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LABORATORY CO_2 PHOTOLYSIS STUDIES RELATED TO PLANETARY ATMOSPHERES

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I. SUMMARY

The work carried out under this contract has been designed to investigate and solve the problems that have arisen in laboratory studies of CO_2 photolysis in the vacuum uv spectral region, and to apply any new information thus obtained to models of the Martian and Venusian atmospheres. The program has been successful; accomplishments include development of an oxygen resonance radiation source for determining $O(^3P)$ atom concentrations by resonance fluorescence, measurements of primary $O(^1D)$ and secondary $O(^3P)$ quantum yields in CO_2 photolysis, measurements of the rate of the three-body CO_2 recombination reaction, $O(^3P) + CO + M \rightarrow CO_2 + M$, determination of the $O(^1D)$-CO_2 interaction rate, and the first observations in a new area of spectroscopy involving forced resonance fluorescence processes in certain CO triplet systems. The CO_2 studies indicate that the participation of CO_3 in processes taking place in the planetary atmospheres is unlikely.

II. INTRODUCTION

The study of CO_2 photolysis processes is of great relevance to the Martian and Venusian atmospheres, because CO_2 appears to be the principal component of these atmospheres. However, the question of what precisely happens when CO_2 is subjected to dissociating radiation has been a matter of considerable controversy, both from the point of view of laboratory studies, and also from the evidence obtained from planetary probes and ground-based observations of the planets.

The laboratory studies have indicated two areas of uncertainty. First, the photolysis of CO_2 in the 1200 to 1700-Å region is expected to lead to CO and O_2 as products, in a ratio of 2:1. Over the last ten years, measurements of this ratio have varied from 100:1 to 1.5:1, and

hypotheses variously involving ozone formation, CO_3 formation, and wall effects have been put forward to explain these observations. Second, dissociation in this wavelength region is expected to produce an oxygen atom in the excited ^1D state; studies of the deactivation rate of this atom by CO_2 have varied by two orders of magnitude, and the actual rate constant is of considerable importance in modeling the planetary atmospheres.

The planetary measurements have indicated that, contrary to expectation, the CO_2 atmospheres appear to be stable. In other words, there appears to be an efficient recombination process for reforming CO_2 from the CO and O atoms that are certainly being produced under the influence of solar radiation. The evidence for this is that the concentrations of O_2, CO, and O atoms are all very small compared to what would be expected at an equilibrium involving known processes. The most recent hypothesis to explain such an atmospheric composition has involved the CO_3 molecule.

The present work was undertaken to achieve a greater understanding of the CO_2-CO-O system. Our previous experience had indicated that it would be useful to develop resonance fluorescence as a method for measuring ground state oxygen atoms, and a good deal of the effort was put into developing and testing the technique on reactions of interest, with an eye to future applications on rocket probes. It also became apparent that resonance fluorescence involving CO was a matter of great interest, and some fundamental studies in this area were carried out, which are expected to be of considerable use in the future.

III. RESULTS

The following are the results of the various investigations undertaken:

A. Oxygen Resonance Lamp

All of the studies of $O(^3P)$ atom reactions were carried out by means of a new technique, resonance fluorescence of OI resonance radiation at 1302, 1305, and 1306 Å. A simple microwave-powered lamp using a 1% O_2-Ar mixture was the light source, and the radiation was monitored by a solar blind photomultiplier. With no further improvement in the design, $O(^3P)$ concentrations in the 10^8 to 10^{12} atoms/cm^3 range can be measured, which is just the range of interest in the earth's atmosphere, making the technique of great interest for rocket probe measurements.

B. $O(^3P)$ Production in 1470 Å CO_2 Photolysis

Evaluation of the $O(^3P)$ yield produced in CO_2 photolysis relative to that produced in O_2 photolysis shows that for equal absorptions, exactly half as many atoms are made from CO_2 as from O_2. Since, in the O_2 case, absorption is into the Schumann-Runge continuum, there are certainly two O atoms formed for every photon absorbed. Thus, for CO_2, one $O(^3P)$ atom results from each absorbed photon. This observation hopefully solves completely the problems encountered in previous studies, where product analyses showed O_2/CO ratios varying from 0 to 0.6, instead of the stoichiometric value of 0.50. It is now clear that $O(^3P)$ is formed in the expected amount, so that the subsequent losses resulting in low O_2 amounts are due to wall interactions or, depending

on conditions, to ozone formation, but are not due to peculiarities of the CO_2 photolysis process or to CO_3 formation.

C. $O(^1D)$ Quantum Yield From CO_2 Photolysis at 1470 Å, and $O(^1D)$-CO_2 Interaction Rate

Although one $O(^3P)$ atom results from each absorbed photon, the initial photodissociation proceeds through the reaction $CO_2 \xrightarrow{h\nu} CO + O(^1D)$. The fact that all the O atoms are subsequently observed as $O(^3P)$ means that deactivation of $O(^1D)$ must be the only result of an $O(^1D)$-CO_2 interaction: $O(^1D) + CO_2 \rightarrow O(^3P) + CO_2$. To demonstrate that $O(^1D)$ is indeed the initial product, competitive quenching experiments with H_2 were used to show that H_2, a known reactant with $O(^1D)$ [$O(^1D) + H_2 \rightarrow OH + H$], can prevent formation of $O(^3P)$. Analysis of the data shows that there can be no $O(^3P)$ produced in the initial photodissociation. Stern-Volmer plots of competitive quenching between CO_2, H_2, and N_2 were evaluated to obtain a value of 0.26 for k_{N_2}/k_{CO_2}, the relative rate constant ratio of N_2 and CO_2 for quenching $O(^1D)$. This number is in agreement with the results of five previous studies. As k_{N_2} is known, the CO_2 rate constant turns out to be $(3\pm1) \times 10^{-10}$ cm^3 $molec^{-1}$ sec^{-1}. The disagreement between our present (and former) results and those of Noxon[1] for this rate constant have now been resolved in our favor, as Noxon has concluded that his interpretation of his experiment was in error.

D. Rate Constants for $O(^3P) + CO + M \rightarrow CO_2 + M$

Because of the possible importance of this reaction in the planetary atmospheres, and in order to try out the resonance fluorescence

[1] J. F. Noxon, J. Chem. Phys. 52, 1852 (1970).

technique on a poorly understood reaction, rate constants were evaluated for the CO_2 recombination reaction. Problems were encountered with surface $O(^3P)$ losses caused by the presence of CO, which may bear some relationship to processes taking place in the planetary atmospheres. Using pulsed excitation techniques, and measuring the subsequent decay of the $O(^3P)$ resonance fluorescence signal (the atoms being produced from O_2 photolysis at 1470 Å), absolute rate constants were determined for M = He, Ar, and N_2. The most probable value for M = CO_2, the species of principal interest, is 2×10^{-35} cm^6 $molec^{-2}$ sec^{-1} at 300°K. Temperature measurements are now needed to determine the rate constant at the much lower temperatures of the Mars and Venus atmospheres; the rate constant is expected to be higher, but not enough to make the recombination of much significance at high altitudes.

To demonstrate the accuracy of the technique, the reactions $O(^3P) + O_2 + M \rightarrow O_3 + M$ and $O(^3P) + NO + M \rightarrow NO_2 + M$ were also studied, and reaction rate constants agreed with those obtained by others.

E. The Role of CO_3

There is no indication of any effects due to CO_3 during CO_2 photolysis. The fact that $O(^1D)$ deactivation proceeds at collision frequency, and may even involve fast $O(^1D)$ atoms, tends to preclude processes such as $CO_2 + O(^1D) \rightarrow CO_3^* \rightarrow CO_3 + h\nu$, as two-body recombinations of this type are invariably slow. Even if CO_3 were formed, the appearance of the total expected amount of $O(^3P)$ would indicate that it is not a very stable species. Furthermore, CO_3 is of value in the atmospheric models only if it keeps the CO concentration down, by the reaction $CO_3 + CO \rightarrow 2\ CO_2$. Addition of CO to CO_2 during photolysis has only a slight effect, and if it is entirely attributed to this reaction, an upper

bound of 10^{-15} cm^3 $molec^{-1}$ sec^{-1} is obtained for the rate constant, a value too low to be important in the atmospheric models.

F. CO Perturbation Spectrum

Construction of the first oxygen lamp revealed that its output was contaminated by the CO Fourth Positive system, which resulted in fluorescence in both the uv and visible spectral regions when the lamp was directed into a cell containing CO. The uv fluorescence is the expected resonance fluorescence,[2] but the visible fluorescence is a new phenomenon, and was investigated further using lamps deliberately contaminated with CO. High resolution spectra of the emission led to the conclusion that the excitation process was also resonance fluorescence, but whereas in the uv the absorption is $A^1\Pi \leftarrow X^1\Sigma^+$, a fully allowed transition, the visible emission ($d^3\Delta \rightarrow a^3\Pi$) is due to $d^3\Delta \leftarrow X^1\Sigma^+$ absorption. This is a forbidden transition, but because of perturbations between certain rotational levels of the $d^3\Delta$ and $A^1\Pi$ states, it becomes allowed for these levels, so that a method for populating the $d^3\Delta$ state becomes available. This is a process that had been predicted[3] but the present work is the first experimental verification. This is the most efficient photolytic process yet observed for populating the $a^3\Pi$ state, and will make detailed studies of its reactions possible.

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[2] T. G. Slanger and G. Black, J. Chem. Phys. 51, 4534 (1969).

[3] G. Herzberg, private communication.

IV. PUBLICATIONS

The experimental results have been or are soon to be published under the following titles:

1. "The Perturbation Spectrum of CO," Chem. Phys. Letters 4, 558 (1970).

2. "Reaction Rate Measurements of $O(^3P)$ Atoms by Resonance Fluorescence. I. $O(^3P) + O_2 + M \rightarrow O_3 + M$, $O(^3P) + NO + M \rightarrow NO_2 + M$," J. Chem. Phys. 53, 3717 (1970).

3. "Reaction Rate Measurements of $O(^3P)$ Atoms by Resonance Fluorescence. II. $O(^3P) + CO + M \rightarrow CO_2 + M$," J. Chem. Phys. 53, 3722 (1970).

4. "The CO_2 Photolysis Problem" (submitted to J. Chem. Phys.)

The last paper appears as an Appendix. Eighty-five percent of the research involved in these four publications was supported by this NASA contract. Graham Black was co-author on all the publications.

