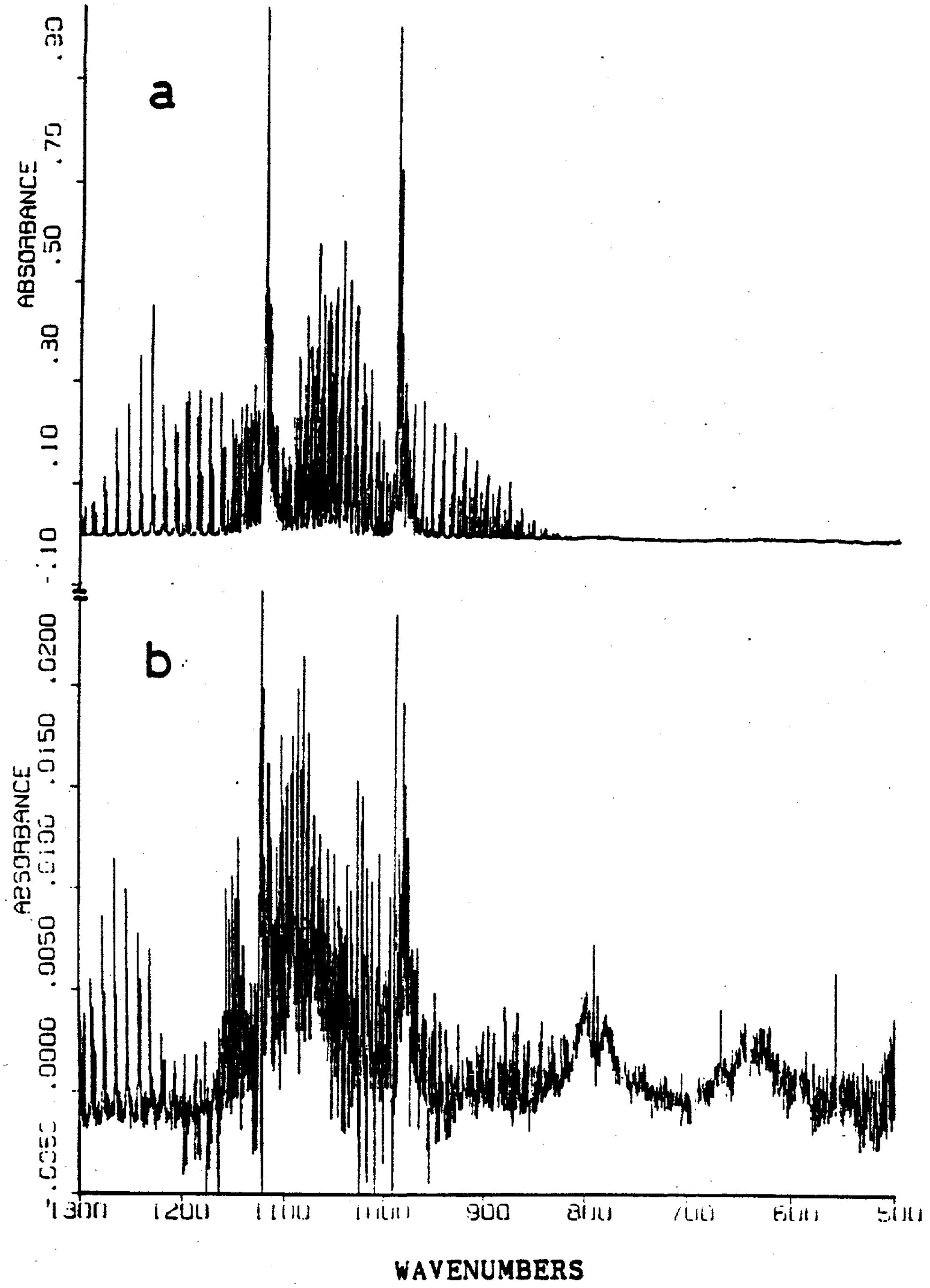

Fig. 3 (a) The FT-IR absorption spectrum of photoirradiated gaseous PH_3 (50 torr) at 184.9 nm for 30 sec.
(b) The difference spectrum of the same mixture, after subtraction of the spectrum of pure PH_3.

