4) The minimum at 0.34 μm, which is apparent in Glushneva's spectrum at a phase angle of 45°, seems either to have disappeared or to have shifted to shorter wavelengths in the spectrum at 87°.

A decreased strength of the ferric band in the near ultraviolet could be due to lower concentrations of either Fe^{3+} or HCl, or both, in the upper layer of haze. Such a decrease may reflect more favorable conditions for the condensation of H_2O vapor at higher altitudes, due to the lower temperatures. Alternatively, larger Fe^{3+} concentrations at lower altitudes could be due to increases in the supply of silicate dust from volcanic eruptions on the surface. Physically, the ultraviolet features could represent holes; local deficiencies of iron in the upper clouds; or local concentrations of iron, possibly related to the surface distribution of active volcanoes, in the lower clouds.

In the far-infrared spectrum of Venus, three minima appear to be present at 8, 9.5, and 11 μm. The depression at 9.5 μm is probably due to a CO_2 band at 9.4 μm, although there is no sign of a minimum at 10.4 μm, where another CO_2 band is located. The 8-μm feature may be an absorption band of hydrochloric acid. The minimum at 11 μm may be associated with silicate aerosol nuclei. Silicates possess emissivity minima in the range from 9 to 11 μm due to the Si-O vibration band. The location of the band depends on the composition; it is shifted toward 9 μm for acidic rocks and toward 11 μm for ultrabasic silicates. Carbonates also have an emissivity minimum at 11 μm (*31*).

In order for silicate bands to be seen in emission, silicates would have to be abundant at the level from which the thermal radiation originates. However, the hydrochloric acid band must be seen in absorption, which requires a relatively lower silicate and higher HCl concentration at greater altitudes. Thus, the ultraviolet markings and the thermal infrared bands may be closely associated, and simultaneous monitoring of Venus in these two spectral regions may prove highly informative.

Finally, it must be stressed that these conclusions apply only to the visible clouds. Other substances may be important in the lower atmosphere.

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Photolysis of Formaldehyde as a Hydrogen Atom Source in the Lower Atmosphere

Abstract. *The rates of formaldehyde photodecomposition into hydrogen and formyl radicals and hydrogen and carbon monoxide molecules in sunlight-irradiated atmospheres have been estimated from extinction data and photochemical results. These data should prove useful in the development of models for the chemical changes that take place in the polluted atmosphere.*

Formaldehyde is a common product of the incomplete combustion of hydrocarbons. It is a significant minor product present in atmospheres polluted with auto exhaust where it amounts to some 40 to 50 percent of the total aldehydic compounds from this source (*1*). Formaldehyde may be introduced directly into the atmosphere or formed in the atmosphere by a variety of reactions; these include reactions of ozone with terminal olefins and reactions of oxygen with alkyl and alkoxyl radicals. The highest recorded total aldehyde concentration from data available up to 1959 was 1.9 parts per million (ppm) reported in Los Angeles (*2*). Typical CH_2O concentrations in Los Angeles in 1961 were in the range 2 to 19 parts per hundred million (pphm) (*1*). The natural processes for the removal of CH_2O in the atmosphere are of increasing concern. In particular, the rate of sunlight photolysis of CH_2O vapor in

Table. 1. Quantum yields ϕ for the primary photochemical processes in the photolysis of CH_2O as a function of wavelength and molar extinction coefficients ϵ of CH_2O vapor integrated over 100-Å bands centered at the given wavelengths.

Wavelength (Å)	$\overline{\phi}_1$	$\overline{\phi}_2$	$\overline{\epsilon}_\lambda$ (liter $mole^{-1}$ cm^{-1}) for 100-Å band
2900	0.81	0.19	8.33
3000	.66	.34	8.51
3100	.52	.48	8.23
3200	.40	.60	6.13
3300	.29	.71	6.19
3400	.18	.82	5.17
3500	.09	.91	2.19
3600	.01	.99	0.46

the atmosphere is of interest in an evaluation of the relative importance of this compound as a source of hydrogen atoms. The HO_2 radicals, which form from the reaction of hydrogen atoms with O_2, are presumed to be involved in the chain sequence leading to the oxidation of NO in CO-containing atmospheres (*3, 4*). We report here reasonable estimates of these rates.