APPENDIX

THE CO_2 PHOTOLYSIS PROBLEM*

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ABSTRACT

The photolysis of CO_2 has been investigated at 1470 Å to determine the $O(^1D)$ quantum yield and the subsequent $O(^3P)$ yield resulting from $O(^1D)$ deactivation, the $O(^1D)$-CO_2 interaction rate constant, and the possible role of CO_3 in the overall process. Utilizing the 1302-1306 Å OI triplet as a resonance fluorescence source, $O(^3P)$ atoms were monitored during O_2 and CO_2 photolysis. By measuring both the intensity and decay time constants for the fluorescence, it could be concluded that each photon absorbed by CO_2 ultimately resulted in an $O(^3P)$ atom. This observation suggests that all previous determinations of low O_2/CO ratios in CO_2 photolysis relate to effects taking place after $O(^3P)$ has been produced, and it is quite likely that wall absorption of $O(^3P)$ is the dominant process. By utilizing competitive quenching between CO_2, H_2, and N_2, it was determined that the $O(^1D)$ quantum yield is unity, and that the rate constant ratio for $O(^1D)$ deactivation by N_2 and CO_2, k_{N_2}/k_{CO_2}, is 0.26, in excellent agreement with other investigations, giving a CO_2 rate constant of $3 \pm 1 \times 10^{-10}$ cm^3 $molec^{-1}$ sec^{-1}. Attempts to find effects attributable to CO_3 participation in the system were unsuccessful, and the implications for planetary atmosphere models are discussed.

INTRODUCTION

The gas phase photolysis of CO_2 in the vacuum uv has been the subject of a considerable number of investigations during the last 15 years,[1-4] generally directed at the observation that the stoichiometry of CO_2 photodissociation did not appear to be correct. The O_2/CO ratio in the products, which should be 0.5, has been found to vary from 0 to 0.6, and the explanations of this effect have usually involved wall processes, ozone formation, and, in the last few years, the elusive CO_3 molecule. All of this work has involved stable product analysis, and it is clear that such measurements are only indirect ways of getting at three basic questions: (1) Is the initial photodissociation step described by the reaction $CO_2 \xrightarrow{1200\text{-}1700\ \text{Å}} CO(X^1\Sigma^+) + O(^1D)$? (2) If so, is the quantum yield for this process unity? (3) What is the product of the CO_2 - $O(^1D)$ interaction?

To answer these questions, it is obvious that the sooner one can make measurements in the chain starting with CO_2 and ending with O_2, the more information is obtainable. If the first step in the chain is the formation of $O(^1D)$, it would be ideal to be able to monitor this species. However, the radiative transition to the $O(^3P)$ ground state has a 100 sec lifetime, and as the deactivation of $O(^1D)$ by CO_2 is extremely rapid, it would be very difficult to observe this emission in the laboratory. Noxon reported detection of $O(^1D)$ emission from CO_2 photolysis[5] and concluded that the deactivation was much slower than others have measured by less direct means;[6-9] however, he has since determined that the observation was erroneous,[10] and there is now general agreement on the very rapid rate of $O(^1D)$ destruction by CO_2.

If direct $O(^1D)$ detection is impractical, the next species in the chain appears to be $O(^3P)$. Earlier work by the authors demonstrated that $O(^1D)$ - CO_2 interaction leads to $O(^3P)$ formation,[6] rather than reaction via $O(^1D) + CO_2 \rightarrow O_2 + CO$, and this has been confirmed by Paraskevopoulos and Cvetanović.[8] Therefore, monitoring the $O(^3P)$ concentration should be a valid way of studying CO_2 photolysis processes, and this was done in our earlier work by means of NO_2 chemiluminescence. However, the system was quite complicated: $O(^1D)$ was generated from O_2 photolysis, large amounts of NO were needed, and it was felt that the discrepancy between our measurements and Noxon's might involve these additional gases. For this reason, it was decided to restudy the system, using resonance fluorescence as a technique for measuring $O(^3P)$ atoms. The advantages were that measurements would be made by physical rather than chemical means, causing minimum system perturbation, and that CO_2 could be used as the $O(^1D)$ source (which was not practical before because CO_2 and NO have similar absorption cross sections for 1470 Å radiation, and similar pressures were required).

The practical importance of CO_2 photolysis studies is that the principal atmospheric component on Venus and Mars is CO_2, and planetary probes and ground-based spectrometry indicate that the CO and O_2 concentrations are much lower than expected on the basis of the supposedly known CO_2 photodissociation rate.[11,12] McElroy and Hunten[13] have proposed an atmospheric model using CO_3 to explain these observations, and it is clearly important to carry out laboratory studies to determine the feasibility of such an explanation.

Although the strongest feature in the solar emission spectrum in the region of interest (1200-1750 Å) is Lyman α at 1216 Å, the use of 1470 Å radiation as the photolysis source is somewhat more representative of the CO_2 photodissociation process. This is because 1470 Å is near the center of the CO_2 absorption continuum leading to $O(^1D)$ formation, whereas L-α is at the short wavelength edge, where the absorption coefficient is quite low. Using the data presented by Detwiler, et al.[14] on solar radiation as a function of wavelength and the absorption coefficietn values of Watanabe, et al.,[15] it may be calculated that only 10% of the $O(^1D)$ produced by CO_2 photodissociation in the 1200-1750 Å region comes from L-α, whereas 55% is produced by radiation in the 1425-1625 Å range.

EXPERIMENTAL

A schematic drawing of the experimental arrangement is shown in Fig. 1. The O_2 lamp is shown in more detail in an earlier paper,[16] as is the electronic circuitry.[17] The measurement technique has also been previously discussed, but can be quickly summarized. CO_2 or O_2 is dissociated by light from a 1470 Å Xe resonance lamp in a flowing system (cell pumpout time is 1-2 sec). Light from an oxygen resonance lamp, emitting the OI resonance triplet at 1302, 1305, and 1306 Å, is scattered from the $O(^3P)$ atoms that have been produced and is measured by a solar-blind photomultiplier sensitive in the 1100-2000 Å region. The Xe lamp is operated in either a pulsed or steady-state mode. In the former case, the decay time constant of the atoms can be measured after the lamp is turned off. Signal integration techniques are used to make possible addition of a number of decay curves, thereby markedly improving the signal-to-noise ratio. Using 2-sec pulses, 5 to 10-min integration times were used with CO_2, and 1 to 2-min with O_2.

The gas filter chambers A, B, and C are used in various ways to block unwanted light; for example, a 1% O_2-N_2 mixture in chamber C has an optical density of 6.5 for scattered 1470 Å radiation from the Xe lamp, but attenuates the 1302-1306 Å radiation by only 20%. During measurements with CO_2 it is possible that contaminant CO fourth-positive radiation from the O_2 lamp can give resonance fluorescence from the CO produced during photolysis.[18] Therefore chamber A was purged with a 0.04% CO-N_2 mixture, to block the exciting radiation. By use of the

filter chambers, it was established that at least 95% of the O_2 lamp emission transmitted by the O_2 filter was OI resonance radiation.

In the quantum yield measurements, the rf-powered Xe lamp was replaced by a larger microwave-powered non-pulsed lamp, which had an intensity approximately six times greater. This was done to make measurements easier at low CO_2 pressures, and also because the larger lamp had a filter chamber built on to it that could be purged with the CO mixture. To establish a base line for each data point, the chamber was purged with O_2, thus blocking the 1470 Å radiation. By this method, the contribution of the oxygen lamp to $O(^3P)$ production can be ignored.

All of the gases were used without further purification and had the following stated purities: Ar - 99.998%, He - 99.995%, CO_2 - 99.99%, O_2 - 99.95%, N_2 - 99.997%, H_2 - 99.997%, and CO - 99.5%.

RESULTS AND DISCUSSION

A. $O(^3P)$ Quantum Yield from CO_2

Our previous measurements[6] of the $O(^3P)$ quantum yield from CO_2 photolysis at 1470 Å, using NO_2 chemiluminescence as an $O(^3P)$ monitor, gave a value of 0.97 ± 0.05. For reasons mentioned earlier, it was considered desirable to repeat the experiment in a pure CO_2 system. As in the earlier work, the measurements were made relative to O_2, for which it is well substantiated that the processes taking place upon photodissociation in the Schuman-Runge continuum are

$$O_2 \xrightarrow{h\nu} O(^1D) + O(^3P) \qquad (1)$$

and

$$O(^1D) + O_2 \rightarrow O(^3P) + O_2^*, \qquad (2)$$

so that the quantum yield of $O(^3P)$ in a pure O_2 system may be taken as 2.0.

The primary data for the quantum yield determination are the intensity of $O(^3P)$ resonance fluorescence as a function of CO_2 and O_2 pressures. This is shown in Fig. 2, with the CO_2 intensities multiplied by 10. To this data a number of corrections must now be made related to the $O(^3P)$ lifetime in the system and the screening of 1304 Å radiation by O_2 and CO_2.

The fluorescence intensity is a relative measure of the $O(^3P)$ atom production rate only as long as the $O(^3P)$ loss rate is constant. For this reason, it is not possible to compare the intensities of the two curves in Fig. 2 without being certain that they are referred to the same $O(^3P)$ loss rate. The loss rate of $O(^3P)$ atoms in this system is

principally determined by interaction at the walls. Certainly the CO_2 environment is inert to $O(^3P)$, and the three-body $O + O_2 + M$ recombination rate is quite slow compared to the measured time constants (100-400 msec), as is the cell pump-out time of 1-2 sec. Therefore, intensity measurements will reflect changes in the wall conditions, which is an annoyance since the wall recombination rate is a rather uncontrolled function of the cell history and the gases present during an experiment. Such a problem is avoided with the NO_2 chemiluminescence technique, since sufficient NO can be added to make the $O(^3P)$ atom loss at the walls unimportant compared to the volume loss.

The cell depicted in Fig. 1 has a path length for 1304 Å radiation of approximately 30 cm; over this distance the light can be absorbed by O_2 or CO_2. For O_2, the average absorption coefficient between 1302 and 1306 Å at 300°K, as measured by Watanabe, et al.[15] and confirmed by our measurements, is 9.7 cm^{-1} atm^{-1}. For CO_2, the absorption coefficient is too discontinuous in the 1300 Å region to use published values, so the required CO_2 value was obtained by observing the attenuation of 1302-1306 Å radiation scattered from the cell walls, and comparing it with the attenuation observed with O_2. Figure 3 shows the data, plotted as light attenuation vs pressure, and the resulting ratio of $\sigma_{CO_2}/\sigma_{O_2}$ gives a value for the average CO_2 coefficient for the three lines of 20.0 cm^{-1} atm^{-1}. A correction factor to the data may then be calculated using the 30-cm path length, and appears as curve A in Fig. 4 for CO_2 and in Fig. 5 for O_2.

In order to keep the corrected data linear over the 0 to 0.3 torr range shown in Fig. 2, it is necessary to put in a correction for the

fact that, particularly for O_2, the measurements are made well beyond the linear absorption range. The required factor is given by $p\sigma\ell/[1 - \exp(-p\sigma\ell)]$, where $\sigma_{O_2} = 320$ cm^{-1} atm^{-1}, $\sigma_{CO_2} = 14$ cm^{-1}, and $\ell = 24$ cm. The value for σ_{O_2} is from Watanabe, et al.,[15] the value for σ_{CO_2} is a recent measurement by Inn,[19] and the ratio $\sigma_{O_2}/\sigma_{CO_2} = 23$ is exactly that found from an experiment analogous to that shown in Fig. 3, performed with scattered 1470 Å light (Fig. 6). These corrective factors are shown as curve B in Figs. 4 and 5.

