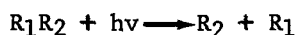


LABORATORY OBSERVATIONS OF THE PHOTOCHEMISTRY OF PARENT MOLECULES: A REVIEW

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Introduction

Many years ago K. Wurm (1) suggested that the photodissociation of stable molecules such as H_2O , HCN , CH_4 , NH_3 , etc., could account for the observed cometary radicals. This postulate can be represented schematically by the following photochemical reaction,



In this particular reaction R_1R_2 represents the parent molecule, R_1 the cometary radical and R_2 may or may not be a stable molecule. The original postulate of Wurm has been largely confirmed by the satellite observations of the overwhelming abundances of cometary H and OH (2), the spectroscopic identification of H_2O^+ (3) and the radio detection of CH_3CN (4), HCN (5), and H_2O (6) in comets. All of the cometary radicals cannot be explained by CH_3CN , HCN , and H_2O which suggest the presence of other parent molecules. An important clue to the identity of other parent molecules is the observations of complex molecules in the interstellar mediums (7). Present theories on the origin of comets (8) suggest that the interstellar molecules are also likely candidates for parent molecules in comets. This review on the status of the photochemistry of parent molecules in comets will use the known interstellar molecules as a guide to the identity of parent molecules.

The photochemical investigation of any molecule should attempt to answer certain basic questions. The qualitative identification of each of the primary products should be made along with the quantitative measurement of the yields of each of these primary products. A photochemical reaction has a threshold energy E_t so that if the energy of the photon E_h used to initiate the reaction is greater than E_t , the excess energy

$\Delta E = E_h - E_t$ must be divided among the primary products. The nature of this energy partitioning, i.e. the division between translational, vibrational, rotational, and electronic energy, is extremely important in any photochemical study. All of these questions must then be answered as a function of the wavelength of the incident photon.

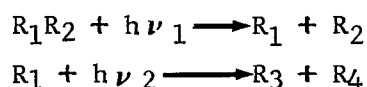
The importance to cometary astrophysics of the qualitative and quantitative identification of each of the primary products is obvious. However, the importance of understanding the energy partitioning among the primary products is not generally appreciated so that a few examples of how this information affects our interpretation of cometary observations will be given. The scale lengths of radicals, atoms, and parent molecules are determined from monochromatic isophotes of the emission of the radicals and ions. These scale lengths are the product of the velocity (v) and the lifetime, t , of the particular species. The velocity of neutral cometary fragment is determined by the energy partitioning among the fragments. Thus, a knowledge of this energy partitioning is essential if we are to obtain the maximum information available in the observed isophotes.

Another example of the importance of understanding energy partitioning is in the interpretation of the relative intensities of radical emission from comets in the infra-red region. Specifically, Meisel and Berg (9) has measured the infra-red emissions of the CN and OH radicals in comet Kohoutek. If an equilibrium model is used to interpret these measurements, then the calculated production rates for CN would be higher than the OH production rates. We know from the UV observations, which we understand, that the situation is just opposite. The net result is that IR radiation is greater for CN than it should be. A possible way out of this dilemma

is to explain the excess IR radiation upon the photochemical formation of vibrationally and rotationally excited CN radicals.

At this point, a few elements of caution should be injected into the discussion about applying laboratory photochemical data to comets. First, there is a large difference between the collision frequency in the laboratory and the collision frequency in comets. For example, in a typical photochemical experiment the total pressure is generally greater than 0.1 torr. At these pressures, one obtains collision frequencies of the order of 10^6 per sec. In comets the collision frequency at the nucleus when the comet is 1 AU away from the sun is of the order of 10^3 to 10^4 collisions per sec. which is three orders of magnitude less than the laboratory values. The net result is that there is a much lower probability in comets for the collisional stabilization of any excited molecules produced in the primary process.

Another process that one could expect to be more probable in comets than in the laboratory is the phenomena of two stage photolysis. Consider the following sequence of events,



In the first reaction the molecule R_1R_2 is photolyzed to produce the radical R_1 . Suppose the lifetime for process 1 at 1 AU is 10^4 sec., and that R_1 absorbs in the near u.v. region of the spectra so that its lifetime is 10^3 sec., then if R_3 is an observable radical or ion its net lifetime will be 10^4 sec. This type of processes is generally unimportant in the laboratory because the collision frequency is high enough so that R_1 reacts before it can undergo secondary photolysis.