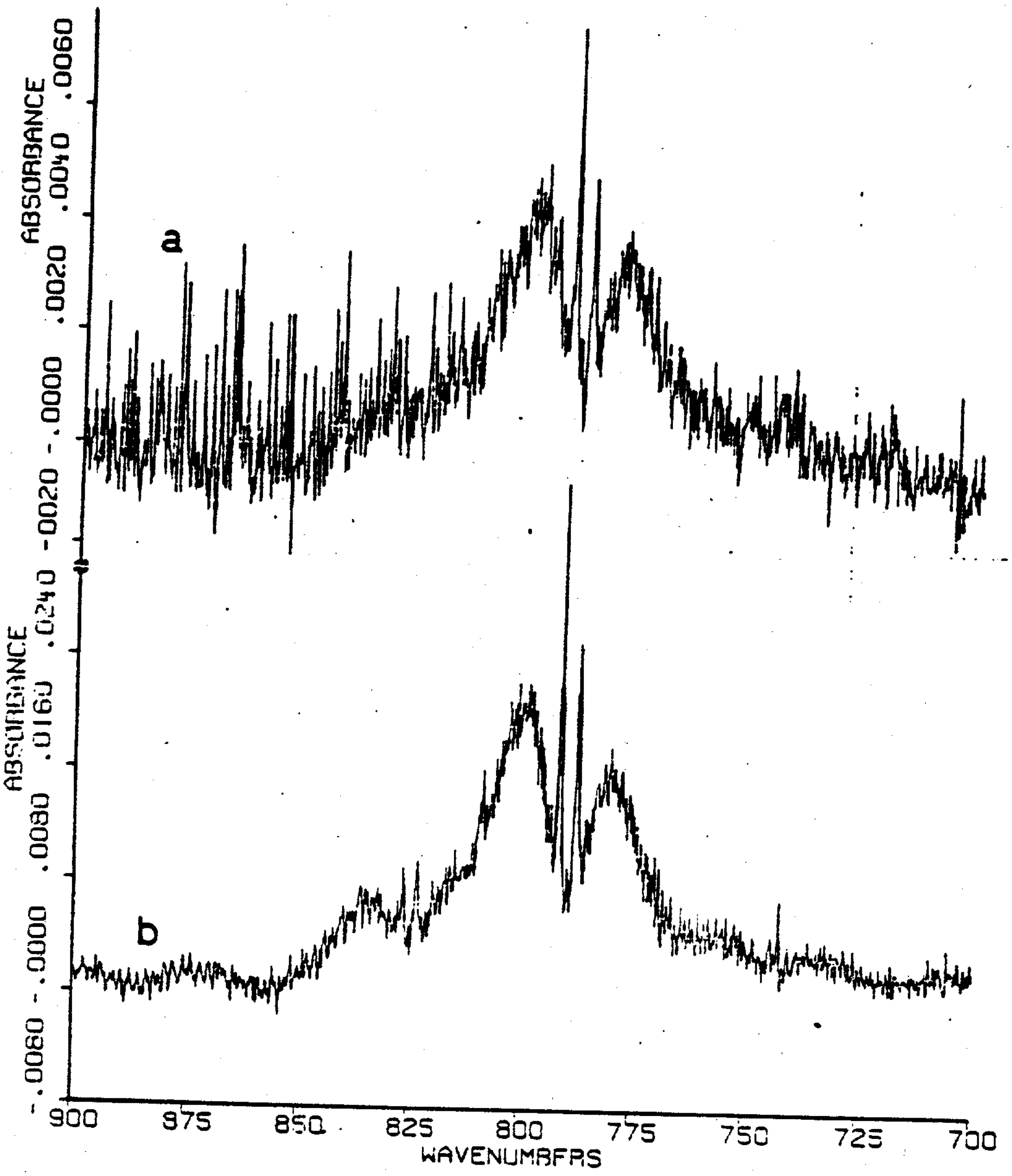

Fig. 4. Comparison of FTIR absorption spectrum (a) of authentic P_2H_4 and the differencespectrum (b) of photoirradiated PH_3.

spectrum was observed which might be assigned to the as yet unknown molecule PH_2NH_2. Formation of N_2H_4 is expected from the photolysis of NH_3, but its loss by adsorption on the walls of glass or quartz is documented [16]. The measured yields of P_2H_4 formed is these photolytic experiments are summarized in Table 1.

The solid products formed on the cell surface during the photoirradiation of these gaseous mixtures were usually yellow in color. The material was, however, not yellow phosphorus because it was not soluble in CS_2, ether or ethanol, nor did it self-ignite when exposed to air. Mass spectrometry suggests a polymeric material containing both P and CH_3 groups. The UV-visible absorption spectra of elemential phosphorus produced by photoirradiating PH_3 at 184.9 nm is shown in Figure 5. The corresponding spectra of solid products formed in the irradiation of PH_3-C_2H_2 mixture and PH_3-NH_3 mixture are shown in Figures 6 and 7 respectively. In general, these spectra show similar absorption patterns. As seen in Figure 6, the product from PH_3-C_2H_2 mixture irradiation shows different absorption spectra depending upon the method of irradiation -- through the window of the cell or through the cylindrical walls of the cell. The solid product formed in the irradiation of PH_3-NH_3 mixture appeared "redder" than that from PH_3 alone.

The products formed in the photolysis of gaseous P_2H_4 at 184.9 nm or 214 nm are PH_3, H_2 and polymeric phosphorus. The UV-visible absorption spectra of the solid product formed in the irradiation of solid P_2H_4 at 78 K are shown in Figure 8. Although the solid product when collected appeared yellowish white, red coloration was observable on the cell surface, suggesting the possibility that it might have a role in the color

Table 1 Yields of P_2H_4 in photolysis of PH_3

PH_3, Torr	added gases, Torr		light source[a]	irrad. time, sec	Yields of P_2H_4 by FT-IR, Torr[b]		Yields of P_2H_4 by UV, Torr[c]	
5.00			Hg	30	○[d]	0.13[f]	0.18	
5.00	NH_3	2.00	Hg	30	○[d]	○[d,f]	0.17	0.08[h]
5.00	NH_3	5.00	Hg	30	○[d]	○[d,f]	0.18	0.09[h]
20.0			Hg	30	○[d]			
20.0	H_2	647	Hg	30	0.22		0.27	
50.0			Hg	30	0.36		0.38	0.32[h]
50.0	NH_3	2.00	Hg	30	○[d]			
50.0	NH_3	5.00	Hg	30	○[d]	0.30[f]	0.30	
50.0	NH_3	200	Hg	30	—[e]	—[e]		
50.0	C_2H_2	2.00	Hg	30	—[e]	0.32[f]	0.36	0.31[h]
50.0	C_2H_2	100	Hg	30			0.52[g]	
50.0	C_2H_4	2.00	Hg	30	0.39		0.40	0.33[h]
30.0	NH_3	3.00	Zn	1200	—[e]			
50.0			Zn	1200	—[e]			
50.0	C_2H_4	2.00	Zn	1200	—[e]			
500			Zn	1200	○[d]			
500	C_2H_4	2.00	Zn	1200	○[d]			

a) Hg: The low pressure mercury lamp (184.9nm) and the cell which was shown in Fig.1 were used.

