

Organic synthesis in the coma of Comet Hale–Bopp?

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ABSTRACT

Several organic molecules have now been detected in the coma of Hale–Bopp. These species may either emanate from the nucleus, or, as has been suggested by Bockelée–Morvan et al., could be synthesized in the coma. We have modelled the gas phase chemistry which occurred in the coma of Hale–Bopp, concentrating on the observed organic molecules HCOOH, HCOOCH₃, HC₃N and CH₃CN. We find that gas phase chemical reactions are unable to synthesize the observed abundances of these molecules, so all these species are most probably present in the nuclear ice. We briefly discuss the implications of this result for the connection between cometary and interstellar ices.

Key words: comets: general – comets: individual: Hale–Bopp.

1 INTRODUCTION

The recent apparition of Comet Hale–Bopp led to the discovery of many new cometary molecules (e.g. Lis et al. 1999; Bockelée–Morvan et al. 2000). Many of these are known interstellar molecules and so offer the prospect of advancing our understanding of the interstellar–comet connection. The principal problem in determining the chemical inventory of comets is that the actual nucleus is obscured by the coma, the cloud of dust and gas that has sublimed from the nuclear surface and is expanding out into space. It is well known from models of protostellar ‘hot core’ sources, where ices have been sublimed, that the observed gas phase composition does not give a clear picture of the original ice composition; gas phase reactions produce new molecules which can then give the deceptive appearance of being mantle products. Careful theoretical modelling is necessary to ‘reconstruct’ the original mantle composition (Charnley, Tielens & Millar 1992). Despite the fact that the physical conditions encountered by molecules subliming from the comet nucleus are significantly different from those in hot cores, it is possible that chemical reactions in the coma could also modify molecular abundances. It is therefore crucial to model the coma chemistry in detail, in order to draw meaningful conclusions about the nucleus from coma observations.

For example, the detection of HNC and the associated HNC/HCN ratios in Comets Hyakutake, Hale–Bopp and Lee (Irvine et al. 1996, 1998; Biver et al. 1999, 2000) could suggest an interstellar origin for the HNC. However, we (Rodgers & Charnley 1998, 2001a) have studied the HNC/HCN ratio in comets from the perspective that the HNC is actually produced in the coma. We found that ion–molecule reactions were ineffective in producing the observed amount of HNC, but that isomerization of the parent molecule HCN induced by fast hydrogen atoms could produce the

high ratios and the variation with heliocentric distance seen in Hale–Bopp. In Comets Hyakutake and Lee, however, insufficient HNC is produced by this mechanism, so we conclude that HNC must either be a parent species (unlikely, since HNC was not present in the nucleus of Hale–Bopp), or most likely, produced via the photolytic decomposition of complex organic polymers. The purpose of this letter is to extend this methodology to other coma molecules. In order to assess whether or not the new organic molecules detected in Hale–Bopp were actually present in the icy nucleus, we investigate all potential gas phase production routes for these species.

The molecules we study – HCOOCH₃, HC₃N, CH₃CN, and (CH₃)₂O – all have quite well understood gas phase synthesis pathways in interstellar sources (Le Teuff, Markwick & Millar 2000). In particular, the detection of methyl formate (HCOOCH₃) in Hale–Bopp has important implications for the interstellar–comet connection. Interstellar methyl formate is only observed in star-forming regions and there is some debate as to whether HCOOCH₃ forms by gas phase reactions involving methyl cation transfer from CH₃OH₂⁺ to H₂CO and/or HCOOH (Blake et al. 1987; Millar, Herbst & Charnley 1991; Charnley 1997), or whether it forms on icy grain mantles. The proposed interstellar gas phase processes are very efficient, all the reactants were present in Hale–Bopp, and so we would like to see which gas phase route, if any, can match the HCOOCH₃ production rate.

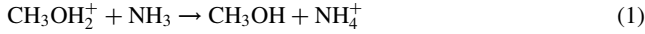
2 MODEL

We employ a combined hydrodynamic and chemical model appropriate for a steady spherically symmetric outflow. A brief description is given in Rodgers & Charnley (1998) and a full description of the model is given elsewhere (Rodgers & Charnley, in preparation). The chemical reaction scheme includes 101 species linked by over 1200 reactions and is based on interstellar hot core chemistry (Charnley et al. 1995; Rodgers & Charnley

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2001b), with additional reactions taken from the UMIST data base (Le Teuff et al. 2000). Photodissociation rates appropriate for the solar UV field were taken from Huebner, Keady & Lyon (1992) and Crovisier (1994). Some additional reactions (principally electron impact reactions) were taken from Schmidt et al. (1988).