For O_2, a correction is required for the fact that the $O(^3P)$ loss rate is increased as O_2 is added, due to the reaction $O(^3P) + O_2 + Ar \rightarrow O_3 + Ar$, the rate for which has been measured in this system[16] as 4.4×10^{-34} cm^6 molec^{-2} sec^{-1}. The required factor depends on the $O(^3P)$ lifetime in the system at the time the data in Fig. 2 were taken. This value was 120 msec, measured with 0.1 torr O_2 and 10 torr Ar, and the correction factor is given as curve D in Fig. 5.

One further correction is required for CO_2, and it is the hardest to assess. Our data show that the lifetime of an $O(^3P)$ atom is significantly longer in O_2 than in CO_2, at low pressures where the $O + O_2 + M$ recombination is unimportant, and this appears to be due entirely to the effect of these gases on the wall recombination coefficient. We have also noted that after NO has flowed through the system, the $O(^3P)$ lifetime becomes much longer, an effect observed in other experiments.[20] Conversely, CO often has the opposite effect, making $O(^3P)$ wall loss rates much faster.[21] Table I shows how the $O(^3P)$ lifetime varies under different conditions; the two sets of data were taken on different days, and in the chronological order shown.

Table I

EFFECT OF $O(^3P)$ SOURCE ON $O(^3P)$ LIFETIME

$[CO_2]$	$[O_2]$	Lifetime
0	40 mtorr	167 msec
0.3 torr	0	134
0	50 mtorr	169
0.6 torr	0	143
1.5 torr	0	168
0	0.2 torr	183 msec
0.1 torr	0.2 torr	177
0.2 torr	0.2 torr	179
0.3 torr	0.2 torr	181

From these figures it may be seen that there are two effects appearing in the CO_2 data; at minimum pressures, the loss rate in CO_2 is faster than in O_2, and increasing the CO_2 pressure increases the $O(^3P)$ lifetime. The former effect is certainly related to the surface condition, but the latter could involve either the surface condition or diffusional phenomena. That diffusion is apparently not involved is indicated by the second set of data in Table I, which shows that in the presence of 0.2 torr O_2, the $O(^3P)$ lifetime is independent of CO_2. To calculate a correction factor, it is necessary to extrapolate the lifetime in CO_2 to zero CO_2 and then relate both the O_2 and CO_2 data to a base lifetime of 120 msec at zero O_2, the O_2 system lifetime pertaining to the experiment of Fig. 2. A 125 msec lifetime (8.00 sec^{-1} time constant) is a reasonable extrapolation of the CO_2 data, giving a value 2.05 sec^{-1} greater than the value at low O_2 (168 msec). Normalizing to an O_2 value of 8.33 sec^{-1} (120 msec) then gives a zero CO_2 value of $8.33 + 2.05 = 10.38$ sec^{-1}, and a value at 0.3 torr CO_2 of $10.38 - 1000 (1/125 - 1/134) = 9.84$ sec^{-1}. The correction curve resulting from this admittedly crude calculation is shown as curve C in Fig. 4.

Curve E in Figs. 4 and 5 shows the total corrections to be applied to the data of Fig. 2, and, when this is done, the plots of Fig. 7 result. If the $O(^3P)$ quantum yield from CO_2 is unity, then the expected ratio of the slopes is $2 \times \sigma_{O_2}/\sigma_{CO_2}$, where the absorption coefficient ratio refers to 1470 Å radiation and has the value of 23. The measured slope ratio (the dotted lines show the deviation of the curves from linearity) is 46, a clear indication that the most probable value for the $O(^3P)$ quantum yield is 1.0, confirming our previous observations.

The greatest source of error is obviously the lifetime correction in the CO_2 case. The other principal uncertainties are the appropriate path lengths for the 1304 and 1470 Å radiation, which would require careful lamp and photomultiplier collimation to minimize. However, only the lifetime correction is required to compare the initial slopes of the data in Fig. 2. The initial slope ratio is 57.5, or 1.25 times the corrected value of 46, which is exactly the total correction required by curve E in Fig. 4. The linearity of the O_2 plot, which involves a maximum $O(^3P)$ concentration of about 2×10^{11} atom/cm^3, shows that the optical depth for the OI resonance radiation is still small and that the average absorption coefficient is less than 10^6 cm^{-1} atm^{-1}, an indication that the lines are partially reversed. Error limits of ±10% should be set on the quantum yield determination, but there is little reason to believe the value to be other than unity. It naturally follows that the CO quantum yield is also 1.0, in contrast to the value of 0.27 obtained by Ung and Schiff.[2]

This experiment shows rather clearly that whatever problem there is in measuring the O_2 quantum yield does not develop until after $O(^3P)$ is formed in the system. Various experiments have shown that diffusion to the walls plays an important role in determining the O_2 yield, and we believe the indications are now strong that the O_2 loss is due entirely to absorption of $O(^3P)$ on the cell walls. It should be noted that the low buffer gas pressure conditions used for obtaining the data in Fig. 2 are just the conditions required for observing very low O_2/CO ratios. Experiments of Felder, et al.[22] have also shown that CO is absorbed on the walls during CO_2 photolysis; after the photolysis experiment

is completed and the cell pumped out, continued uv irradiation of the empty cell yields CO (detected by resonance fluorescence).

B. $O(^1D)$ Deactivation Rates

The $O(^1D)$ deactivation rate by CO_2 is no longer in serious doubt, but measurements relative to the rates for H_2 and N_2 were carried out to see how well resonance fluorescence measurements would agree with the quite complex NO_2 chemiluminescence method used previously.

$O(^1D)$ was generated from CO_2 by 1470 Å photolysis, and the $O(^3P)$ resonance fluorescence intensity was measured as a function of H_2, a molecule known to react with (but not deactivate) $O(^1D)$.[6,8] The two competing reactions are

$$O(^1D) + CO_2 \xrightarrow{k_1} O(^3P) + CO_2 \qquad (3)$$

and

$$O(^1D) + H_2 \xrightarrow{k_2} OH + H. \qquad (4)$$

The $O(^3P)$ loss mechanisms are wall recombination and possibly reaction with H_2:

$$O(^3P) + H_2 \xrightarrow{k_3} OH + H. \qquad (5)$$

The latter is a slow reaction, having a rate constant[23] of $<10^{-17}$ cm^3 $molec^{-1}$ sec^{-1} and can be expected to have a negligible effect on the $O(^3P)$ loss rate for the H_2 concentrations used.

A steady-state treatment of the system (measurements were again made with the large nonpulsed lamp) shows that the expected intensity attentuation upon H_2 addition is given by

$$I_0/I = 1 + \frac{k_2[H_2]}{k_1[CO_2]}, \qquad (6)$$

assuming that the addition of H_2 does not change the $O(^3P)$ loss rate by either volume or surface processes. Plots of I_0/I vs $[H_2]$ are presented in Fig. 8, and it may be seen that they are indeed straight lines, conforming to Eq. 6. However, an anomaly is encountered when $O(^3P)$ decay time measurements are made under the same conditions, because there is some effect of H_2 on the decay time; for the curve at 1.54 torr CO_2, the $O(^3P)$ loss rate is increased by ~40% by 2.5 torr H_2. The fact that this effect does not appear as upward curvature in the plots of Fig. 8 (corresponding to a second term in H_2 in Eq. 6) implies that there is an additional production of $O(^3P)$ associated with H_2 addition, balancing the increased loss rate. It is difficult to imagine a volume process involving OH or H in a CO_2-H_2 system that could lead to a significant $O(^3P)$ production source, and, again, surface phenomenon are more likely to provide an explanation. A monolayer of $O(^3P)$ atoms covering the surface of the reaction vessel involves approximately 10^{18} atoms. The photodissociation rate is $\sim 10^{15}$ molecules/sec. The additional $O(^3P)$ production rate required to balance the increased $O(^3P)$ loss rate is $\sim 10^{14}$ atoms/sec. Obviously, any process that slightly disturbs the absorbed $O(^3P)$ monolayer (even assuming only 1% coverage) could cause the observed effect. One possibility is that H atoms could displace O atoms from the surface. Another possibility is that the process $H + O + O \rightarrow OH + O$ could take place on the surface, with the O atom being ejected back into the system. It is not easy to evaluate these speculations, and further study is really required to clarify the observations.

From Eq. 6 it may be seen that the reciprocal slopes of the data of Fig. 8, when plotted against $[CO_2]$, should give a line with slope

k_1/k_2. Figure 9 shows such a line, and it is indeed straight; more data are included than appear in Fig. 8. The slope of the line is 0.78, compared to the previously determined range of values[6] of 0.77-1.2 and the value determined by Paraskevopoulos and Cvetanović[8] of 0.50.

The deactivation rate constant for N_2 was then measured to determine a new value for k_{N_2}/k_{CO_2}. For a CO_2 pressure of 0.23 torr, Stern-Volmer plots of I_0/I vs $[H_2]$ were made for various N_2 pressures. The system is then described by a modification of Eq. 6.

$$I_0/I = 1 + \frac{k_2[H_2]}{k_1[CO_2] + k_4[N_2]}, \tag{7}$$

where k_4 is the rate constant for the reaction

$$O(^1D) + N_2 \xrightarrow{k_4} O(^3P) + N_2. \tag{8}$$

Plots of I_0/I vs $[H_2]$ are again linear, as shown in Fig. 10. The reciprocal slopes vs $[N_2]$ are plotted in Fig. 11, giving a line with slope k_4/k_2 equal to 0.20. Since $k_4/k_1 = \frac{k_2}{k_1} \cdot \frac{k_4}{k_2}$, the value of k_{N_2}/k_{CO_2} is 0.26, compared to our earlier value of 0.22. There are now six determinations of this ratio,[6-9,24] all contained within the value 0.26 ± 0.04. Based on the present range of values for k_{N_2} of 5-10 × 10^{-11} cm^3 $moles^{-1}$ sec^{-1}, the value for k_{CO_2} is then 3±1 × 10^{-10} cm^3 $molec^{-1}$ sec^{-1}.

The problem of the variation of the $O(^3P)$ loss rate with H_2 addition presumably enters into the N_2 data as well and can be expected to cancel out in an evaluation of k_{N_2}/k_{CO_2}, as is indicated by the agreement between our value and the others. We believe that the $O(^1D)$-H_2 rate is still uncertain by a factor of ~2 and can be given a value of 4±1.5 × 10^{-10} cm^3 $molec^{-1}$ sec^{-1}. It should be pointed out that the pos-

sibility of a significant fraction of the initial CO_2 photodissociation giving $O(^3P)$ directly is ruled out by the linearity of the plots in Figs. 8 and 10. If this were to occur, the signal attenuation would follow the relationship

$$I_o/I = \frac{(k_1[CO_2] + k_2[H_2])}{(k_1[CO_2] + Ak_2[H_2])}, \tag{9}$$

where A is the fraction of photodissociation giving $O(^3P)$ directly, and this expression is not linear in $[H_2]$.

