PHOTOCHEMICAL REACTIONS IN INTERSTELLAR GRAINS
PHOTOLYSIS OF CO, NH$_3$, AND H$_2$O

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Abstract. A simulation of the organic layer accreted onto interstellar dust particles was prepared by slow deposition of a CO:NH$_3$:H$_2$O gas mixture on an Al block at 10 K, with concomitant irradiation with vacuum UV. The residues were analyzed by GC–MS, HPLC, and near IR; a reaction pathway leading from NH$_3$ to complex alcohol, fatty acid, and amide products in 27 stages is postulated. The astronomical relevance and significance of the observations are discussed.

1. Introduction

Interstellar gas and grains comprise about 10 % of the mass of the stars in our galaxy. A typical grain consists of a silicate core and a mantle. If the grain is present in a diffuse cloud of interstellar gas, the mantle consists of relatively non-volatile higher molecular weight organic compounds. Grains in denser clouds of interstellar dust are believed to be coated with volatile inorganic and organic compounds (H$_2$O, CH$_4$, CO$_2$, CO, NH$_3$) along with the higher molecular weight organics. Previous studies (Greenberg, 1982a) focussed on modeling the photochemical processes which may occur on grains when the volatile inorganic compounds are converted to the non-volatile organic compounds ('yellow stuff') (Greenberg, 1984).

With the increase in evidence that interstellar grains are the basic building blocks of comets (Greenberg, 1982b, 1983; A'Hearn and Feldman, 1984; Whipple, 1983) and with the realization that comet collisions with the earth may have occurred at a much higher frequency than earlier assumed (Davis *et al.*, 1984; Whitmore and Jackson, 1984), it may be presumed that interstellar dust chemistry played an important role in the early chemistry of the earth. The results of the chemical analysis of the non-volatile organics formed by photolyses of CO, NH$_3$, and H$_2$O at 10 K is presented in this report. The products at 10 K are compared with those observed at 77 K and 298 K.

2. Interstellar Dust

The chemical evolution of interstellar grains and their contribution to the composition of comets and to other members of the solar system such as carbonaceous meteorites

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has been detailed elsewhere (Greenberg, 1983). We summarize here briefly a few key stages in this evolution.

The grains which contain the bulk of the organics start out as elongated silicate particles of mean radius $\sim 0.05\,\mu m$ formed in the atmospheres of cool evolved stars and are blown out into space. These little 'rocks' cool to 10 K in space and are the seeds on which atoms and molecules of the gas condense within molecular clouds to form mantles. Along with the condensation, the ultraviolet light from distant stars photolyzes the mixture creating new molecules and radicals. In this way each grain accumulates a complex organic mantle which is partially eroded when the cloud becomes less dense (diffuse) and is regenerated when the cloud is more dense (molecular). This passage from the diffuse cloud to the molecular cloud phase occurs more than 20 times during the grain's lifetime with each phase lasting, in the mean, some 100 million years. Thus the ultimate mantle material is a result of photolysis which has occurred over some billions of years.

The volatile molecular mantle of interstellar grains is an evanescent component which is observed in molecular clouds but which appears to be rapidly destroyed in diffuse clouds, leaving only a non-volatile mixture in the mantle. The wavelength dependence of the extinction of starlight leads to a grain size which requires that this mantle be about $0.07\,\mu m$ thick on the $0.05\,\mu m$ radius silicate core. This is the model which we adopt for quantitative calculations. Based on this model, about 20% of a comet is predicted to consist of the yellow stuff (Greenberg, 1982b). This prediction is consistent with the 'missing carbon mystery' (Delsemme, 1982).

3. Experimental

3.1. PREPARATION OF RESIDUES, PHOTOLYSIS AT 10 K

The details of some of the laboratory procedures have been published earlier (Hagen *et al.*, 1979). Relevant aspects are summarized below. The process of accretion of interstellar gases on a dust particle is simulated by slow deposition of a gas mixture on an aluminum block at a temperature of 10 K. The actual laboratory temperature may vary above this by as much as 5 degrees. The photolysis of the accreting gases by interstellar UV photons is simulated by exposing the sample during deposition by vacuum ultraviolet radiation produced by a microwave stimulated hydrogen flow lamp. One hour of irradiation in the laboratory is equivalent to 1000 years in the less dense regions of interstellar space.

3.1.1. *Preparation of Gas Mixture*

The gas mixture is prepared by filling a bulb sequentially with gases which have increasing vapor pressures. The bulb is connected via a valve to a tube which has been filled with the required amount of gas. The valve is then opened to let the gas in. Starting with an evacuated bulb, this process is repeated for each gas component and, in each case, an overpressure between the gas in the tube and in the bulb is maintained to prevent back flow into the tube.

