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Oxidation of organic materials with perchlorates: Relevance to the chemistry on the Martian surface

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ABSTRACT

No organic materials have been found on the Martian surface, based on the results from the Viking and Phoenix missions. The Phoenix mission detected the inorganic perchlorates in the Martian soil. Perchlorates are potent oxidizing substances. The high-temperature oxidative properties of perchlorates may promote combustion of organics in pyrolytic experiments. This may compromise the ability of Phoenix's TEGA (Thermal and Evolved Gas Analyzer) experiments to detect organics. The high temperature conditions of TEGA instrument are not representative of the environment on Mars. In this paper we pose a question if organic materials can survive oxidation with perchlorates at less drastic temperatures. We have surveyed the literature on oxidations of various groups of organic materials by perchlorates. Several amino acids, notably glycine and alanine, are quite resistant to this oxidation. The same is true for some heterocycles, purines and pyrimidines. These organic materials may have survived perchlorate oxidation in the natural environment on Mars.

Keywords: perchlorates on Mars, perchlorate oxidation, oxidation of amino acids with perchlorates, oxidation of heterocyclic compounds with perchlorates, oxidation of purines and pyrimidines with perchlorates, survival of organic compounds on Mars

1. INTRODUCTION

The search for life on Mars continues. The Viking results were negative, but not everybody agrees with this conclusion. The controversy over the Viking's results is continuing. This subject is well reviewed¹. The negative results also came from the Phoenix mission². However, the latter mission indicated the presence of water on Mars, which is highly encouraging for the presence of life³. An unexpected result was the presence of perchlorates in Martian soil². Since perchlorates are powerful oxidizing agents, a possibility is considered if the organic materials are being destroyed by oxidation with perchlorates. The Viking results also indicated the oxidizing nature of the Martian soil¹. The problem caused by the internal high temperature conditions of the TEGA (Thermal and Evolved Gas Analyzer) of the Phoenix mission has been addressed^{2, 4, 5}. At high temperatures oxygen is released from perchlorates and then may promote combustion of organics in pyrolytic experiments, which would adversely influence the TEGA's experiment to detect organics^{2, 4, 5}. Oxygen release from perchlorate decomposition may have also interfered with the detection of organics in the Viking's GC-MS⁴. The presence of perchlorates on Mars was confirmed by two methods, within the WLC (Wet Chemistry Laboratory) and TEGA². The finding of perchlorates thus appears secure. The propensity of the organic materials to undergo oxidation with perchlorates under the conditions that are more relevant to the Martian surface than the drastic temperatures in the TEGA and GC-MS instruments needs to be addressed. This is the subject of our paper. The first impulse is to create model experiments for oxidation of various organics, especially those that are relevant to life, under simulated Martian conditions. This is a formidable goal, which, in time, will be achieved. The first step, however, is to look for the available data from the literature on the oxidations of organic materials with perchlorates, and see if any of these results can guide us towards design of a good model for the oxidations under the Martian conditions. In this paper we have accomplished such a goal. Much more remains to be done for the development of the model experiment, since various inorganic materials that are present on the Martian surface may be powerful catalysts for oxidation with perchlorates. The temperature factor is also of interest. If one simulates Martian temperature, the reactions are bound to be very slow. It is useful to look at the reactions which occur at higher temperatures, to obtain

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the reaction outcome within the reasonable period of time. The same is true of the concentrations of the organic materials. In Martian models such concentrations should be low. In a preliminary survey of the reactions, higher concentrations would give us quicker results. The question of pH is important as well. The Martian soil at the Phoenix Lander site was found to be slightly basic, pH 7.7, consistent with the Viking data ². However, Mars rover results implied widespread acidic soil ². The nuances of the pH of the Martian soil will have to be reflected in the model experiments. Again, in the preliminary considerations, it is useful to look first at the pH which gives the fastest reaction. Model reactions may be studied in the Atacama Desert, since it has perchlorates ⁶, and it resembles Martian surface in other aspects ⁷.