Photochemical Lifetimes and the Fractional Probability for Dissociation

The total photochemical lifetime (t_T) may be defined in terms of the absorption coefficient σ_λ , the quantum yield ϕ_λ , and the intensity of the incident light I_λ by the following relationship (10),

$$t_T = \frac{1}{\int \sigma_\lambda I_\lambda \phi_\lambda d\lambda}$$

The average intensity of solar radiation at 1 AU for 50 nm intervals between 100.0 and 400 nm is given in figure 1. This figure illustrates how sharply the solar radiation decreases below 300 nm. In fact, not only does the magnitude decrease but below 150 nm, the character shifts from a continuum to a line spectra. This has the effect that an accurate measure of the total lifetime in this region can best be obtained by using a high resolution spectra of the gas along with a high resolution spectra of the sun. Fortunately, the only really important line between 100.0 and 150.0 nm is the Lyman alpha line at 121.6 nm. This line has been removed from the rest of the spectra because of its high intensity and will be considered separately. No attempt will be made to take into consideration the light below 100 nm because except in special cases for gases, such as CO and N₂, that have high thresholds for dissociation this region has a negligible effect on the photochemical lifetime.

Knowing the absorption coefficient of the gas and assuming ϕ_λ is equal to 1 for all wavelengths, the data in figure 1 can be used to calculate the minimum photodissociation lifetime for parent molecules in comets. These results are given in table 1. The important point to note is that most molecules have lifetimes below $2 \times 10^{+4}$ sec. at 1 AU. This is in contradiction to the earlier work of Potter and Del Duca (11) where most of the molecules had much longer lifetimes. In their work only the