Gas mixtures for the experiments reported on here have been limited to CO, NH_3, and H_2O in various proportions. The glass bulb is connected to the deposition tube by a metal O-ring compression connector. The deposition tube (1 mm I.D.) passes through the vacuum chamber containing the aluminium block cold finger and is directed towards one side of the cold block. The gas flow is regulated by a needle valve and controlled by a flow meter at a rate of about 1.5×10^{16} molecules s^{-1}. During deposition the pressure in the vacuum chamber rises only slightly, indicating that almost all the molecules are directly frozen on the surface of the block. The flux of the hydrogen discharge lamp is about 1.5×10^{15} photon $cm^{-2} s^{-1}$ with peaks of intensity at 160 nm and at $L\alpha$ (122 nm). This is about one tenth the molecular deposition flux thus making it equivalent to radiation in a molecular cloud whose hydrogen density is $10^4 cm^{-3}$ and whose ultraviolet flux is a factor of a thousand less than its free space mean value. The total deposition/irradiation time for each cube side was 24 hr after which time the sample was about 50 μm thick. We note that the photon penetration is less than the sample thickness after about 0.5 μm so that every photon is absorbed.

After completing the deposition on all four sides, the sample is slowly warmed to room temperature while maintaining vacuum. In order to prevent runaway chain reactions which blast off the material (d'Hendecourt et al., 1982), warming is ceased whenever the vapor pressure appears to increase rapidly and to allow the free radicals to anneal out. In general, the reaction vessel is warmed in steps of about 5 to 10 K and at each stage allow about $\frac{1}{4}$ hr annealing time. Above a temperature of 60 K, by which temperature the major fraction of free radicals have already diffused and reacted (Hagen, 1982), the refrigerator is turned off and the sample is allowed to rise to room temperature over a 10 hr period. At room temperature small translucent spots (about 0.5 mm) of non-volatile yellow colored residue material, which we call organic refractory, are left on the block.

The vacuum chamber is purged with nitrogen and the block is encased in a sealed glass chamber in a nitrogen atmosphere and kept for further analysis. The sample (< 1 mg) was rinsed from the aluminum block with about 0.5 ml of Fisher certified ACS methanol. An aliquot of the extract was used for high performance liquid chromatography (HPLC) analysis and an aliquot was used for combination gas chromatographic-mass spectrometric (GC–MS) analysis. The methanol was removed from both aliquots by evaporation under vacuum, using a rotary evaporator, at room temperature and the samples were dried in a vacuum desiccator overnight.

Compounds were identified by direct comparison with authentic samples obtained from commercial sources. Glyceramide was prepared from acrylonitrile by the procedure of Payne and Williams (1961): mp. 88–90 °C, lit. mp. 92 °C. The 200 MHz ^{1}H NMR spectrum of the product was consistent with the assigned structure.

3.2. PHOTOLYSIS AT 298 K AND 77 K

These experiments were performed by Dr H. Khwaja at RPI using procedures developed previously for PH_3 photolysis (Ferris et al., 1984). The CO and NH_3 were degassed by three freeze-pump-thaw cycles before use. A mixture of 101 torr CO and

19.8 torr NH_3 was irradiated at 298 K for 12 hr in the first experiment and 453 torr of CO and 9 torr of NH_3 were mixed and then irradiated at 77 K in the second experiment. The vapor pressure of CO is 400 torr and the vapor pressure of NH_3 is essentially 0 torr at 77 K so a mixture of 53 torr of CO and 9 torr of NH_3 condensed on the walls of the photolysis cell in this experiment. The samples were irradiated in a 10 cm × 2.2 cm diameter cylindrical quartz cell using a low pressure mercury lamp with principal emissions at 185 and 254 nm. After the photolysis was terminated, the cell was immersed in a dry ice-acetone bath (195 K) and the volatiles were pumped off. The residue was rinsed from the cell with 1 ml of methanol-water (9 : 1) and concentrated to dryness at room temperature using a rotary evaporator. The residues were silylated as described below for GC-MS analysis.

3.3. GC-MS ANALYSIS

To the dried residue was added 50 μl of pyridine and 50 μl of Regisil™ (a mixture of 99% bis(trimethylsilyl)trifluoroacetamide and 1% trimethylchlorosilane obtained from Pierce, Rockford, ill.) and the mixture was heated at 60 °C for 15 hr. Samples (5 μl) were chromatographed on a 6 ft, 2 mm ID, glass column containing 3% OV-17 on 80–100 mesh Chromosorb W using a Varian 2400 FID chromatograph with nitrogen carrier gas and a temperature program of 70–280 °C at 10 °C min^{-1}. GC–MS was performed on a Carlo Erba GC coupled to a Kratos MS–25 mass spectrometer with an SGE open-split interface. The sample was injected directly on a J&W DB–5 (5% phenyl silicone and 95% methyl silicone) capillary column (30 m × 0.2 mm ID). The column was maintained at 65 °C for 10 min before temperature programming at 6 °C min^{-1} to 280 °C. The open split was swept with helium from 2 min until 16 min into the run. The mass spectrometer was operated at an ionization voltage of 70 eV, a trap current of 0.26 mA, a source voltage of 2 kV and a source temperature of 270 °C.