2. OXIDATION OF ORGANIC MATERIALS WITH PERCHLORATES

2.1 Background

Perchlorates, specifically perchloric acid, have two central uses in the organic chemistry. The first use is as a reagent to modify the organic compounds, for example the epoxide ring openings to the diols ^{8, 9}, and various other specific reactions ⁸. The second use is for destruction of the organic matter prior to elemental analyses. In contrast with dry ashing, the perchlorate oxidation occurs in the aqueous solution, and is thus termed a “wet” oxidation ¹⁰⁻¹¹. Its emphasis is on destruction of the organic material, not on any useful transformation. A complete destruction is desirable, since the subsequent analysis of the residues will be cleaner. The protocol for the wet oxidation was designed to this effect. The first important information is about the types of the organic compounds that are destroyed by the perchlorate oxidation. The second, and to us more exciting information, is if any organics can survive, even partially, such vigorous oxidation. If the answer to the second question is positive, we can use this as a guide for the design of the Martian model. In the first approximation we may state that the organics which survive aqueous perchlorate oxidation, under the temperature and pH conditions that were chosen for the favorable destruction rate, ought to survive on Mars with the presence of the perchlorates under less drastic temperature and moderate pH conditions.

2.2 Specific results

The authors ¹⁰ evaluated the effectiveness of wet perchloric acid oxidations of 85 different organic substances. The samples were subjected to a mixture of perchloric and nitric acids, in a 2:1 ratio, and then heated gradually from 20-120°C, at which point the nitric acid began to distil. The nitric acid was removed in the 120-140°C range. The temperature then rose quickly to 203°C, the boiling point of the perchloric acid- water azeotrope (72.5% HClO₄). The samples were maintained at this temperature for 30 min., cooled and analyzed. Screening for organic residues was done by a range of methods, including proton NMR (Nuclear Magnetic Resonance), UV (Ultra Violet) and IR (Infra Red) spectroscopy, MS (mass spectrometry) and carbon microanalysis. Certain samples were resistant to or only partially oxidized in this procedure. Approximately half of the samples retained measurable carbonaceous matter in solution. Table 1 represents selected results. In this protocol a mixture of perchloric and nitric acids was used. Sulfuric acid may be used instead of nitric. Mixtures of nitric and sulfuric acids are less commonly used because the reaction is slower and charring occurs ¹¹. Once char is formed it is extremely slow to oxidize without perchloric acid. In the perchloric-nitric mixture, the nitric acid destroys easily oxidized material, before the perchloric acid becomes sufficiently concentrated to become effective on the material that is not so easily oxidized ¹¹. The oxidation strength of perchloric acid can be varied by changing temperature and concentration. Sugars are very susceptible to the oxidation with perchlorates. Glucose, for example, undergoes oxidative degradation with 40% perchloric acid at 40°C to give a mixture of products, which include gluconic, glucaric, glucuronic, tartaric, oxalic, citric, succinic, and levulinic acids. The degradation is gradual. Total degradation of glucose and starch to CO₂ is achieved with concentrated perchloric acid at reflux temperature ¹¹. Perchloric acid can be used with glacial acetic acid, a protocol particularly useful for the determination of butterfat in milk and milk products ¹¹⁻¹². Since concentrated sulfuric acid is not used, no charring of sugars occurs. Much can be learned from the book by Smith ¹³, which summarizes applications of mixed perchloric, sulfuric and phosphoric acids

Table 1. Residual carbon content and the identity of the residues after wet perchloric acid oxidation of selected organic compounds¹⁰

Sample	% C	Identified Organic Residue
<i>Amino Acids</i>		
Glycine	20	Glycine
Alanine	67	Alanine, acetic acid
Serine	0	
Threonine	0	
Leucine	3	Leucine
Phenylalanine	0	
Tyrosine	0	
Hydroxyproline	2	
Proline	52	Proline
Cystine	0	
Methionine	52	
Histidine	9	Histidine
Tryptophan	0	
Glutamic acid	14	
Lysine	42	
Arginine	0	
<i>Heterocycles</i>		
2,2'-Bipyridine	59	2,2'-Bipyridine
Pyridine	88	Pyridine
Quinoline	72	Quinolinic acid
2,4,6-Trimethylpyridine	100	2,4,6-trimethylpyridine, chloro-dimethylpyridinecarboxylic acid
<i>Purines and Pyrimidines</i>		
Adenine	3	
Barbital	14	Acetic acid
Caffeine	26	Methylamine
Cytosine	2	
Guanine	2	Guanine
Uracil	1	
<i>Other Compounds</i>		
Anthracene	0	
Camphor	4	Camphor
Cholesterol	0	
Riboflavin	1	

