Radiation equilibria pertinent to planetary atmospheres

By P. HARTECK, R. R. REEVES, Jr., B. A. THOMPSON, and R. W. WALDRON,
Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York, U.S.A.

(Manuscript received January 25, 1966)

ABSTRACT

Radiation equilibria due to ionizing radiation or ultraviolet light, or both, on systems such as air, oxygen, carbon dioxide, and their mixtures are of major importance to planetary atmospheres. To investigate the radiation equilibria in the ultraviolet region, a special "Bromine" lamp has been developed which gives 10^{17} quanta/sec at 1582 and 1633 A where the latter is the most intense Br line. Since the absorption coefficients of O_2, CO_2, O_3 and other gases are substantial at these wavelengths, radiation equilibria can be obtained in reasonable times (between 1 hr and a few days, depending on conditions) in our 500 ml sample volume. Since the temperature can also be varied, the conditions prevailing in any region of an atmosphere can be simulated. The wall effects are negligible for pressures down to a few mm.

The irradiation of O_2, CO, CO_2, N_2 and mixtures of these gases are discussed. The effects of trace amounts of water vapor on the equilibria are noted.

Introduction

Much interest exists today in the chemistry of the atmospheres of the earth and Venus. For both planets solar radiation impinging on the upper atmospheres causes photodissociation and various recombination reactions result in the establishment of steady-state equilibria. Most of the recombination reactions of interest take place in the region of the chemosphere. In the earth's atmosphere, photodissociation of oxygen is the source of steady-state concentrations of O-atoms and ozone. Although many investigations have been made of the manner in which these species interact, the rate constants of some of the reactions are not known with sufficient accuracy to predict steady-state conditions occurring in various regions of the atmosphere. The role which minor constituents such as H-atoms and OH radicals may play in the atmospheric chemical equilibria is also of great interest as is the origin of some of the trace constituents such as N_2O.

The principal observable constituent of the Venus atmosphere is carbon dioxide. It might be expected that photodissociation of this would lead to appreciable steady-state concentrations of oxygen and carbon monoxide. However, these two compounds are not observed and upper limits have been set for their presence which correspond to 0.1 % of the CO_2. A study of the photochemical equilibrium of this system would thus be very valuable for an understanding of the chemistry of the Venus atmosphere.

The iodine lamp, emitting the 2062 A ultraviolet line of iodine, has been used in this laboratory to study the reactions of (HARTECK, REEVES & THOMPSON, 1964) CO ($a^3\Pi$) molecules and for this work a similar lamp, the bromine lamp (THOMPSON, HARTECK & REEVES, 1965) was used. The bromine lamp emits radiation at 1633 A which is absorbed by CO_2 and O_2. The high total radiation intensities obtainable from these lamps make them especially suitable for radiation equilibrium studies.

Experimental

The bromine lamp used for these studies has been described in detail elsewhere. THOMPSON *et al.*, 1965. Basically it consists of a central discharge tube through which argon containing a trace of bromine vapor is passed. The bromine is introduced through a capillary leak from a reservoir. A vacuum jacket is provided between the central discharge tube and the sample reservoir for thermal insulation. The innermost walls are constructed of Suprasil quartz to permit transmission of the 1633 A bromine line. Each 1 mm thickness of Suprasil transmits about

50% of the 1633A radiation so that about 25% of the initial intensity is transmitted to the sample reservoir. The only other ultraviolet line which might be present is the 1582A line and only a minor amount of this wavelength should have been received by the sample because each 1 mm thickness of Suprasil transmits only 10% of the radiation of this wavelength. Thus only 1% of the initial 1582A radiation would penetrate to the sample cell. An outer jacket is provided through which liquid can be circulated at any desired temperature. The temperature in the sample reservoir was checked by gas thermometer techniques and found to be within 1 or 2 degrees of that in the outer jacket. Studies were made at various temperatures from 300° K to 200° K. Gas samples could be withdrawn for analysis at any time during irradiation.

