Cometary Impact and Amino Acid Survival − Chemical Kinetics and Thermochemistry[†]

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The Arrhenius parameters for the initiating reactions in butane thermolysis and the formation of soot, reliable to at least 3000 K, have been applied to the question of the survival of amino acids in cometary impacts on early Earth. The pressure/temperature/time course employed here was that developed in hydrocode simulations for kilometer-sized comets (Pierazzo and Chyba, 1999), with attention to the track below 3000 K where it is shown that potential stabilizing effects of high pressure become unimportant kinetically. The question of survival can then be considered without the need for assignment of activation volumes and the related uncertainties in their application to extreme conditions. The exercise shows that the characteristic times for soot formation in the interval fall well below the cooling periods for impacts ranging from fully vertical down to about 9° above horizontal. Decarboxylation, which emerges as more rapid than soot formation below 2000−3000 K, continues further down to extremely narrow impact angles, and accordingly cometary delivery of amino acids to early Earth is highly unlikely.

Introduction

The likelihood that significant quantities of amino acids and other organic materials were delivered to prebiotic Earth and survived cometary impact remains an important question bearing on Earth's early biochemistry and life's origins, and two recent accounts by Pierazzo and Chyba[1] and Blank et al.[2] have considered the issue from a chemical kinetics perspective. Pierazzo and Chyba applied kinetic parameters to models of the collisions of kilometer-size comets developed in hydrocode simulations in which temperatures and pressures fell from peak values of near 10 000 K and 100 GPa to nominal levels over several seconds. While recognizing that earlier estimates suggested survival was unlikely, they noted that there had been no reliable high-temperature chemical kinetics data available to allow a clear-cut description of the fate of organic substances at the extreme conditions. Using kinetic parameters developed in a new study by Rodante with amino acids conducted to about 900 K,[3] they then concluded that some amino acids might have survived after all. They cautioned that the parameters they employed were from conditions still quite modest, however, and they advised that the issue be revisited when the appropriate data became available.

In their account, Blank et al. emphasized the challenges in developing an understanding of organic survival under shock conditions from a chemical kinetics approach. They noted that in principle the severe pressures at impact could stabilize organic structures that would otherwise be wholly destroyed at the extreme impact temperatures. Using shock impulse techniques, they subjected concentrated amino acid solutions to heating and cooling rates of hundreds of degrees/μs, with peak conditions of up to 870 K and 20 GPa over microsecond intervals. They found that significant fractions of the acids not only survived, but that small peptides were formed in trace quantities as well. The conditions, however, were far less extreme and the cooling rates considerably greater than those afforded in the Pierazzo−Chyba profiles. Survival at true comet impact scales thus remains an open question.

The exercise reported here was conducted from the perspective that (i) the Rodante data may have seriously underestimated the rates of decomposition at impact conditions, and that (ii) well-established kinetic data and mechanistic models from the alkane pyrolysis and soot formation literature were dependable to at least 3000 K and thus applicable to the problem. A representative impact profile described by Pierazzo and Chyba is employed, first examining the prospective protective effects of the very high impact pressures, and then applying the kinetics parameters for some likely key initial steps in an alkane-to-soot model and appraising the chances for organic survival.

Background and Approach

The Pierazzo and Chyba modeling included the impact of spherical comet bodies 1−5 km in radius impacting the early oceans, and a temperature/pressure profile for the vertical impact of a 2-km comet traveling at 20-km/s is shown in Figure 1.[4] The figure shows that the pressure falls rapidly to below 1 GPa in the first 0.2 s. The temperature falls at a slower rate to about 2000 K in that interval, and then falls even more slowly out to beyond 1 s. The figure is partitioned at about 0.05 and 0.2 s to depict the points at which the shifts in the density of water over the spread of conditions alter its qualities and solvent character. (The densities were estimated from the equation of state for water by Belonoshko and Saxena.[5]) Thus, immediately after impact where densities range around 2 g/mL, water is fully ionized to H_3O^+ and OH^- and is essentially a fused salt.[6] The medium then briefly passes through a liquidlike zone, and for the remaining period is essentially a vapor.

