

THE PHOTOCHEMICAL FORMATION OF COMETARY RADICALS

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Summary

The present state of our knowledge of the photochemical formation of cometary free radicals is reviewed. The evidence shows that the photodissociation of water can explain the formation of O, OH, H and H_2O^+ . Some of the other radicals such as CN and NH_2 can also be explained by the photodissociation of stable compounds such as HCN, CH_3CN and NH_3 . Other radicals such as NH, C_2 , and C_3 do not appear to originate from the direct photolysis of any stable parent compound. The photolysis of free radicals that are formed as primary products in the photolysis of stable parent molecules has been suggested as an alternate source for these radicals. It is shown that such a process would be consistent with the currently available laboratory data and with cometary observations.

Introduction

Over forty years ago Wurm [1] suggested that the radicals and ions observed in comets result from the photodissociation and ionization of stable molecules. Recent observations of comets in the vacuum ultra-violet [2], the near infra-red [3], and the radio regions of the spectra [4 - 6] have confirmed this hypothesis. The interpretation of these recent observations of comets requires a knowledge of the photochemical properties of the potential parent molecules and an understanding of the properties of the free radicals observed in comets. This particular paper will review some of the cometary observations and show what kinds of laboratory data are needed to further our understanding of these results.

Cometary morphology

A schematic diagram of the various regions of a comet is given in Fig. 1. The smallest and probably the most important part of the comet

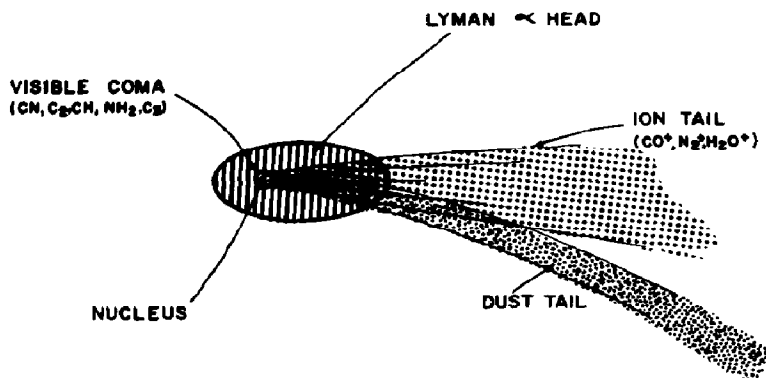


Fig. 1. Schematic diagram of a comet.

is the nucleus. All of the other parts of the comet are the result of transitory phenomena that result from the interaction of the comet with the environment around the sun. The general consensus among astronomers is that the nucleus is a large solid body with a radius of the order of a few kilometers composed of frozen gases such as H_2O , HCN , NH_3 and dust particles. As this solid body approaches the sun the surface heats up evolving both gas and dust. It is the evolved material that contributes to the other parts of the comet that we see. There is now some direct evidence which will be presented later for the existence of these frozen gases.

Light from the sun dissociates these evolving gases forming the free radicals that make up the visible and Lyman alpha comas. The visible coma has a radius of from 10^5 to 10^6 km, while the Lyman alpha coma is a factor of ten or a hundred larger than this. The dust tail extends to distances of the order of 10^6 km and the ion tail extends as far as one astronomical unit, *i.e.*, the distance from the earth to the sun. These dimensions make the comet the largest body in the solar system, although it is certainly not the most massive.

The density of the nucleus is probably of the order of 1 g/cm^3 , and has the consistency of a dirty snowball. The total gas density of the coma at the surface of the nucleus is of the order of 10^{13} molecules/ cm^3 and decreases approximately as the inverse square of the distance from the nucleus. The evaporation rate of the gases depends upon the heat input from the sun and will also vary as the inverse square of the distance from the comet to the sun. The above gas density applies to a comet at 1 astronomical unit (A. U.) from the sun. At large distances from the nucleus the gas density is expected to fall more rapidly than $1/r^2$ since dissociation of the evaporated gases has to be taken into account. At the extremes of the visible coma, in the Lyman alpha coma, and in the ion tail, the number densities are expected to be of the order of a few per cm^3 .

