

EXTRATERRESTRIAL ATMOSPHERIC PHOTOCHEMISTRY

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1. Introduction

Our knowledge of the atmospheres of the planets and satellites in the solar system has advanced enormously [1 - 3] in the years since the first issue of the *Journal of Photochemistry* appeared. Orbiters, "fly-bys" and landers have reached the atmospheres of distant bodies to provide the first *in situ* measurements, and these data have been supplemented by the results from increasingly sophisticated Earth-based investigations. Table 1 summarizes some of the most important recent space missions that have included atmospheric observations as an objective [4 - 19], and the table also shows what is planned for the immediate future.

In the paragraphs that follow I have presented a very personal selection of topics that are specifically photochemical in nature.

2. Inner planets

One of the fascinating aspects of the photochemistry of the inner planets has been the identification of the part that catalytic cycles play in determining composition [20 - 23]. For Mars and Venus, such cycles are vital, because photolysis of the bulk atmospheric constituent, CO₂,



produces CO (and O) which could not otherwise be oxidized back to CO₂. Present day CO concentrations could be produced in a few years on Mars and a few hundred years on Venus, and the entire atmospheres would be modified in a few thousand years. On Mars [20, 21], catalytic cycles involving HO_x species can be readily identified, with the reaction



playing a dominant role in the oxidation of CO. Odd hydrogen compounds are supplied by photochemical decomposition of H₂O, either directly by photolysis or in attack by O(¹D) derived from CO₂, O₂ and O₃ photolysis. A small branch of the HO_x reactions leads to the formation of H₂ that ultimately escapes as H from the Martian exosphere. Since the reaction is fed

TABLE 1

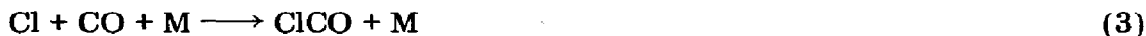
Some recent and proposed missions

<i>Date</i>	<i>Name</i>	<i>Objective</i>	<i>References</i>
July - September 1976	Viking 1, 2	Mars Entry Science and Lander	[4, 5]
December 1978	Pioneer Venus	Orbiter and "Bus" carrying entry probes to Venus	[6 - 9]
December 1978	Venera 11, 12	Soviet probes to Venus	[9 - 11]
March 1979	Voyager 1	Closest approach to Jupiter	[12]
July 1979	Voyager 2	Closest approach to Jupiter	[13]
September 1979	Pioneer 11	First ever fly-by of Saturn	[14, 15]
November 1980	Voyager 1	Closest approach to Saturn	[16 - 18]
August 1981	Voyager 2	Closest approach to Saturn	[17, 19]
March 1982	Venera 13, 14	Soviet sounders to Venus	
June 1984	"VEGA" (Venera 15, 16)	Launch December 1984 to visit Venus (June 1984) and on to comet Halley (April 1986) (U.S.S.R.-France)	
April 1986	Giotto	Comet Halley mission (ESA; launch, summer 1985)	
March - April 1986	Planet C	Comet Halley mission (Japan)	
1986	Voyager 2	First ever fly-by of Uranus	
1989	Galileo	Jupiter orbiter (NASA; launch, 1986)	
1989	Voyager 2	First ever fly-by of Neptune	

ESA, European Space Agency; NASA, National Aeronautics and Space Administration.

by the leak of H_2O that is permanently destroyed, escape of two hydrogen atoms is necessarily accompanied by the escape of one oxygen atom [21]. Ionospheric processes [24] are responsible for this O loss, as well as for the loss of N [21]. The H_2O lost over the age of the solar system would correspond to an ice layer of 2.5 m thickness. Incidentally, since there is only an *atmospheric* reservoir of nitrogen, the slightly higher loss rate of ^{14}N compared with ^{15}N has led to an isotopic enrichment of the heavier isotope in the atmosphere.

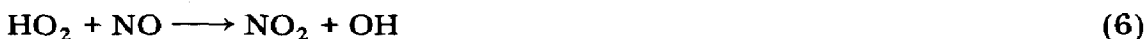
The catalytic cycles which effect the union of CO and O on Venus are rather more complex and subtle than those operating on Mars, because there is insufficient H_2O to yield the necessary concentration of HO_x radicals [23]. Considerable interest attaches to the possible roles [22, 23] of ClO_x and SO_x species in catalytic cycles because of the presence of HCl and SO_2 in the upper atmosphere. In the Earth's atmosphere, ClO_x only catalyses the conversion of odd oxygen to O_2 , but on Venus a dual role is possible, with two sequences leading to recombination of O with CO. Three-body formation of chloroformyl radicals (ClCO) and then of peroxychloroformyl radicals ($ClCO_3$) is involved in both cases:



followed by attack of either Cl or O on ClCO₃ to yield CO₂. Sulphur-containing species are also implicated in the (photo)dissociation of O₂ [23], with sulphur atoms, ultimately derived photochemically from SO₂, attacking the molecular oxygen. More interestingly, the SO product of SO₂ photolysis can react with ClO:



to synergize the ClO_x catalytic chain. The mechanism bears an interesting analogy with the tropospheric oxidation cycle on Earth, of which a part may be represented



On Venus, SO₂ plays the role of NO₂, and ClO_x the role of HO_x. Mesospheric hazes of ice, dust and acid aerosols [25] bear a further analogy with terrestrial phenomena!