The kinetic parameters used by Pierazzo and Chyba were developed in thermo-gravimetric and calorimetric studies on the solid acids at temperatures up to 900 K,[3] and a comment regarding their applicability is appropriate. Critical to the

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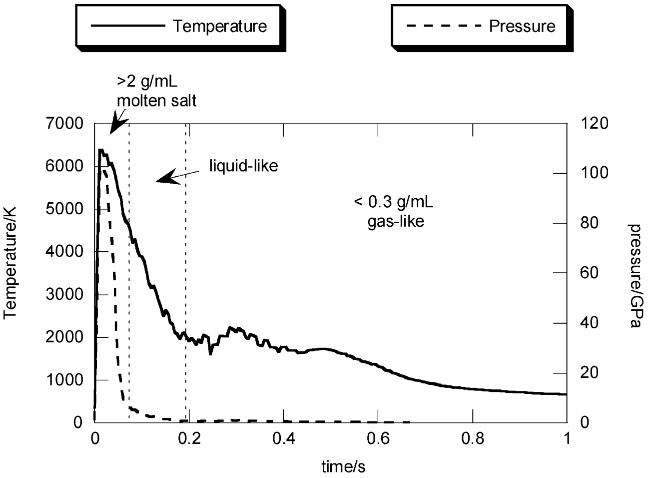


Figure 1. Time/temperature/pressure profiles as developed by Pierazzo and Chyba. The vertical partitions designate the regions where the shift in the density of water affects its solvent qualities.

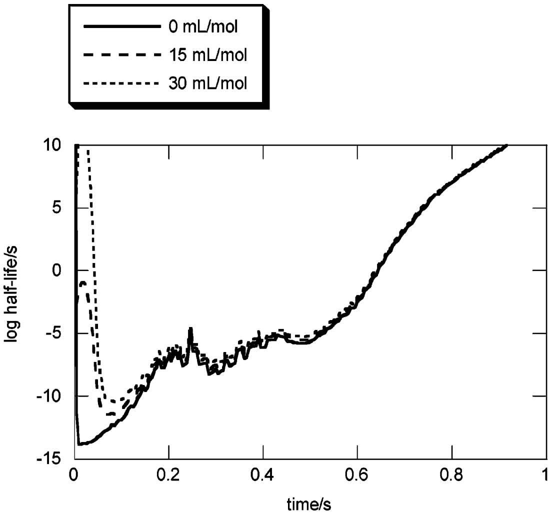
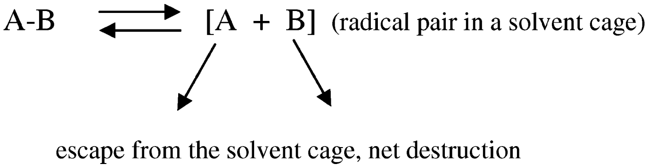


Figure 2. Half-lives of C−C bond scission in butane over the Pierazzo and Chyba temperature/pressure course employing a range of activation volumes.

modeling is the fact that kinetic parameters applied to conditions well beyond the range in which the parameters were developed will not represent higher activation energy processes that can emerge at the more extreme conditions and eclipse the lower temperature reactions. This complication can be underscored for the present case by recognizing that reaction sequences at high temperatures tend to be initiated with bond scissions; they are entropically driven with *A*-factors generally in a relatively narrow 10^{14}−10^{17} s^{-1} range.[7] It is notable that the *A*-factors listed by Rodante varied widely over some 30 orders of magnitude, and as such they must reflect a very broad range of reactions. Those with *A*-factors in the 10−10^{6} s^{-1} range are for the most part paired with strikingly low activation energies, and they most likely represent complex reactor wall-catalyzed sequences that should be far slower than homolytic scission in a cometary impact setting. It follows that an analysis employing those parameters at impact conditions would severely underrate reaction velocities.

As for the reaction routes themselves, homolytic scission reactions at pressures up to about 0.5 GPa have been studied widely[8] and are simply represented by the sequence:



A measure of the consumption of A−B is the competition between the rate of reformation of the A−B bond on the one hand, and the escape of the radicals from the solvent cage on the other. That competition in turn is a function of the viscosity of the medium,[9,10] which of course generally increases with pressure and decreases with temperature.

It would seem then that some sense of amino acid survival could be developed directly with an application of the viscosity of water at shock conditions to the reaction kinetics. Unfortunately, the picture is clouded by some serious disagreement extending over several orders of magnitude as to just what the viscosity of high pressure/temperature water is,[11,12] and so that route of analysis is not available. (It is not helpful, moreover, to recognize that no less a notable than Sir Francis Crick, who worked in the field for a while, referred to the viscosity of water at extreme conditions as “the dullest problem imaginable”.[13])

That limitation can be bypassed, however, by considering high temperature processes taking place within the solvent cage, and specifically those reactions leading to soot. The Arrhenius equation describing the behavior of a rate constant with temperature can be extended to include the effects of pressures in the expression