The cometary morphology that has been presented raises certain questions that are related to the photochemistry of the parent molecules

in comets. In particular one would like to know the identity of the parent molecules that are the precursors of the observed radicals and ions. There are questions about the distribution of the excess energy available from the photodissociation of these compounds since the partitioning of energy among the photochemical fragments determines the velocity of the observed fragment. This velocity along with the lifetimes of the parent and daughter molecules determine the size of an observed cometary cloud for a particular radical. The question of energy partitioning among the photochemical fragments may also be important in explaining discrepancies that may arise in observations of a fragment species in different regions of the spectra. For example, the CN and OH radicals have been observed in both the violet [6, 7] and in the near infra-red [8] regions of the spectra. In the violet regions of the spectra the results are well understood and it is easy to show that they indicate that the OH production rate is much higher than the CN production rate. The intensities that are observed in the infra-red region would suggest the opposite conclusions. In reality the infra-red observations may just reflect the photochemical energy that has gone into vibrational excitation of the radicals. These questions suggest that comprehensive photochemical studies are needed to supply data for the astronomers to use in interpreting their observations. A detailed consideration of these questions will show how present photochemical knowledge is used and what future studies are needed to explain the observations of cometary astrophysics.

Parent molecules

Short of direct sampling of the volatile material around a comet, there are ways of determining the identity of the parent molecules in comets. A parent molecule may be identified by direct spectral observation of a line in the infra-red or radio region of the spectra, or by spectral observations of dissociation or ionization products of the stable molecules. The latter technique is not a unique determination of a parent molecule but it is highly suggestive of their existence and their identity. Both techniques may be illustrated in the explanation of the observations of H_2O^+ , OH, H and $\text{O}(^1\text{D})$ in comets.

The forbidden red line of oxygen was observed in comets some time ago. These observations led Biermann and Trefftz [9] to suggest that this emission could only be explained by the dissociative excitation of some molecule such as H_2O , CO_2 , etc. This dissociative excitation could have been initiated either by photons, electrons, or ions. They favored photodissociation as the origin of this cometary emission. Later Delsemme [10] presented detailed arguments to support the idea that H_2O was the source of the OH and O^1D emissions observed in comets. The observations of Code 2 of the large amount of OH relative to the other radicals and the presence of the large Lyman alpha cloud was additional support for these

TABLE 1

Radio observations of parent molecules in comets

Molecule	Heliocentric distance (a. u.)	Production rate (mol/s steradian)	Comet	Source
H ₂ O	1.2	3×10^{29}	Bradfield (1974 b)	Jackson <i>et al.</i>
CH ₃ CN	0.8	10^{30}	Kohoutek (1973 b)	Uhlich and Conklin
HCN	0.4	5×10^{26}	Kohoutek (1973 b)	Heubner <i>et al.</i>
NH ₃	1.0 to 1.6	$< 4 \times 10^{27}$	Kohoutek (1973 b)	Mango <i>et al.</i>
CH ₃ OH	1.2	$< 1 \times 10^{29}$	Kohoutek (1973 b)	Mango <i>et al.</i>
N ₂ O	1.0	$< 2 \times 10^{31}$	Kohoutek (1973 b)	Mango <i>et al.</i>

views. These results led Clark *et al.* [11] to attempt to determine the presence of water directly from radio observations in comets Bennett, Kohoutek and Bradfield. Their efforts were finally successful in comet Bradfield [12] even though by this time there had been stronger evidence for the existence of water in comets with the identification of the H₂O⁺ emission in comet Kohoutek. A strong impetus to the radio searches for water was the rather complete knowledge of the photochemistry of H₂O. This knowledge permitted astronomers such as Bertaux *et al.* [13], and Keller *et al.* [14], to fit detailed models to the observed Lyman alpha isophotes observed in comets. These models agreed with the results even before the H₂O molecule had been detected.

In addition to water several other parent molecules have been detected in the radio region. These are listed in Table 1 along with the upper limits from some unsuccessful searches. These upper limits are often not very stringent, in part, because they may be much higher than the production rates of H₂O, derived from the observations of the most predominate species in comets, OH and H. All of these upper limits are derived from thermodynamic models and as such they cannot account for parent molecules in excited vibrational-rotational levels. The models assume that collisions can maintain the equilibrium but the rate of collisions is generally too low inside the coma to accomplish this for excited levels. Meaningful upper limits can only be estimated in these cases by doing a rate calculation. Such a calculation would be speculative with our meager knowledge of the conditions in comets.