C. The Search for CO_3

One of the current theories[13] to explain the low level of $O(^3P)$ and CO in the atmospheres of Venus and Mars is that CO_3 is formed in a two-body reaction following photodissociation by

$$O(^1D) + CO_2 \xrightarrow{k_5} CO_3^* \rightarrow CO_3 + h\nu \tag{10}$$

and that CO_2 regeneration then occurs quantitatively by

$$CO_3 + CO \xrightarrow{k_6} 2CO_2. \tag{11}$$

The reason for proposing such a scheme is that the normal three-body recombination,

$$O(^3P) + CO + M \xrightarrow{k_7} CO_2 + M, \tag{12}$$

is too slow,[21] as are various catalytic schemes involving OH and HO_2, which also involve three-body steps. It appears that eddy diffusion rates would have to be enormous to bring $O(^3P)$ and CO down to low enough altitudes quickly enough for the three-body mechanisms to become operative in maintaining the observed low concentrations.

Various laboratory studies dealing with CO_3 have been reported. The original observation of Moll, et al.[25] have since been confirmed by Weissberger, et al.[26] and Arvis,[27] but so far the only identification of the molecule purported to be CO_3 has been by IR absorption in matrices; attempts to characterize it by mass spectrometry, ESR, or gas-phase IR absorption have been unsuccessful.

The minimum requirements for the CO_3 scheme to be practical are that the two-body recombination reaction (reaction 10) takes place at the measured $O(^1D)$ loss rate, with a constant of $\sim 3 \times 10^{-10}$ cm^3 moles^{-1} sec^{-1}, that stabilized CO_3 be inert to collisions with CO_2, and that reaction 11 have a rate fast enough to prevent both CO buildup and competition with the analogous $O(^3P)$ reaction

$$O(^3P) + CO_3 \rightarrow CO_2 + O_2. \qquad (13)$$

The idea that a two-body recombination reaction can take place at every collision goes against all experience from kinetic studies, even for thermalized reactants. In the photolysis of CO_2 at 1470 Å, the $O(^1D)$ can have as much as 0.5 eV kinetic energy, depending on the degree of vibrational excitation of the CO, and it is inconceivable that under such conditions every collision with CO_2 will result in a CO_3^* molecule stable for at least 10^5 vibrations (the minimum time required for emission of a photon).

Nevertheless, if it is granted that CO_3 can somehow be formed, there is certainly no indication from the quantum yield data that it has a long enough lifetime in the system to be pumped out; this is, however, not a significant test, because wall collisions could well de-

compose the CO_3 to CO_2 + $O(^3P)$. A more revealing experiment involves the addition of CO to CO_2 during photolysis. If reaction takes place, then the $O(^3P)$ quantum yield should decrease drastically, as CO_3 would then react via reaction 11, and $O(^3P)$ would not be regenerated. Lack of an effect would indicate that reaction 11 is much slower than the diffusion time to the walls (or that CO_3 is not produced). Table II presents the results of time decay measurement in which CO was added to CO_2 during photolysis.

Table II

EFFECT OF CO ON $O(^3P)$ PRODUCTION RATE FROM CO_2

CO_2	CO	Ar	Fluorescence Intensity	$O(^3P)$ Lifetime	Intensity/ Lifetime
0.6 torr	0	10 torr	15.4 units	515 msec	29.9
0.6 torr	50 mtorr	10 torr	15.9	458	34.7
0.6 torr	0	10 torr	16.2	473	34.3
0.5 torr	0	30 mtorr	10.0 units	268 msec	37.3
0.5 torr	0	0	11.3	279	40.3
0.5 torr	30 mtorr	0	8.8	273	32.2

The time constants are much shorter in the absence of a buffer gas, demonstrating the effect of diffusion. This set of measurements shows longer time constants than the comparable data of Table I, a result of the intervening history of the cell. As discussed in an earlier paper,[21] under certain conditions the wall loss coefficient for $O(^3P)$

atoms is increased in a semipermanent manner by CO. However, for the small amounts of CO added in the experiments of Table II, this effect is apparently not operating, because the time constants are reproducible.

The parameter of interest is the production rate of $O(^3P)$ atoms and its variation with CO. The steady-state intensity, given in the table, is related to two factors, given that the Xe lamp intensity is constant. These are the $O(^3P)$ loss rate (the reciprocal of the lifetime) and the screening effect of CO for the OI and Xe radiation. The CO absorption coefficient for Xe resonance radiation[28] is 0.18 cm^{-1}, and thus of no concern. The $O(^3P)$ production rate, P, is then given by

$$P = \frac{I}{\tau} (1 - f)$$

where f is the fraction of the 1302-1306 Å radiation absorbed by CO, I is the fluorescence intensity, and τ is the $O(^3P)$ lifetime. The factor f can be approximated from the data of Fig. 3, which indicates that 30-50 mtorr. CO causes only 1-2% attenuation of the OI lamp radiation. However, measuring the attenuation of the total scattered 1302-1306 Å light is not exactly equivalent to determining the attentuation by CO of the resonance radiation scattered from $O(^3P)$ atoms. This is because the CO absorption is not due to a continuum, but to the $CO(A^1\Pi \leftarrow X^1\Sigma^+)$ fourth-positive system, so that the CO absorption coefficient for the OI radiation may be different for each spectral line.

Figure 12 shows the attenuation of each OI line by CO, the lines being dispersed by a 0.5 meter Jarrell-Ash vacuum monochromator, and it is obvious that the behavior of the 1306 Å line is quite different from that of the other two.

A comparison of the OI triplet wavelengths and the transitions tabulated by Simons, et al.[29] for the CO system show the following closest energy matches (Table III), all for the $CO(A^1\Pi \leftarrow X^1\Sigma^+)$ 9,0 band.

Table III

BEST ENERGY MATCHES BETWEEN OI LINES

AND CO FOURTH-POSITIVE TRANSITIONS

Oxygen Line	$\Delta\epsilon(cm^{-1})$	Rotational Number
1302 Å	3.48	6 (P-branch)
1305 Å	1.64	19 (Q-branch)
1306 Å	0.21	22 (Q-branch)

The close resonance of the 1306 Å line with the J = 22 CO line (one Doppler width at 300°K) is reflected in the behavior of the 1306 Å line in Fig. 12, and it may be predicted that a high resolution examination of the 1302-1306 Å oxygen radiation that has been observed in the Martian atmosphere[30] will show a depletion in the 1306 Å line. It is worth noting that similar attenuation measurements with CO_2 and O_2 for each OI line do not show any curvature as in Fig. 12, indicating lack of such fine structure in this wavelength region for the two molecules.

As the CO absorption coefficient is different for each OI line, using the data of Fig. 3 is only strictly correct if the 1302:1305:1306 Å ratio is the same for the lamp radiation and the resonantly scattered radiation. For the optically thin conditions in the absorption cell, the ratio will be the statistically determined value of 5:3:1, but the same will not hold true in the lamp, as the optical

thickness was not as carefully controlled as in the experiments of Parkes, et al.[31] However, for present purposes the 1-2% attenuation value can be used, as it will lead to a maximum rate constant for k_6. Thus, $p \sim I/\tau$, and the data in Table II shows a maximum $O(^3P)$ production rate decrease of ~15%. Attributing this all to reaction 11, and assuming that CO_3 is destroyed at each wall collision, we may conclude that $\tau_D^{-1} = 7k_6[CO]$. A diffusion time of ~100 ms then leads to a maximum value for k_6 of $\sim 10^{-15}$ cm^3 $moles^{-1}$ sec^{-1}. This means that at least 3×10^5 collisions with CO are required before reaction, and in the Martian atmosphere, where the CO mixing ratio[32] is about 10^{-4}, CO_3 will undergo at least 3×10^9 collisions before reaction. At an altitude where the pressure is 1 mtorr, and the collision rate is roughly 3×10^3 collisions/sec, the CO_3 lifetime will then be at least 10^6 sec. As a consequence of such a long lifetime against reaction with CO, CO_3 will build up to high concentrations which will be balanced by destruction by photolysis and $CO_3 + CO_3$ reaction, neither of which will be useful in stopping the buildup of CO produced by CO_2 photodissociation. Therefore, the CO_3 hypothesis does not appear to be helpful in explaining the Mars and Venus atmospheres. It may of course be argued that the present experiments do not duplicate the planetary atmosphere conditions, in that whereas $O(^1D)$-CO_2 interaction may lead to an excited CO_3^* which can stabilize itself by radiation in the atmosphere, at the pressure required in the laboratory (to prevent wall deactivation) collision with Ar or CO_2 will lead to dissociation ($CO_3^* + M \rightarrow CO_2 + O + M$). Similar reasoning to explain the lack of any hard evidence for CO_3 may be continued indefinitely, but it is probably more useful to explore

other avenues as an explanation for the problems posed by the planetary atmospheres. It is worth remembering that a certain impetus was given the CO_3 hypothesis by the conflicting observations of the $O(^1D)$ deactivation rate by CO_2.[33] As this is now resolved, there is no longer any justification based on laboratory evidence to make further investigations into a possible role for CO_3.

A phenomena that does require further study is the very rapid $O(^3P)$ loss that occurs on the walls of a vessel after CO has been photolyzed or discharged in it. Such an effect suggests that at any altitude in the planetary atmospheres where aerosols or particulate matter may be present, they may act as traps for CO, and subsequent collisions of these particles with $O(^3P)$ could then cause very efficient CO_2 recombination. In effect, the three-body recombination process would be replaced by two two-body reactions, where the intermediate species is stable. This process could probably not be operative in the tenuous upper atmosphere of Mars but might become important at intermediate altitudes before normal chemical processes could begin to account for the recombination rate.

CONCLUSIONS

The important results of this investigation are: 1) The quantum yield of $O(^3P)$ from CO_2 photolysis at 1470 Å has been established as unity, and by implication, the initial $O(^1D)$ and CO quantum yields are also unity. 2) The rate of $O(^1D)$ deactivation by CO_2 has been found to be of the same magnitude as previously measured and occurs at every collision. 3) No evidence has been discovered for CO_3 as an intermediate species in CO_2 photolysis, and, of particular importance, there is no indication that the reaction $CO_3 + CO \rightarrow 2CO_2$ is of any significance, even if CO_3 is formed. 4) The study of surface interactions involving CO and $O(^3P)$ may be an important area of investigation.

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FIGURES

1. Reaction cell.

2. Resonance fluorescence intensity vs pressure. [Ar] = 10 torr.

3. 1302-1306 Å scattered light attenuation vs pressure.