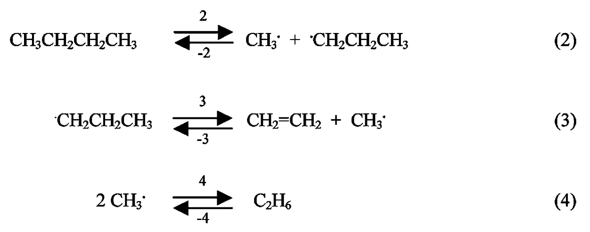
$$\log k = \log A - E_a/2.303RT - p\Delta V^{\ddagger}/2.303RT \qquad (1)$$

where $\Delta V^{\ddagger}$ is the activation volume of the reaction.[14] Activation volumes refer to the volume changes associated with the movement of a reactant from its starting state to the activated complex. Generally they are positive for unimolecular reactions involving bond breaking and negative for bimolecular bond making reactions, ranging typically from 15 to −40 cm^3/mol.[8] Because activation volumes themselves are pressure sensitive, however, the question can be raised as to how reliably they and eq 1 can be applied to the extreme ranges of conditions considered here. The very large spread of solvent qualities, moreover, will encourage a range of prospective reaction routes, running from highly ionic to strictly free radical, and so the assignment of dependable rate parameters becomes a major challenge.

To deal with these issues, and because as maintained by eq 1 the effects of high pressures are offset by high temperatures, it is desirable to survey the interplay of the conditions over the route depicted in Figure 1. The homolytic scission of the terminal C−C bond in *n*-butane, the first step in the model used below to assess impact survival, can be employed for that purpose. The Arrhenius parameters for the reaction are log *A* = 16.6/s^{-1} and E_a = 365.7 kJ/mol, and for demonstration purposes activation volumes of 0 (i.e., no pressure correction), 15, and 30 mL/mol have been used.

The result is presented in Figure 2, which reveals that if the effects of pressure are ignored, the lifetime of a C−C bond would be measured in picoseconds over the first few milliseconds after impact, and organic survival is in that case clearly not possible. However the figure shows that if pressure effects are included, eq 1 projects lifetimes of near a second at a minimum in that initial interval.

The picture quickly changes beyond that period as a result of the rapid pressure falloff, however, and it appears that by



$$CH_3CH_2CH_2CH_3 \underset{-2}{\overset{2}{\rightleftarrows}} CH_3^{\cdot} + {}^{\cdot}CH_2CH_2CH_3 \qquad (2)$$

$${}^{\cdot}CH_2CH_2CH_3 \underset{-3}{\overset{3}{\rightleftarrows}} CH_2{=}CH_2 + CH_3^{\cdot} \qquad (3)$$

$$2\ CH_3^{\cdot} \underset{-4}{\overset{4}{\rightleftarrows}} C_2H_6 \qquad (4)$$

Reaction	Rate constant[a]	Comment
2	$10^{16.6}$ exp(-365.7/RT)	The rate constants for C-C scission and recombination for propane were used here.
-2	$10^{10.0}$	
3	$10^{13.0}$ exp(-63.1/RT)	
-3	$10^{3.4}$ $T^{1.6}$ exp(-23.8/RT)	
4	$10^{13.8}$ $T^{-1.18}$ exp(-2.7/RT)	
-4	$10^{16.1}$ exp(-371.5/RT)	

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a. The rate constants are in liter-mole-sec units and the activation energies in kJ/mol. For those cases with a pressure dependence the expression listed is that for the high pressure limit. All of the constants were taken from the web site maintained by the Gas Research Institute at http://www.me.berkeley.edu/gri_mech/ and are valid to at least 3000 K.

Figure 3. Initial pyrolytic sequence leading to soot.

about 0.2 s the effects of pressure have become insignificant. The analysis can therefore be directed to the events in this region and beyond because there will then be no need to deal with an assignment of activation volumes. Moreover, because by that period the temperature has fallen below 3000 K and the medium is essentially a vapor, the amino acids will be in their molecular rather than their zwitterionic forms. The analysis is thus suitably within the range where a hydrocarbon model should work well, and reliable Arrhenius parameters for alkane pyrolysis can be employed.

Results

The pyrolytic destruction of organic compounds is known to take place over several degradative steps to polynuclear aromatic substances, ultimately leading to soot[15] (or diamond at conditions within the diamond stability field). It is described by the global process

$$\text{organic compound (with O and/or N)} \rightarrow m\mathrm{H}_2 + n\mathrm{C}\ (+\mathrm{H_2O}\ \text{and/or}\ \mathrm{NH_3})$$

which is exoergic and kinetically significant generally at temperatures greater than about 1300 K.[16]

Figure 3 displays the first three steps along the route to soot in the pyrolytic sequence for butane;[17] the species in the string are those that would be formed in, and remain in, the solvent cage following impact. The three equilibria comprise the initiation steps in what at lower temperatures and pressures, and presumably lower viscosities, would be an autoaccelerating chain process propagated by migration of reactive free radicals from the cage and their subsequent reaction with butane in the medium.