3.4. HPLC ANALYSIS

The dried sample was dissolved in 1 ml of double distilled water and 5 μl aliquots were injected on a Waters μ Bondpak C–18 column, 30 cm × 7.8 mm, and double distilled water was used as the mobile phase. The separations were as efficient as those reported using 1% KH_2PO_4 (pH 6) (Murray *et al.*, 1982). The present method has the advantage that the purified materials can be collected and recovered after removing the water by freeze drying. The amides in the product mixture were detected using a Waters Lambda-Max 481 variable wavelength detector operating at 200 nm.

4. Results and Discussion

4.1. REACTION PRODUCTS

In the first reported studies on the photolysis of NH_3 in a CO matrix using a hydrogen discharge lamp it was observed the formaldehyde, formamide, cyanic acid and the formyl radical were reaction products (Miligan and Jacox, 1965). In more recent studies CO_2, formic acid, and the carboxyl radical were detected in addition to those

TABLE I

Products from the photolysis of $CO:NH_3:H_2O$ mixtures[a]

			10 K			77 K	298 K
			$CO:NH_3$ 5:1	$CO:NH_3:H_2O$ 5:1:1	$CO:NH_3:H_2O$ 5:1:5	$CO:NH_3$ 6:1[b]	$CO:NH_3$ 5:1
	Compound	Formula					
1.	ethylene glycol	$HOCH_2CH_2OH$	trace[c]	4[c]	2[c]	1[c]	trace[c]
2.	lactic acid	$CH_3CH(OH)CO_2H$	3	2	2	1	1
3.	glycolic acid	$HOCH_2CO_2H$	1	2	47	—	trace
4.	hydroxy-acetamide	$HOCH_2CONH_2$	18	14	7	1	trace
5, 6	urea/ biuret	$NH_2CONH_2/$ $NH_2CONHCONH_2$[d]	13	10	2	68	48
7.	oxamic acid	$NH_2\overset{O}{\overset{\|}{C}}CO_2H$	7	6	6	—	1
8.	glycerol	$HOCH_2CH(OH)CH_2OH$	1	2	4	5	1
9.	oxamide	$NH_2\overset{OO}{\overset{\|\|}{C}C}NH_2$	49	53	14	25	50
10.	glyceric acid	$HOCH_2CH(OH)CO_2H$	1	1	9	1	—
11.	glycer-amide	$HOCH_2CH(OH)CONH_2$	9	5	8	—	—

[a] Listed in order of elution from the GC trace shown in Figure 1. Yields are given in percent based on the response of the mass spectrometer assuming the same sensitivity for each compound.

[b] Approximate ratio in condensed phase. See Experimental Section for details.

[c] Identification of ethylene glycol not certain due to interferences.

[d] The TMS derivatives of biuret and urea do not separate in our system. The presence of each was confirmed by HPLC.

products reported by Milligan and Jacox (1965) when a mixture of $CO:NH_3:H_2O$ and CO_2 was irradiated at 10 K (Hagen *et al.*, 1979). Photolysis of mixtures of CO and NH_3 at room temperature resulted in the formation of formamide, ammonium cyanate, HCN, urea, biurea and semicarbazide (Ferris *et al.*, 1974; Hubbard *et al.*, 1975).

Oxamide, hydroxyacetamide, urea, biuret, glyceramide, and oxamic acid are the major non-volatile reaction products obtained from the photolysis of a solid matrix of $CO:NH_3$ at 10 K using a 160 nm light source and then warming the mixture to room temperature in vacuo (Table I). These compounds were indentified by GC–MS analysis of their trimethylsilyl derivatives (Butts, 1972). A typical GC–MS ion monitor trace is given in Figure 1 with the relative intensities based on the total ion current between 180–500 mass units.

