standard calcite, aragonite (*9*), and carbonate sediments sampled from the slope adjacent to station 10 (Fig. 1). The sediments were raised from a depth of 2000 m and sieved to the size range 32 to 42 mesh (0.35 to 0.50 mm) before use in the saturometer cell. X-ray diffraction analyses revealed no traces of aragonite in the calcite standard, whereas calcite traces were present in the standard aragonite. The sediment separate used in experiments was found to be pure calcite; however, traces of aragonite were found in the finest fraction of the sediment.

The data (Fig. 2) show a correlation between the degree of carbonate saturation of seawater and the carbonate content of the sediments at the same depth. The results of the in situ carbonate measurements suggest that the intermediate waters of the central Pacific, between approximately 1000 and 3500 m, are close to saturation ($IP/K'\text{sp} \approxeq 0.95$) with respect to calcite (*10*). At about 3750 m, the degree of saturation profile exhibits a break and deviates toward undersaturation. Measurement of seawater saturation with respect to the local sediments duplicates that with respect to standard optical calcite, except that deviation toward undersaturation seems to start at a somewhat shallower depth. However, the significance of this difference cannot be assessed because of the scatter in the data and the small number of replicate measurements.

The profile of seawater saturation with respect to aragonite parallels that with respect to calcite, but is shifted toward undersaturation, because aragonite is more soluble than calcite (*7*). Hence, there is good consistency between the experiments conducted with calcite, aragonite, and local sediments. Further, the data from station 11 correlate well with the data from station 10, which suggests similar carbonate solubility reactions along the two profiles.

The data reported here reveal that the zone between high and low carbonate content in the sediments coincides with the break in the calcite-seawater saturation profile (Fig. 2). This observation is in accord with data on carbonate dissolution rates in the central Pacific obtained by measuring the weight loss of carbonate material suspended for several months on mooring lines (*11*). Dissolution rates of both optical grade calcite and foraminiferal ooze were found to increase rapidly below approximately 3700 m.

Conceivably, the carbonate compensation depth may be depressed with respect to the break in the calcite saturation profile in areas with high productivity, that is, a high sedimentation rate of biogenic $CaCO_3$. We believe that further studies are essential before this can be proved.

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9. Materials were obtained from Ward's (Monterey, California). The calcite was an optical grade mineral from Chihuahua, Mexico, and the aragonite was from Farka, Switzerland. The minerals were crushed, sieved to the size range 32 to 42 mesh (0.35 to 0.50 mm), washed, and then dried overnight in an oven at 105°C.
10. Laboratory experiments seem to indicate that the slight undersaturation observed may be due to the presence of traces of a high-solubility phase in the carbonate material used, and does not represent the characteristics of the bulk solid.
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Hot Hydrogen Atoms: Initiators of Reactions of Interest in Interstellar Chemistry and Evolution

Abstract. *Photochemically generated hot hydrogen atoms initiate reactions with simple molecular substrates including methane to produce organic alcohols, amines, acids, amino acids, and other compounds. The typical quantum yields for the formation of amino acids are 2×10^{-5} to 4×10^{-5}. Hot hydrogen atoms may be important initiators of reactions in interstellar space and in planetary atmospheres.*

Considerable effort has been made to elucidate the pathways by which biologically significant molecules arose prior to the existence of living things (*1*). Many of the techniques consisted of conventional electric discharge and ultraviolet irradiation or the heating of mixtures of various simple molecules such as NH_3, CH_4, and water. In most cases, prime areas of interest included the chemical synthesis of amino acids, purines, and pyrimidines, and ultimately polypeptides and polynucleotides. In a more recent effort, H_2S irradiated in the presence of a mixture of simple gases yielded certain amino acids (*2*). In addition, there is considerable interest in the mechanism of formation of molecules in interstellar space. We report here the formation of some amino acids and other organic compounds initiated by "hot" hydrogen atoms in mixtures of simple gases chosen from among CH_4, C_2H_6, H_2O, and NH_3. The hot hydrogen atom donors include both H_2S and CH_3SH.