The spacing of the energy levels for bromine is such that no emission lines are observed in the region between 1633A and about 3000A (TECH, 1963). However, fairly intense "continua" similar to those found with I_2 KIESS & CORLISS, 1959) are observed in the 2500A–3000A region. This radiation could interfere with the study of equilibria involving ozone, which absorbs strongly in this wavelength region, and therefore it was minimized by keeping the bromine partial pressure very low (a few tenths of a micron or less). For these experiments it was desirable to have as nearly monochromatic radiation as possible; however, it is clear from the above remarks that by using a higher bromine pressure so that the "continua" were more intense, a pseudo-"solar" radiation spectrum could be obtained which might be very useful in some studies.

All gases used were obtained from the Matheson Company. CO_2 (Coleman Grade) was purified from traces of air and water by fractional distillation at low temperatures. Oxygen and argon were dried by passing through liquid oxygen traps. CO always had to be purified from traces of iron carbonyl which might have interfered with the equilibria under study. This was done by bubbling through sodium hydroxide solution. The CO was then dried by passing through a series of liquid oxygen traps.

Gas analyses were made with a Consolidated Electrodynamics Corp. mass spectrometer, model 21–130, except for ozone which was determined by bubbling through potassium iodide solution and titrating the liberated iodine.

Results and discussion

Oxygen-ozone radiation equilibrium

A preliminary discussion of the results observed with this system is given elsewhere (THOMPSON, HARTECK & REEVES, 1965). The most significant feature of the results is that at low temperatures the steady-state ratio of O_3 to O_2 at any given temperature was essentially a constant, independent of the total pressure. When pure O_2 was irradiated at 201°K the equilibrium O_3/O_2 ratio was about 0.46; at 242°K the ratio was about 0.15. At 273°K the ratio was about 0.09 with a slight pressure dependence. The precision of the data in each case was about ±10%.

The O_2-O_3 equilibrium can be considered to be controlled by the following series of reactions:

$$O_3 + h\nu \xrightarrow{\alpha_1} O_2^* + O(^1D), \qquad (1)$$

$$O_2 + h\nu \xrightarrow{\alpha_2} O(^3P) + O(^1D), \qquad (2)$$

$$O(^3P) + O_2 + M \xrightarrow{k_3} O_3 + M, \qquad (3)$$

$$O(^3P) + O_3 \xrightarrow{k_4} O_2 + O_2, \qquad (4)$$

where it is considered that all excited O_2 molecules and $O(^1D)$ atoms are immediately quenched by collisions and do not affect the subsequent reactions. From the steady-state equations for O-atoms and for O_3 the following expression for the equilibrium O_3/O_2 ratio can be derived:

$$\frac{(O_3)}{(O_2)} = \frac{-1 + \sqrt{1 + 4(\alpha_1 k_3 (M)/\alpha_2 k_4)}}{2\alpha_1/\alpha_2}, \qquad (I)$$

where α_1 and α_2 are the absorption coefficients for O_3 and O_2 for the incident light. It is obvious that this O_3/O_2 ratio is not pressure independent.

Alternately, it could be considered that the equilibrium is being controlled by a mechanism involving exited or energetic atoms and molecules. One possible sequence is the following:

$$O_3 + h\nu \xrightarrow{\alpha_1} O_2^* + O(^1D), \quad (1)$$

$$O_2 + h\nu \xrightarrow{\alpha_2} O(^3P) + O(^1D), \quad (2)$$

$$O(^3P) + O_2 + M \xrightarrow{k_3} O_3 + M, \quad (3)$$

$$O(^1D) + O_3 \xrightarrow{k_5} O_2 + O_2, \quad (5)$$

$$O(^1D) + O_2 \xrightarrow{k_6} O_2^* + O(^3P), \quad (6)$$

$$O_2^* + O_3 \xrightarrow{k_7} O_2 + O_2 + O, \quad (7)$$

$$O_2^* + O_2 \xrightarrow{k_8} O_2 + O_2, \quad (8)$$

where the O_2^* formed in Reaction (1) and the $O(^1D)$ formed in Reactions (1) and (2) have initially considerable kinetic energy. O_2^* is considered to be either the $(a^1\Delta g)$ or the $(b^1\Sigma g^+)$ state. The reaction