Zn: The zinc lamp (214nm) and the cross-shaped cylindrical cell with two KBr windows and two Suprasil windows were used.

b) The pressure of P_2H_4 was determined by the baseline method on IR absorvance at 791.2cm^{-1}.

c) The pressure of P_2H_4 was determined by the UV absorvance of the photolysate at 245nm.

d) Open circles mean that P_2H_4 was observed, however, yields of P_2H_4 could not be determined because of the interruption by IR absorvance of added gas or too small amount of P_2H_4.

e) P_2H_4 was not observed in IR spectra.

f) In case there are overlaping between the absorptions of the added gases and P_2H_4, the P_2H_4 was measured after the separation.

g) This yield of P_2H_4 might not be correct, because the yellowish white photoproduct was apt to be formed and it was assumed that the UV absorvance at 245nm was not due to the presence of P_2H_4.

h) There is no need to separate, however, the separations were carried out in order to compare with the results of FT-IR. The decrease of 20% in average on the quantity of P_2H_4 was observed by the separation.

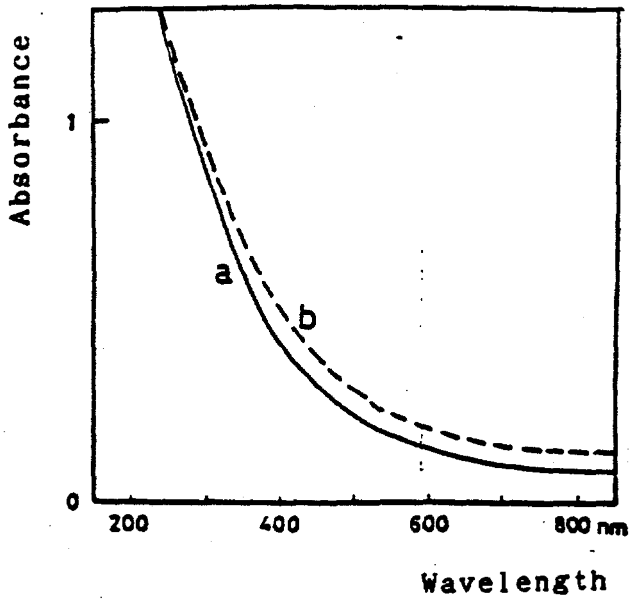

Fig. 5 The UV-Vis absorbance spectra of the elemental phosphorus produced by photoirradiating at 184.9nm for 30 min (uncorrected for surface reflection)
(a) 10 Torr PH3, (b) 50 Torr PH3

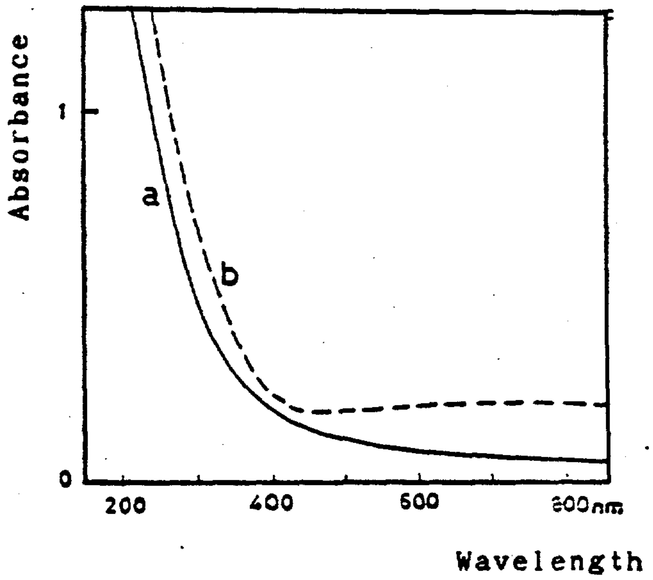

Fig. 6 The UV-Vis absorbance spectra of the solid photolysis product of 50 torr Ph_3 amd 100 Torr C_2H_2 mixture. Photoirradiations were carried out at 184.9nm for 30 min. (uncorrected for surface relection)

(a) The cylindrical cell is photoirradiated through the one window

(b) The cylindrical cell is photoirradiated through its cylindrical wall.