The overall conversion in Figure 3 is the equilibrium

$$CH_3CH_2CH_2CH_3 \rightleftarrows CH_3CH_3 + CH_2{=}CH_2 \qquad (5)$$

and simple calculations show that up to the highest temperatures and pressures considered here it is overwhelmingly favored to the right. The question then becomes how rapidly equilibrium is attained with respect to the rate of cooling in Figure 1, and an analysis of the kinetics of the scheme is required.

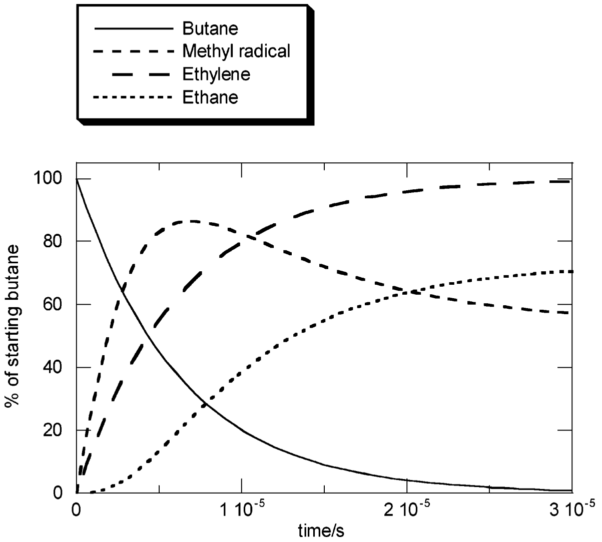

Figure 4. Profiles for the reaction sequence in Figure 3 at 1700 K.

The analysis focuses on the temperature interval 0.2−0.5 s where the temperature ranges from 2000 down to about 1700 K, and the reaction kinetics were developed specifically for the lower temperature with Acuchem, a program providing numerical solutions for complex kinetic systems.[18] The results are shown in Figure 4.

The figure shows that at 1700 K butane is virtually fully consumed over tens of microseconds. The formation of ethylene (C_2H_4) is complete, and the C_2H_6/CH_3 equilibrium in reaction

4 is fully attained over that period as well. (The propyl radical ($CH_3CH_2CH_2^{\bullet}$) also rapidly attains a steady state in the interval, but at levels several decades below those of the substances in the figure.) Because materials in the impact wave are at temperatures no lower than 1700 K over the interval 0.2−0.5 s, it then follows that whatever may happen over the first 0.2 s after impact, butane and by extension amino acids will be fully destroyed by the 0.5 s mark.

This analysis for a vertical collision can be extended to the broader case of angular impacts, recognizing that the post-shock temperatures and pressures scale, respectively, as $\sin^{0.8} \theta$ and $\sin \theta$ (where θ is the impact angle in degrees as measured from the horizontal).[19] Application of this dependence to the model shows that for impacts inclining increasingly to the horizontal, the zone of thermolytic destruction slides back along the time line to earlier stages after impact. Destruction continues to be complete down to a narrow impact of about 9°, at which point the post-shock temperature falls from 1500 to 1300 K over the first 35 ms while the half-life of butane at 1300 K is about 10 ms. While shock temperatures drop to values below those for butane thermolysis at even more slender impact angles, it evolves that the decarboxylation of amino acids surpasses soot formation as the dominant mode of destruction at these lower temperatures, and continues down to glancing angles bordering on a near-miss event.[20] On this basis, it is apparent that their impact survival overall is quite unlikely.

A potential qualification that should be addressed is the fact that amino acids can associate with mineral materials in a comet through acid−base and polar forces, and those associations could provide some level of protection against thermolysis. Surface binding apparently offers little protection, however, as shown by Buchanan et al. who studied the thermolysis of silica-bound molecules containing pyrolytically sensitive C−O and C−C bonds.[22] It thus seems clear that a Pierazzo−Chyba impact should destroy all amino acids in kilometer-sized impactors.