SOLAR PHOTON FLUX

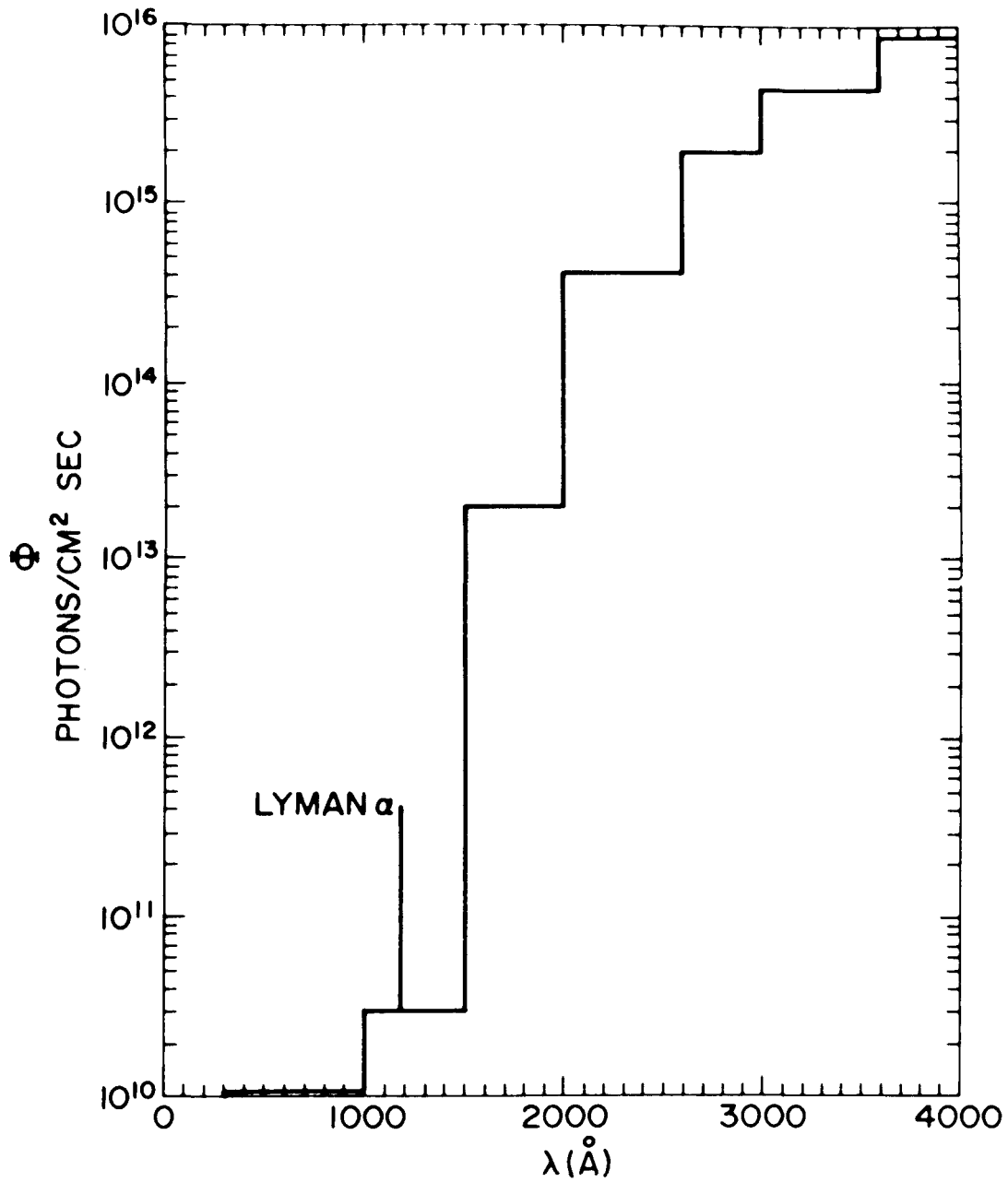


Figure 1. The Integrated Solar Flux at one Astronomical Unit

Table 1

PHOTOCHEMICAL LIFETIME (t_r) AND PARTIAL DISSOCIATION FRACTION P_f FOR PARENT MOLECULES AT 1 A.U.

Molecule	t_r (sec.)	P_f				Source for Absorption Cross- Section
		100-150 nm	150-200 nm	121.6 nm	200 nm	
NH ₃	2.1×10^3	0.09	0.16	0.012	0.82	J.A.R. Samson and J.A. Meyer, Geographical Corp. Rept. #TR-69-7-N "Absorption Cross-Section of Minor Constituents in Planetary Atmospheres from 105.0-210.0 nm"
H ₂ O	2.0×10^4	0.05	0.83	0.16	-	J.A.R. Samson, op cite.
CH ₄	1.2×10^5	0.07	-	0.93	-	J.A.R. Samson, op cite.
HCN	9×10^4	0.05	0.14	0.81	-	M. Berry, Private Communication, Univ. Wisc. Chem. Dept.
C ₂ N ₂	1.1×10^4	0.02	0.71	0.27	-	R.E. Connors, J.L. Roberts, and Karl Weiss, J. Chem. Phys. <u>60</u> , 5011, 1974
HC ₂ CN	1.3×10^4	0.10	0.72	0.17	-	R.E. Connors, op cite.
CH ₃ C ₂ H	4.9×10^3	0.006	0.90	0.09	-	T. Nakayama and K. Watanabe, J. Chem. Phys. <u>40</u> , 558, 1964
C ₂ H ₂	5.7×10^3	0.004	0.83	0.17	-	T. Nakayama, op cite.
H ₂ CO	1.9×10^3	0.008	0.17		.82	J.G. Calvert and J.N. Pitts, Jr. "Photochemistry," John Wiley New York, 1966; J.E. Mentall, E.P. Gentiew, M. Krauss and D. Neumann, J. Chem. Phys., <u>55</u> , 5471, 1971
CH ₃ CHO	1.6×10^3		0.25		0.75	J.G. Calvert, op cite. E.E. Barnes and W.T. Simpson, J. Chem. Phys., <u>39</u> , 670, 1963

Table 1 (continued)

HNCO	1.3×10^4	0.01	0.56	0.19	0.24	J.W. Rabalais, J.R. McDonald and S.P. McGlynn, <i>J. Chem. Phys.</i> , <u>51</u> , 5103, 1969 H. Okabe, <i>J. Chem. Phys.</i> , <u>53</u> , 3507, 1970
CH ₃ OH	2.1×10^4	0.005	0.91	0.09	-	D.R. Salahub and C. Sandorf, <i>Chem. Phys. Lett.</i> , <u>8</u> , 71, 1971
HCONH ₂	1.5×10^3	0.001	0.90	0.009	0.09	H. Basch, M.B. Robin and N.A. Kuebler, <i>J. Chem. Phys.</i> <u>49</u> , 5007, 1968
HCOOH	7×10^3	0.004	0.81	0.08	0.11	E.E. Barnes, <i>op cite.</i>
CH ₃ NH ₂	1.5×10^3	0.002	0.17	0.02	0.80	E. Tannenbaum, E.M. Coffin, and A.J. Harrison, <i>J. Chem. Phys.</i> <u>21</u> , 311, 1953
CH ₃ OCH ₃	8.2×10^3		1.00			J.G. Calvert, <i>op cite.</i>

absorption coefficient for the continuum was used in determining the lifetime and as Herzberg (12) has pointed out this ignores predissociation. The effect of predissociation has been included in table 1 by including the absorption of spectral lines.

The partial dissociation fraction (P_f) for a parent molecule can be defined as

$$P_f = \frac{\bar{\sigma}_\lambda \bar{I}_\lambda}{t_r}$$

where $\bar{\sigma}_\lambda$ is the mean absorption co-efficient over the wavelength band and \bar{I}_λ is the mean solar flux over the same wavelength interval. This table shows that for most molecules the important photodissociation region is between 150 and 200 nm, while the region below 150 nm is relatively unimportant.

