47. THE CHEMICAL COMPOSITION OF COMETARY NUCLEI

L. M. SHUL'MAN

Main Astronomical Observatory, Ukrainian Academy of Sciences, Kiev, U.S.S.R.

Abstract. The probable parent-molecules of radicals such as C_3 and N_2^+ are discussed, and it is concluded that cometary nuclei may contain complicated organic molecules, such as C_3H_4, CH_2N_2, and C_4H_2. It is suggested that these molecules are formed by radiation synthesis in solid phase. In a time interval of order 10^7 to 10^9 yr bombardment from cosmic rays would be expected to transform the chemical composition to a depth of 1 m. Solar cosmic rays do not penetrate as far, and as a result the surface layer of the nucleus can be enriched with unsaturated hydrocarbons. After a critical concentration of this explosive material is reached a further burst of solar cosmic rays can initiate an explosion and thus an outburst in the comet's brightness. This mechanism is the only one advanced to date that can explain the synchronism of the energy output over the whole nuclear surface.

1. Introduction

The present paper deals with the chemical composition of cometary ices, a subject about which we have only indirect information. It is well known that spectroscopic data give us information only about the radicals that have appreciable emissivity in the visible region of the spectrum. Many authors, beginning with Wurm, have treated this problem. As a result we have a long list of proposed parent-molecules (see Table I).
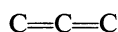
TABLE I

Parent-molecules

Observed radical	Proposed parent-molecules
CO^+, CO_2^+	CO_2
N_2^+	$N_2(?)$, $C_2N_2(?)$
C_2	C_2H_2, C_2H_4, $C_2H_6(?)$
C_3	$C_3H_8(?)$
OH	H_2O, H_2O_2
CH	CH_4
CH_2	CH_4
NH	NH_3
NH_2	NH_3, N_2H_4, CH_3NH_2
CN	C_2N_2, HCN

The choice of these molecules is based mainly on their simplicity. We ought to admit that simplicity is not a sufficient criterion for the selection and take into consideration other criteria too. Cometary ices must consist of sufficiently volatile substances. The molecules of the substances must contain the observed radicals, and the radicals must be weakly bonded in parent-molecules. The dissociation energy of an observed radical must exceed the escape energy of the radical from its parent-molecule. The

parent-molecule structure must allow the formation of the observed radical in the easiest way, i.e., in the minimum number of elementary stages that have the maximum possible cross-section. We must reject any mechanisms for the formation of the cometary neutrals demanding three-body collisions in the inner coma.

## 2. Formation of the C_3 Radical

There are many substances that satisfy the above criteria. However, for several radicals the number of possible parent-molecules is very restricted, so we can predict the parent-molecules almost exactly. Radicals of this type include C_3. Each suggested parent-molecule must contain a group
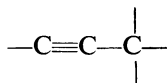
$$C{=}C{=}C$$

or

$$\underset{-C\underline{\hspace{1.2cm}}C-,}{\overset{C}{\diagup\diagdown}}$$
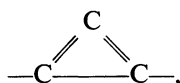
with double bonds between carbon atoms. The molecules with

$$-\overset{|}{C}-\overset{|}{C}-\overset{|}{C}-$$

or

$$-C{\equiv}C-\overset{|}{C}-$$
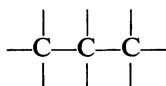
are not suitable owing to the relationship between the binding-energies of single (2.5 to 3.5 eV), double (4 to 6 eV) and triple (7.5 to 8 eV) bonds.

So we can assume that the simplest molecules able to produce C_3 are $H_2C:C:CH_2$, $HC:C:CH$ and $(CH_3)_2C:C:C(CH_3)_2$. In the last case C_3 escapes more easily because the binding energy of the CH_3 radical is ~ 3 eV, as opposed to ~ 4 eV for H.