In some but not all of the photolysis experiments, 1,2,4-trichlorobenzene and the bistrimethylsilyl derivatives of catechol and *ortho*-and/or *para*-cresol were identified by their mass spectra. The source of the 1,2,4-trichlorobenzene was not established. It was not detected in a control where the complete experiment was performed except the mixture was not irradiated with ultraviolet light. However, the trimethylsilyl derivat-
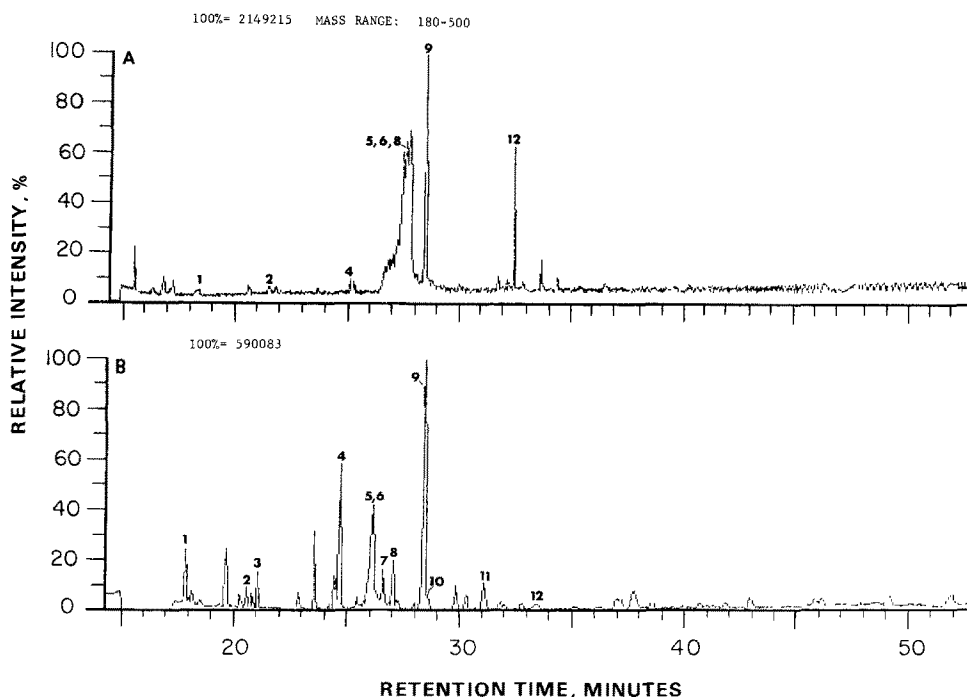
Fig. 1. Mass spectrometric ion monitor trace based on the total signal in the 180–500 mass range. The compounds identified as their TMS derivatives are numbered and listed in Table I. (A) 5 : 1 CO:NH$_3$ at 298 K. (B) 5 : 1 CO:NH$_3$ at 10 K. The structure of 12 was not established.

ives of the following compounds were detected in this control and were later found to be due to their presence in trace amounts in the methanol used to dissolve the sample: ethylene glycol, propylamine, cresol, glycerol and an unknown with a m/e of 186. It is not clear whether glycerol and ethylene glycol are formed by the photochemical experiments or they are just contaminants in the methanol. This will be the subject of future studies.

The relative amounts of urea and biuret could not be determined by GC–MS because the gas chromatographic procedure converts biuret to a compound similar to but not identical with the silyl derivative of urea. Table II lists the retention indices (Kovats, 1958) and characteristics ions for all the compounds looked for in the reaction mixtures.

Some of the GC–MS findings were confirmed by comparison of the HPLC retention times of the underivatized product mixture with that of authentic samples (Figure 2). Biuret and urea were separated by HPLC and were shown to have the same retention times as components of the photolysis mixture by coinjection of authentic samples with the mixture. Further evidence for the presence of urea and biuret is their previous identification in studies of the gas phase photolysis of CO—NH$_3$ mixtures (Ferris *et al.*, 1974; Hubbard *et al.*, 1975).

Three minor products, glycolic acid, glyceric acid, and lactic acid were also identified

TABLE II

Products searched for in photolysis mixture

	Kovats index	Molecular weight	Characteristic ions
Ethylene glycol (TMS)$_2$	1056	206	191
Propane diols (TMS)$_2$	1071	220	205
	1121		205, 177
Lactic acid (TMS)$_2$	1149	234	190, 191, 219
Glycolic acid (TMS)$_2$	1161	220	161, 177, 205
Propylamine (TMS)$_2$	1200	203	203, 174, 144
Cresol (TMS)	1210	180	180, 165, 135, 91
Oxalic acid (TMS)$_2$	1217	234	190, 219
1,2,4-Trichlorobenzene	1223	181	184, 182, 181
Hydroxyacetamide (TMS)$_2$	1235	219	188, 204, 219
Valine (TMS)$_2$	1231	261	144, 218, 246
Urea (TMS)$_2$	1262	204	189, 204, 171
Biuret (TMS)$_3$	1262	319	171, 189, 204, 186
Oxamic acid (TMS)$_2$	1271	231	174, 189
Leucine (TMS)$_2$	1277	275	158, 218, 232, 260
Glycerol (TMS)$_3$	1282	308	205, 218, 293
Glycolaldehyde(dimer) (TMS)$_2$	1285	264	161, 191, (249, 263
	1290		tr.)
Proline (TMS)$_2$	1305	259	142, 216, 244, 259
Oxamide (TMS)$_2$	1335	232	174, 189, 217, 232
Glyceric acid (TMS)$_3$	1340	322	307, 292, 322, 189, 205
3-Aminopropanol (TMS)$_3$	1362	291	174, 248, 291, 276
Serine (TMS)$_3$	1388	321	204, 218, 278, 306
Glyceramide (TMS)$_3$	1430	321	306, 189, 205, 216
Semicarbazide (TMS0)$_4$	1440	363	188, 348, 363, 272, 291
Glyceraldehyde(dimer) (TMS)$_4$	1708	468	204, 218, 234, 307,
	1734		363, 378, 453, 468