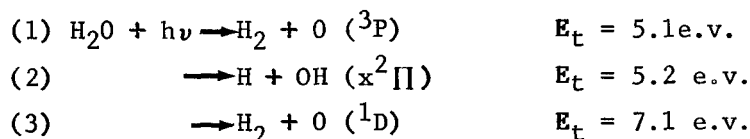
Triatomic Parent Molecules

(H₂O)

The most important parent molecule in comets is the triatomic molecule (H₂O) water. The photochemistry of H₂O is probably better understood than any other parent molecule. Table 1 shows that the principle wavelength regions for the photodissociation of H₂O are the first continuum between 150-200 nm and the Lyman alpha line of the sun at 121.6 nm. Of the two regions the first absorption band is the most important with 83% of the H₂O molecules decomposing in this region.

150.0 - 200.0 nm

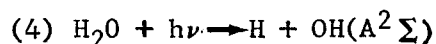
The three possible primary processes in this wavelength region are:



The first primary process which produces H₂ and ground state O atoms is spin forbidden and is of negligible importance. The latest available evidence (13) indicates that the relative quantum yields for the production of H atoms to the quantum yield for the production of O atoms in this region is greater than 99 to 1. Thus, even the spin allowed processes is of negligible importance. The solar photon energy is between 5.8 and 8.3 e.v. in this region so that the products of reaction 2 have to dispose of 0.6 to 3.1 e.v. of excess energy. The work of Sthul and Welge (14, 15) shows that the OH radical produced in the vacuum ultraviolet flash photolysis of H₂O is not vibrationally or rotationally excited. All of the excess energy for reactions (2) and (3) must go into the relative translational motion of the fragments. Masanet and Vermeil (16) using a chemical method to determine the amounts of excess translational energy produced in reaction (2) have confirmed this observation.

121.6 nm

Most of the H₂O molecules that are not photodissociated in the first continuum will be dissociated by Lyman alpha. At this wavelength there is strong evidence (13) that some of the H₂O is photodissociated to yield H₂ and O(¹D) atoms. A new primary process is also observed (17) namely,

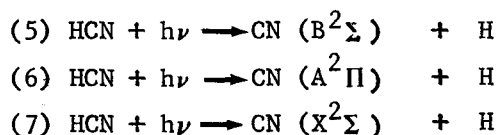


This reaction has been known to occur for almost 30 years and the work of Carrington (17) shows that the quantum yield for the production of the A²Σ state of OH is ~ .05 at 121.6 nm. The uncertainty in the absolute measurement of the intensity are such that as much as 15% of the H₂O could dissociate to form the A state of OH. Steif (13) has shown that 89% of the H₂O dissociates to form OH plus H in the 105.0 - 145.0 nm wavelength

region along with 11% to form H_2 and $O(^1D)$. If these results are applicable at the single wavelength of 121.6 nm, then less than 17% of the total OH formed at this wavelength is in the A state. Most of the energy in reaction (4) that must be distributed among the products ends up as rotational energy in the hydroxyl radical (17) but chemical evidence (16) has been presented that the H atom produced in the photolysis at 121.6 nm are translationally hot which suggest that reaction (4) is not important. The authors of this particular study have also suggested that reaction (3) is pressure dependent and quote a lifetime for the suggested (C^1B) intermediate state of H_2O of 2×10^{-8} sec. The relative quantum yield measurements of Steif et al. were done by quenching the (O^1D) to the (O^3P) state and subsequent detection of this state using an O atom resonance fluorescence lamp. This method of necessity requires high pressures and could lead to error in the determination of the yield of (O^1D) if the product is formed by the predissociation of the (C^1B) state of H_2O .

HCN

More than 82% of the HCN will be photodissociated by the Lyman alpha radiation from the sun. At this wavelength all three of the following primary processes are energetically possible.

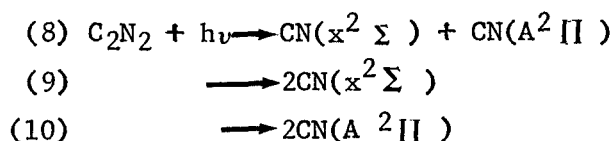


The first two processes have been observed (18) by Mele and Okabe in the photolysis of HCN at 123.6 nm. Both the A and the B state of the CN radicals were produced with a large amount of excess vibrational and rotational energies. No information exists on the quantum yields for the production of the X, A, and B states at this wavelength.

Most of the remaining HCN will be photolyzed in the 150 to 200 nm region. M. Berry (19) has recently studied the photolysis of HCN in this wavelength region where only the A and the X states can be produced. He used gain measurements of the laser lines that result from the A to X transition when HCN is photolyzed. With this technique he was able to show that the production of A state radicals is the principle primary processes. Most of these radicals were formed in the $v' = 0$ with a few of them in the $v' = 1$ level. Most of the remaining energy will be converted into the translational motion of the H atom.



