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LABORATORY CO₂ PHOTOLYSIS STUDIES RELATED TO PLANETARY ATMOSPHERES

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Prepared for:

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Attn: Chief Planetary Atmospheres, Code SL

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Introduction

This work under NASA sponsorship (Contract No. NSR 05-019-252) was undertaken to increase our understanding of the details of CO₂ uv photolysis processes, including determination of the initial dissociation products, and the paths and rates of the subsequent secondary reactions. Monitoring of the O(³P) concentration by means of resonance fluorescence was chosen as a desirable method of achieving these ends, because of the minimum perturbation induced in the system by such a technique. We hope results will clarify the processes taking place in the Mars and Venus atmospheres; a secondary benefit is that development of an effective O(³P) resonance lamp can be useful in measurements of O(³P) concentrations in planetary atmospheres, including that of the earth.

Achievements

During the first six months efforts, reported here, a primary objective has been to construct a lamp emitting the OI 1302-1306 Å resonance triplet with sufficient intensity at the line centers to make resonance fluorescence measurements of O(³P) atom concentrations produced in O₂ and CO₂ photolysis practical. This has been accomplished. The lamp is a flowing microwave discharge of 1% O₂ in Ar, with a MgF₂ window; at present, experiments carried out with O₂ as the O atom source give signal to noise ratios on the order of 500. The original lamp design was not ideal because a considerable amount of the resonance light emitted was reversed, and therefore could not be absorbed by O(³P). This resulted in the signal due to scattered light from the walls being approximately equal to the fluorescence signal. Although such a situation does not present a serious problem, a new lamp has been constructed that greatly increases the absorbable light and increases detection sensitivity for O(³P) atoms.

Experiments with O₂ and CO₂ photolysis have been underway for two months and some interesting observations have been made, although it must be stressed that the findings are preliminary and subject to reinterpretation. Results to date are as follows:

1. The measurement of the $O(^3P)$ produced from CO_2 photolysis shows, when compared to results from O_2 photolysis, that $O(^3P)$ is produced with a quantum yield of 1.0. This means that if CO_3 is formed as a step in the $O(^1D)$ deactivation [$O(^1D)$ is the initial CO_2 dissociation product] by a reaction $CO_2 + O(^1D) \rightarrow CO_3$, the CO_3 must then decompose to $O(^3P) + CO_2$ before any of it leaves the system, i.e., within 0.25 seconds.
2. When H_2 is added to CO_2 during photolysis of the latter, it removes the $O(^1D)$ without affecting the $O(^3P)$, and it does so at a rate comparable to the rate at which CO_2 deactivates $O(^1D)$ to $O(^3P)$, as our previous work indicated. This is most important, because the crux of the argument over CO_2 photolysis is whether $O(^1D)$ is deactivated by CO_2 at the rapid rate previously measured by us, or at the rate 100 times slower measured by Noxon.^{*} As things now stand, we can rationalize Noxon's data by assuming that our fast rate is correct, and that his data involves CO_3 . On the other hand, we can find no explanation for our results, now twice demonstrated by entirely different methods, and recently confirmed by Paraskevopoulos and Cvetanović,[†] if Noxon's slow rate is correct.
3. Measurements of the loss rates of $O(^3P)$ in our flow system have been made in the presence of CO_2 and O_2 , and there is no significant difference between them. In both cases, the loss is governed by the pump-out time of the system. This means that differing $O(^3P)$ concentrations measured in the two instances will reflect the production rate of $O(^3P)$, and not the loss rates, an important point in interpreting the data.

^{*} J. F. Noxon, Can. J. Chem. 47, 1873 (1969).

[†] G. Paraskevopoulos and R. J. Cvetanović, J. Am. Chem. Soc. 91:27, 7572 (1969).

When this project was started, it was first necessary to carry out some studies of CO resonance fluorescence, as this subject has a bearing on our observations. The results of a part of this work are soon to be published in Chemical Physics Letters under the title "The Perturbation Spectrum of CO." The paper describes observations on forced resonance fluorescence processes involving forbidden electronic transitions, which take place because of intramolecular perturbation effects. A copy of the paper has already been forwarded to NASA.

Plans for Completion of Project

As stated above, a new lamp has been designed which will improve the system considerably. Further experiments are planned with O₂, CO₂, and combinations thereof, to confirm the observations made so far. The effect of CO addition will also be investigated, as its behaviour has been previously found to be somewhat anomalous. With reference to CO₃, various tests will be devised to search for concrete evidence for this species. Experiments will be carried out with a pulsed Xe lamp in order to determine if there is any time lag between the start of a pulse and the appearance of O(³P). Such experiments will set an upper limit on the lifetime of a CO₃ intermediate. As yet, our results do not require any hypothesis involving CO₃; it is needed only to reconcile Noxon's results with ours.