$$O_2^* + O_2 \rightarrow O_3 + O \quad (9)$$

cannot occur with either O_2 $(a^1\Delta g)$ or O_2 $(b^1\Sigma g^+)$. It occurs with O_2 $(A^3\Sigma u^+)$ (HARTECK & REEVES, 1964) but this is not formed in the above series of reactions. Using Reactions (1) through (8) steady-state equations can be set up for O_3, O-atoms, and $O(^1D)$. Combining these three equations the equilibrium O_3/O_2 ratio is found to be:

$$\left| \frac{(O_3)}{(O_2)} = \sqrt{\frac{\alpha_2 k_6}{\alpha_1 k_5}}, \right. \quad (II)$$

where α_1 and α_2 are defined as above. This ratio is pressure independent, even though Reaction (3) contains a term dependent on pressure, because this reaction is not a controlling reaction, but a consecutive reaction to Reactions (2) and (6). The reaction of $O(^3P)$ with O_3 is neglected in this sequence, assuming that under these conditions, due especially to its heat of activation, this reaction does not significantly compete with Reaction (3). Therefore, in the steady-state the rate of formation of ozone is equal to the rate of formation of $O(^3P)$ by Reactions (2) and (6). Such an excited atom mechanism is thus compatible with the observed O_2-O_3 equilibrium results under these conditions.

When mixtures of 10% O_2 in argon were irradiated, a constant O_3/O_2 ratio, independent of pressure, was again observed for a given temperature; however, the value was about a factor of two higher. The O-atoms produced in Reaction (2) by 1633A radiation will have additional kinetic energy of about 5 kcal and thus may react faster with ozone than normal thermal atoms. Addition of argon would be expected to thermalize these atoms and thereby increase the steady-state ozone concentration as observed. However, the addition of argon should have little or no effect on depopulating the excited electronic states.

When traces of H_2 were added to the oxygen the equilibrium O_3/O_2 ratio decreased, as might be expected on the basis of the known rapid reaction of H-atoms with O_3. However the effect was by no means as dramatic as observed with CO_2 (REEVES *et al.*, to be published).

CO_2 radiation equilibrium

The photochemical equilibrium of CO_2 can be considered to be controlled by the following two reactions in addition to Reactions (1) through (4) above:

$$CO_2 + h\nu \xrightarrow{\alpha_3} CO + O(^1D), \quad (10)$$

$$CO + O(^3P) \xrightarrow{k_{11}} CO_2 + h\nu, \quad (11)$$

where again the excited atoms and molecules have been assumed to be immediately quenched. It may be noted that Reaction (11) has been reported as a two-body reaction by MAHAN & SOLO (1962). By the application of steady-state relationships (REEVES *et al.*, to be published), the following equation can be derived for the equilibrium CO/CO_2 ratio:

$$\left| \frac{(CO)}{(CO_2)} = \frac{-1 + \sqrt{1 + 4(\alpha_1 k_3 (M)/\alpha_2 k_4)}}{2\alpha_1 k_{11}/\alpha_3 k_4}, \right. \quad (III)$$

where α_1, α_2, and α_3 are the absorption coefficients of O_3, O_2 and CO_2 for the incident light. It is interesting that if the above series of reactions is solved for the O_3/O_2 ratio, equation (III) reduces to equation (I), since Reaction (10) is essentially the reverse of Reaction (11). Our experimental results confirm this since the O_3/O_2 ratio found in the irradiated CO_2 was comparable to that obtained with pure O_2.

Substitution into equation (III) of values for absorption coefficients and rate constants

(REEVES *et al.*, to be published) gives CO/CO_2 ratios of 52 at 200°K and 28 at 300°K.

In these experiments dissociation of the CO_2 proceeded at a uniform initial rate consistent with a quantum yield of unity in agreement with the results of GROTH (1937). As mentioned above, O_3 was present and the O_3/O_2 ratio was comparable to that obtained when pure oxygen was irradiated at the same temperature. The ratio of CO to O_2 was determined mass spectrometrically and, including the oxygen from the O_3, was found to be the stoichiometric 2:1 ratio. This is in contrast to the results of some other workers (cf. WARNECK, 1964) who have reported finding less than the stoichiometric amount of oxygen. However their experimental conditions were quite different; in particular, a much smaller fraction of the CO_2 was dissociated in their experiments.