This particular molecule has not been observed in the interstellar medium but is expected to occur since it represents the dimer of the CN radical. Most of the photodissociation (71%) of C_2N_2 occurs in the 150 to 200 nm region. The remaining amount of this dissociation occurs at L_α . The photodissociation in the 150 to 200 nm region has been extensively studied by the author (20, 21, 22) and M. Berry (19). The primary processes that are energetically possible at this wavelength are,



M. Berry states that most of the radicals are formed in the A state. The author and his co-workers (22) were able to determine how the excess energy is partitioned among the fragments. Most of the available energy, 82%, goes into the translational motion of the fragments. Of the energy that remains, 11% goes into vibrational excitation and 6% into rotational excitation.

NH₃

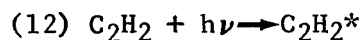
Ammonia has been considered a probable parent molecule for a long time. Most of the NH₃ will be photodissociated in the first absorption bands. In this wavelength region it is energetically possible to produce NH₂ in the ground (X²B) state and in the (\tilde{A} ²A₁) excited state. The evidence (23) is that the principle photochemical process occurring for NH₃ in this band is,



even though several others are energetically possible and have been searched for (25). The quantum yield for photodissociation via reaction (11) is one throughout this wavelength region. Nothing is known about the partitioning of energy in this molecule.

C₂H₂

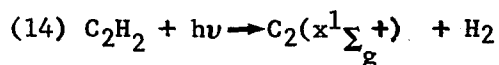
It has been supposed for a long time that acetylene is the source of C₂ in comets. No laboratory evidence exists (25) at the present time to support this contention. The principle wavelength region for photodissociation of acetylene is the 150-200 nm region where it is estimated that 83% of the C₂H₂ decomposes. Most of this decomposition (76%) occurs at the 153 nm peak. The principle photochemical process in this wavelength region (26) is thought to be the formation,



of a long lived excited acetylene molecule. This excited molecule then either undergoes polymerization reactions or decomposes to yield C₂H and an H atom. This reaction is 5.38 e.v. endothermic (27) and a photon at 153 nm has an energy of 8.10 e.v., which leaves 2.72 e.v. for partitioning

between the C₂H and H fragments. This is not enough energy to form electronically excited C₂H so the excess energy has to be in either internal energy of C₂H or translational motion of the H atom. No information exists at the present time relating to this question.

Earlier it was mentioned that there is no direct evidence for C₂ production from acetylene. This problem is complicated by the known participation of C₂H₂* in the photodissociation. There is an observation by Steif et. al (28) that suggests that C₂ might be a primary product, being produced via reaction 14. This postulate,

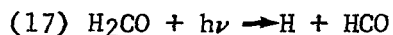
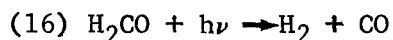


is based upon the observation that substantial amounts of molecular hydrogen appear to be formed at low total pressures. It would be extremely important to try to observe the C₂ in some direct manner in the gas phase photolysis of C₂H₂ since the Swann band is one of the most prominent emissions in comets. These bands result from the fluorescent pumping of X³Π_u ground state radicals. The direct production of the triplet ground state of C₂ via a molecular processes is only slightly more endothermic, 6.3 e.v. versus 6.2 e.v., than the production of the singlet state. However, the triplet processes is spin forbidden. It is possible, however, that the selection rule might be violated via an intersystem crossing to a highly vibrationally excited triplet state of C₂H₂ (30). This state then can decompose to yield the (X³Π_u) state of C₂. A direct observation of this radical is needed to clear up this point.

H₂CO

This molecule was one of the first fairly large molecules observed in the interstellar space (7). It is also one of the molecules that will undergo appreciable amounts of photodissociation above 200 nm since it does have

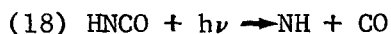
a reasonable absorption coefficient in the 250 to 350 nm meter range. As table 1 shows 99% of the formaldehyde will be decomposed in this wavelength range. The two primary photochemical processes (30) are,



The relative yields of these two reactions is a function of wavelength with the quantum yield of the molecular process 16 increasing from 0.2 to 0.8 as the wavelength decreases from 256 to 330 nm. In addition to the very short photochemical lifetime of H_2CO , an extremely interesting observation is that the molecular processes is only .06 e.v endothermic. So that from 3.8 to 4.8 e.v. of energy has to be distributed between the products. A recent theoretical treatment of this problem (31) suggests that dissociation of the formaldehyde occurs from a highly excited vibrational level of the singlet ground state. The products of this dissociation should be both vibrationally and rotationally excited but not electronically excited.