Electronically excited species do not appear to play any major direct part in the bulk chemistry of the neutral atmospheric components, although they may be involved in ionospheric processes [24, 26] that ultimately affect the neutral chemistry. They are also, of course, intimately connected with airglow emissions. UV airglow studies [27 - 30] have afforded considerable insight into the distribution of atomic and other minor constituents of the atmospheres of Mars and Venus, but we concentrate here on emissions from the metastable singlet states of O₂ [31]. IR Atmospheric Band emission, due to the O₂(¹Δ_g → ³Σ_g⁻) transition, is observed in the airglow of both Mars [32, 33] and Venus [34]. In the Martian atmosphere, O₂(¹Δ_g) is almost certainly excited, as it is in the terrestrial dayglow, by the UV photolysis of O₃ [31]; seasonal and latitudinal intensity variations [33] are entirely consistent with the variability of [O₃]. O₃ photolysis can account [35] for only about 10% of the observed intensity on Venus because of the low oxygen column densities [36]. Alternative excitation mechanisms that have been proposed include [31] recombination of atomic oxygen and exothermic reactions of ClO_x species, but the proposals await experimental confirmation. A big impetus to the study of the higher lying (about 4.05 eV) c¹Σ_u⁻ state of O₂ was provided by the identification [37] of a Herzberg II (c → X) progression in a nightglow spectrum obtained [38] by the Soviet Venera 9, 10 mission. Subsequently, it was shown [39] that the c → X emission was also present in the Earth's nightglow, although much weaker [39, 40] than in the Venusian nightglow, and with an entirely different vibrational distribution. In the Martian airglow, the Herzberg II system is weaker [41] even than it is in the Earth's. Laboratory studies [37, 42 - 45] have shown that recombination of O(³P) atoms populates O₂(c¹Σ_u⁻), especially when CO₂ is the third body.

Atomic oxygen is a particularly efficient [44, 46] quencher of $O_2(c^1\Sigma_u^-)$, and the relative intensities of the Herzberg II bands on Venus, Earth and Mars may reflect the abundance of O as well as of O_2 and the nature of the third body [44, 47]. Great importance attaches to the question of whether $O_2(c^1\Sigma_u^-)$ can excite $O(^1S)$, $O_2(a^1\Delta_g)$ or $O_2(b^1\Sigma_g^+)$ in collisions with O or O_2 [31, 44 - 49], and it seems that these studies will continue to excite much interest.

We can hardly leave the topic of non-equilibrium emission processes without some reference to "natural lasers" [50] operating in the CO_2 atmospheres of Venus and Mars. Absorption of energetic solar radiation by CO_2 , followed by *partial* collisional deactivation, may populate vibrationally excited CO_2 in the upper atmospheres [51]. Thermally emitted photons from the lower atmosphere can then stimulate emission from these molecules. Stimulated emission of this kind may account for up to 7% of the total radiation at $\lambda \approx 10 \mu m$ [51], but speculations are now appearing [50, 51] that this weak natural laser could be turned into a huge man-made one by placing large mirrors in orbit parallel to one another!

3. Outer planets and Titan

Jupiter and Saturn are made up *almost* entirely of hydrogen and helium, although CH_4 and NH_3 are present in abundances rather greater than the solar ones; Uranus and Neptune probably have a rocky core, and a correspondingly greater departure from solar composition [52, 53]. The temperature structures in the atmospheres of the four planets, and of Saturn's moon Titan, all show minima, with a tropopause separating regions analogous to Earth's troposphere and stratosphere. The temperature minima act as "cold-traps" which limit the mixing ratios of condensable gases in the upper atmosphere, with condensates remaining as aerosols or clouds at the appropriate levels.