Hot hydrogen atoms are those with kinetic (or translational) energy in excess of that to be expected if they were in thermal equilibrium with the surroundings. In our case, they are generated by photolysis of the donor molecules as

$$CH_3SH \xrightarrow{h\nu} CH_3S\cdot + H\cdot \text{ (hot)} \quad (1)$$

The excess kinetic energy of hydrogen from HR is

$$E_k(H) = (h\nu - D - I)\frac{M_R}{M_{HR}} \quad (2)$$

where $h\nu$ is the energy of light, D is the bond dissociation energy, I is the internal energy remaining in the fragment R, and M is the mass. For the donors used, the mass ratio is essentially equal to 1 and the amount of internal energy left in R is approximately 5 to 17 percent of the maximum kinetic energy of the hydrogen atom over the wavelength band used for the photolysis (*3*) (220 to 280 nm). Based on the foregoing, the average kinetic energies of the hot hydrogen atoms range from approximately 17 to 32 kcal/mole (onset of H_2S absorption at 266 nm). These hot hydrogen atoms lose the excess kinetic energy by either nonreactive or reactive collisions with the surrounding molecules (*4*). In our case the chemical reaction of interest, based on the nature of the substrates and energies of the hot hydrogen atoms, is

$$RH + H\ (\text{hot}) \rightarrow R\cdot + H_2 \qquad (3)$$

All gases used were chemically pure grade (Matheson), and the H_2O was both distilled and deionized. The C_2H_5OH was absolute pure grade (U.S. Industrial Company). In one reaction, CH_4 of ultrahigh purity (minimum purity 99.97 percent, Linde Company) was used to provide assurance that the products were not formed by reactions of contaminant C_2H_6. Figure 1 shows the reaction vessel and accompanying circulation system. The total volume was approximately 6 liters. The temperature of the heated side (coil A) was kept at 150°C, and the remainder of the system was maintained at 30° or 50°C. When water was used, 3 ml was introduced into trap B and carefully degassed. The pressure of each gas reactant was measured with a Bourdon gauge (mercury gauges can introduce mercury vapor and cause mercury photosensitized reactions). After all gases had been introduced, heating element A was turned on and the gases were allowed to mix for about 12 hours. A small portion of gas was removed for analysis prior to reaction. After the completion of a reaction, a small portion of gas was transferred to storage bulbs and trap B was cooled with ice while the gas mixture was circulated for several hours. Nitrogen was then introduced to a total pressure of 1 atm, and the trap was disconnected; one to two drops of product were removed from the trap for analysis. For those reactions for which amino acids were expected, the entire system was washed with water; the wash water was then filtered and concentrated by rotary evaporation at 50°C. The concentrated solution was passed through a Dowex 50-X4 ion-exchange resin. The eluent was dried and analyzed for amino acids with a Technicon amino acid analyzer. Organic acids were analyzed according to the method of Gerhke and Goerlitz (*5*) except that the black silver salt was isolated from the solution for esterification instead of the water solution. All reactants and products (except amino acids) were analyzed by means of a combined gas chromatograph–mass spectrometer (LKB model 9000).

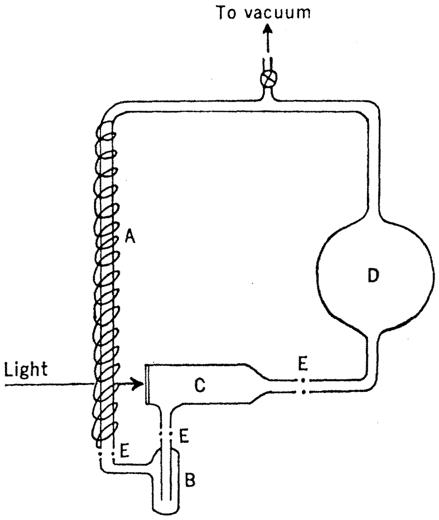

Fig. 1. Experimental apparatus; *A*, heating coil; *B*, cold trap; *C*, reaction vessel; *D*, 5-liter flask; and *E*, O-ring joint.

