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CO + O-Atom Reaction

During a study of the CO reaction with O-atoms it was found that the addition of NO_2 resulted in an unexpectedly high increase in the formation of CO_2. This phenomenon was investigated in some detail because NO and NO_2 are common impurities and because they are often used for analytical purposes in kinetic studies. It was found that the enhanced CO_2 formation occurred only when moisture was added to the O_2 stream by passing through concentrated H_2SO_4 prior to discharging (a common practice to increase stability). It did not occur with " dry" O_2, with "wet" CO, with NO instead of NO_2, or with no discharge (i.e., no O-atoms). Also the effect could be eliminated with a large excess of NO_2. Maximum enhancement was obtained with a concentration of NO_2 very close to the O-atom concentration and with a relatively high CO to O-atom ratio. Considering all the data it is clear that the oxidation does not occur in one simple step but over a more complex mechanism such as the following series of reactions involving excited species:

$$NO_2 + O \rightarrow NO + O_2^* \qquad (1)$$

$$O_2^* + H \rightarrow OH^* + O \qquad (2)$$

$$OH^* + CO \rightarrow CO_2 + H \qquad (3)$$

A paper discussing these results is to be presented at the New York ACS meeting in September.

Isotopic Enrichment Using the Bromine Lamp

Recently Dr. Liuti of this laboratory has reported the formation of carbon suboxide enriched in C-13 by irradiation of CO with the 2062 A iodine line. We have now found that the irradiation of NO with the 1633 A bromine line results in the formation of N_2 substantially enriched in N-15. Various experimental conditions have been studied and enrichments as high as a factor of three over the normal N-15/N-14 ratio have been observed. The results at different temperatures indicate that the energy transfer reaction:

$$NO^* + NO \rightarrow NO + NO^* \qquad (4)$$

may be competing with reactions such as

$$NO^* + NO \rightarrow N_2 + O + O \qquad (5)$$

$$NO^* + N_2O \rightarrow N_2 + N + O + O \qquad (6)$$

and thus tending to reduce any primary isotopic effect.

When NO was irradiated with the 2062 A iodine line the same products were formed but the enrichment of the N_2 produced was much less. Other gases being investigated are N_2O, H_2S, CS_2, and NH_3. When N_2O was irradiated with the bromine line a depletion of N-15 in the product N_2 was observed.

Radical Resonance Studies

This work has continued with emphasis on refining the equipment to permit more accurate precise experiments to be carried

out. A paper on the preliminary results with OH radicals was presented at the 7th Informal Photochemistry Meeting and has been submitted to The Journal of Physical Chemistry. Extensive efforts have been made to apply the method to the detection and measurement of CH radicals, but to date these efforts have been unsuccessful.

Microwave Emission

A paper entitled " Some Comments on The Venus Temperature," in which the results of the microwave experiments are discussed, has been accepted for publication in The Journal of Geophysical Research. Review of this work is still in progress and the direction of future efforts will be guided in part by the response to this paper.

N-Atom Recombination

The study of the reaction order and mechanism of the N-atom recombination and afterglow has not been completed yet. Variations in derived rate coefficients are higher than desirable and more precise data are being obtained.

Publications and Presentations

" Photochemical Equilibrium Studies of Carbon Dioxide and Their Significance for the Venus Atmosphere" by R. R. Reeves, Jr., P. Harteck, B. A. Thompson, and R. W. Waldron has been published in The Journal of Physical Chemistry 70, 1637 (1966).

" Some Comments on the Venus Temperature" by D.C. Applebaum, P. Harteck, R.R. Reeves,Jr., and B.A. Thompson has been accepted for publication in The Journal of Geophysical Research.

" OH Radical Detection and Measurement by Resonant Radiation" by R. Fuhrman, P. Harteck, R.R. Reeves,Jr., and B.A. Thompson has been submitted for publication to The Journal of Physical Chemistry. This paper was also presented at the 7th Informal Photochemical Meeting held at R.P.I., June 20-23, 1966.

" Catalyzed Oxidation of Carbon Monoxide" by R. Bergendahl, P. Harteck, R.R. Reeves,Jr., and B. A. Thompson will be presented at the American Chemical Society Meeting in New York City, September, 1966.

" Gaseous Reactions in the Upper Atmosphere" by P. Harteck was presented at a Symposium on the Physics and Chemistry of the Upper Atmosphere, The Chemical Institute of Canada, Saskatoon, June 5-8, 1966.

Dr. Harteck was honored by being awarded an Honorary Doctorate by the University of Bonn. Following the presentation Dr. Harteck gave an address on Atmospheric Chemistry.