Above the clouds on the planets, photochemical transformations can take place [54]. Molecular hydrogen is converted, directly or via an ionic mechanism, to hydrogen atoms at $\lambda < 100 \text{ nm}$. CH_4 is photolysed at longer wavelengths to yield mainly singlet and triplet CH_2 radicals [54]. Hydrogen abstraction by CH_2 leads to CH_3 and ultimately C_2H_6 . C_2H_4 is also probably formed, but is photolysed itself to yield C_2H_2 which is photochemically rather stable (because the dissociation products C_2H and C_2 react with H_2 to regenerate C_2H_2). Higher hydrocarbons, and possibly even polymeric materials, can be formed by reactions of C_2H_2 (as, for example, with 3CH_2 to yield methyl acetylene, CH_3CCH , an observed species). NH_3 is photolysed to NH_2 , some of which combines to yield hydrazine, N_2H_4 , as a condensed haze. A minor photochemical pathway leads, via N_2H_4 , to N_2 , and, were it not for the condensation of N_2H_4 , molecular nitrogen would be the major nitrogen-containing species [54]. Analogous reactions lead from PH_3 to P_2H_4 , with some elemental phosphorus being formed [54, 55]. There is naturally some speculation [55] about whether phosphorus contributes to

the wide variety of colours found on the bodies of the outer solar system. Colouration by complex organic molecules is another possibility, and in this context the presence of HCN, at least on Jupiter, may be significant. It is, in fact, rather difficult to account for the formation of HCN in these atmospheres [56]; one promising pathway is the photolysis of aziridine (ethyleneimine), itself formed directly from NH_2 radicals and C_2H_2 [56].

Although the atmospheres of Jupiter and Saturn are usually thought of as totally reducing, the discovery of CO on Jupiter proves that photochemical processes involving oxygen species do occur. An extraplanetary source of oxygen seems implicated [57], H_2O being supplied by meteors, material from the satellites and even from the rings for Saturn. Oxygen in any form is virtually bound to be converted to CO, which is then chemically and photochemically stable.

Saturn's largest satellite, Titan, is the only satellite in the solar system to possess a massive atmosphere [58 - 60]. Emission lines from molecular and atomic nitrogen, characteristic of electron-excited N_2 , are emitted from the upper atmosphere. The atmosphere is predominantly N_2 (with a few per cent of CH_4 , and some other minor compounds) exerting a surface pressure of 1.6 (Earth) atm. Titan is the only body in the solar system besides Earth that has an atmosphere composed largely of nitrogen. The satellite is covered by coloured clouds that must be aerosols derived from gaseous organic compounds, and are thus Titan's equivalent of photochemical smog; above the cloud layer lies a thinner haze of aerosol particles [61].

Escape of H and H_2 from Titan's atmosphere is ensured by the combination of very low escape velocity (2.1 km s^{-1}) and the thermal structure of the atmosphere. Build-up of heavier hydrocarbons, such as C_2H_6 and C_3H_8 , occurs at the expense of CH_4 , and H_2 is a minor constituent. Absence of H_2 , and the presence of N_2 , modify considerably Titan's atmospheric chemistry from that of Jupiter or Saturn [58, 59]. Radicals such as CH_3 or NH_2 no longer return most frequently to CH_4 or NH_3 . Hydrogen-deficient hydrocarbons are favoured, with mixing ratios of C_2H_6 and C_2H_2 far larger than on Saturn; C_2H_4 is detected on the satellite but not on the planet. Nitrogen quenches $^1\text{CH}_2$ to $^3\text{CH}_2$, and C_2H_2 formation is particularly important. The radicals CH_3 , $^3\text{CH}_2$ and C_2H can yield [59] many of the compounds, such as CH_3CCH_3 (diacetylene) and CH_3CCH , observed [58] in the atmosphere. HCN formation is easier to explain on the satellite than on Saturn because the nitrogen source is N_2 itself, with known routes to HCN existing from photochemically derived N and N^+ . Photolysis of HCN generates CN that can react with known atmospheric constituents to yield two other species detected in the atmosphere (HCCCN and C_2N_2).

Recent discoveries of CO [62] and CO_2 [63] on Titan have opened up new vistas in the chemistry of reducing atmospheres. Continued input of H_2O to the satellite is demanded in order to maintain any CO_2 at all; without H_2O , photolysis would convert CO_2 to CO, and there would be no route for reversing the process in reaction (2), as we discussed in connection with Mars. If the large postulated influx of H_2O is borne out by further observation,

H₂O could be an important species on Saturn as well. CO may therefore be present in Saturn's upper atmosphere as it is in Jupiter's. The chemistry of H₂O, CO and CO₂ may ultimately prove to be as significant to reducing atmospheres as that of the "trace constituent" reduced compounds (e.g. CH₄, H₂) is for oxidizing ones [63].

For the immediate future, refinement of the data from the Voyager encounters with Jupiter, Saturn and their satellites continues to yield new information which challenges the interpretative skills of photochemists. If all goes well, Voyager 2 will visit Uranus and Neptune in 1986 and 1989 and should provide a wealth of observational data. In 1986 as well, there is a chance of an encounter with Halley's comet to investigate the tail of gas that bears some similarity to an atmosphere. Knowledge of chemistry at the limits of the solar system should thus be expanding enormously when the *Journal of Photochemistry* reaches its fiftieth volume.

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