HNCO

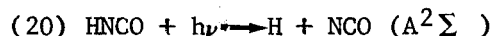
This molecule is fairly unique since substantial decomposition occurs throughout the solar spectrum. There is a large amount of qualitative data available on the states of the photochemical products, but no work on the quantum yields or the internal energy distribution of these products appears to be available. H. Okabe (32) has summarized most of this work. In the 200 to 230 nm the two principle primary processes are,



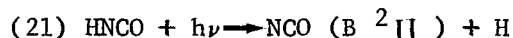
Both radical intermediates have been observed (33,34) in the flash photolysis of this compound. The particular transition of NH that was observed was the

NH ($X^3\Sigma$) \rightarrow NH ($A^3\Sigma$) transition. Reaction 18 would violate the spin selection rule if NH was produced directly in the $X^3\Sigma$ state. It has been suggested that the NH in 18 is produced in the $A^1\Delta$ state which is then quickly quenched to the $X^3\Sigma$ state. This quenching reaction also violates the selection rule so this question deserves further study. The two processes, 18 and 19, are 3.4 and 4.9 e.v. endothermic so between 2.8 and 1.2 e.v. of energy has to be partitioned among the fragments.

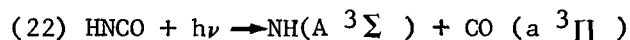
In the next absorption region between 150 and 200 nm a new primary processes occurs in which the NCO fragment is electronically excited to the $A^2\Sigma$ state. The threshold for this processes is at 160.5 nm so that this processes is probably not too important for comets:



The last important absorption region at Lyman alpha (121.6 nm). Two new primary can now occur. The first of these (21) is the excitation of the NCO to the ($B^2\Pi$) state. This reaction,



has been observed by Okabe (32). The other reaction that is energetically possible is the production of two triplet molecule via,

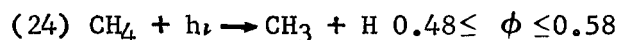
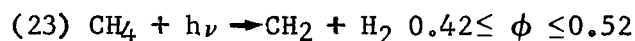


Reactions of this type may be extremely important if the $\text{CO}(a^3\Pi)$ is produced in rotational levels where little mixing occurs with allowed transition. In this manner the lifetime of CO against photoionization might be substantially lowered since this metastable ($a^3\Pi$) state can be photoionized at longer wavelengths.

CH₄

Methane has not been observed in the interstellar medium but is expected to be very abundant there and in comets. This expectation is based primarily upon the fact that this is the most thermodynamically stable

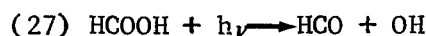
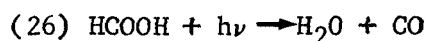
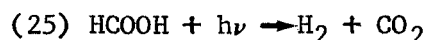
carbon compound in a hydrogen rich atmosphere. Since methane does not absorb above about 140 nm, the most important solar wavelength for photodecomposition is for Lyman Alpha at 121.6 nm. There are two important primary processes (35) in this region, one of which involves the molecular detachment of H₂, the other is the formation of atomic H. The measured values of these quantum yields are given below. No information exists on



the energy partitioning among the products.

HCOOH

This is the simplest organic acid but very little is known about its photochemistry. Apparently, the only photochemical studies that have been reported (36, 37) are in the region above 200 nm which only accounts for 11% of the photodissociation if this molecule occurs in comets. The principle primary processes that have been reported in this region are,

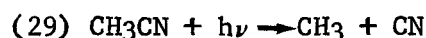
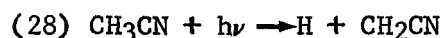


No measurements have been made on the partitioning of energy among the products; however, the interesting point is that reactions 25 and 26 are almost thermoneutral. The reaction which forms H₂ plus CO₂ is exothermic by 0.15 e.v. while the reaction forming H₂O + CO is endothermic by 0.3 e.v. The result is that in each case large amounts of energy have to be converted into either recoil or internal energy of the products. Since formic acid has a relatively short photochemical lifetime and 81% will be decomposed in the 150 to 200 nm region, the products of 25 and 26 could have as much as 8 e.v. of energy. If this energy went into exciting a long lived

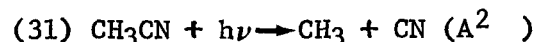
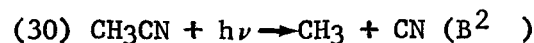
metastable state of CO, then only 6 e.v. of energy would be needed to ionize this state. The solar flux (36) that would be available for ionizing this metastable state of CO is 10^{13} . Thus, with an effective ionization, cross section of 10^{-16}cm^2 the photoionization lifetime of metastable CO would be only 10^3 sec. This is many orders of magnitude lower than lifetime of ground state CO.