by GC–MS. It was not possible to identify these compounds by HPLC because of their weak ultraviolet absorption at 200 nm. The formation of lactic acid was initially surprising since it was difficult to imagine the reduction of CO to a methyl group. However, the recent report of the conversion of CO to CH_4 and compounds containing methyl groups (e.g., CH_3OH, CH_3CHO) (Bar-Nun and Chang, 1983) is consistent with the formation of lactic acid in the present study.

A mixture of $CO:NH_3$ was selected for the initial experiments at 10 K because the results could be compared with earlier photochemical studies performed at 298 K (Ferris *et al.*, 1974; Hagen *et al.*, 1979; Hubbard *et al.*, 1975; Milligan and Jacox, 1965). The volatile products reported in the 1974–75 research (formamide, HCN and ammonium cyanate) were not detected in the present study because they would have been pumped off when the sample is warmed to room temperature. The five minor products detected in the present study (Table I) were not observed in the 1974–75 study. This is because they are formed in very low yield and thus could not be detected by the techniques used at that time. When the volatile and minor photoproducts noted above are excluded from consideration, the differences in the reaction products detected when
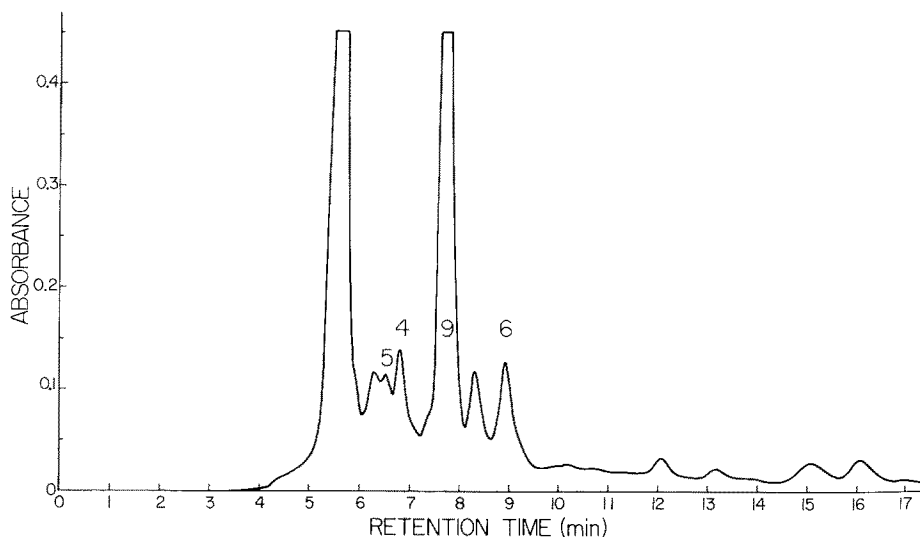
Fig. 2.   HPLC trace of 1.25 μg of the products formed by irradiation of a 5 : 1 CO:NH₃ mixture of 10 K. The compounds identified are numbered and listed in Table I. The intensity of the first peak eluted was greatly diminished in other samples. The cause of this variation could not be established. See experimental section for HPLC conditions.

the photolyses are performed at 10 K and 298 K appear to be primarily in relative abundances. Hydroxyacetamide and glyceramide were not detected in photolyses performed at 298 K while semicarbazide and biurea were not detected at 10 K.

Since there were similarities in the products obtained at 10 K and 298 K, the gas phase studies were reinvestigated to determine if the variation in reaction products is due principally to the temperature difference in the two studies (10 K versus 298 K). The other difference in the two studies, was the use of a hydrogen lamp with principal emission at 160 nm and a low pressure mercury lamp with principal emissions at 185 and 254 nm, respectively. Photolyses were performed at two temperatures; 298 K and 77 K. After the photolysis was terminated, the volatile reactants and products were pumped off before analysis of the non-volatile residue by GC–MS and HPLC. Both CO and NH₃ were irradiated in the gas phase study at 298 K while a portion of the CO and all the NH₃ was condensed on the cell walls at 77 K. The results of the present study at 298 K differ from the 1974–75 findings (Hubbard *et al.*, 1975) by the observation of oxamide as a major product and the absence of biurea and semicarbazide as photoproducts. The difference in reaction products may be due to thermal reactions resulting from contact of the photoproducts with the hot coil of the low pressure mercury lamp in the earlier studies (Ferris and Morimoto, 1981). In the present study the samples were photolyzed in quartz cells which were separate from, and not heated by, the UV lamp. Surface effects in the photolyses performed at 10 K may also account for the difference in reaction products.