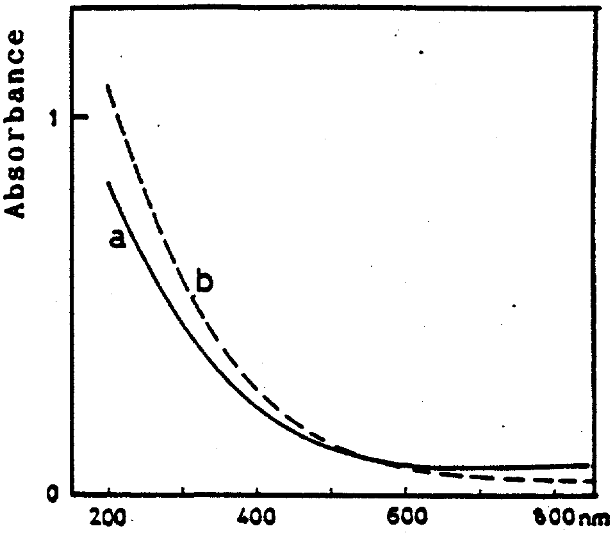

Fig. 7. The UV-Vis absorbance spectra of the solid photolysis product at 184.9 nm for 10 min. The cylindrical cell is photoirradiated through the one window. (uncorrected for surface reflection)
(a) 10 torr PH_3 alone
(b) The mixture of 10 torr PH_3 and 100 torr NH_3

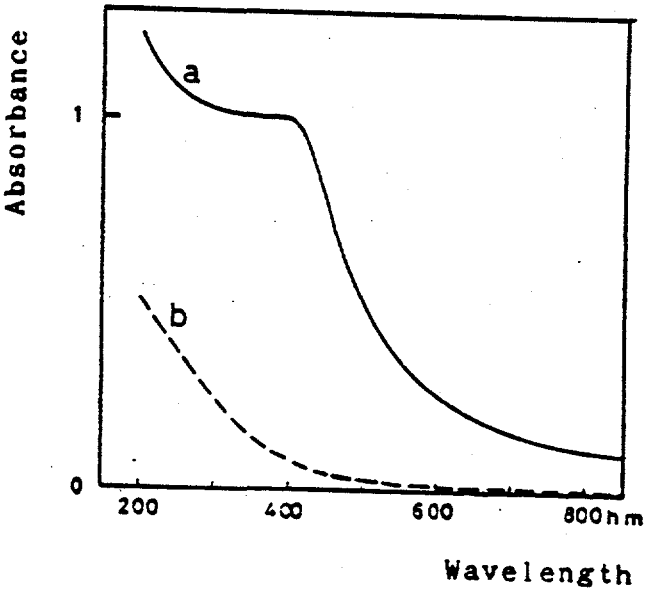

Fig. 8. The UV-Vis absorbance spectra of the product formed by photolysis of solid P_2H_4.
(a) (solid line) 0.3 mg, or (b) (broken line) 0.06 mg of P_2H_4 was condensed on the quartz plate at 78 K and photoirradiated with 214 nm zinc lamp.

of the GRS in Jupiter. Further investigations are needed for a complete understanding of the photochemistry of gaseous or solid P_2H_4 and to determine any role that PH_3 or P_2H_4 might have for the color of the GRS.

References

1. S.T.Ridgway, L.Wallace, and U.Fink, Astrophys. J., 207, 1002 (1976)
2. R.G.Prinn and J.S.Lewis, Science, 190, 274 (1975)
3. J.S.Lewis, Icarus, 10, 393 (1969)
4. C.Sagan and B.N.Khare, Astrophys. J., 168, 563, (1971)
5. T.Scattergood, P.Lesser, and T.Owen, Nature, 247, 100 (1974)
6. C.Ponnamperuma, Icarus, 29, 321 (1976)
7. H.Melville, Proc. Roy. Soc. London, 138, 374 (1932)
   ibid. 139, 541 (1933)
8. R.Norrish and G.Oldershaw,Proc. Roy. Soc. London, 262, 1 (1961)
9. H.G.V.Ruiz and F.S.Rowland, Geophys. Res. Lett., 5 ,407 (1978)
10. J.P.Ferris and R.Benson, J. Am. Chem. Soc.,103, 1922 (1981)
11. J.P.Ferris, A.Bossard, H.Khwaja, J. Am. Chem. Soc.,106, 318 (1984)
12. D.F.Strobel, Astrophys. J., 214, L97 (1977)
13. J.A.Kaye and D.F.Strobel, Icarus, 59, 314 (1984)
14. N.Noy, M.Podolak, and A.Bar-Nun, J. Geophys. Res.,86, 11985 (1981)
15. E.P.Nixon, J. Phys. Chem., 60, 1054 (1956)
16. J.R.McNesby, I.Tanaka, and H.Okabe, J. Chem. Phys., 36, 605 (1962)

II. Photolytic Studies with Radioactive Tracers

The HO initiated oxidation of CS_2 in the presence of O_2 or air has been studied using ^{14}C labelled $^{*}CS_2$ in order to acquire additional information about mechanism of the photochemical reactions of CS_2 under atmospheric conditions. Earlier studies accomplished in this laboratory on the reaction of HO with $^{*}CS_2$ indicated that in the absence of O_2, the bimolecular reaction of CS_2 with HO has a rate constant 3×10^{-15} cm^3 $molecule^{-1}$ s^{-1} at 295 K, consistent with the findings of other research laboratories using different experimental techniques [1-3]. Two of the reported studies on the oxidation of CS_2 by HO in the presence of O_2 have indicated rapid removal of CS_2 with the formation of OCS and SO_2 as products, thus identifying a tropospheric sink for CS_2 and source for tropospheric OCS and SO_2 [4,5]. The mechanism which has been proposed for this oxidation process involves the formation of a CS_2OH adduct which either dissociated back to the reactants or reacted with O_2 to form the observed products:

$$CS_2 + HO + M \qquad CS_2OH + M \qquad (1)$$

$$CS_2OH + O_2 \qquad \text{Products} \qquad (2)$$

The details of the mechanism of conversion of CS_2 to OCS and SO_2 are not well elucidated.