After a few per cent of the CO_2 had been dissociated, back reactions began to compete and a steady-state was reached. The position of the equilibrium was found to be somewhat variable with a maximum CO/CO_2 ratio observed of 0.35, much lower than the theoretical value predicted above. Some evidence of catalysis of the back reaction due to the presence of traces of water vapor was provided by irradiations of CO-O_2 mixtures and of CO_2 with traces of H_2 added. For example, it was found that with as little as 0.1 % water vapor present complete recombination to CO_2 occurred ($O_2/CO_2 < 0.005$). With 0.01 % H_2O the equilibrium shifted slightly toward increased decomposition ($O_2/CO_2 \sim 0.03$). When 0.1 % H_2 was added to CO_2 before irradiation, the dissociation was completely inhibited ($O_2/CO_2 < 0.005$), and with 0.01 % H_2 dissociation occurred to a small extent ($O_2/CO_2 \sim 0.02$). In these latter experiments it could be seen mass spectrometrically that most of the added hydrogen remained as H_2 and only a very small fraction was converted to H_2O during the time of irradiation. These results are described in more detail elsewhere (REEVES *et al.*, to be published). It was concluded that under these conditions the equilibrium is being controlled by such reactions as:

$$CO + OH \rightarrow CO_2 + H, \qquad (12)$$

$$O_3 + H \rightarrow O_2 + OH, \qquad (13)$$

$$OH + O_3 \rightarrow HO_2 + O_2, \qquad (14)$$

$$CO + HO_2 \rightarrow CO_2 + OH. \qquad (15)$$

Reactions (12) and (13) constitute a cycle; however, the heat of activation of Reaction (12) has been reported to be at least as high as 7 kcal (AVRAMENKO & KOLESNIKOVA, 1964). At low temperatures, therefore, this cycle would be insufficient to account for the observed recombination and additional cycles such as that represented by Reactions (14) and (15) may be operating. Other reactions of a similar nature may also be involved.

Since the O_2-O_3 equilibrium was believed to be controlled by excited or energetic species, as discussed above, it could be considered that a similar situation exists with CO_2. The following reactions represent a possible sequence:

$$O_3 + h\nu \xrightarrow{\alpha_1} O_2^* + O(^1D), \qquad (1)$$

$$O_2 + h\nu \xrightarrow{\alpha_2} O(^3P) + O(^1D), \qquad (2)$$

$$O(^3P) + O_2 + M \xrightarrow{k_3} O_3 + M, \qquad (3)$$

$$O(^1D) + O_3 \xrightarrow{k_5} O_2 + O_2, \qquad (5)$$

$$O(^1D) + O_2 \xrightarrow{k_6} O_2^* + O(^3P), \qquad (6)$$

$$O_2^* + O_3 \xrightarrow{k_7} O_2 + O_2 + O(^3P), \qquad (7)$$

$$O_2^* + O_2 \xrightarrow{k_8} O_2 + O_2, \qquad (8)$$

$$CO_2 + h\nu \xrightarrow{\alpha_3} CO + O(^1D), \qquad (10)$$

$$CO + O(^1D) \xrightarrow{k_{12}} CO_2 + h\nu. \qquad (12)$$

Subjecting this system to a steady-state treatment one finds the equilibrium CO/CO_2 ratio to be given by:

$$\frac{(CO)}{(CO_2)} = \sqrt{\frac{\alpha_3^2 k_5 k_6}{\alpha_1 \alpha_2 k_{12}^2}} \qquad (IV)$$

where α_1, α_2 and α_3 are defined as above. Thus in an extremely clean system the CO/CO_2 ratio at any temperature might be expected to be a constant, independent of pressure. The pressure independence arises from the same considerations discussed above for the oxygen-ozone equilibrium.