These studies establish that the temperature variation between 298 K and 10 K and the change from the gas to solid phase effects the photoproducts. Hydroxyacetamide,

oxamic acid and glyceramide, major products at 10 K, consist of less than 1 % of the product mixture at 77 K and 298 K. Urea and/or biuret are formed in larger amounts at the higher temperatures instead of these compounds. The differences in the reaction products probably reflect temperature and surface effects on the rates of reaction of the photochemically-generated radicals. Even the rates of radical processes, which normally have very low activation energies, will be effected by temperature changes of more than 200 °C. In addition, the concentration of radicals and reactant molecules is much greater in the solid matrix irradiated at 10 K as compared to the irradiation of a gaseous mixture.

Since water has been found to be a major component of interstellar grains (Gillett and Forrest, 1973; Greenberg et $al.$, 1983; Greenberg, 1982a, b; Hagen, et $al.$, 1979), $CO:NH_3:H_2O$ mixtures, where the proportions were $5:1:1$ and $5:1:5$, were photolysed at 10 K. The same reaction products were obtained both in the presence and absence of water (Table I) but the proportion of more highly oxygenated molecules increased as the proportion of water was increased. The proportion of glycolic acid and glyceric acids increased markedly with increasing water content while oxamide and urea and/or biuret showed a corresponding decrease. If the amount of C and O is summed over all the identified products one can calculate that the C:O ratio decreases from $1:2$ to $1:13$ going from a $5:1:1$ to a $5:1:5$ ratio of $CO:NH_3:H_2O$ in the starting material. This trend is consistent with the depletion pattern for atoms in the diffuse cloud medium (Greenberg, 1982a).
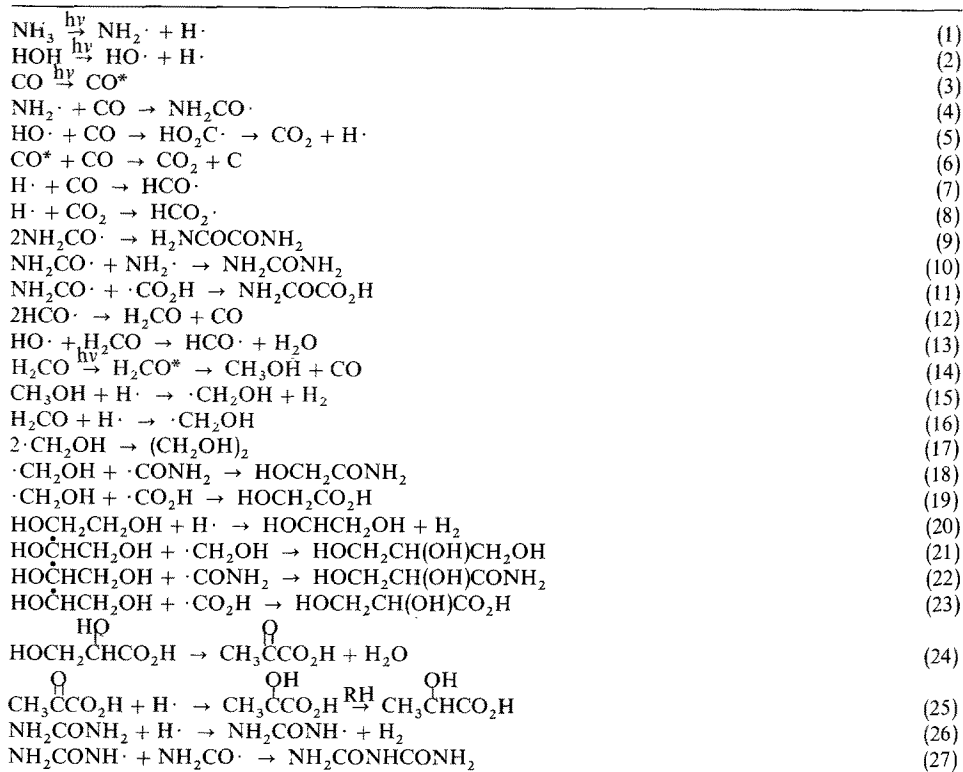
4.2. REACTION PATHWAY

A reaction pathway (Scheme 1) is proposed on the basis of the variation in photo products with reactants, the reaction intermediates detected by infrared analysis during the initial stages of irradiation at 10 K, and the reported photochemical reactions of the starting compounds. It is assumed that the principal reaction pathway is initiated by photolytic cleavage of NH_3 and H_2O although it is recognized that CO also absorbs 160 nm light (Huber and Herzberg, 1979) but is not dissociated at that wavelength.