in analysis, with numerous examples, such as the determination of chromium in chrome-tanned leather, determination of sulfur in organic compounds, and determination of silica in plant products, among others. Determination of chromium in leather¹⁴, sulfur in coal¹⁵⁻¹⁶, iron in blood¹⁷, and isolation of spores from coal¹⁸ are useful examples of the oxidative power of perchloric acid in the destruction of particular organic materials. Variants of the protocol were used. They include a mixture of perchloric and periodic acids¹⁶, and ammonium perchlorate in a mixture with nitric and hydrochloric acids¹⁹, among others. An interesting variation utilizes a mixture of solid perchloric acid and 50% perchloric acid for isolation of spores from coal¹⁸. More can be learned about the oxidative behavior of perchloric acid from references²⁰⁻²⁶. Naturally occurring perchlorates can be distinguished from man-made, which are typically manufactured for the military and industrial applications⁶. The manufactured perchlorates are used as solid rocket propellants, and are thus used by NASA⁶. Natural perchlorates have a unique oxygen isotope signature²⁷. This work may come in handy in the future astrobiological studies of perchlorates. Likewise, the biological reduction of perchlorate is of a definitive importance for astrobiology, since it illustrates that life is not inconsistent with the presence of perchlorates²⁸.

3. CONCLUSIONS

We have surveyed the literature on vigorous wet oxidations of various organic materials by perchlorates, under the conditions that were designed to destroy the organic matter. However, various organics survived or were only partially oxidized. Among those are several amino acids, notably glycine and alanine, which are quite resistant to this oxidation. The same is true for some heterocycles, purines and pyrimidines. In the first approximation we may state that the organics which survive aqueous perchlorate oxidation, under the temperature and pH conditions that were chosen for the favorable destruction rate, ought to survive on Mars in the presence of the perchlorates under less drastic temperature and moderate pH conditions.

REFERENCES

- [1] "An Astrobiology Strategy for the Exploration of Mars", National Research Council of The National Academies, The National Academies Press, Washington, D.C., pp. 27-35, 2007.
- [2] Hecht, M. H., Kounaves, S. P., Quinn, R. C., West, S. J., Young, S. M. M., Ming, D. W., Catling, D. C., Clark, B. C., Boynton, W. V., Hoffman, J., DeFlores, L. P., Gospodinova, K., Kapit, J., and Smith, P. H., "Detection of perchlorate and the soluble chemistry of Martian soil at the Phoenix Lander site", *Science*, 325, 64-67 (2009).
- [3] Smith, P. H., Tamppari, L. K., Arvidson, R. E., Bass, D., Blaney, D., Boynton, W. V., Carswell, A., Catling, D. C., Clark, B. C., Duck, T., DeJong, E., Fisher, D., Goetz, W., Gunnlaugsson, H. P., Hecht, M. H., Hipkin, V., Hoffman, J., Hviid, S. F., Keller, H. U., Kounaves, S. P., Lange, C. F., Lemmon, M. T., Madsen, M. B., Markiewicz, W. J., Marshall, J., McKay, C. P., Mellon, M. T., Ming, D. W., Morris, R. V., Pike, W. T., Renno, N., Staufer, U., Stoker, C., Taylor, P. Whiteway, J. A., and Zent, A. P., "H₂O at the Phoenix Landing Site", *Science*, 325, 58-61 (2009).
- [4] Sutter, B., Ming, D. W., Boynton, W. V., Niles, P. B., Hoffman, J., Lauer, H. V., Golden, D. C., "Summary of results from the Mars Phoenix Lander's Thermal Evolved Gas Analyzer", 40th Lunar Planet. Sci. Conf., Abstract 8004.
- [5] Ming, D. W., Lauer, Jr., H. V., Archer, Jr., P. D., Sutter, B., Golden, D. C., Morris, R. V., Niles, P. B., and Boynton, W. V., "Combustion of organic molecules by the thermal decomposition of the perchlorate salts: Implications for organics at the Mars Phoenix Scout Landing site", 40th Lunar Planet. Sci. Conf., Abstract 2241.
- [6] Duncan, P. B., Morrison, R. D., and Vavricka, E., "Forensic identification of anthropogenic and naturally occurring sources of perchlorate", *Environmental Forensics*, 6, 205-215 (2005).
- [7] Navarro-González, R., Rainey, F. A., Molina, P., Bagaley, D. R., Hollen, B. J., de la Rosa, J., Small, A. M., Quinn, R. C., Grunthaner, F. J., Cáceres, L., Gomez-Silva, B., and McKay, C. P., "Mars-like soils in the Atacama Desert, Chile, and the dry limits of microbial life", *Science*, 302, 1018-1021 (2003).
- [8] Fieser, L. F., and Fieser, M., "Reagents for organic synthesis", J. Wiley and Sons, Inc., New York, 1967, pp. 796-802.
- [9] Li, J. J., Limberakis, C., and Pflum, D. A., "Modern organic synthesis in the laboratory. A collection of standard experimental procedures", Oxford Univ. Press, Oxford, 2007, p. 40.
- [10] Martinie, G. D., and Schilt, A. A., "Investigation of the wet oxidation efficiencies of perchloric acid mixtures for various organic substances and the identities of residual matter", *Analytical Chem.*, 48, 70-74 (1976).
- [11] Schilt, A. A., "Perchloric acid and perchlorates", Published by the G. F. Smith Chem. Co., Columbus, OH, 1979, pp. 69-95.
- [12] Smith, G. F., and Fritz, J. S., "The determination of butterfat in ice cream employing mixed perchloric and acetic acids", *J. Dairy Science*, 31, 905-908 (1948).
- [13] Smith, G. F., "Mixed perchloric, sulfuric and phosphoric acids and their applications in analysis", Second Ed., Published by the G. F. Smith Chem. Co., Columbus, OH, 1942.
- [14] Smith, G. F., and Fritz, J. S., "Mixed perchloric and sulfuric acids in the analysis of chrome tanned leather", *J. Amer. Leather Chemists Assoc.*, 42, 195-201 (1947).
- [15] Smith, G. F., and Deem, A. G., "Determination of sulfur in coal by perchloric acid method", *Industrial and Engineering Chem., Analytical Ed.*, 4, 227-229 (1932).
- [16] Spielholtz, G. I., and Diehl, H., "Wet ashing of coal with perchloric acid mixed with periodic acid for the determination of sulphur and certain other constituents", *Talanta*, 13, 991-1002 (1966).