4. Intensity correction factors for CO_2.

   A = 1304 Å attenuation

   B = Linear absorption

   C = $O(^3P)$ lifetime

   E = Total

5. Intensity correction factors for O_2.

   A = 1304 Å attenuation

   B = Linear absorption

   D = Ozone formation

   E = Total

6. 1470 Å scattered light attenuation vs pressure.

7. Corrected fluorescence intensity vs pressure. [Ar] = 10 torr.

8. I_0/I vs $[H_2]$. [Ar] = 10 torr.

   ○ 0.16 torr CO_2

   ▲ 0.23

   □ 0.35

   ● 0.47

   △ 0.50

   ■ 1.54

9. Reciprocal slopes vs $[CO_2]$. [Ar] = 10 torr.

10. I_0/I vs $[H_2]$. $[CO_2]$ = 0.23 torr. [Ar] = 10 torr.

    △ no N_2

    ● 0.35 torr N_2

    □ 0.71

▲ 1.10 torr N_2

o 1.59

11. Reciprocal slopes vs $[N_2]$. $[CO_2]$ = 0.23 torr. [Ar] = 10 torr.

12. I_o/I vs [CO] for oxygen resonance lines. ℓ = 101 cm.

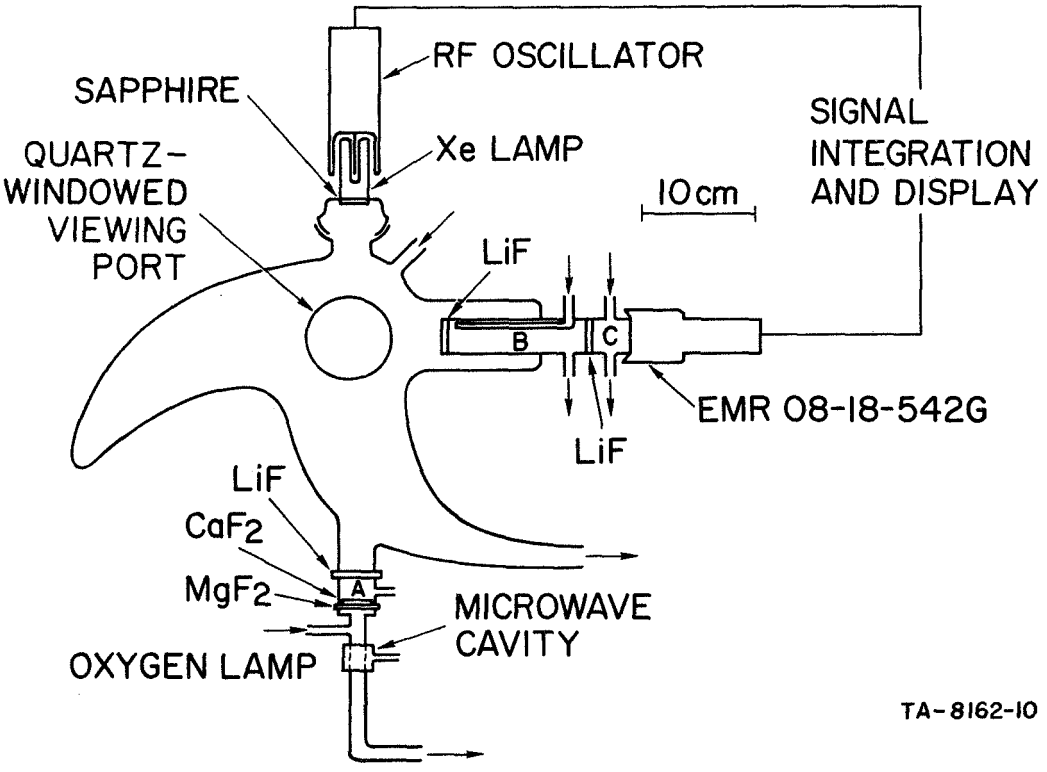
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Fig. 1

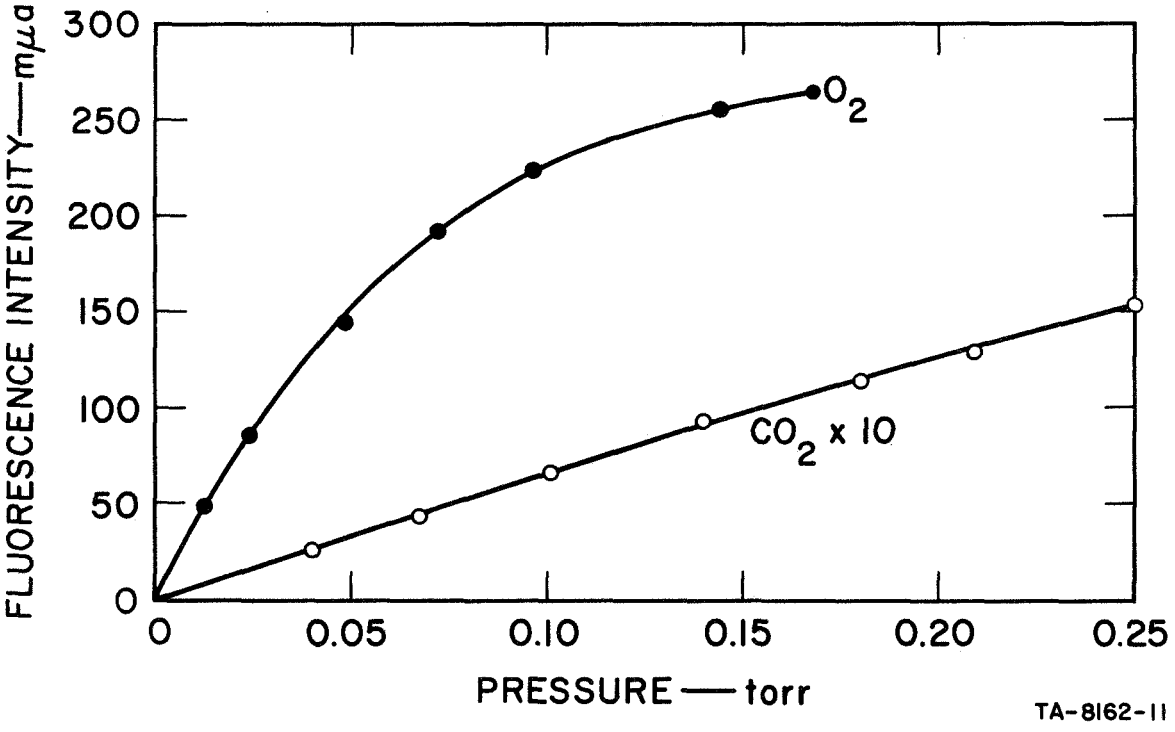
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Fig. 2

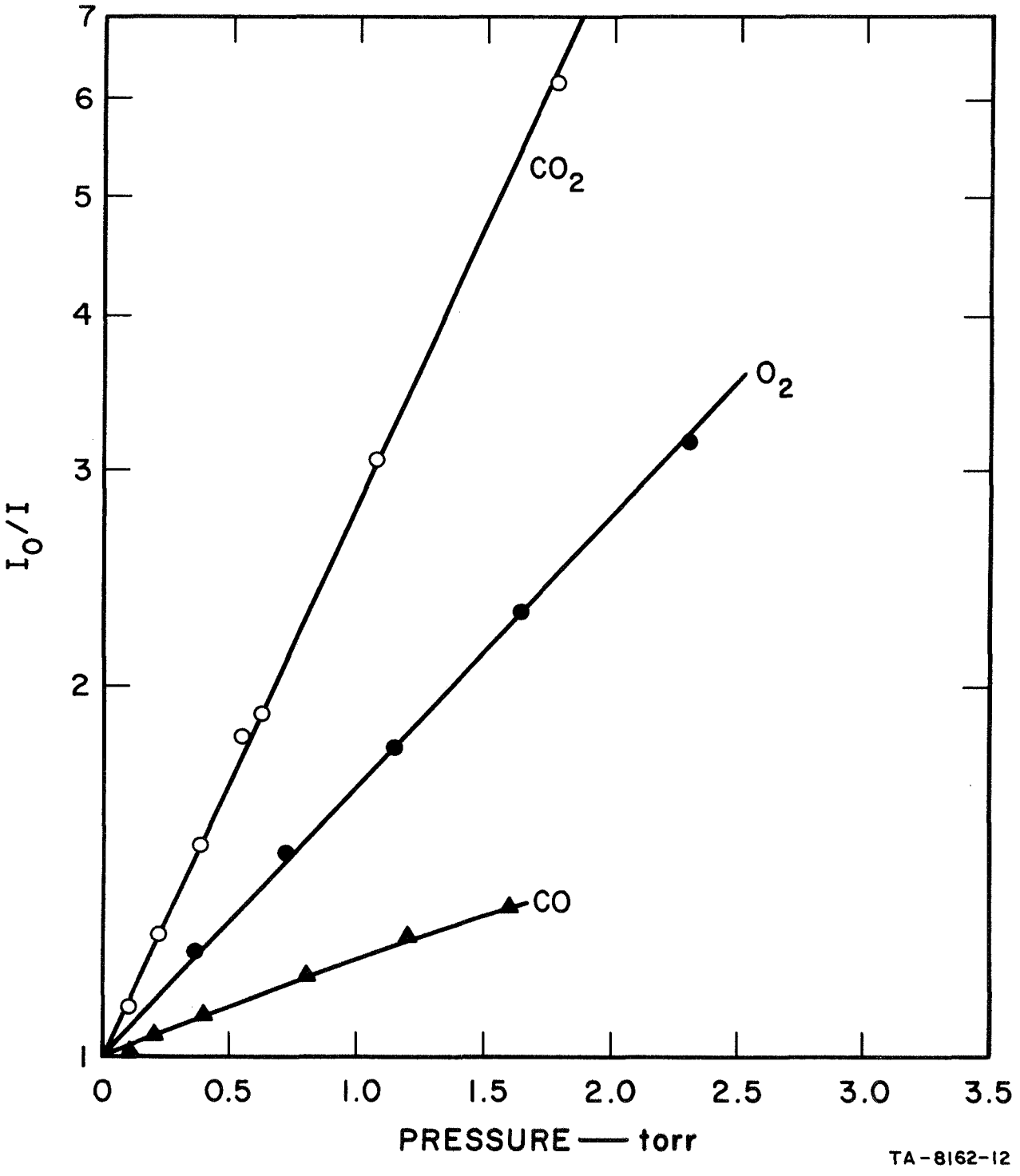
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Fig. 3