The chemistry which occurs in the coma is driven by ion–molecule reactions, where the ions originate from the photoionization of parent molecules. The most important reactions are proton transfer reactions (cf. Giguere & Huebner 1978). Thus, in order to calculate accurately the abundances of the principal ions, we must include *all* exoergic proton transfer reactions, many of which are absent from the UMIST data base. In particular, the reaction

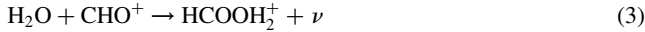


is crucial, because it controls the CH_3OH_2^+ abundance, which in turn affects the HNC production rate (Rodgers & Charnley 1998) and the rates of methyl cation transfer reactions that form large O-bearing organics (Rodgers & Charnley 2001b). All such new reactions were assumed to proceed with a rate coefficient of $2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, and the exoergicity of each reaction was calculated from the proton affinity data of Hunter & Lias (1998).

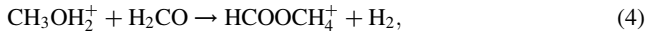
The chemistry of large oxygen-bearing molecules in hot cores has been modelled by Millar et al. (1991) and Charnley et al. (1995), and many of the important reactions in our model have been discussed in detail by these authors. Formic acid (HCOOH) is formed directly by the reaction (Le Teuff et al. 2000)



and indirectly through the reaction



followed by proton transfer or dissociative recombination. Methyl formate is formed via methyl cation transfer reactions of protonated methanol with formaldehyde or formic acid,



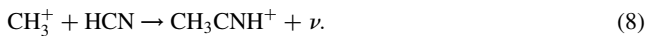
again followed by proton transfer or dissociative recombination. A similar reaction with methanol can lead to dimethyl ether $[(\text{CH}_3)_2\text{O}]$:



Hot core nitrogen chemistry is discussed by Rodgers & Charnley (2001b) and Charnley & Rodgers (in preparation). Cyanoacetylene (HC_3N) is produced by the reaction of acetylene with the CN radical,



whereas methyl cyanide (CH_3CN) is formed via the radiative association of CH_3^+ and HCN,



All of the above reactants are known to be abundant in cometary comae, so we have investigated the potential of reactions (2)–(8) to form the observed amounts of cometary organic molecules.

Because the molecules we are interested in have so far only been detected in Hale–Bopp, when this comet was at a heliocentric distance of ~ 1 au (Bockelée–Morvan et al. 2000), we have chosen our initial conditions accordingly. We assume a

nuclear radius of 20 km (Weaver et al. 1997), a surface temperature of 100 K (Biver et al. 1999), and an initial H_2O production rate of $10^{31} \text{ molecule s}^{-1}$ (Dello Russo et al. 2000). The initial chemical composition was based on table 4 of Bockelée–Morvan et al. (2000) and is shown in Table 1.

3 RESULTS

Fig. 1 shows our calculated molecular abundances as a function of cometocentric distance, R . Note that we have included HCOOH as a parent species, with an initial abundance equal to the observed value of 0.001 relative to H_2O (Bockelée–Morvan et al. 2000). This is because when we ran the model with no initial HCOOH, reactions (2) and (3) failed to produce sufficient HCOOH by a factor of 10^3 . Since HCOOH is a possible precursor to HCOOCH_3 (reaction 5), we have included it as a parent in order to maximize the amount of HCOOCH_3 synthesized in the coma.

Because the number densities of molecules are changing throughout the coma, the observed column density depends on the size of the telescope beam, and the offset between the centre of the beam and the nucleus. HCOOH, HCOOCH_3 , and HC_3N were detected in Hale–Bopp between 1997 February 20 and April 5 using the CSO, IRAM 30-m and IRAM Plateau-de-Bure telescopes (Bockelée–Morvan et al. 2000). During these dates the comet was at a geocentric distance, Δ , of 1.3–1.6 au. The

Table 1. Initial abundances assumed for parent species, relative to water.

Species	Abundance (%)
H_2O	100
CO	20
CO_2	6
CH_3OH	2.4
NH_3	0.7
H_2CO	0.5
CH_4	0.6
C_2H_6	0.3
C_2H_2	0.1
HCN	0.25
HCOOH	0.1
N_2	0.1

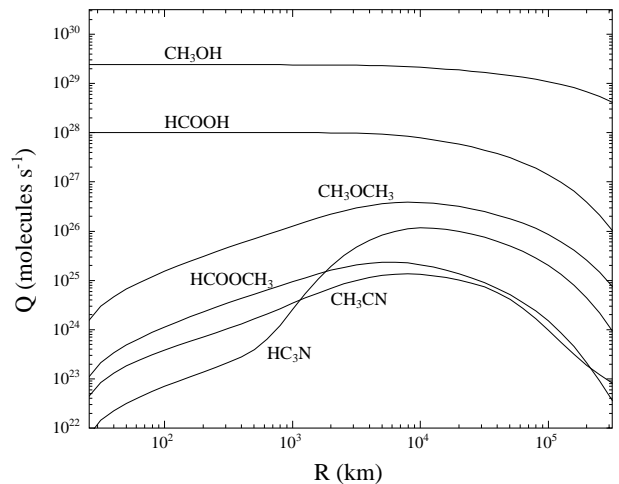


Figure 1. Molecular abundances, $Q(=4\pi n v R^2)$, versus cometocentric distance, R , for large organic molecules. The initial value for H_2O (not shown) is $10^{31} \text{ molecule s}^{-1}$.