It should be emphasized that while the reaction sequence given in Scheme 1 is plausible, it is speculative. It is based, in part, on previously established gas phase photochemical reaction pathways for these compounds (Okabe, 1978; von Sonntagg and Schuchmann, 1977; Bar-nun and Chang, 1983; Hubbard et $al.$, 1975; Jones et $al.$, 1973) as well as the experimental findings noted previously. The reaction pathways at 10 K and 77 K may be strongly influenced by surface as well as temperature effects.

The radicals $HCO\cdot$, $\cdot NH_2$ and $\cdot CO_2H$ have been detected by their infrared absorption after irradiation of a $CO:NH_3:H_2O:CO_2$ mixture for 2 hr at 10 K (Hagen et $al.$, 1979; Milligan and Jacox, 1965; van IJzendoorn et $al.$, 1983) and therefore, must have a central role in the formation of the observed products. Even though CO_2 was not a starting material in the present study, it is formed very efficiently by the reaction of hydroxyl radicals with CO (Equation (5)) (Bar-Nun and Chang, 1983, and references therein) as well as by the reaction between excited CO (CO^*) and CO (6) (Hagen, 1982). The formation of most of the observed reaction products can be rationalized

SCHEME 1

$$NH_3 \overset{h\nu}{\rightarrow} NH_2\cdot + H\cdot \tag{1}$$
$$HOH \overset{h\nu}{\rightarrow} HO\cdot + H\cdot \tag{2}$$
$$CO \overset{h\nu}{\rightarrow} CO^* \tag{3}$$
$$NH_2\cdot + CO \rightarrow NH_2CO\cdot \tag{4}$$
$$HO\cdot + CO \rightarrow HO_2C\cdot \rightarrow CO_2 + H\cdot \tag{5}$$
$$CO^* + CO \rightarrow CO_2 + C \tag{6}$$
$$H\cdot + CO \rightarrow HCO\cdot \tag{7}$$
$$H\cdot + CO_2 \rightarrow HCO_2\cdot \tag{8}$$
$$2NH_2CO\cdot \rightarrow H_2NCOCONH_2 \tag{9}$$
$$NH_2CO\cdot + NH_2\cdot \rightarrow NH_2CONH_2 \tag{10}$$
$$NH_2CO\cdot + \cdot CO_2H \rightarrow NH_2COCO_2H \tag{11}$$
$$2HCO\cdot \rightarrow H_2CO + CO \tag{12}$$
$$HO\cdot + H_2CO \rightarrow HCO\cdot + H_2O \tag{13}$$
$$H_2CO \overset{h\nu}{\rightarrow} H_2CO^* \rightarrow CH_3OH + CO \tag{14}$$
$$CH_3OH + H\cdot \rightarrow \cdot CH_2OH + H_2 \tag{15}$$
$$H_2CO + H\cdot \rightarrow \cdot CH_2OH \tag{16}$$
$$2\cdot CH_2OH \rightarrow (CH_2OH)_2 \tag{17}$$
$$\cdot CH_2OH + \cdot CONH_2 \rightarrow HOCH_2CONH_2 \tag{18}$$
$$\cdot CH_2OH + \cdot CO_2H \rightarrow HOCH_2CO_2H \tag{19}$$
$$HOCH_2CH_2OH + H\cdot \rightarrow HOCHCH_2OH + H_2 \tag{20}$$
$$HO\overset{\bullet}{C}HCH_2OH + \cdot CH_2OH \rightarrow HOCH_2CH(OH)CH_2OH \tag{21}$$
$$HO\overset{\bullet}{C}HCH_2OH + \cdot CONH_2 \rightarrow HOCH_2CH(OH)CONH_2 \tag{22}$$
$$HO\overset{\bullet}{C}HCH_2OH + \cdot CO_2H \rightarrow HOCH_2CH(OH)CO_2H \tag{23}$$
$$HOCH_2\overset{HO}{\overset{|}{C}}HCO_2H \rightarrow CH_3\overset{O}{\overset{\|}{C}}CO_2H + H_2O \tag{24}$$
$$CH_3\overset{O}{\overset{\|}{C}}CO_2H + H\cdot \rightarrow CH_3\overset{OH}{\overset{|}{C}}CO_2H \overset{RH}{\rightarrow} CH_3\overset{OH}{\overset{|}{C}}HCO_2H \tag{25}$$
$$NH_2CONH_2 + H\cdot \rightarrow NH_2CONH\cdot + H_2 \tag{26}$$
$$NH_2CONH\cdot + NH_2CO\cdot \rightarrow NH_2CONHCONH_2 \tag{27}$$

starting with $HCO\cdot$, $\cdot NH_2$, and $\cdot CO_2H$. Urea, oxamide and oxamic acid are formed as a result of direct combination reactions (Equations (9), (10), and (11)). The hydroxymethylene radical, formed either from methanol (Equation (15)) or for-maldehyde (Equation (16)), is a potential source of ethylene glycol, hydroxyacetamide and glycolic acid (Equations (17), (18), and (19) respectively). The radical of ethylene glycol (Equation (20)) is a plausible source of glycerol (Equation (21)), glyceramide (Equation (22)) and lactic acid (Equations (23)–(25)) while biuret may be formed from the radical or urea (Equations (26) and (27)). The carboxylic acid groups observed in some of the products of the 5 : 1 $CO:NH_3$ mixture may have been formed from $\cdot CO_2H$ produced by reactions (6) and (8).