Our recent experiments have involved the use of ^{14}C labeled $^{*}CS_2$ to examine the reaction of CS_2 with HO in the presence of O_2 in a static photolytic system and radio gas chromatographic measurements of both ^{14}C-product yields and $^{14}CS_2$ removal. A rapid removal of $^{*}CS_2$ with rates increasing with O_2 concentration was observed in these experiments consistent with the findings of Jones et al. [4] and of Barnes et al. [5]. However, the products spectrum observed in our experiments differs from those of earlier studies. We observed that the reaction of $^{14}CS_2$ with HO in the presence of O_2 produces not only $O^{14}CS$, but also ^{14}CO in yields comparable to that of $O^{14}CS$ and minor yields of $^{14}CO_2$. In these experiments we confined our measurements to $^{14}CO_2$ in yields comparable to that of $O^{14}CS$ and minor yields of $^{14}CO_2$. In these experiments we confined our measurements to ^{14}C-product yields and did not measure SO_2 formation quantitatively. Additional eperiments with ^{35}S-labelled CS_2 will allow measurements of both $OC^{35}S$ and $^{35}SO_2$ by radio gas chromatography and will be useful for better understanding of the CS_2 oxidative process in the atmosphere.

In our recent experiments, mixtures of $^{*}CS_2$, C_3H_8, H_2O_2, O_2 and N_2 at a total pressure of one atmosphere were irradiated at 302 nm. The photolytic decomposition of H_2O_2 served as the source of HO radicals. The loss of C_3H_8 through reaction with HO served as a standard for monitoring the HO fluxes in these irradiations. The ^{14}C product yields and the loss of $^{14}CS_2$ were determined by radio gas chromatography of the photolytic mixture. The effect of irradiation time on the product yields is shown in Figure 1. Linear increase in yield was observed for all three products $O^{14}CS$, ^{14}CO, and $^{14}CO_2$ for irradiation periods up to two hours. The loss of C_3H_8 measured by its thermal conductivity response was also linear with irradiation time as shown in Figure 1. The ratios of the percent product yield to the percent C_3H_8 loss in

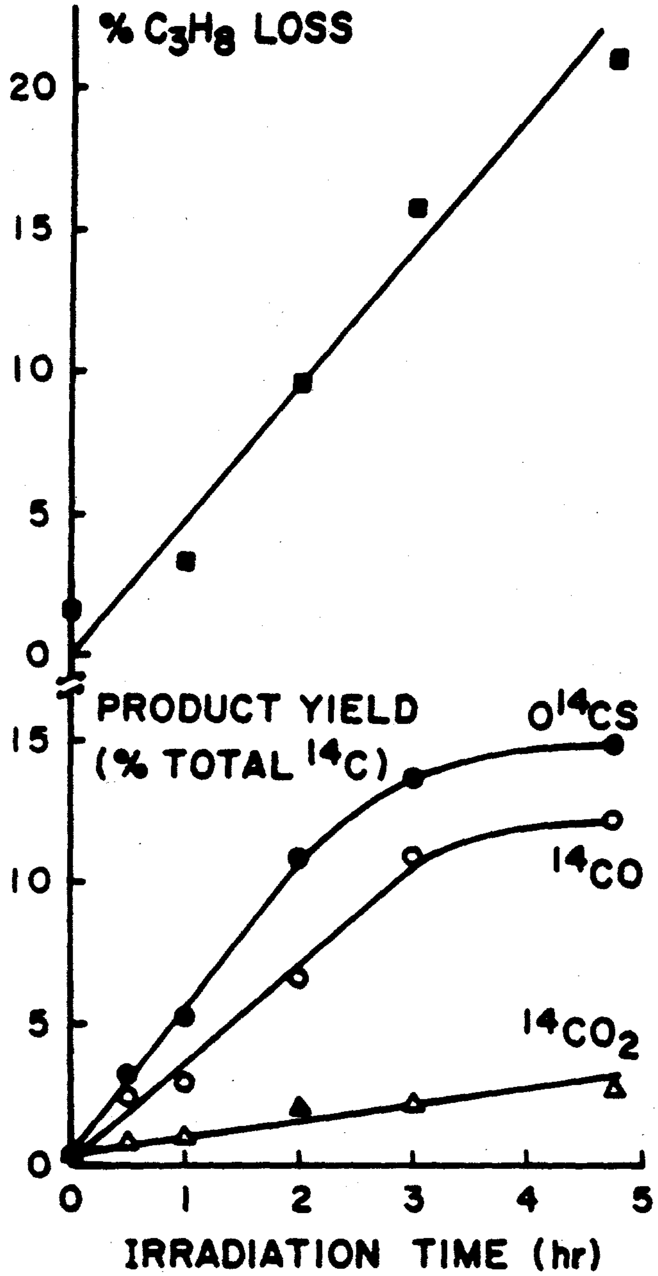

Figure 1. Effect of irradiation time on % ^{14}C-product yields and % C_3H_8 loss in the 302 nm irradiation of mixtures of H_2O_2 (~2 torr), *CS_2 (~0.9 torr), C_3H_8 (~1.5 torr), O_2(172 torr) and N_2(590 torr).

short irradiations (less than two hours) in these experiments represent an effective rate constant for ^{14}C product formation relative to the rate constant for removal of C_3H_8 reaction with HO. Using the known value of the rate constant ($1.2x10^{-12}$ cm^3 molecule^{-1}) for the HO + C_3H_8reaction, these ratios could then be converted into "effective" rate constants for $O^{14}CS$, ^{14}CO, and $^{14}CO_2$ formation. In samples containing 172 torr of O_2 and one atmosphere total pressure, these effective rate constants at 295 K were determined to be $(1.42\pm0.41)x10^{-12}$, $(0.90\pm0.12)x10^{-12}$ and $(0.26\pm0.10)x10^{-12}$ cm^3 molecule^{-1} s^{-1} respectively for $O^{14}C$ ^{14}CO and $^{14}CO_2$ formation.