Table 2. Comparison of observed and predicted abundances relative to H₂O.

Molecule	Date (1997)	Telescope	[X]/[H ₂ O] × 10 ⁴	
			Observed	Model
HCOOH ^a	Mar. 20–21	PdB	9.0	0.01 ^d
HCOOCH ₃ ^a	Apr. 5	30-m	8.0	0.02 ^e
HC ₃ N ^a	Feb. 19–21	CSO	2.4	0.09
...	Mar. 6	PdB	2.3	0.09
...	Apr. 3–5	30-m	1.7	0.07
CH ₃ CN ^b	Many	All	2–3	0.01 ^f
(CH ₃) ₂ O ^c	–	–	<45	0.33 ^f

^aObservational data from Bockelée–Morvan et al. (2000).

^bCH₃CN was observed between Aug. 96 and Aug. 97 by Biver et al. (1999).

^cUpper limit from Crovisier (private communication).

^dAssuming no initial HCOOH injection.

^eWhen no HCOOH is present in the nucleus, the HCOOCH₃/H₂O ratio equals 1.6×10^{-6} . With HCOOH injected at the 0.1 per cent level, the value is 1.9×10^{-6} .

^fCalculated assuming a 20-arcsec FWHM beam and $\Delta = 1.5$ au.

angular widths (FWHM) of the telescope beams at 230 GHz are 31, 11 and 22 arcsec respectively, which implies linear beam sizes of $\sim 1\text{--}3 \times 10^4$ km. In order to compare our results with the observations, we have convolved our number density profiles with a Gaussian beam of the appropriate linear width for the telescope used and Δ on the date of each observation. The resulting values are listed in Table 2.

It is clear that chemical reactions are unable to form the observed abundances of all four species. Therefore, we conclude that they must have been present in the nucleus of Hale–Bopp. We also show results for (CH₃)₂O in Fig. 1 and Table 2, because we find this to be the most abundant large organic daughter molecule. However, our predicted abundance is a factor of 100 below the upper limit determined for Hale–Bopp, and as this was an exceptionally active comet we expect that (CH₃)₂O will be very difficult to detect in other comets. Note that (CH₃)₂O is formed via self-alkylation of CH₃OH (reaction 6), so the production rate is proportional to the square of the methanol abundance. Hence, future searches for this molecule should focus on methanol-rich comets.

Finally, reaction (5) could alternatively lead to protonated acetic acid (Charnley & Rodgers, in preparation). The limits on CH₃COOH in Hale–Bopp have not yet been evaluated (Crovisier et al. 1999), but our calculations also imply that it could not be formed in the coma in significant quantities.

4 DISCUSSION

We have shown that HCOOH, HCOOCH₃, CH₃CN and HC₃N cannot be produced in the coma by ion–molecule chemistry, and so were most likely present in the nucleus of Comet Hale–Bopp. All these species are also observed in the interstellar medium. As differences between cometary and interstellar ices can be used to constrain the degree of processing which occurred as material accreted into the protosolar nebula, we briefly compare cometary and interstellar values (cf. Bockelée–Morvan et al. 2000; Irvine et al. 2000; Ehrenfreund & Charnley 2000).

Solid-state formic acid has been detected by *ISO* toward the high-mass protostars W33A and NGC 7538, with an abundance relative to H₂O of $\sim 1\text{--}3$ per cent (Schutte et al. 1996, 1999). This is ten times higher than the value in Hale–Bopp, which suggests that HCOOH is depleted in cometary ices. HCOOH is thought to

be formed via surface chemistry on interstellar grains, through atomic O and H addition reactions to CO (Tielens & Hagen 1982). However, HCOOH is not seen toward low-mass protostars or field stars, and experimental work by Hudson & Moore (1999) has shown that HCOOH is produced by energetic processing (radiolysis) of H₂O + CO ices. Therefore, the large HCOOH abundances seen by *ISO* may trace highly processed ices, and will not reflect the values in the natal cloud which collapsed to form the Solar System. Alternatively, it is possible that Bockelée–Morvan et al. (2000) underestimated the HCOOH abundance in Hale–Bopp. Bockelée–Morvan et al. assumed a photodissociation rate of $3.2 \times 10^{-5} \text{ s}^{-1}$, which ensures that the scalelength over which the molecule is destroyed is larger than the telescope beam width of $\sim 10^4$ km. Huebner et al. (1992) obtained a value of $8.8 \times 10^{-4} \text{ s}^{-1}$ for the photodestruction rate at 1 au. If this latter value is correct, then Bockelée–Morvan et al. will have underestimated the HCOOH production rate by a factor of around four, or even more if the beam was not centred on the nucleus.