Formaldehyde photolysis may be described in terms of two primary dissociative processes (*5, 6*):

$$CH_2O + h\nu \rightarrow HCO + H \qquad (1)$$

$$CH_2O + h\nu \rightarrow H_2 + CO \qquad (2)$$

The lifetimes of the electronically excited CH_2O states that lead to these chemical changes are very short, and it is unlikely that these states suffer any significant deactivation by interaction with the atmospheric gases. The quantum efficiencies of the two processes are a function of wavelength. The results of both of our two studies suggest that the primary quantum yields ϕ of reactions 1 and 2 are nearly equal at 3130 Å; $\phi_1 \cong \phi_2 \cong 0.5$. However, these studies give conflicting results on the dependence of ϕ_1/ϕ_2 on the wavelength of the exciting light. The results of McQuigg and Calvert (*6*) provide the best present data on this dependence. The work of DeGraff and Calvert (*5*) involved a very limited number of experiments at wavelengths other than 3130 Å; the purity of the light was low in experiments at "3340," "2654," and "2537" Å, and estimates of the fraction of the incident light absorbed in these experiments must be of low precision. The primary quantum yields of reactions 1 and 2 derived from the data of McQuigg and Calvert (*6*) are summarized in Table 1. The observed trend in the efficiency of radical formation with wavelength is consistent with qualitative observations made by Bufalini and Brubaker (*7*) in their study of the photolysis of mixtures of CH_2O and O_2 at wavelengths near 3130 and 3660 Å. Table 1 also lists data on the absorption coefficients for CH_2O vapor (*6*) which can be coupled with estimates of the actinic irradiance of Leighton (*8*) to derive estimates of the specific rate of sunlight absorption (k_a) for CH_2O vapor, and the specific rate constants for H and HCO radical generation (k_1) and molecular H_2 and CO formation (k_2) in the sunlight-irradiated lower atmosphere. These data are summarized in Table 2 for various solar zenith angles.

Table 2. Estimated specific absorption rates (k_a) and the specific rates of primary reactions 1 (k_1) and 2 (k_2) for CH_2O vapor in sunlight in the lower atmosphere; the actinic irradiance was taken from the estimates of Leighton (*8*) which presumably apply to representative atmospheric conditions (atmospheric pressure, 1000 mb; thickness of the equivalent layer of ozone at standard temperature and pressure, 2.2 mm).

Solar zenith angle (deg)	k_a (hour^{-1})	k_1 (hour^{-1})	k_2 (hour^{-1})
0	0.55	0.16	0.39
20	.53	.15	.38
40	.43	.12	.31
60	.26	.067	.19
80	.068	.016	.042

The data of Table 2 should prove very useful in the development of models for atmospheric chemistry involving CH_2O vapor. The approximate rate of CH_2O destruction by both reactions 1 and 2 should be given by $k_a[CH_2O]$, whereas the rates of occurrence of reactions 1 and 2 are given by: $k_1[CH_2O]$ and $k_2[CH_2O]$, respectively. The rate data predict that the half-life of CH_2O due to photodestruction in the sunlight-irradiated lower atmosphere is about 75 minutes.

The formyl radical formed in the atmosphere may react with O_2 largely by disproportionation (*7, 9*)

$$HCO + O_2 \rightarrow HO_2 + CO \qquad (3)$$

and hydrogen atoms are expected to react with O_2 in the atmosphere to form HO_2 as well

$$H + O_2 + M \rightarrow HO_2 + M \qquad (4)$$

where M is N_2 or O_2. Thus, the rate of generation of HO_2 radicals from CH_2O photolysis in sunlight will be given approximately by $2k_1[CH_2O]$. Under the conditions found in most urban atmospheres which are high in auto-exhaust pollution, it appears that CH_2O photolysis can be a significant source of HO_2. Thus, for CH_2O concentrations of 2 and 19 pphm, the rates of HO_2 generation at a solar zenith angle of 20° would be 0.6 and 5.7 pphm per hour, respectively. These rates are comparable to those expected from alternative atmospheric sources: nitrous acid photolysis (*4, 8*) and the attack of $O(^1D)$ on H_2O (*10*). In the natural CO-containing atmospheres the importance of NO oxidation in the sequence of reactions 5, 6, 4, 5 . . . , has been suggested (*3, 4*)

$$HO_2 + NO \rightarrow OH + NO_2 \qquad (5)$$

$$OH + CO \rightarrow CO_2 + H \qquad (6)$$

The relative importance of the alternative sources of HO_2 and OH radicals is obviously a function of the composition of the polluted atmosphere. However, each of these sources, and possibly others, should be included in attempts to simulate the chemistry of the polluted atmosphere.

We expect the rather unique result of H_2 formation even in the strong oxidizing atmosphere of the urban community as a result of CH_2O photodissociation in reaction 2. The simultaneous analyses for CH_2O and H_2 concentrations in sunlight-irradiated atmospheres polluted with auto exhaust could provide an interesting test of our present rate estimates. There is very little information on the H_2 concentrations in the polluted atmosphere. However, King (*11*) has observed a small increase in the atmospheric H_2 concentration in polluted atmospheres in New Jersey; 0.75 ppm in the morning hours had increased to 1.0 ppm at noon. This observation is consistent with our thesis, but the limited data now available provide no firm test of it.

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