The effect of O_2 concentration on product yields in the irradiation at 302 nm of mixtures of $*CS_2$-C_3H_8——H_2O_2-O_2-N_2 at a total pressure of one atmosphere is shown in Figure 2. In the range of O_2 concentrations used in these experiments (0-248 torr, the relative yield ratio $\%0^{14}CS/\%C_3H_8$ loss, increased continuously with $[0_2]$ as shown in Figure 2. The corresponding ratios for ^{14}CO and $^{14}CO_2$ also indicated increases with $[0_2]$ as shown in Figure 2. The corresponding ratios for ^{14}CO and $^{14}CO_2$ also indicated increases with $[O_2]$ but remained constant for $[0_2]>100$ torr. From the measured relative loss of $^{14}CS_2$ vs C_3H_8. the effective rate constants (k_{eff}) for the removal of CS_2 were determined at various $[0_2]$ using the known rate constant or the H0 + C_3H_8 reaction. As shown in Figure 3, these effective removal rates increased with $[0_2]$. The values of k_{eff} reported by Barnes _et_ _al_. and by Jones _et_ _al_. are also shown in Figure 3. Our values of k_{eff} are in agreement with those of Barnes _et_ _al_., but are approximately 2.5 times higher than those reported by Jones _et_ _al_. Additionally,

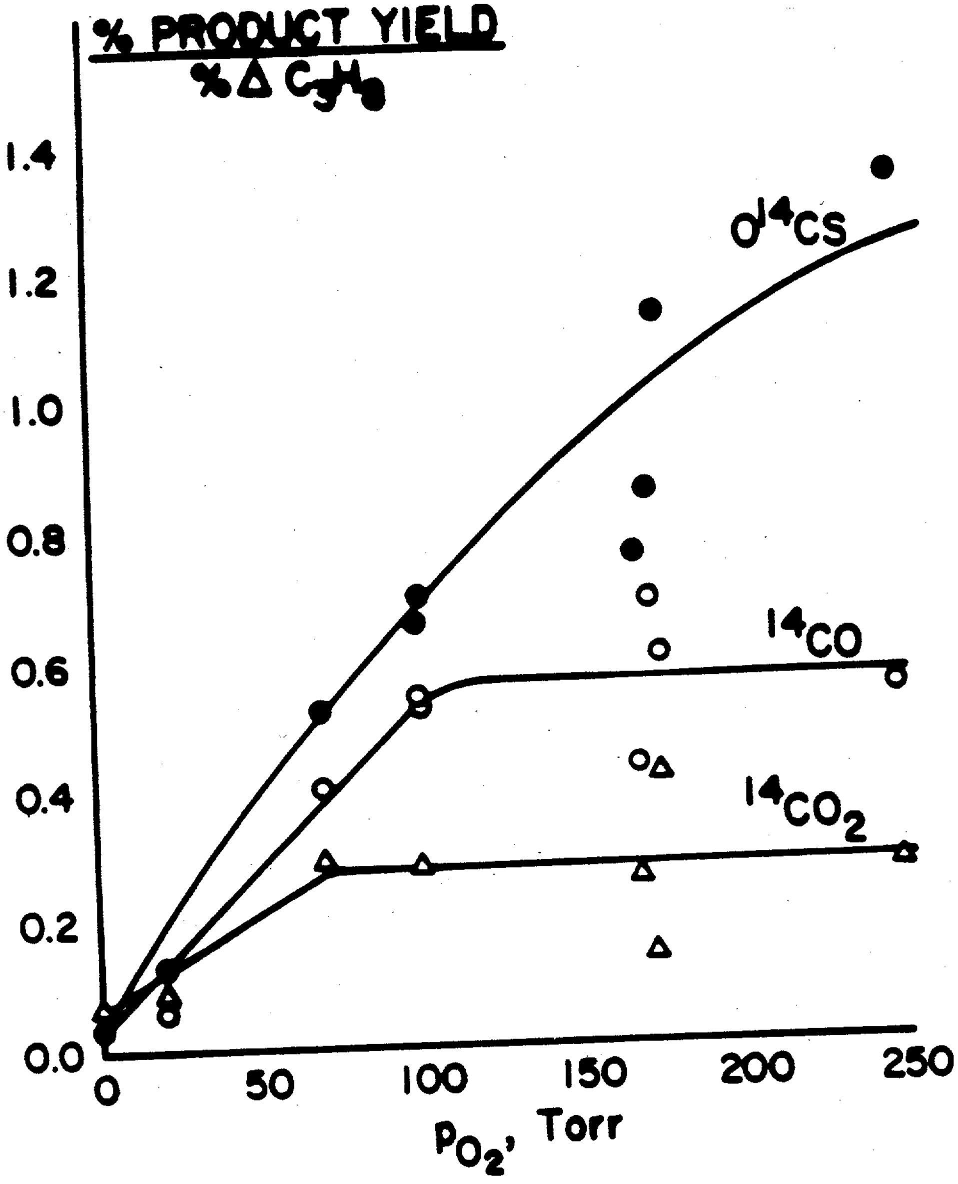

Figure 2. Effect of O_2 concentration on product yields in the 302 nm irradiation of mixtures of H_2O_2 (~2 torr), $*CS_2$ (~0.9 torr), C_3H_8 (~1.5 torr), O_2 (0-248 torr) and N_2 (balance to form total of one atm.)