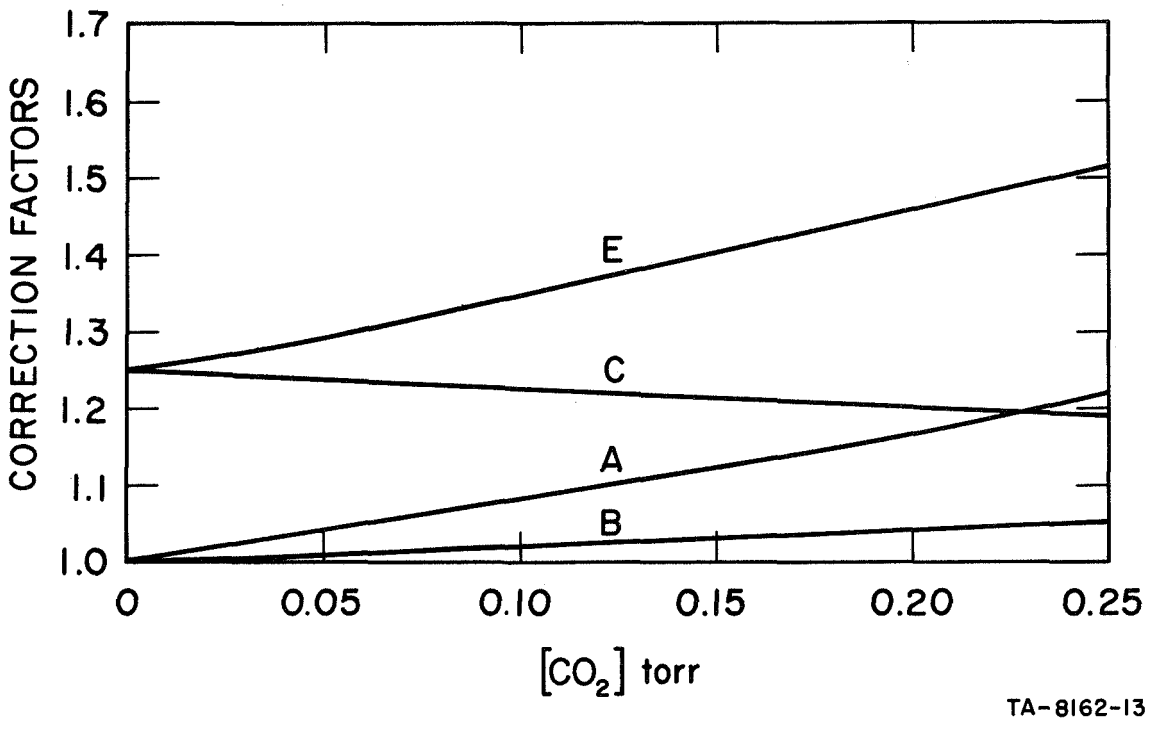
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Fig. 4

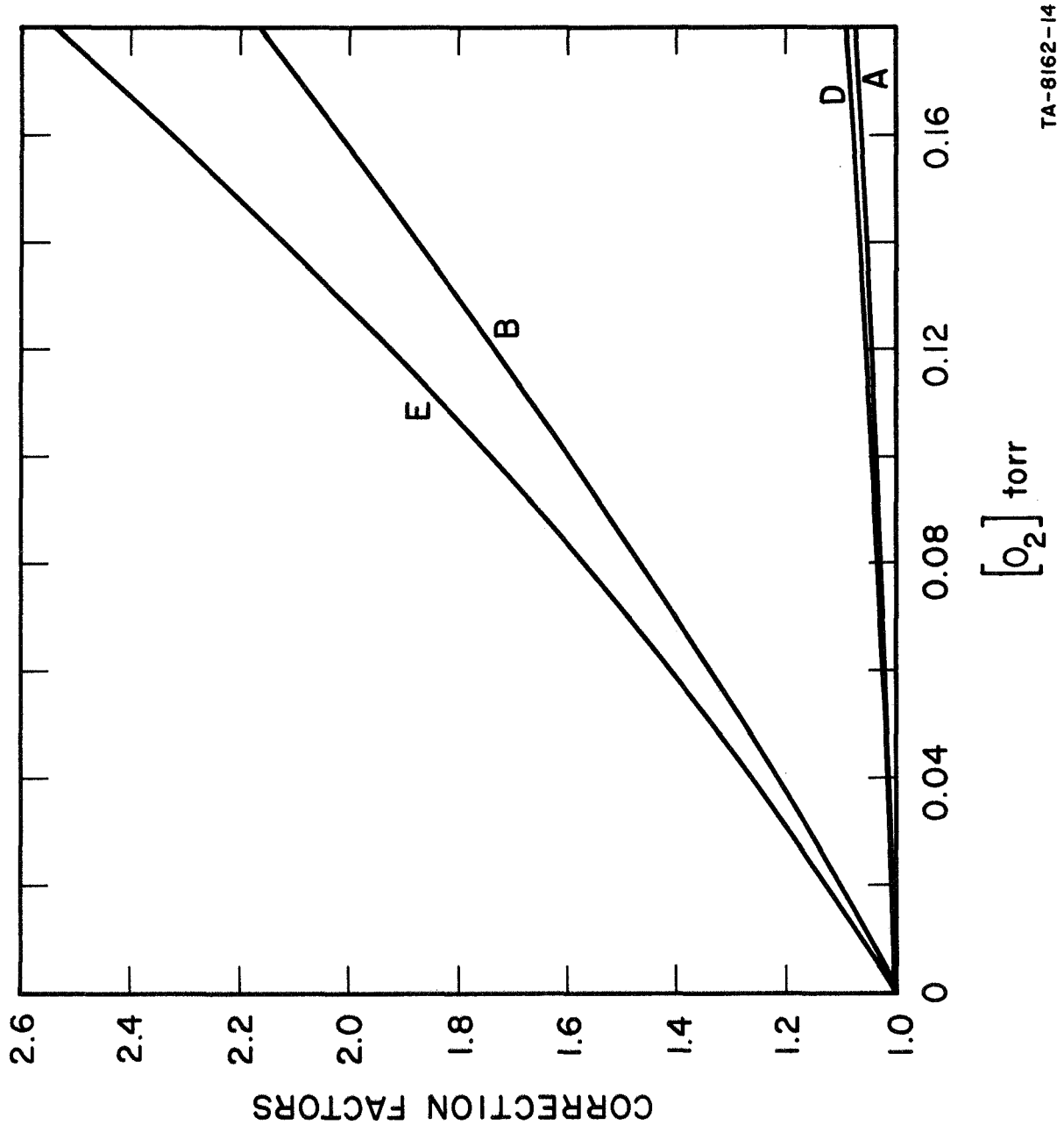
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Fig. 5

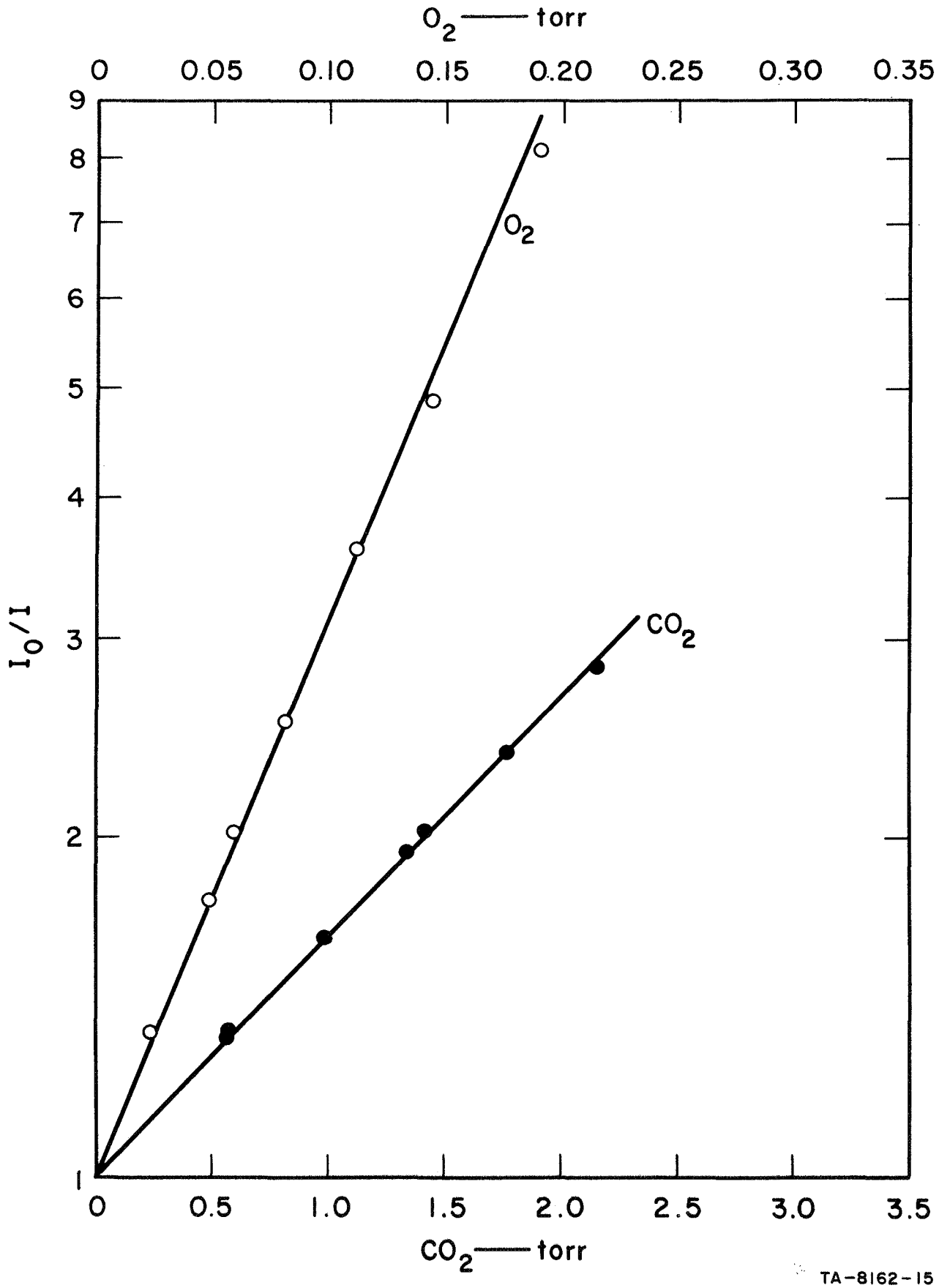
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Fig. 6