The light sources for the photolysis of the H_2S or CH_3SH were 1000-watt xenon or 500-watt mercury lamps coupled with a filter system [water, Corning filter 9-54, and Cl_2 (5-cm cell) at 1 atm]. The band pass was from 220 to 280 nm with a maximum of 54 percent transmittance at 252 nm. In some cases, a yellow film would form on the window but would disappear if the light source was turned off and the gases were allowed to circulate for some period.

Table 1 presents a summary of all experiments completed to date with the results. Brief comments on some of the experiments follow.

Experiment II was carried out in the absence of light, but we utilized the same procedures as for all other experiments for which amino acids were analyzed. No amino acids were detected, and this experiment thus provides a blank test.

Experiment IV was done to provide some insight into the mechanism and intermediates of the reaction giving amino acids. The products C_2H_5OH (or CH_3OH), CH_3COOH, and C_2H_5COOH were detected.

Experiment V was carried out because C_2H_5OH was produced in experiment IV. A larger number of amino acids were produced in experiment V than in experiment III. The real significance of this comparison between experiments III and V regarding the number of amino acids is not clear because of a change in the light source. The quantum yield of amino acids was $\sim 2 \times 10^{-5}$ to $\sim 3 \times 10^{-5}$.

Experiment VI provided an interesting result. The primary difference between this experiment and experiment V was the addition of water plus some liquid C_2H_5OH. However, the consequence was quite marked. Roughly equal amounts of the various amino acids were produced in experiment V, whereas in experiment VI approximately 95 percent was glycine (0.05 mg). However, the number and nature of the amino acids was the same in both experiments. The quantum yield of formation of amino acids was $\sim 3 \times 10^{-5}$ to $\sim 4 \times 10^{-5}$.

Experiment VIII is important in that a substrate containing only one carbon atom, CH_4, was sufficient for the production of amino acids of the same nature and number as from C_2H_6. Very pure CH_4 (99.97 percent minimum purity) was used so that contaminant C_2H_6 could be ruled out as the carbon source.

Experiment VII shows that alkyl amines can be produced in hydrocarbon-NH_3 systems induced by hot hydrogen atoms.

Several important conclusions can be drawn from the results of these experiments. (i) Hot hydrogen atoms can initiate reactions among simple molecules to produce biomolecules of significance. (ii) The one-carbon reactant CH_4 can participate in reactions leading to the formation of amino acids containing more than one carbon atom. This is important because large amounts of CH_4 existed on the primitive earth, are now present near some planets, and may occur in interstellar space (clouds). The two-carbon reactant C_2H_6 is not a necessary reactant. (iii) In addition to amino acids, other important molecules can be produced by reactions initiated by hot hydrogen atoms such as CH_3OH, C_2H_5OH, CH_3COOH, C_2H_5COOH, and organic amines. Furthermore, it appears that some of these could be intermediates in the production of the amino acids. (iv) The first intermediate formed after attack by the hot hydrogen atom is a free radical. These in turn attack other reactants giving other free radicals. In some cases, the radicals combine to give products such as C_2H_5OH, $C_2H_5NH_2$, or CH_3NH_2, but in other cases, such as for the amino acids, the mechanism is not known. (v) The ambient temperature in interstellar space and clouds is very low so that chemical reactions either would not occur or would be extremely slow. However, the conditions for the formation of molecules in interstellar space are substantially displaced from thermodynamic equilibrium (*6*). It is just this possibility of a nonequilibrium condition in which some atoms are hot (0.5 to 50 ev) and not in thermal equilibrium that would permit reactions of relatively high activation energies to occur which ordinarily could not (*7*). The importance of such a possibility is not limited to these conditions but is also important in planetary atmospheres where the number of such reactions is still higher because of the greater density of molecules. Hydrogen sulfide is present in interstellar space and was probably present on the primitive earth (*8*). However, any other hydrogen atom (hot) source would be equally effective.

We wish to comment briefly on

Table 1. Summary of the results of experiments on hot hydrogen atoms.