A catalyzed back-reaction of the type represented by Reactions (12) through (15) could

obviously explain the high abundance of CO_2 in the Venus atmosphere with no more than traces of either CO or O_2. Recent spectroscopic observations from a balloon (BOTTEMA *et al.*, 1964) have indicated the presence of small amounts (a few cm-atm) of water vapor in the Venus atmosphere. Thus, impinging solar radiation should result in the establishment of OH radicals and H-atoms down to the cloud layer. The above results have shown that only traces of moisture are required for catalysis of the back reaction and therefore it seems reasonable to conclude that any CO and O_2 formed in the Venus atmosphere recombine in the above manner to regenerate CO_2. Also, under the influence of solar radiation, additional ozone may be dissociated by radiation in the 2500 A region, increasing the relative level of O-atoms, which in turn may enhance the rate of CO_2 formation.

It may be noted that the observed temperature of the Venus cloud layer is 235°K (SINTON, 1961) which is not too different from the lower temperatures used in these experiments. Only a very small amount of actual water vapor is possible at such low temperatures because in this region the vapor pressure of water is only a few microns. Such a recombination catalyzed by the presence of trace amounts of water vapor has an analogy in the Earth's upper atmosphere where relatively small amounts of H-atoms lead to strong emission of the Meinel bands as a result of catalytic decomposition of ozone by H-atoms.

Any excess CO which might occur in the atmosphere as a result of volcanic exhalations or other such sources could be expected to react to form carbon suboxide under the influence of solar radiation. Thus it might be expected that the Venus clouds are composed, at least in part, of carbon suboxide or a polymer or organic product derived from the suboxide (HARTECK & GROTH, 1957).

Photodissociation of atmospheric water vapor, followed by escape of H-atoms from the upper atmosphere might be considered as a source of excess atmospheric oxygen. The calculations of HARTECK & JENSEN (1948), KUIPER (1952), and UREY (1959) have shown that oxygen in the earth's atmosphere may originate in part from such a source. However, production of oxygen in the Venus atmosphere in this way should be negligible due to the combination of higher total pressure and very low temperature at the cloud layer which would limit the transport of water vapor through the atmosphere.

It may be noted that if excess O_2 should be formed in some other manner it could soon be consumed by reducing substances such as sub-oxides which may be expected to be present on the Venus surface (HARTECK *et al.*, 1963).

N_2O radiation equilibrium

The origin of N_2O in the Earth's atmosphere may be biological or to a certain extent photochemical. We have irradiated mixtures of nitrogen and oxygen with the bromine lamp at a variety of temperatures and pressures to determine whether N_2O could be produced by the action of the 1633 A radiation. We were unable to detect any N_2O and may set an upper limit to the quantum yield of $\sim 10^{-4}$. GROTH & SCHIERHOLZ (1957) have reported the formation of N_2O with a quantum yield of 10^{-4} with the 1470 A and 1295 A lines of xenon which have substantially higher energy. In general, however, it seems doubtful that significant amounts of N_2O are produced in the atmosphere by this type of radiation. One alternate possibility which might be considered is that of a negative ion chain mechanism such as:

$$N_2 + O^- \rightarrow N_2O + e^-, \qquad (16)$$

$$e^- + O_3 \rightarrow O_2 + O^-. \qquad (17)$$

Such a chain could produce considerable amounts of N_2O. It is known that N_2O can be formed by passing air through an ozonizer and also by irradiating nitrogen-oxygen mixtures with ionizing radiation, indicating the possibility of such a mechanism.

Acknowledgement

This work was carried out under a Research Grant from The National Aeronautics and Space Administration. This paper was presented in part at the CACR Symposium on Atmospheric Chemistry, Circulation and Aerosols held at Visby, Sweden, August 18–25, 1965.

REFERENCES

See AVRAMENKO, L. I., and KOLESNIKOVA, R. V. 1964, Mechanisms and rate constants of elementary gas phase reactions involving hydroxyl and oxygen atoms; pp. 25–62 in *Advances in Photochemistry*, Vol. 2, Interscience Publishers, New York.

BOTTEMA, M., PLUMMER, W., and STRONG, J., 1964, Water vapor in the atmosphere of Venus. *Astrophys. J.*, **139**, p. 1021.

HARTECK, P., and GROTH, W., 1957, Discussed by G. P. KUIPER in The atmosphere and the cloud layer of Venus, pp. 78–86 in *The Threshold of Space*, M. ZELIKOFF, Ed., Pergamon Press, London.