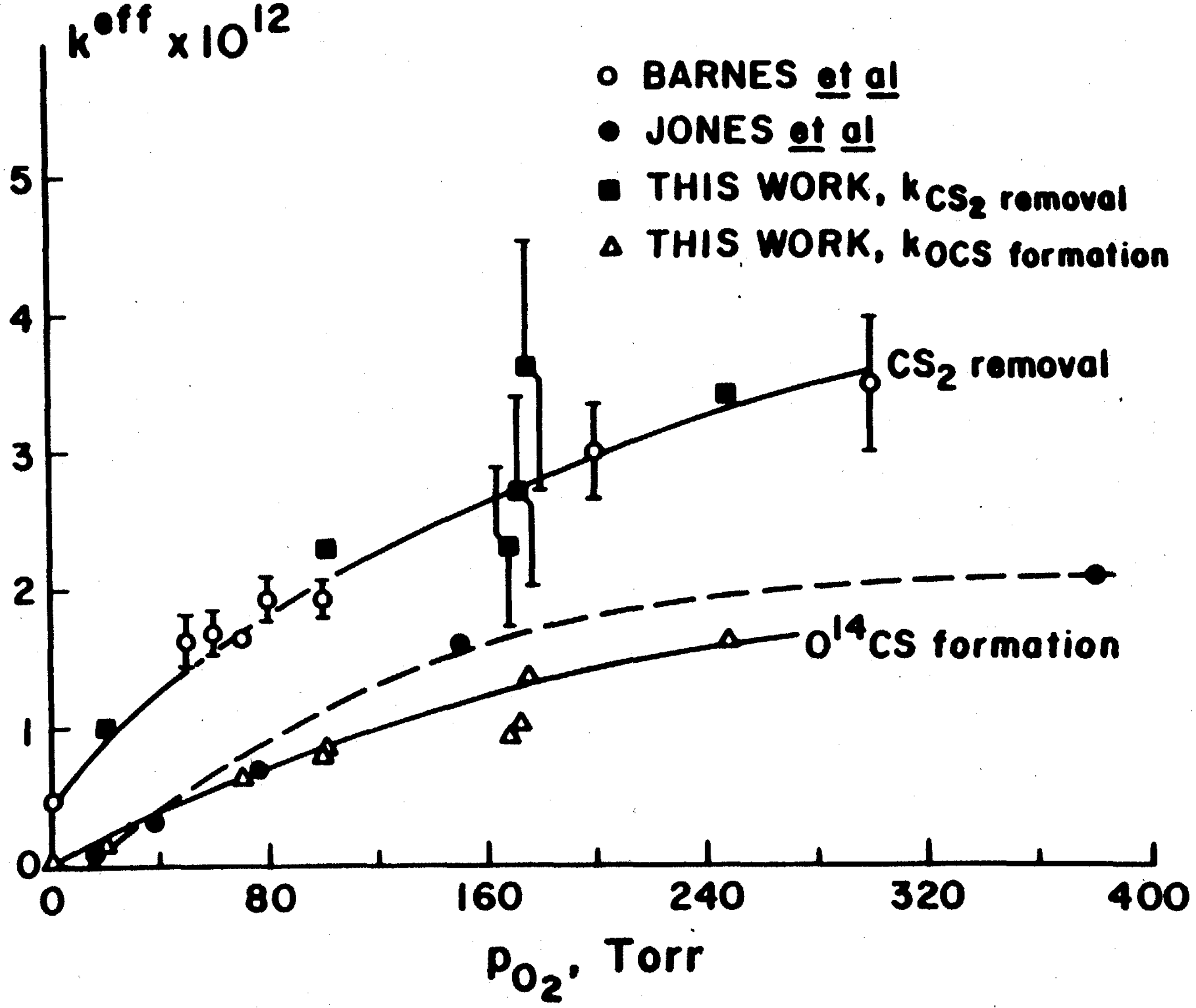

Figure 3. Measured k_{eff} values for the removal of CS_2 and for OCS formation at 1 atm. pressure and 295 K vs. O_2 concentration.

both the earlier studies reported one to one equivalence of CS_2 loss to the yields of OCS and SO_2, while in our experiments the $O^{14}CS$ formation accounts for only about half the fraction of $^{14}CS_2$ removed, as can be seen from the effective rate constants for $O^{14}CS$ formation shown in Figure 3. The observation of only low yields of the three products $O^{14}CS$, ^{14}CO and $^{14}CO_2$ in irradiated mixtures containing no H_2O_2, the source of HO radicals, and the enhanced, $[O_2]$ dependent yields observed for all three products when both H_2O_2 and O_2 are present in the irradiation mixtures, leads us to believe that routes for formation of all three products exist in the $HO + CS_2 + O_2$ system. The dependence of k_{eff} on $[O_2]$ can be accounted for by the proposed reactions (1) and (2); but the mechanism by which the CS_2OH adduct is converted to the observed products is unclear. Further studies are needed for a better understanding of this complex mechanism and we propose to continue our studies on this system using ^{35}S labeled CS_2.