The water production rate, which is calculated from the strength of the radio signals, is at least an order of magnitude higher than the rate calculated from the observations of the emissions of H and OH. The excitation mechanism for these u.v. observations is well understood, while at present there is no satisfactory explanation for radio observations of H₂O and CH₂CN. The accepted densities of electrons, ions, or neutral molecules are not high enough to maintain the observed populations [12]. The observed excitation could be the result of a transitory phenomena such

TABLE 2

Potential parent molecules

Cometary radical	Interstellar molecule
OH	H ₂ O
CN	HCN, CH ₃ CN, HC ₂ CN, H ₃ C ₂ CN
O(¹ D)	H ₂ O
H	H ₂ O
CH	CH ₄ *
CH ₂	CH ₄ , CH ₂ CO*
NH	HNCO
NH ₂	NH ₃ , NH ₂ CHO (P), CH ₃ NH ₂
C ₂	HC≡CH*, HC≡C CN, CH ₃ C≡CH, H ₂ C≡CHCN
C ₃	H ₂ C=C=CH ₂ *, CH ₃ C≡CH, HC≡C CN, HC≡C C≡CH*
CO ⁺	CO
N ₂ ⁺	N ₂
H ₂ O ⁺	H ₂ O

*Has not been observed in interstellar medium.

as a flare. It could also be due to the build-up of the population in these excited levels as a result of some radiative pumping mechanism.

The molecules that have been observed in comets in the radio region cannot explain all of the radical and ions that have been observed. There must be other parent molecules that have not yet been identified. A clue to the possible parent molecules in comets is the observations, in the radio region, of complex organic molecules in space. Table 2 lists all of the interstellar molecules which could be the precursors of the observed radical and ions. While all of these molecules are possible sources, one would like to determine the most likely source. One key to this puzzle is the lifetime of the parents in the solar radiation field. If the photochemical lifetime is long, then the density of the parent molecule must be high to compensate for the long lifetime. If we use water as a benchmark, one might be able to eliminate some of the possible parent molecules from the list in Table 2. Figure 2 is a plot of total photodissociation lifetime of various parent molecules. The remarkable thing about this graph is that it shows that H₂O, HCN, CH₃OH, and CH₄ are among the most stable parent molecules. Thus, if all of the parent compounds in Table 2 were present in equal amounts, the photodissociation products from these stable compounds would be present in the lowest concentration. Table 3 gives the relative abundances of the principal cometary radicals. What this Table shows is that most of the radicals observed in the visible region of the spectra are only minor constituents in the cometary atmosphere. Since the parents of these minor constituents have shorter photochemical lifetimes, they in turn must not be present in very high concentrations in comets. This conclusion is encouraging since it tends to confirm the feelings of most astronomers that H₂O is the most abundant cometary species.

TOTAL PHOTODISSOCIATION LIFETIME OF COMETARY PARENT MOLECULES

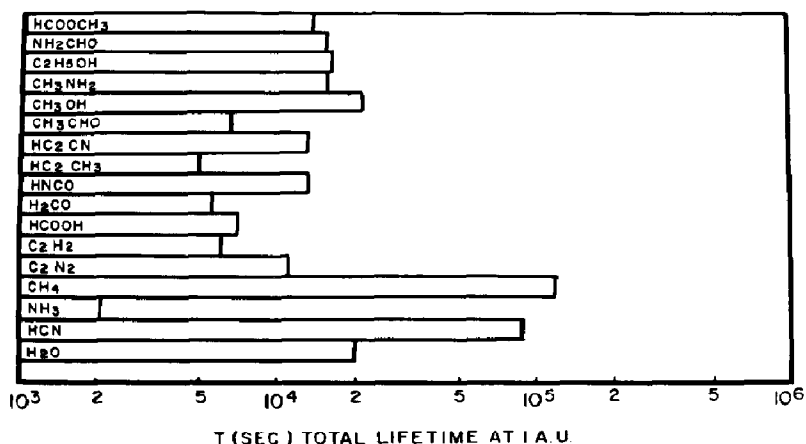


Fig. 2. The total photodissociation lifetime for a comet at 1 astronomical unit (a. u.), i.e. the distance from the earth to the sun.

TABLE 3

Relative radical abundances in comets at 1 a. u.

Radicals	Relative abundances
H	1.0
OH	1.0
CN	10 ⁻²
NH	10 ⁻³
NH ₂	10 ⁻³
C ₂	10 ⁻²
C ₃	10 ⁻³
CH	10 ⁻³

Table adapted from: A. H. Delsemme, *Icarus*, 24 (1975) 95.