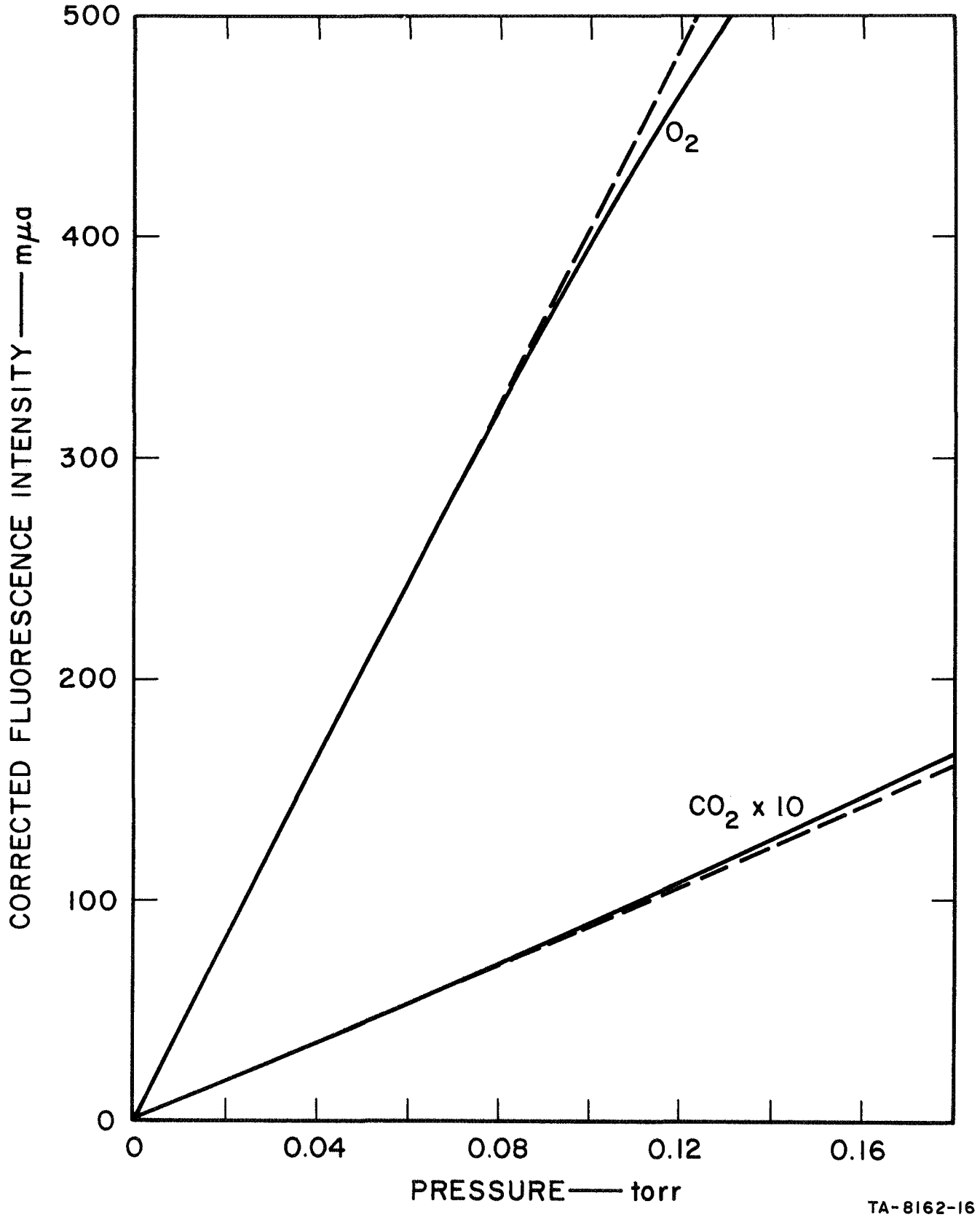
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Fig. 7

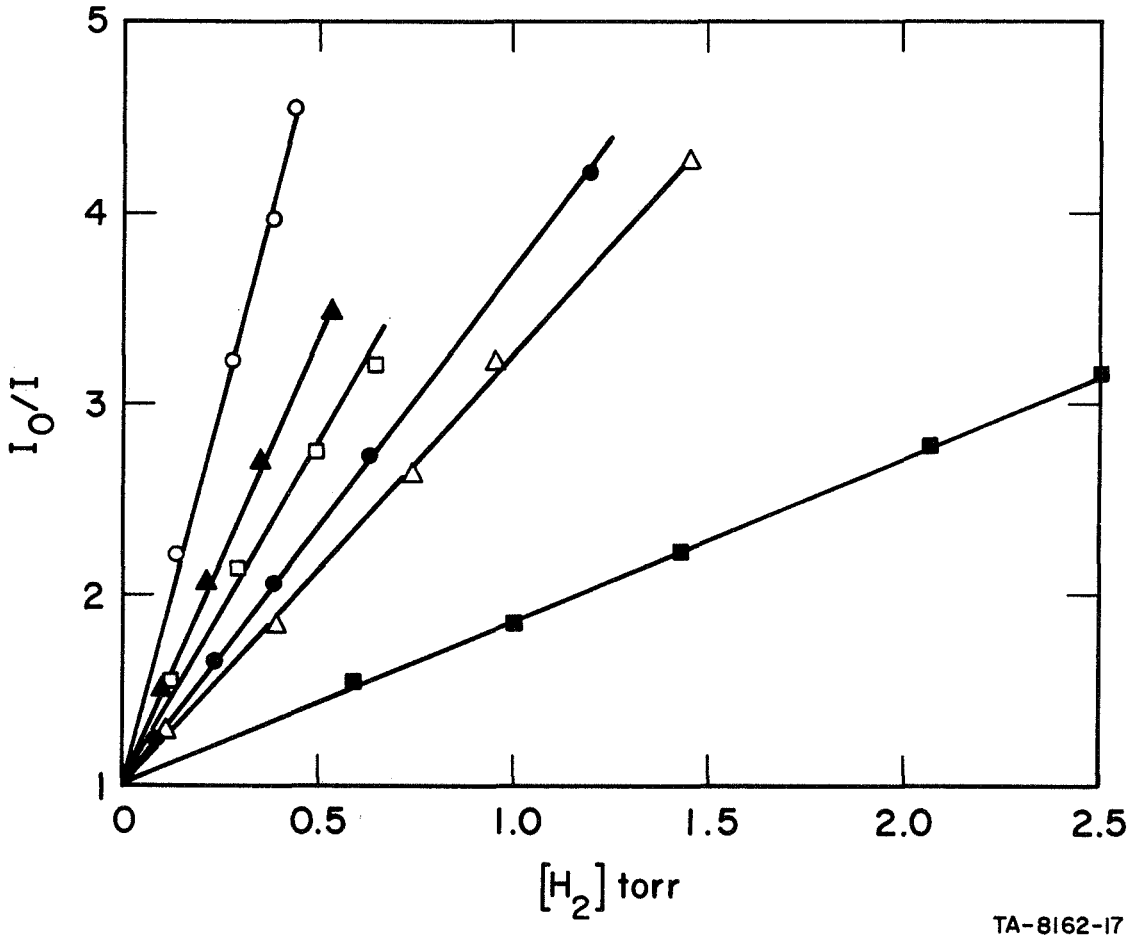

Fig. 8

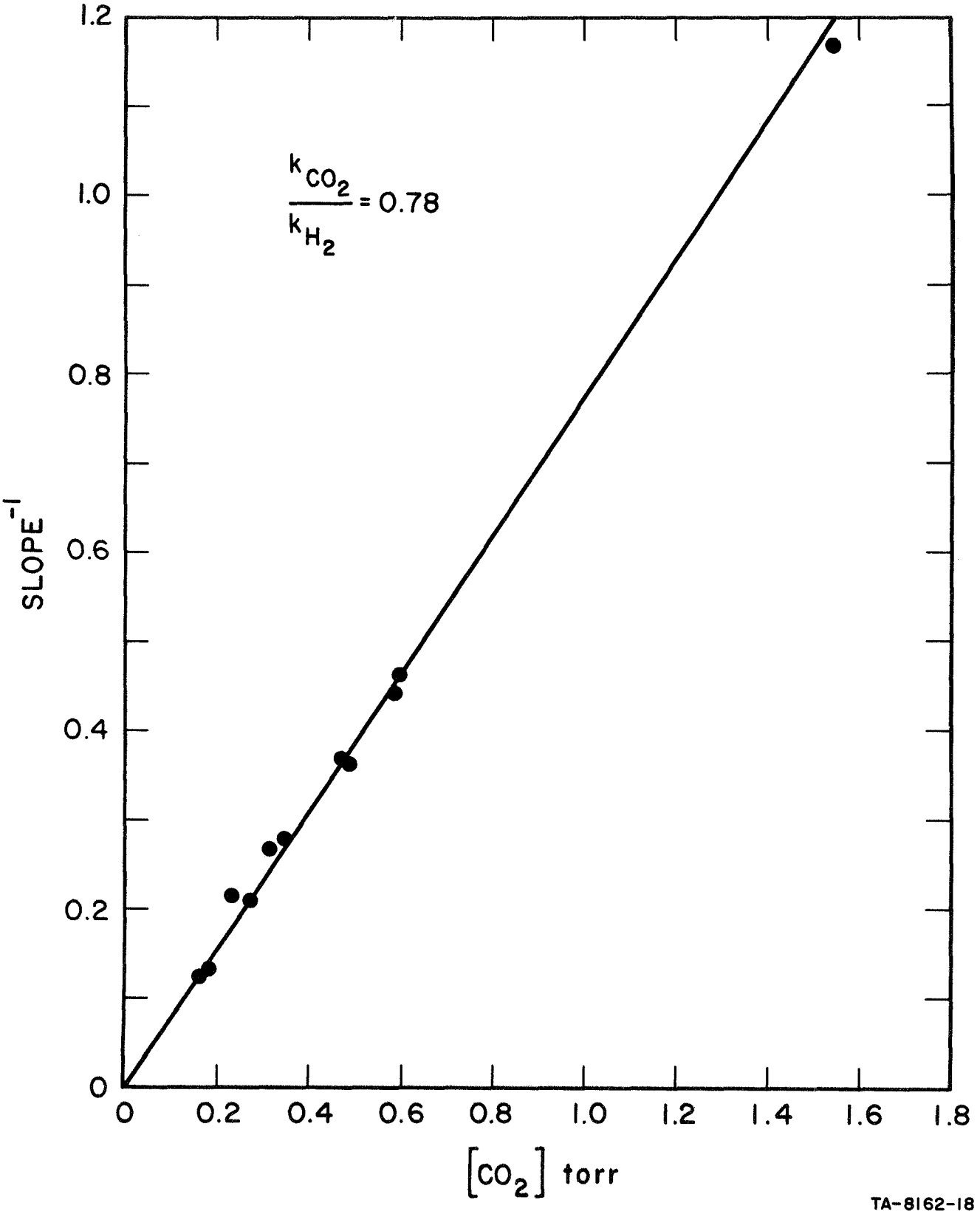
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Fig. 9