REFERENCES

1. R. S. Iyer and F. S. Rowland, Geophys. Res. Lett. 7, 797(1980).
2. P. H. Wine, R. C. Shah, and A. R. Ravishankara, J. Phys. Chem. 84 , 2499 (1980).
3. M. T. Leu and R. H. Smith, J. Phys. Chem. 86, 958 (1982).
4. B. M. R. Jones, R. A. Cox, and S. A. Penkett, J. Atm. Chem. 1, 65 (1983).
5. I. Barnes, K. H. Vecker, E. H. Fink, A. Reimer, F. Zabel, and H. Niki, Int. J. Chem. Kinet. 15, 631 (1983).

III. Heterogeneous Reactions of Atmospheric Interest

The study of the heterogeneous reactions of chlorine nitrate with H_2O and with HCl in reactions (1) and (2), begun under this contract in 1984, has continued with later support from N.A.S.A., and the first

$$H_2O + ClONO_2 \longrightarrow HOCl + HONO_2 \qquad (1)$$

$$HCl + ClONO_2 \longrightarrow Cl_2 + HONO_2 \qquad (2)$$

aspects have now been published. In brief, the first of these showed an equivalent bimolecular rate constant of (1-13) × 10^{-19} cm^3 $molecule^{-1}$ sec^{-1} on all of the normally inert surfaces tried, rate constants which are a factor of 10^2 to 10^3 faster than those found with the 5800 liter reaction vessel at the University of California Riverside. Reaction (2) was even faster, with equivalent rate constants in the 10^{-16} cm^3 $molecule^{-1}$ sec^{-1} range.

Because catalysis on usually passive surfaces is so effective in the laboratory, the possibility becomes quite plausible that $ClONO_2$ molecules striking ice crystals in the stratosphere may very well react with them. The heterogeneous reaction of HCl with $ClONO_2$ is less likely in the actual atmosphere because it requires that both molecules strike the particulate matter in the stratosphere, and that the first to strike must be held long enough to encounter the second. However, the extremely rapid catalysis in the laboratory keeps open the possibility that such sticky collisions and rapid reactions cannot be eliminated from consideration on the basis of present knowledge.

An important new phenomenon in stratospheric chemistry is the observation of a very striking loss of ozone (to 50%) during the spring season over the Antarctic continent. While such losses have not been simulated by two-dimensional models of the atmosphere with the "standard" chemical reactions (about 150 in number), the large losses over Antarctica have been successfully simulated with the inclusion of either one of reactions (1) or (2), as reported by S. Solomon, R. R. Garcia, F. S. Rowland and D. J. Wuebbles, Nature, 321, 231 (1986). This successful simulation demonstrates only that reactions such as (1) and (2) are consistent with the Antarctic ozone loss observations, but not that the heterogeneous reactions are actually occurring at the necessary rates in the actual stratosphere.

The postulated sequence of chemical reactions which is involved in the rapid ozone loss during the Antarctic spring includes:

$$\mathrm{Cl} + \mathrm{O_3} \longrightarrow \mathrm{ClO} + \mathrm{O_2} \qquad (3)$$

$$\mathrm{HO} + \mathrm{O_3} \longrightarrow \mathrm{HO_2} + \mathrm{O_2} \qquad (4)$$

$$\mathrm{HO_2} + \mathrm{ClO} \longrightarrow \mathrm{HOCl} + \mathrm{O_2} \qquad (5)$$

$$\mathrm{HOCl} + \text{u.v.} \longrightarrow \mathrm{HO} + \mathrm{Cl} \qquad (6)$$

The slow steps in this chain sequence are reactions (5) and (6), but uncertainty exists in both. Other postulated reactions which may also participate include:

$$\mathrm{ClO} + \mathrm{ClO} + \mathrm{M} \longrightarrow \mathrm{ClOOCl} + \mathrm{M} \qquad (7)$$

$$\mathrm{ClOOCl} + \text{u.v.} \longrightarrow \mathrm{OClO} + \mathrm{Cl} \qquad (8)$$

$$\mathrm{ClO} + \mathrm{BrO} \longrightarrow \mathrm{OClO} + \mathrm{Br} \qquad (9)$$

$$\mathrm{Br} + \mathrm{O_3} \longrightarrow \mathrm{BrO} + \mathrm{O_2} \qquad (10)$$

In all of these sequences, the chain reactions sum to $2\ \mathrm{O_3} \longrightarrow 3\ \mathrm{O_2}$, in contrast to the sum $\mathrm{O_3} + \mathrm{O} \longrightarrow 2\ \mathrm{O_2}$ which characterizes the $\mathrm{ClO_x}$ and $\mathrm{NO_x}$ chains operating in the stratosphere for temperate and tropic latitudes. These ozone loss processes are able to proceed even in the relative absence of O atoms which characterizes the Antarctic spring stratosphere.

IV. Reactions of Tritium, ^{38}Cl and ^{18}F Atoms from Nuclear Recoil

A thesis "Thermal ^{18}F Atom Addition to Olefins" by P. J. Rogers has been completed, and the work is now being prepared for journal publication.

The experiments involving the thermalization of energetic tritium atoms are successfully continuing, and one journal article has been published.

The study of the reactions of thermalized ^{38}Cl atoms with H_2S has been completed, and a preliminary report published in the Journal of Physical Chemistry.