The total photodissociation lifetime has not proved to be a very useful tool in deciding among the various possible parent molecules. Another possible approach is to determine the fractional dissociation probability, i.e., the primary processes, in an effort to isolate those molecules with the highest probability for being the parent of a particular radical. After all, it does not matter if a parent compound has a short photochemical lifetime if it does not dissociate to the observed cometary radical. To do this we must have some idea about the wavelength dependence of the lifetime for photodissociation. In Fig. 3 the fractional dissociation probability has been plotted for the known interstellar molecules for three spectral ranges. The three spectral ranges were chosen to represent the most important regions of the solar spectrum from the photochemical point of view [15]. Above 200 nm the solar spectrum is rather smooth over a 100 nm range. From 150 to 200 nm, the continuum

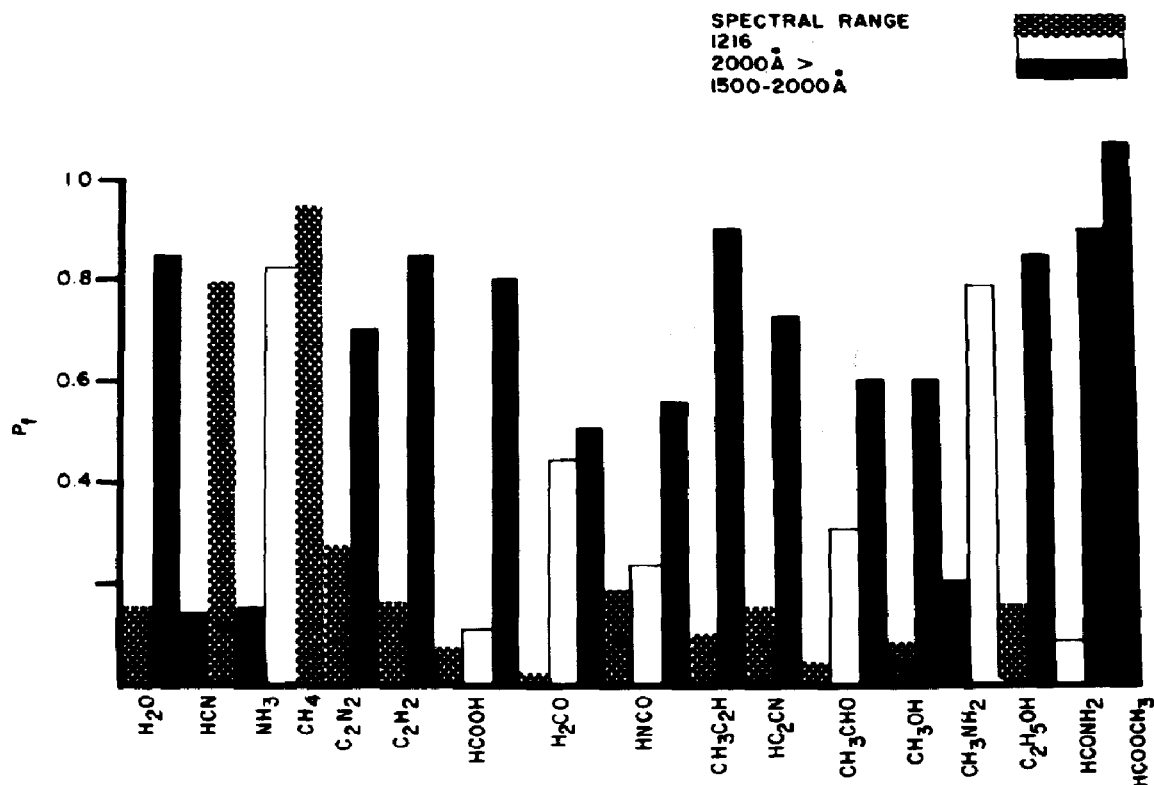
FRACTIONAL DISSOCIATION PROBABILITY P_f FOR PARENT MOLECULES

Fig. 3. The fractional dissociation probability for parent molecules in the different spectral regions.

is falling rapidly, while below the 150 nm the most important single factor is the large intensity of the Lyman alpha line. This figure shows that if a molecule absorbs and dissociates above 200 nm, most of the photochemical decomposition will occur there since the solar intensity is several orders of magnitude higher than it is below this region. Otherwise, the next most important photochemical region is between 150 and 200 nm. The Lyman alpha line is only important in those cases where the absorption in other regions is weak. All we now need is some knowledge of the mechanism for the various possible primary processes that may occur in each of these wavelength regions. This type of information has been recently reviewed [16] and will not be repeated here, rather in this paper each of the observed free radicals will be discussed in an attempt to ascertain if any of the proposed parent molecules are likely candidates for these radicals.