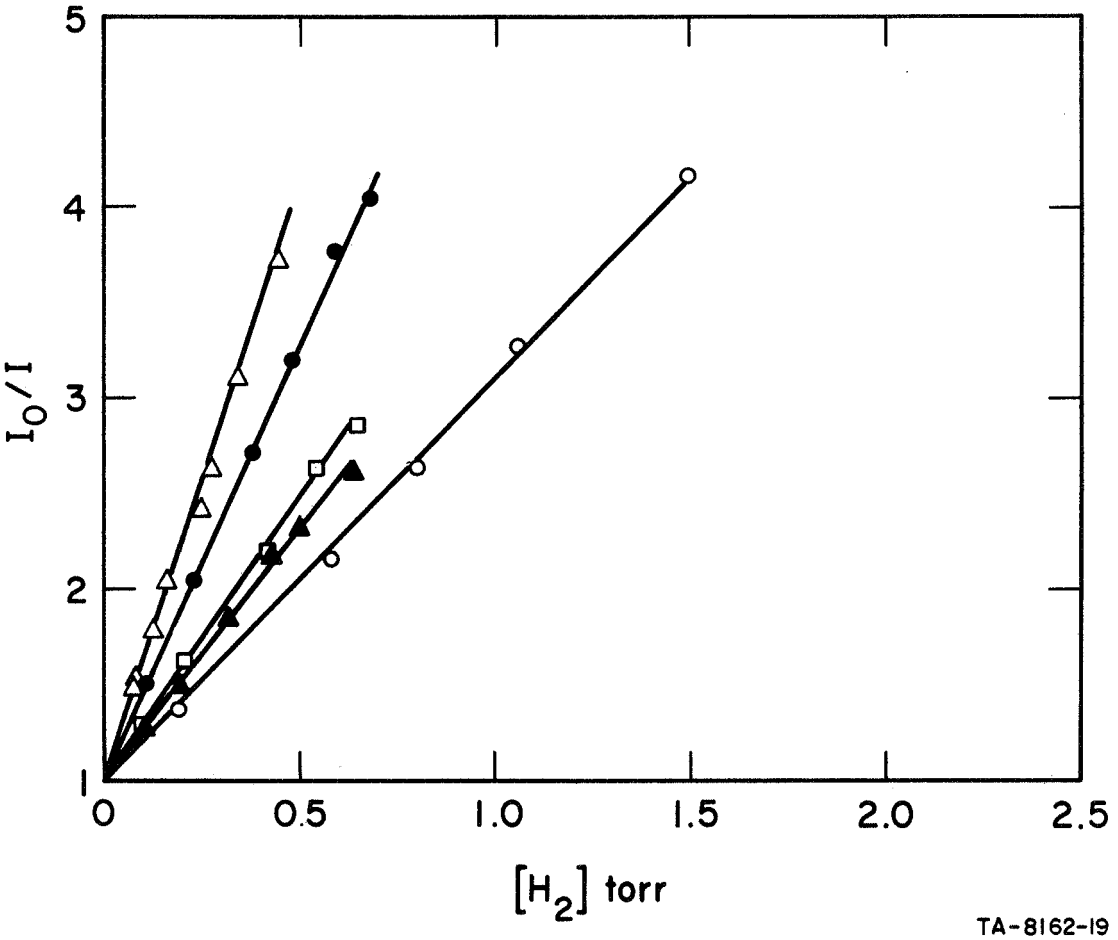
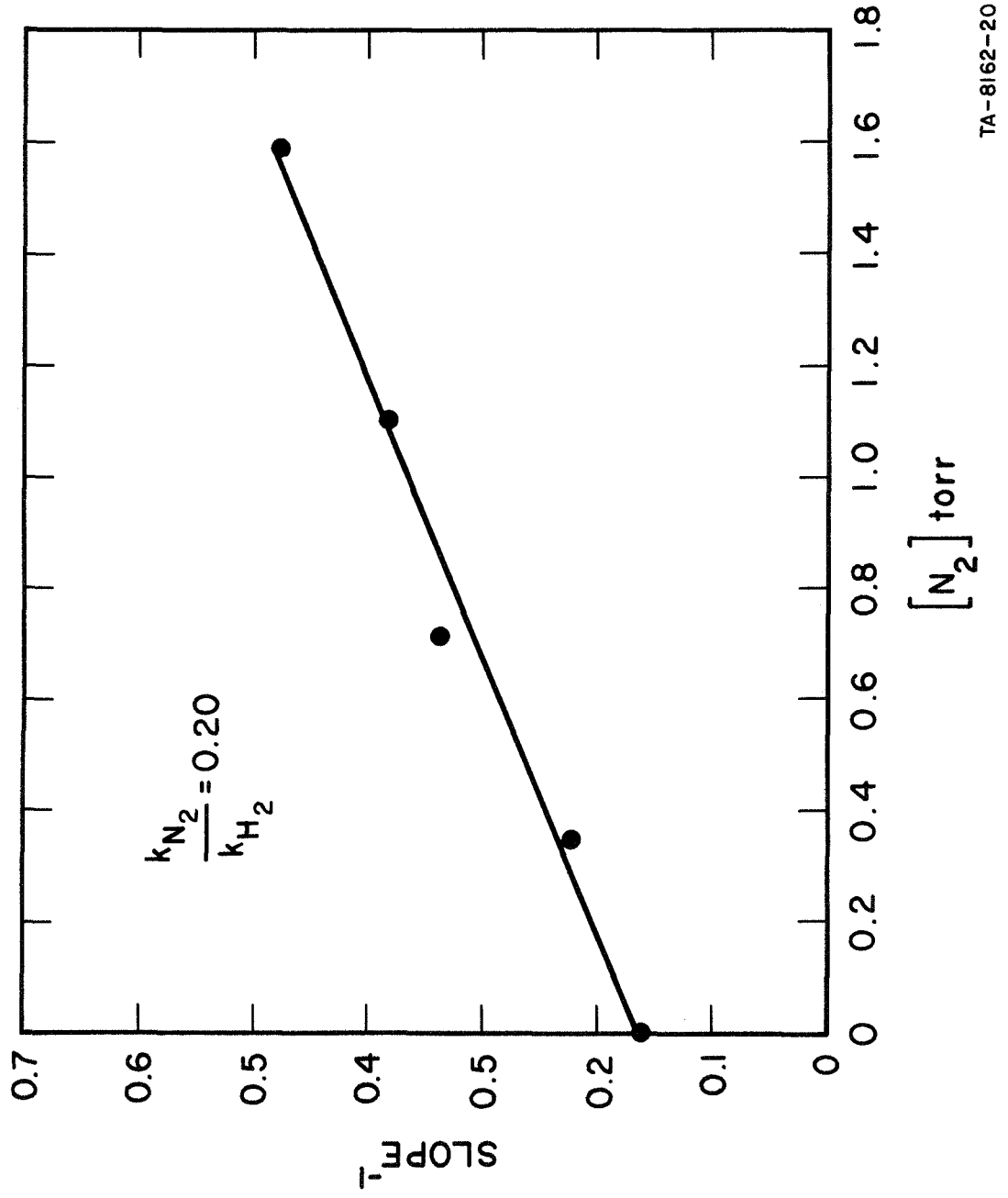


Fig. 10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TA-8162-20

Fig. 11

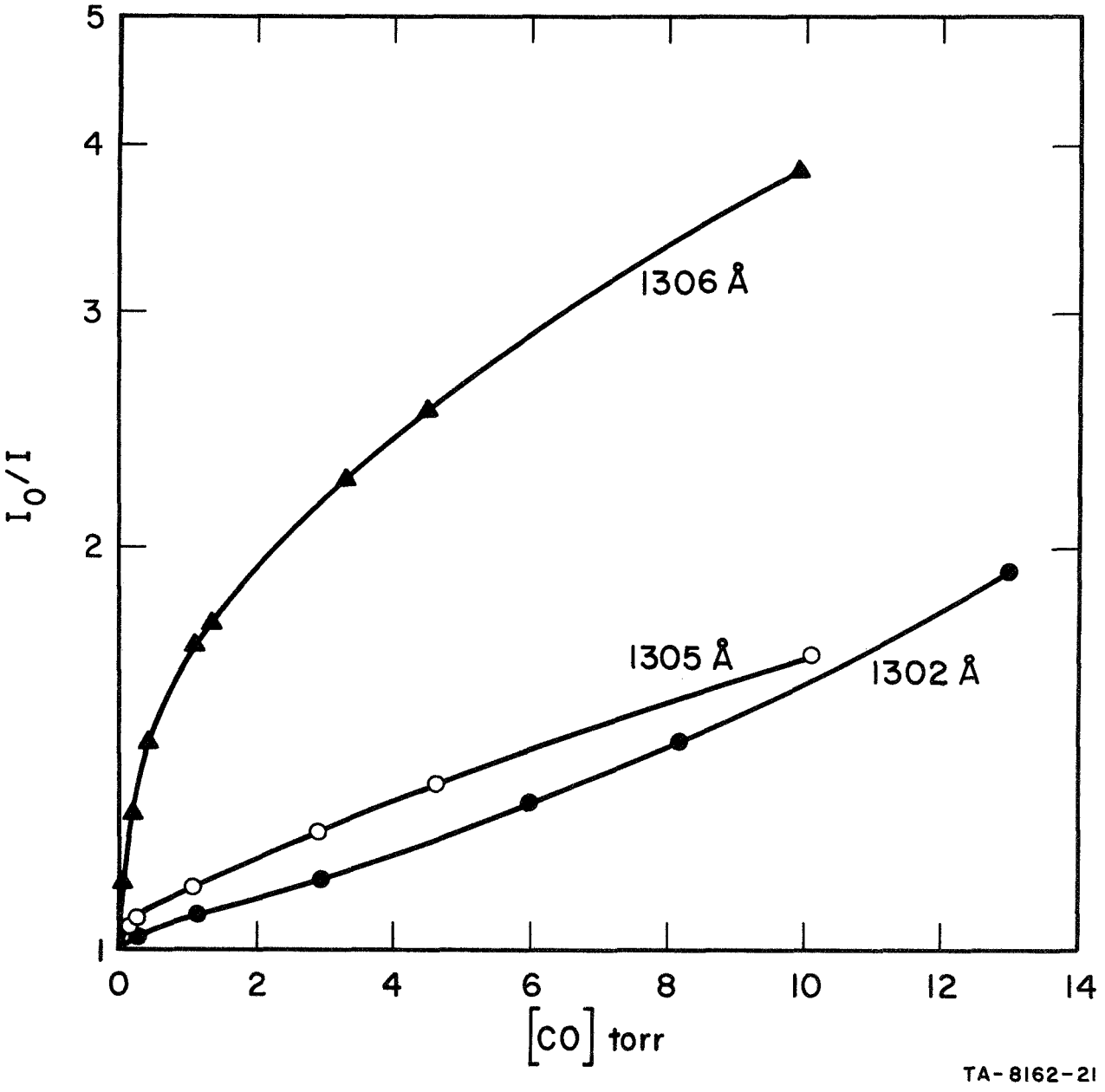

Fig. 12