The absorption coefficient of this compound has not been measured so the important photochemical region of the spectra cannot be determined. Two studies have been reported on the photochemistry of acetonitrile. The first was a classical photochemical study (37) where the following reactions were postulated:



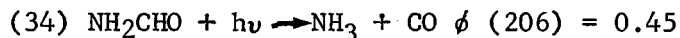
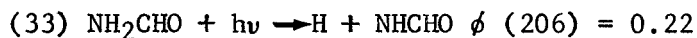
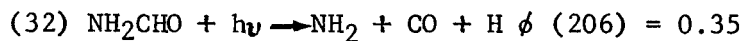
In that study it was determined that at 184.9 nm the quantum yield for H production is much greater than the quantum yield of CH_3 production. At the shorter wavelength, 121.6 nm, the photodissociation leads the formation of electronically excited CN radicals via the following processes,



Reaction 30 has been observed by Okabe (38) who measured the relative fluorescence yield as a function of the wavelength of the light. M. Berry (19) has observed lasing from the $\text{A}^2\Pi$ to the $\text{X}^2\Sigma$ state in the flash photolysis of CH_3CN which indicates that reaction 31 occurs. No information is available on the partitioning of energy among the internal degrees of freedom.

NH₂CHO

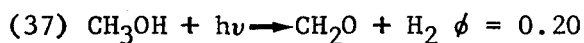
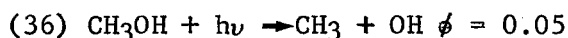
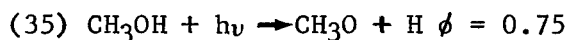
Formamide has been studied (39) at 206 nm and the quantum yields of the following primary processes were determined.



In the wavelength region above 200 nm only 9% of the formamide will be decomposed. No measurement has been reported for the vacuum ultraviolet region below 200 nm and neither have any studies been reported on energy partitioning among the fragments. An energy partitioning study in the region below 200 nm would be extremely valuable since reaction 34 probably has a lot of excess energy that must be disposed of.

CH₃OH

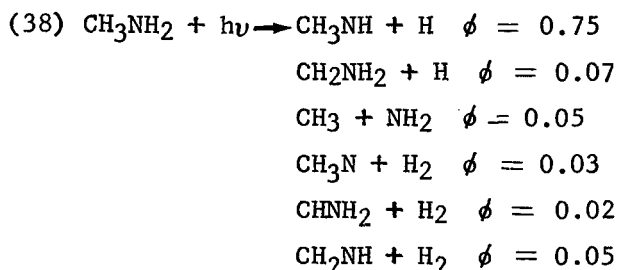
This molecule is dissociated primarily in the region between 150 and 200 nm. The following primary processes are thought to occur (40) with the associated quantum yields:



All of these reactions are thought to be a result of this collision induced predissociation (42) of excited methanol. If this is the case throughout this region, then the photolysis of CH₃OH needs to be studied very carefully as a function of time between collisions. In comets where the time between collisions at the surface of the nucleus is of the order of a few tenths of a millisecond, processes like collision induced predissociation would be rare.

CH₃NH₂

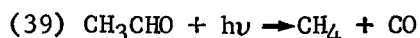
Methylamine is dissociated mostly by light in the 200 to 250 nm region. In this region the principle primary product (43) is the formation of the methylamine radical and an H atom. There are, however, five minor primary processes in this region. The limits to their respective quantum yields (41) are given as follows:



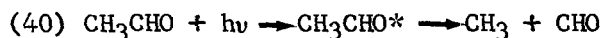
Nothing is known about the photochemistry in the wavelength region below 200 nm nor have any energy partitioning studies been reported.

CH₃CHO

Acetaldehyde is a homolog of formaldehyde and like formaldehyde, a molecular processes and a free radical process occurs in the photodissociation process (42) above 200 nm. The molecular process has a quantum yield (43) of



less than or equal to 0.5 and the free radical process results from the decomposition of an intermediate state. Like formaldehyde the molecular products

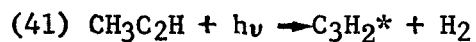


in reaction 39 have to carry away ~ 5 e.v. of excess energy because of the near thermoneutral character of the reaction. The free radical products are known (44) to carry away only 0.5 e.v. of rotational energy.

CH₃C₂H

Propyne has not been adequately studied in the 150 to 200 nm region which is the most important photochemical region from the cometary point of

view. The one study (45) reports only product yield and gives no mechanism. There has been a rather extensive study (46) at 123.6 nm in which an excited $C_3H_3^*$ intermediate is postulated. This intermediate then decomposes to give C_3 and H_2 .



In comets since few collisions occur, it has been suggested by Steif (47) that propyne might be a good source for C_3 .