OH, H and O¹D

The most likely parent for all of these species is the water molecule. This molecule has been detected in the radio region of Comet Bradfield. Both the astronomical evidence and the photochemical evidence is overwhelming that water is the principal precursor to the above unstable species.

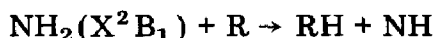
CN

The discovery of HCN and CH₃CN radio emissions in Comet Kohoutek is strong evidence that these molecules are the parents of the CN radical. This molecule has about the same abundance as the C₂ radical, but is at least two orders of magnitude less abundant than the decomposition products of water. The lifetime of the HCN molecule is a factor of five larger than the lifetime of the water so that the HCN to H₂O ratio would have to be of the order of 0.05 to explain the radical abundance in Table 3. The observed ratio derived from the radio observations of Heubner *et al.* [5], and the u.v. observations of Carruthers *et al.* [16], is about 0.025. This is excellent agreement for cometary work. Additional CN may come from a variety of other molecules such as CH₃CN, HC₂CN and H₃C₂CN. The first of these molecules was the very first parent molecule discovered in comets by Uhlich and Conklin [4] and later confirmed by Heubner *et al.* [5].

NH and NH₂

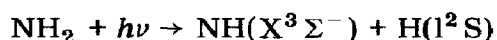
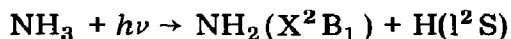
The most obvious choice of a parent molecule for these two radicals is the NH₃ molecule that has been observed in the interstellar medium but not detected in comets. Figure 4 shows that ammonia is dissociated almost exclusively in the region above 150 nm. At these wavelengths it is well known that the principal primary process [16] is the one that produces NH₂ (X²B₁) along with a ground state hydrogen atom. This would explain the NH₂ radical but would not explain the formation of the NH radical. The quoted abundance of NH and NH₂ is only one thousandth of the OH abundance so the ammonia production rate would have to be only one thousandth of the water production rate. This would certainly agree with the upper limits of the NH₃ production rates derived from cometary radio observations. The only problem appears to be that NH cannot be produced directly from the photolysis of NH₃. The key here is the word *directly* because an examination of the total lifetimes in Fig. 2 shows that ammonia will dissociate in 2000 s at one astronomical unit or within ~ 2000 km of the nucleus. This is very close to the nucleus that there are several possibilities that might explain the appearance of NH

in comets. First, the NH_2 radical could react with the other molecules present in the comet producing the NH radical by the following reaction:



R must be a free radical if the rate of the reaction is to be fast with a low activation energy. The principal radicals will be either H or OH which results from the photodissociation of water. The average ammonia molecule has a high probability of being dissociated when it is >2000 km from the nucleus. The total radical concentrations at this distance is a factor of two hundred less than the molecular concentrations. Molecules escaping from this region will undergo only one collision before they enter the collision free zone. Since the radical concentration is so low, the NH_2 radical will only have about one chance in 200 of reacting with another free radical before it escapes into this collision free zone. One concludes then that secondary reactions of the NH_2 radical are unable to explain the formation of the NH radical.

Another possibility is secondary photolysis of the NH_2 radical that was originally formed as the result of primary photolysis. This can be represented by the following reaction scheme:



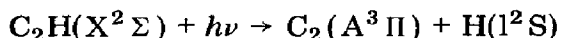
This mechanism also explains the observation of triplet NH in the photochemical reaction without violating the spin conservation rule. Is such a process likely? To answer this question we must first consider the photon energy necessary to dissociate the NH_2 radical. We also must ask ourselves whether there is any evidence for an accessible dissociation state. The bond dissociation energy of the NH_2 radical is 86 kcal/mole or about 3.7 eV. Wavelengths of the order of 330 nm or less would be needed to dissociate this radical. No absorption, at wavelengths less than 400 nm, has been observed for the NH_2 radical. This negative evidence might be the strongest evidence for the presence of a continuous absorption at shorter wavelengths. Continuous absorption bands are very difficult to detect and so that there is a high probability that they would have been overlooked. What is needed is a concentrated effort to detect such absorption. A weak absorption with an absorption cross-section of about $10^{-19} \text{ cm}^2/\text{mol}$ would be enough to explain the cometary result if it occurred between 200 and 250 nm. Otherwise, a fairly strong absorption between 150 and 200 nm would be needed. An estimate can be made of the required cross-section in the region below 200 nm by considering the fact that one would need a photodissociation lifetime in this region of the order of a few thousand seconds at one astronomical unit. This leads to an estimated absorption coefficient of the order of $5 \times 10^{-17} \text{ cm}^2/\text{mol}$. This is a perfectly reasonable absorption coefficient for this region of the spectra. With a photodissociation lifetime of the order of a few thousandths of a second very few of the NH_2 radicals would survive past 10,000 km. These

considerations would suggest that the NH_2 emissions should not extend to large distances from the nucleus of the comet, which is exactly what has been observed in comets.

C_2 and C_3

One of the oldest problems in cometary photochemistry is the origin of the C_2 Swan system. This band system is one of the strongest observed in comets indicating that the C_2 radical is at least as abundant as the CN radical. Yet, no good photochemical source for this species has been discovered. The most obvious source is the primary photolysis of the acetylene molecule which should be very abundant in comets. Figure 3 shows that most of the acetylene is photodissociated in the region between 150 and 200 nm. Of the material that is dissociated in this region, 92% of it occurs at the 153 nm band of acetylene. The principal primary process in this region produces an excited C_2H_2^* molecule which dissociates to yield the C_2H radical and a H atom. No evidence has been obtained for the production of a C_2 radical in the primary process even though there have been extensive efforts to look for this radical. This then suggests that we must look for some other source or at least a different mechanism for the production of this radical.

A likely prospect is the secondary photolysis of the C_2H radical. The bond dissociation energy has been recently measured by Okabe [17], who reports a dissociation energy of 123 kcal or a threshold wavelength of 232.4 nm. The C_2H radical would have to absorb light below this wavelength if secondary photolysis is to explain the formation of the C_2 radical via the following reaction:



This reaction obeys the spin selection rule so that it should occur below the threshold wavelength. The bands that lead to dissociation probably lie below 150 nm since Graham *et al.* [18] reported that he did not see any absorption between 150 and 250 nm. Additional support for this mechanism comes from the recent identification [19] of the C_2H radical in interstellar space.

The presence of the C_3 radical has also been difficult to explain in comets because no single primary process appears to yield this radical. The suggestion by Stief [20] that propyne, $\text{CH}_3\text{C}_2\text{H}$, might be a source of C_3 runs into some difficulty on the following grounds. First, most of the propyne in comets is photolyzed in the 150 to 200 nm region. In this region the only way it is energetically possible to produce C_3 from the absorption of a single photon is by the elimination of two molecules of hydrogen *via* the following mechanism:



This reaction probably will not occur in a single step, but rather by a two-step mechanism. First, a hydrogen molecule is eliminated, leaving an excited $C_3H_2^*$ fragment which subsequently falls apart into a H_2 molecule and a C_3 radical. The difficulty is that the principal photochemical reaction in the 150 to 200 nm region is the formation of either C_3H_3 or C_3H . This being the case, it is entirely feasible that the C_3 radical is produced by the secondary photolysis of one of these intermediate radicals. This suggestion has the attractive feature that it might explain the early appearance of C_3 before C_2 . If secondary photolysis is responsible for the formation of these radicals, then the photolysis of the radical precursors of C_3 may occur at wavelengths longer than the wavelengths required for secondary photolysis of the C_2H .

Conclusion

The production of some of the free radicals in comets has been explained by evoking a mechanism that relies upon the photolysis of radicals formed in the primary dissociation of more stable compounds. There is very little experimental evidence obtained from laboratory studies of gas phase photolysis that at present can support such a postulate. There have been several studies of the photolysis of compounds in an inert gas matrix [18, 21, 22] that do show that radicals can be photolyzed to yield some of the cometary free radicals. Studies are now in progress to try to obtain experimental verification of the postulates that are contained in this review. These studies should confirm or negate some of the proposals that have been made. Until these studies are concluded, the proposal mechanism does at least explain the observations in a manner that does not contradict either the astronomical observations nor the current laboratory photochemical studies.

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