The results of the study of Blank et al., conducted at lower temperatures, significantly shorter durations, and higher cooling rates, fall into a different category.[2] The same analysis for material in the solvent cage, but shifted down to 870 K, shows a half-life for butane based on the three equilibria of tens of hours. The stability remains, moreover, even when the effects of pressure are ignored. Because the impact periods in the study were no longer than several microseconds, there is little question that amino acids are quite stable to soot-forming chemistry at the Blank et al. conditions. Other possible routes for decomposition would include decarboxylation and the complex pyrolytic processes seen in the calorimetric studies of Rodante.[3] The half-lives at 870 K for those two routes, once again ignoring pressure effects, are about 2 and 10 ms, respectively. (The former value is developed from the data of Snider and Wolfenden for glycine;[21] the latter is for alanine, one of the least stable amino acids in the Rodante study.) These values too are far larger than the shock periods, and it therefore seems safe to conclude that even at ambient pressures, amino acids are stable at 870 K over microsecond periods. Accordingly, their recovery in the studies by Blank et al. is not unexpected.

Moreover, given the high concentrations of their starting amino acid solutions, nominally 0.1 M, neither are the observations of peptides. This conclusion can be developed from the thermochemistry for aqueous glycine and its dipeptide over a range of temperatures up to the critical temperature of water (647 K),[23] where it can be shown that the conversions of a 0.1 M glycine solution to the peptide range from about 0.03% at 300 K to more than 3% at the critical temperature. That trend should be maintained beyond that point at water densities greater than about 0.3 g/mL, and since at the Blank, et al. conditions the density was >1 g/mL,[5] peptides can be expected in quite significant fractions.

(Indeed, it might be argued that the small levels of conversion to peptides observed in the work were kinetics-based and that higher yields would have been observed over longer reaction periods. The results in that case would be reminiscent of the findings of Fox,[24] Hennon et al.,[25] Rohlfing,[26] and others who showed that polyamino acids are readily prepared by simply heating amino acids. They, moreover, would be an interesting extension of the views of Shock,[27] who proposed that peptide-forming reactions (included in a broad collection of dehydratively formed links with biochemical significance) could be thermochemically feasible in water at hydrothermal conditions.)

Conclusions

On the basis of this analysis, it seems clear that amino acids and other organic materials will not survive a route of cometary impact that includes temperatures of 2000−3000 K and pressures below about 30 GPa over periods of tens of milliseconds. While these values were likely common to the collisions of the majority of prebiotic colliders kilometers in size, organic substances are delivered to Earth in meteorites[28] and it is of interest to bridge these two limits in behavior. (The author thanks a reviewer for raising this question.) Meteorites are in a different class from the bodies dealt with here in that they are considerably smaller (i.e., meters in extent) and are largely ablation-cooled in their passage through the atmosphere. Accordingly, the organic material in their interiors can survive. While the organic content is of interest fundamentally, however, its contribution to the inventory of exogenous organic materials on early Earth falls orders of magnitude below that from other external sources, including interplanetary dust particles, which are the largest single exogenous source.[29] Larger bodies up to about 100 m are subject to extreme aerobraking and drag heating, and they generally do not reach the ground but are destroyed in airbursts.[30]

For the still larger bodies that do land, Pierazzo and Chyba note that impact temperatures are not influenced significantly by impactor size.[1] A decrease in size merely decreases the heating periods in the interior because the shocked material is released from the shock by the rarefaction wave reflected back from the face opposite the impact point. Thus, presuming simple first-order initiation chemistry, the surviving fraction of organic substances will scale as e^{-d} where d is the impactor diameter. Overlaying this relationship on the model described here shows that destruction remains complete with drop in impactor size down to about 100 m.

It can be noted parenthetically that a massive impact that has been recognized as anomalously gentle was probably not. The Sudbury Basin in Canada, the second largest impact crater in the world and the result of the arrival of a 10-km body, is described as having attained impact temperatures no greater than a remarkably cool 1300 K.[31] A reexamination of the kinetic data leading to that conclusion, however, suggests that the impact was probably a conventional event, with the extreme pressures and temperatures expected for such a cataclysm.[32] Thus, although it appears that the notion that life's "building blocks" arrived in comets has entered our popular culture,[33] overall it seems safe to conclude that comets were not a meaningful source of any organic material to prebiotic Earth. The cradle of the first biochemistry is yet to be revealed.

While the understanding of the start of life remains uncertain and problematic,[35] it is worth noting in conclusion that a core feature of the trend toward the chemical organization required for life's operation is kinetics-based. In studies dealing with the fundamental nature of the catalytic function of enzymes, Snider and Wolfenden have observed that enzymatic structures undergo evolutionary changes that drive them to provide rates approaching encounter rates in solution.[35] This remarkable facility of enzymes, which are little more than amino acid polymers, to adapt structurally to approach catalytic efficiencies at the limits of physical law is stunning and must reflect a prime component of the mechanism of life's beginnings. Accordingly, it seems clear that an understanding of the very foundations of life and its origins can be developed with an improved appreciation of its ties to chemical kinetics.

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