SUMMARY

The photochemistry of possible parent molecules of comets has been reviewed. The survey of the available literature suggests that a great deal of work remains. The quantum yield for many of the primary processes are unknown. Energy partitioning among the fragments has not been extensively investigated. This latter question might be extremely valuable in understanding the presence of cometary ions such as CO. Finally, a few of the studies have been performed as a function of the number of collisions that the excited molecules undergo, so that possible differences that may occur in a cometary environment may be ascertained.

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DISCUSSION

H. Keller: I looked also at the lifetime of H₂O by photodissociation and my lifetime is definitely higher than 2×10^4 seconds.

I figured out it would be between 7 and 10 times 10^4 seconds.

W. Jackson: We'll have to get together and see. It may be due to the fact that I used old values of the solar flux.

H. Keller: And I integrated in 25 angstroms intervals.

W. Jackson: I won't argue about the exact value. I was trying to illustrate the general principle.

W. F. Huebner: I have two quick questions.

First of all was predissociation taken into account?

W. Jackson: Yes.

W. F. Huebner: The second question is, do you have similar numbers for ionization lifetimes?

W. Jackson: No, I don't, but in general the photon flux below a thousand angstroms drops by several orders of magnitude, and even if they have the same absorption coefficient the photoionization lifetimes are going to be several orders of magnitude longer.

M. Dubin: This is an inverse question and not the subject of your talk, but can you determine the parent molecules from the spectrum of the radicals? I mean, this is one of the objectives.

What about the inverse problem? Is it possible to determine on a kinetics basis what the parent molecule distribution will be, given the solar abundances, in the atomic form? And is anybody doing any work in this regard to give a pattern of parents based on the number of elements?

W. Jackson: The difficulty with doing that, you have to know quite a bit about the origin of comets, which means that you have to know whether you have equilibrium. Then you would have to know all the kinetic equations for the formation of the particular species.

At least, I'm not doing it. There may be some other people who are.

DISCUSSION (Continued)

C. Cosmovici: Are the results you have shown on photodissociation of parent molecules all experimental?

W. Jackson: They're all experimental results.

C. Cosmovici: That means you have detected these product molecules?

W. Jackson: That means that in one way or another the photochemists have decided that that was one of the possible parent molecules.

There are any number of ways of doing that. You can do kinetic spectroscopy, for example; analyze the products and using suitable isotopic labeling, you might use mass spectrometry; or you might use laser-induced fluorescence.

To get into the many different techniques that photochemists would use would take me the rest of the week.

C. Cosmovici: No, I just wanted to know if it's possible to detect all these product molecules experimentally?

W. Jackson: It is possible to detect atoms; it is possible to detect free radicals by resonance fluorescence spectrum, using a tunable dial laser. We've shown that with CN. Welge and Braun have shown earlier that you can detect atoms, using resonance fluorescence method.

Yes, it's possible to detect them all. The most sensitive method is resonance fluorescence, of course.

C. Cosmovici: Also for complex molecules?

W. Jackson: Well, complex molecules, you would probably have to look at absorption, or you might have to get cute.

Now, there are cute ways of doing suitable isotopical labeling and look at the product distribution. You can do high intensity flash photolysis, but you have to be careful because you get secondary processes that would affect your results for photodissociation.

You might do something like flash photolysis producing, say, C_3H and then have another flash lamp to photodissociate the C_3H and look at the C_3 by resonance fluorescence, using a tunable dye laser.

DISCUSSION (Continued)

C. Cosmovici: Thank you.

The second question was, we spoke about the dissociation of parent molecules, but we didn't speak about the possibility of gas reaction to form parent molecules. And I would like to ask if it is possible in a cometary coma to have chemical reactions in order to get parent molecules?

W. Jackson: That is a question, I think, Bert Donn and I addressed in the Liege symposium, 10 years ago. In fact, we had a table in which we gave what were the relative probabilities of reaction per collision.

Now, a lot of radical, radical reactions don't go on every collision. It's possible, but the region where you form most of the radicals and ions—is also the region where you have the lowest density, so you have to be careful.

I'm not going to say it's impossible. It depends upon the density distribution and so forth.

L. Stief: Just one comment in case people are concerned about all those unknowns.

Nature hasn't been very kind to us. There are two ways we normally do photochemistry. The older way was to look at products, and this was really good for the big molecules because a variety of fragments would give a variety of identifiable products.

The so-called simple molecules mess you up, because no matter what you do you get the same product. You get hydrogen, nitrogen and oxygen, even though you have ten different processes occurring. You can help this somewhat with isotopes, but you're still stuck.

Therefore, you're forced to go to more direct methods. However, you like to do photochemistry with a single line, and when you do the direct method you like to have an intense source that you can turn off quickly and make a time resolve observation.

So both sides have their problems. The products are indirect but at least are monochromatic. The direct methods are becoming monochromatic. We tend to work with wide band sources.