- [17] Smith, G. F., "Destruction of organic matter in blood fibrin and chromacized medical catgut by wet oxidation. Determination of iron in blood and of chromium in sutures", *Industrial and Engineering Chem., Analytical Ed.*, 18, 257-259 (1946).
- [18] Spielholtz, G., Thomas, L. A., and Diehl, H., "Isolation of spores by wet oxidation", *Micropaleontology*, 8, 109-110 (1962).
- [19] Smith, G. F., "Wet oxidation of organic compositions. Mixed nitric and hydrochloric acid with ammonium perchlorate as oxygen donors", *Talanta*, 11, 633-640 (1964).
- [20] Smith, G. F., "The wet ashing of organic matter employing hot concentrated perchloric acid. The liquid fire reaction", *Analytica Chimica Acta*, 8, 397-421 (1953).
- [21] Smith, G. F., and Veraguth, A. J., "The determination of chlorates in the presence of perchlorates. Reduction of chlorates in acid solution employing excess Fe(II) or As (III)", *Analytica Chimica Acta*, 17, 386-389 (1957).
- [22] Smith, G. F., "Wet oxidation of organic matter employing perchloric acid at graded oxidation potentials and controlled temperatures", *Analytica Chimica Acta*, 17, 175-185 (1957).
- [23] Diehl, H., and Smith, G. F., "Wet oxidation of organic matter employing mixed perchloric and sulphuric acids at controlled temperatures and graded high potentials", *Talanta*, 2, 209-219 (1959).
- [24] Smith, G. F., "The role of 70-80% perchloric acid as oxygen donor and the oxidation potentials made available", *Talanta*, 15, 489-496 (1968).
- [25] Smith, G. F., "Perchloric acid. Authentic, scientific and practical considerations relative to its use as an important research and routine analytical chemical reagent with special reference to rapidity, accuracy and economy", Vol. 1 (March, 1931), Second Edition (January 1933), Published by G. F. Smith Chemical Company, Columbus, OH, 1933.
- [26] Smith, G. F., and Diehl, H., "A new general procedure in the low-temperature wet oxidation of organic compositions. Perchloric and periodic acids as oxidants. 'The Periodic acid liquid fire reaction' ", *Talanta*, 4, 185-193 (1960).
- [27] Bao, H., and Gu, B., "Natural perchlorate has a unique oxygen isotope signature", *Environ. Sci. Technol.*, 38, 5073-5077 (2004).
- [28] Gingras, T. M., and Batista, J. R., "Biological reduction of perchlorates in ion exchange regenerant solutions containing high salinity and ammonium levels", *J. Environ. Monit.*, 4, 96-101 (2002).