Reactants* (pressure in cm-Hg)	Lowest temperature	Irradiation time	Light source	Amino acids detected	Other products detected
			Experiment I		
$CH_3SH = 42.5$ $C_2H_6 = 12.5$ $NH_3 = 12.5$ $H_2O = 9$	30°C	14 days	1-kw Xe lamp	Aspartic acid Glycine Cysteine	CH_3SSH, CH_3SSCH_3, and other amino compounds that are either more acidic or more basic than the normal amino acids
			Experiment II		
$CH_3SH = 42.4$ $C_2H_6 = 12.5$ $NH_3 = 12.5$ $H_2O = 9$	50°C for 14 days	None	None	None	Other amino compounds more acidic than all the protein amino acids but no protein amino acids†
			Experiment III		
$H_2S = 47.5$ $C_2H_6 = 12.5$ $NH_3 = 12.5$ $H_2O = 9$	50°C	14 days	1-kw Xe lamp	Aspartic acid Glycine Glutamic acid Alanine Cysteine	Sulfur and maybe one amino compound more acidic than the protein amino acids and possibly some more basic than the protein amino acids
			Experiment IV		
$CH_3SH = 37.5$ $C_2H_6 = 37.5$ $H_2O = 9$	50°C	14 days	500-watt, high-pressure Hg lamp	None expected	CH_3COOH, C_2H_5COOH, C_2H_5OH,‡ CH_3SSCH_3, CH_3SSH
			Experiment V		
$H_2S = 25$ $NH_3 = 12.5$ $C_2H_5OH = 7$	30°C	21 hours	500-watt, high-pressure Hg lamp	Serine or threonine Glycine Alanine Aspartic acid Valine Glutamic acid Leucine Isoleucine Proline	Sulfur and possibly some amino compounds more basic than the protein amino acids
			Experiment VI		
$H_2S = 25$ $NH_3 = 12.5$ $C_2H_5OH = 7$ (2 ml) $H_2O = 3.2$	30°C	37 hours	500-watt, high-pressure Hg lamp	Glycine Serine or threonine Aspartic acid Valine Leucine Isoleucine Glutamic acid Proline (trace amount) Probably alanine	Sulfur and some other amino compounds that are either more acidic or more basic than normal amino acids
			Experiment VII		
$CH_3SH = 25$ $CH_4 = 25$ $NH_3 = 25$	Room temperature	14 days	1-kw Xe lamp	None expected	CH_3SSH, CH_3SSCH_3, CH_3NH_2§
			Experiment VIII		
$H_2S = 25$ $NH_3 = 25$ $CH_4 = 25$‖ $H_2O = 9$	50°C	113½ hours	500-watt, high-pressure Hg lamp	Aspartic acid Serine or threonine Glutamic acid Proline Glycine Alanine Valine Leucine Isoleucine	Sulfur and possibly some amino compounds either more basic or more acidic than the protein amino acids

* In all experiments, the first molecule listed (H_2S or CH_3SH) is the source of the hot hydrogen atom by photolysis according to Eq. 1. † We carefully determined blanks as follows. In one case, after the thermal reaction the same procedure was followed as for all other cases except for passage through the Dowex column. In this case, four peaks were detected prior to the detection of aspartic acid and other protein amino acids. In another blank, water plus NH_3 used to wash the apparatus after the hot hydrogen atom reactions was passed alone through the Dowex column. Three peaks were detected prior to the detection of aspartic acid and other protein amino acids. Finally, the reference amino acid solution was carefully analyzed and one peak was detected prior to the detection of aspartic acid and other protein amino acids. In all cases where any of these peaks apparently appeared from the hot hydrogen atom reactions, they were five to ten times more intense than in the blanks but still were not considered as confirmed reaction products. ‡ If CH_4 is used, CH_3OH is produced but analyses for carboxylic acids were not carried out. § If C_2H_6 is used, $C_2H_5NH_2$ is produced. ‖ Ultrahigh pure grade, minimum purity 99.97 percent (Linde Company).