Another mechanism, proposed by Jackson and Donn (1966), involves a disproportionation reaction following photodissociation of $HC:C.C:CH$, namely

$$C_4H_2 + h\nu \longrightarrow C_3H + CH \tag{1}$$

$$C_3H + R \longrightarrow C_3 + RH, \tag{2}$$

where R is an arbitrary radical. This supposition is based on the experimental results on the photolysis of diacetylene and on their interpretation given by Calloman and Ramsay (1957). Calvert and Pitts (1965) have found this explanation doubtful because a single bond in the C_4H_2 molecule is more likely to be broken up than a triple one:
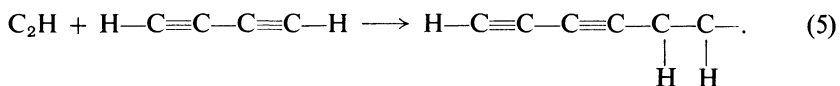
$$C_4H_2 + h\nu \longrightarrow C_2H + C_2H. \tag{3}$$

Calvert and Pitts explain the origin of C_3 radicals in laboratory photolysis of C_4H_2 by another reaction of disproportionation:

$$C_2H + C_2H \longrightarrow C_3H + H. \tag{4}$$

The process (2) follows this reaction.

One can see an essential difference between the processes (1)–(2) and (3)–(4). The second one will take place only when the frequency of C_2H—C_2H collisions is sufficiently high. The number density of C_2H radicals must exceed 10^9 cm^{-3}. In addition, the number density of C_4H_2 must be much less than that of C_2H to prevent polymerization according to the scheme:

$$C_2H + H-C{\equiv}C-C{\equiv}C-H \longrightarrow H-C{\equiv}C-C{\equiv}C-C-C-. \tag{5}$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \underset{H}{|}\ \underset{H}{|}$$

It is interesting to note that the process (5) results in the formation of organic grains, and it may therefore be proposed as one of the possible mechanisms for the origin of dust in the atmospheres of comets.

A third possible way of forming the C_3 radical is fusion, e.g.
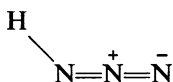
$$C_2 + C \longrightarrow C_3 + h\nu. \tag{6}$$

Besides difficulty with the probability of this process, we have here direct disagreement with observations. Indeed, according to Swings and Haser (1956), the C_3 radical is observed at greater heliocentric distances than C_2.

3. Formation of N_2^+ Ions

Another puzzle of similar character is the origin of the N_2^+ ions. The simplest supposition is that molecular nitrogen exists in the nuclei. But if this were so, nitrogen should have been evaporated at great heliocentric distances, owing to the low temperature and specific heat of evaporation. Another obvious difficulty is that emission of neutral nitrogen has not been observed, and if N_2^+ ions appear as the result of the ionization of N_2, the first negative system of the latter should certainly be present.

So we have evidence that N_2^+ is formed in some other way. If there is no free N_2 in cometary nuclei, we have to find parent-molecules that would give N_2^+ after dissociation, preferably with a charge exchange. The simplest molecules available are

$$\overset{\textstyle H}{\diagdown}$$
$$N{=}\overset{+}{N}{=}\overset{-}{N}$$

and

$$\overset{\textstyle H}{\diagdown}$$
$$C{=}\overset{+}{N}{=}\overset{-}{N}$$
$$\diagup$$
$$H$$

or

$$
\begin{array}{c}
H \\
\diagdown \\
\quad \overset{-}{C}-\overset{+}{N}\equiv N. \\
\diagup \\
H
\end{array}
$$

All these molecules have the groups $=\overset{+}{N}=\overset{-}{N}$ or $-\overset{+}{N}\equiv N$. The following processes may be proposed as mechanisms for the formation of N_2^+ ions:

$$HN_3 + H^+ \longrightarrow HN + N_2^+ + H \tag{7}$$

$$CH_2N_2 + H^+ \longrightarrow CH_3 + N_2^+ \tag{8}$$

$$ \longrightarrow CH_2 + H + N_2^+ \tag{9}$$

or

$$HN_3 + h\nu \longrightarrow NH + N_2^+ + e \tag{10}$$

$$CH_2N_2 + h\nu \longrightarrow CH_2 + N_2^+ + e. \tag{11}$$

There are no experimental data on these processes and any laboratory experiments would be of significant interest.

4. Origin of Complex Parent-Molecules

In summary, we conclude that complicated molecules such as C_3H_4, CH_2N_2, C_4H_2 and others are to be expected in cometary nuclei. But how could they have been formed? It is very likely that the mechanism is radiation synthesis in solid phase induced by cosmic rays. Indeed, a cometary nucleus is exposed to cosmic rays for a long time before it approaches the Sun. The total intensity of galactic cosmic rays $I = 8 \times 10^8$ eV cm^{-2} s^{-1} sr^{-1}. The mean energy of a cosmic proton is $E = 2 \times 10^9$ eV. This corresponds to a penetration depth of

$$l = \frac{60 \text{ to } 80}{\delta} \text{ g cm}^{-2}, \tag{12}$$

where δ (g cm^{-3}) is the average density of the surface layer of the nucleus. Cosmic rays thus penetrate into the nucleus to a depth about 1 m.