HARTECK, P., and JENSEN, J. H. D., 1948, Über den Sauerstoffgehalt der Atmosphäre. *Z. Naturforsch.*, **3a**, p. 591.

HARTECK, P., REEVES, R. R., JR., and THOMPSON, B. A., 1963, Photochemical problems of the Venus atmosphere. NASA Technical Note TN-D-1984.

HARTECK, P., and REEVES, R. R., JR., 1964, Formation and reactions of the excited O_2 ($A^3\Sigma_u^+$) molecules. *Disc. Faraday Soc.*, **37**, p. 82.

HARTECK, P., REEVES R. R., JR., and THOMPSON, B. A., 1964, The iodine lamp; A light source for selective excitation of CO. *Z. Naturforsch.* **19a**, p. 2.

GROTH, W., 1937, Photochemische Untersuchungen in Schumann-Ultraviolett Nr. 3. *Z. Phys. Chem.*, B**37**, p. 307.

GROTH, W., and SCHIERHOLZ, H., 1957, Photochemical formation of nitrous oxide. *J. Chem. Phys.*, **27**, 973.

KIESS, C. C., and CORLISS, C. H., 1959, Description and analysis of the first spectrum of iodine. Ibid., **63A**, p. 1.

KUIPER, G. P., 1952, Planetary atmospheres and their origin, pp. 306 ff. in *The Atmospheres of the Earth and Planets*, G. P. KUIPER, Ed., Univ. of Chicago Press.

MAHAN, B. H., and SOLO, R. B., 1962, Carbon monoxide-oxygen atom reaction. *J. Chem. Phys.*, **37**, p. 2669.

REEVES, R. R., JR., HARTECK, P., THOMPSON, B. A., and WALDRON, R. W., Photochemical equilibrium studies of carbon dioxide and their significance for the Venus atmosphere. To be published.

SINTON, W. M., 1961, pp. 430–34 of Recent radiometric studies of the planets and the Moon, in *Planets and Satellites*, G. P. KUIPER, Ed., Univ. of Chicago Press.

TECH, J. L., 1963, Analysis of the spectrum of neutral atomic bromine (BrI). *J. Res. Natl. Bur. Std.*, **67A**, p. 505.

THOMPSON, B. A., HARTECK, P., and REEVES, R. R., JR., 1965, The bromine ultraviolet lamp. Studies of the oxygen-ozone and carbon dioxide equilibria. *J. Phys. Chem.*, **69**, pp. 3964.

UREY, H. C., 1959, The atmospheres of the planets, pp. 363–418 in *Handbuch der Physik*, Vol. 52, Springer Verlag.

For discussion see WARNECK, P., 1964, Reactions of ^1D oxygen atoms in the photolysis of carbon dioxide. *Disc. Faraday Soc.*, **37**, p. 57. and discussion on pp. 217–218.

РАДИАЦИОННОЕ РАВНОВЕСИЕ, ПРИСУЩЕЕ ПЛАНЕТАРНЫМ АТМОСФЕРАМ

Радиационное равновесие, обусловленное воздействием ионизирующей радиации или ультрафиолетовым светом, или ими обоими, на такие системы, как воздух, кислород, двуокись углерода и их смеси, имеет большое значение для планетарных атмосфер. С целью исследования радиационного равновесия в ультрафиолетовой области была сконструирована специальная «броминовая» лампа, которая излучала 10^{17} квант/сек в интервале 1582–1633 Å, в котором наиболее интенсивно рассеяние на линии брома. Поскольку коэффициенты поглощения O_2, CO_2, O_3 и других газов существенны для таких длин волн, то радиационное равновесие в нашем выделенном объеме в 500 мл может быть получено в разумное время (от 1 часа до нескольких дней в зависимости от условий). Так как температуру также можно изменять, то можно моделировать условия, характерные для любой области атмосферы. Эффекты на стенках пренебрежимы для давлений порядка нескольких миллибар.

Обсуждается переизлучение O_2, CO, CO_2, N_2 и смесей этих газов. Отмечаются эффекты присутствия следов водяного пара на равновесие.