some of these results relative to other comparable published work (*2*). We have demonstrated that amino acids can be produced from a hydrocarbon substrate with only one carbon atom, CH_4, whereas Sagan and Khare (*2*) have stated that the two-carbon substrate C_2H_6 is required for the production of amino acids. They have also suggested that the amino acids from such experiments are very likely not primarily made free but result from the hydrolysis of nitriles or polypeptides (*2*). Our conditions never resulted in the formation of observable amounts of polymer, nor were acid or basic hydrolysis conditions ever employed. Furthermore, we observed the production of amino acids in two experiments utilizing C_2H_5OH as one of the substrates and, considering the nature of the experiments, it would appear that no nitrile-containing molecules could be generated. We detected no HCN or nitrile-containing molecule at the completion of any experiment either in the gas phase or in solution (water trap), using gas chromatographic–mass spectrometric analysis. In view of these facts, we believe that the major yield of amino acids is produced not from the hydrolysis of a polymer but directly by a unique mechanism or mechanisms not hitherto considered.

Note added in proof: An experiment similar to experiment VI was repeated and the products subjected to esterification and acylation to form *N*-trifluoroacetyl isopropyl esters. Gas chromatography–mass spectrometry analysis positively identified the protein amino acids glycine, alanine, valine, leucine, aspartic acid, and glutamic acid plus some other nonprotein amino acids. This constitutes the first verification of protein amino acids from such reactions.

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Global Trends in Total Atmospheric Ozone

Abstract. *Analyses of the mean monthly global distributions of total ozone for the 13-year period from 1957 through 1970 reveal an upward trend of about 7.5 percent per decade in the Northern Hemisphere and about 2.5 percent per decade in the Southern Hemisphere. The increase seems to have started about March 1961 in the Northern Hemisphere and about September 1961 in the Southern Hemisphere. The cause of these trends is at present unknown.*

Studies by Komhyr *et al.* (*1*) of the temporal changes in the amounts of total ozone at a number of individual stations have shown that there was an increase during the 1960's over many parts of the world. The average increase for ten North American stations was determined to be about 5 percent per decade. Calculations based on data from additional individual stations showing similar results have also recently been discussed in the literature (*2*). It is of considerable concern to determine whether or not these reported long-period ozone changes represent a worldwide trend.

Ozone is a minor constituent in the atmosphere, and its principal importance derives from the fact that, even in relatively small amounts, it absorbs solar ultraviolet radiation that would otherwise penetrate down to the earth's surface and have disastrous effects on the biosphere (*3*). In addition, this absorption of solar radiation is responsible for the warm region at the top of the stratosphere (at about 50 km) and thereby helps to determine the thermal structure of that part of the atmosphere. Since ozone is a relatively inert gas below about 25 km, it represents a good tracer substance for atmospheric motions and has been a subject for considerable research by meteorologists and aeronomers (*4*). Added interest in studies of atmospheric ozone stems from recent suggestions that exhaust products from high-flying aircraft might somehow affect the stratospheric ozone distribution and thus change the ultraviolet shielding property of the atmosphere, or inadvertently modify the earth's climate (*5*).

We have been involved in a program of analysis of all of the available total ozone data and have prepared mean monthly maps of the total ozone distribution for each hemisphere covering the 13-year period from July 1957 to July 1970. From the individual monthly maps we have extracted grid point values (for each 10° of latitude and 20° of longitude) of total ozone. These values provide the basic data for the derived global ozone trends as described below.

The average total ozone measured from the earth's surface (that is, the total amount of ozone in a vertical column) is about 300 matm cm (*6*). Although some observations of total ozone were made as early as 1905, data sufficient to enable one to determine its global distribution only became available at the start of the International Geophysical Year (July 1957). At that time routine observations of total ozone were being made at about 50 stations. Since then an increasing number of stations have been involved in the international ozone-observing network, and, by 1970, total ozone data were at hand for at least part of the 13-year period from 150 stations, about 80 percent of them in the Northern Hemisphere (*7*) (see Fig. 1). The distribution of these stations, both geographically and with time, is somewhat uneven. For example, most of the stations in each hemisphere are located in mid-latitudes. Also, there are no data from the large ocean areas except for the observations from a few island stations.

The standard observing instrument used in the ozone network is the Dobson spectrophotometer (*8*), although observers at a few stations, notably in