A molecule in the surface layer absorbs the power

$$\frac{dD}{dt} = \frac{\pi Im}{l\delta} \text{ eV s}^{-1}, \tag{13}$$

and typical values of the radiation synthesis output are in the range

$$G \sim 0.01 \text{ to } 1 \text{ reaction eV}^{-1}. \tag{14}$$

This means that every molecule in the layer will be hit by a cosmic proton (and therefore able to take part in chemical reactions) during a time interval of

$$T = \frac{l\delta}{G\pi Im} = 2 \times 10^7 \text{ to } 2 \times 10^9 \text{ yr.} \tag{15}$$

This estimate shows that the chemical composition of ices in the surface layer of the nucleus may be entirely transformed during a time considerably shorter than the age of the solar system.

Unfortunately, there are no experimental data on the processes mentioned here. But although nobody has exposed the assumed cometary ices (especially the mixtures) to hard radiation, some laboratory results are of interest to the physics of comets. For example, it has been shown (Davis and Libby, 1964) that CH_4 exposed to the radiation of Co^{60} below a temperature of 77 K was transformed into viscous oil. The oil was a mixture of complicated molecules of the C_mH_n type, where the value of m approached 20. It would be very desirable if similar experiments were made with frozen mixtures.

5. Effects of Solar Cosmic Rays

A cometary nucleus is affected, not only by galactic cosmic rays, but also by solar ones. Solar cosmic rays (SCR) are softer and do not penetrate as far as those from the Galaxy. SCR are irregular in time because they are generated during active processes on the Sun.

The power spectrum of SCR is often approximated by the expression:

$$D(E) = D_0 E^\gamma \text{ proton cm}^{-2} \text{ s}^{-1} \text{ sr}^{-1} \text{ MeV}^{-1}, \tag{16}$$

where E (MeV) is the energy of a proton. The spectral index γ approaches values of 4 to 6 during solar flares, and $\gamma = 3$ when flares are absent. The free path l of a proton depends on its energy as

$$l = E^{7/4}/B\delta, \tag{17}$$

where B is a constant depending on the chemical nature of the absorber. For lead and air B is equal to 220 and 417, respectively. We shall accept the value $B = 300$.

It is easy to show that the power P absorbed at a depth h is given by the relation

$$P = \frac{2\pi(\gamma + 1)\Gamma(\tfrac{8}{7})\Gamma[(4\gamma - 3)/7]}{(\gamma - \tfrac{3}{4})\Gamma[(4\gamma + 11)/7]} \frac{D_0}{B^{4(\gamma - 2)/7}(h\delta)^{(4\gamma - 1)/7}} \text{ MeV g}^{-1} \text{ s}^{-1}. \tag{18}$$

For example (Brown and D'Arcy, 1959), the solar flare on 1959 July 14–15 had parameters $D_0 = 6 \times 10^{12}$; $\gamma = 4.5$. It follows that the surface layer (as deep as 1 mm) would receive ~ 0.5 eV per molecule in a time of the order 10^5 s. This energy is sufficient to destroy intermolecular bonds in cometary ices. The above-mentioned flare was extremely intense, and similar flares are seldom observed. Weaker bursts of SCR are more common and involve the radiation synthesis and accumulation of unsaturated hydrocarbons and other explosives in the surface layer of the cometary nucleus. This accumulation will build up until the critical concentration is reached. The next flare can initiate the inevitable explosion and hence an outburst in the brightness of the comet.

It is worth mentioning that SCR synchronize the output of energy over the whole nuclear surface, and thus the envelope thrown off as a result of the surface explosion

will have spherical symmetry. All hypotheses on this subject proposed until now fail to explain fully the synchronization of the explosion.

It is clear that at small heliocentric distances intensive evaporation prevents the storage of explosives on the surface of a nucleus. But this mechanism gives us a key to understanding the outbursts in brightness and expanding shells observed for comets at large heliocentric distances.

References

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