Finally, we note that decomposition of large organics has been proposed as a major source of coma molecules, in order to account for the distributed sources of CO, C₂, C₃, CN and H₂CO (e.g. Eberhardt et al. 1987; Combi & Fink 1997; Greenberg & Li 1998). Recent work by Cottin et al. (2000) has shown that HCOOH is produced by photolysis of polyoxymethylene (POM, the –CH₂O– polymer), which has previously been considered as a possible parent of cometary formaldehyde (Huebner 1987). Cottin et al. obtain a HCOOH yield of around one fifth that for H₂CO. As the H₂CO abundance in Hale–Bopp was ~ 1 per cent at 1 au (Biver et al. 1999), if only half of this came from POM then there is sufficient POM to account for all the observed HCOOH.

Methyl formate has a similar abundance in interstellar hot cores to that seen in Hale–Bopp (see e.g. Bockelée–Morvan et al. 2000, fig. 3b). However, as discussed in the Introduction, HCOOCH₃ is thought to be a daughter molecule in hot cores, formed via reactions (4) and (5) (Charnley et al. 1995). Thus, the presence of HCOOCH₃ in Hale–Bopp has important implications for the processing of interstellar material prior to its incorporation into the Solar system. There are two possibilities. First, CH₃OH and H₂CO may both form readily in interstellar ices (e.g. Charnley, Tielens & Rodgers 1997); formation of HCOOCH₃ thus requires that these ices be evaporated near the proto-Sun and their constituents allowed to react, as in hot cores. The presence of HCOOCH₃ in Hale–Bopp would then require that these products and reactants recondensed on to the icy dust grains that were ultimately assembled into the comet. This could occur either prior to incorporation in the solar nebula, since molecular material accreted in the outer disc will suffer least processing in passing through the accretion shock, or by chemical reactions in the outer disc (cf. Aikawa & Herbst 1999) if gas–dust parcels experience several episodes of modest heating and cooling, i.e. mixing in the disc. Secondly, interstellar HCOOCH₃ is formed on interstellar grains.

Cyanoacetylene and methyl cyanide are seen in hot cores with similar abundances to those in Hale–Bopp. However, they are thought to be daughter species in hot cores, since reactions (7) and (8) proceed efficiently in these regions (Charnley & Rodgers, in preparation). Thus, the presence of these molecules in Hale–Bopp is further evidence for the first scenario discussed in the previous paragraph, i.e. that the chemical composition of comets is consistent with mantle evaporation followed by a hot core-like chemistry followed by recondensation, either during the collapse phase of the natal cloud or in the outer region of the young

protoplanetary disc. Cometary methyl cyanide was first detected in Comet Kohoutek by Ulich & Conklin (1974), although their derived column densities imply an extremely large abundance. More recently, Dutrey et al. (1996) observed CH₃CN in Comet Hyakutake, with an inferred production rate of $1.8 \times 10^{25} \text{ s}^{-1}$. Using the H₂O production rate of $1.7 \times 10^{29} \text{ s}^{-1}$ derived by Mumma et al. (1996) two days earlier, this works out as a CH₃CN abundance of 10^{-4} , half the amount in Hale–Bopp.

In conclusion, we have shown that HCOOH, HCOOCH₃, HC₃N and CH₃CN cannot have been formed by gas phase chemistry in the coma of Hale–Bopp. It appears therefore that all four molecules must have been present in the nuclear ice. The fact that HCOOCH₃, HC₃N and CH₃CN are undetected in interstellar ices, but are produced in abundance in hot cores, suggests that natal presolar material underwent a hot core-like stage during its collapse.

Finally, we end with a brief note of caution. HCOOH and HCOOCH₃ were observed on only one occasion, and HC₃N on three, and we cannot be too confident about extrapolating such meagre data to draw strong conclusions about the general nature of cometary ices. For example, the initial discovery of HNC in Hyakutake was unexplainable by coma chemistry, and so the HNC was supposed to be unprocessed interstellar material (Irvine et al. 1996). Only when HNC was detected in Hale–Bopp, and shown unequivocally to be a daughter species (e.g. Irvine et al. 1998; Blake et al. 1999), was this conclusion revised. It is only through detailed observations, including long-term monitoring of production rates and interferometric mapping of the coma, that we can accurately determine the chemical inventory of comets.

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