The absence of aldehydes and ketones as reaction products is surprising. There is evidence that formaldehyde is an initial photoproduct from infrared studies after 2 hr photolysis at 10 K (Hagen et al., 1979) but no aldehydic or ketonic products observed in the present study. For example, lactic acid but no pyruvic acid was detected. This may represent the facile hydrogen atom addition reaction of the carbonyl group resulting from the high flux of hydrogen atoms formed by the photolysis of NH_3 and H_2O.
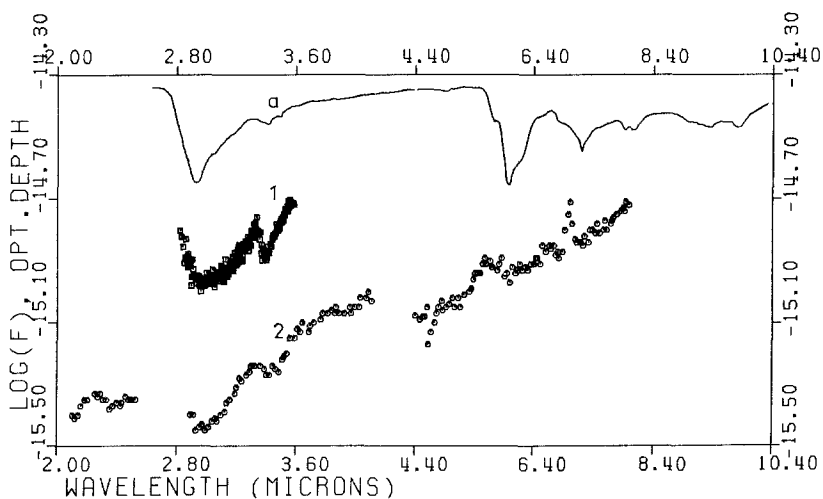
Fig. 3. Infrared absorption spectra of: (a) Residue of CO:H₂O:NH₃ = 5 : 5 : 1. (1) Galactic Centre source
IRS 7. (2) Galactic Centre source Sgr A West.

4.3. ANALYSIS OF THE RESIDUE INFRARED SPECTRUM

The infrared spectrum, particularly in the 'finger-print' region 7.5 μm–25 μm has
provided a classical means for identification of organic compounds. This technique is
also useful for the identification of some of the structural features in complex molecules.

The infrared spectrum of the residue of the 5 : 5 : 1 = $H_2O:CO:NH_3$ (Figure 3) was
compared with the spectra of the molecules in Table I. The lack of quantitative
measures of the absorption cross sections for different molecules makes it difficult to
produce a synthesis of the relative effects of the initial molecules which can be compared
with the total result. We therefore limited ourselves to identification of features.

The molecules that were detected in the residue were divided into three groups:
alcohols, amides and carboxylic acids (Table III).

Of the alcohols, two different molecules were tentatively identified: ethylene glycol
$(HOCH_2CH_2OH)$ and glycerol $(HOCH_2HOCHCH_2OH)$. The following analyses
assumes their photochemical formation from CO, NH_3, and H_2O mixtures. These
molecules have characteristic alcohol absorptions at about 3.0 and 9.4 μm (double
peaked), due respectively to the O–H and the C–O stretch vibrations. There is as well
the C–H stretch absorption at 3.4 μm. The 3.0 μm absorption surely contributes to the
2.93 micron absorption present in the residue spectrum, but the difference in position
and shape of the features indicates that there is at least one other important
contribution. The ratio of the depths of the 3.4 to 3 μm absorption is much larger for the
detected alcohols than for the residue. This also points to another substantial
contribution to the 3 μ residue feature apart from the alcohol absorption. The double
9.4 μm absorption may be responsible for the absorption peaks at 9.35 and 9.80 μm in
the residue spectrum, although this would imply a rather large shift of these absorp-
tions compared to the position in a pure sample.

Of the amides, six species were detected in the residue: urea (H_2NCONH_2),

TABLE III

Absorption characteristics of the molecules detected in the $H_2O:CO:NH_3 = 5:5:1$ residue. The positions of maximum absorbance and FWHM is given in μm, together with an indication of the depth of the absorption relative to the depth of the other absorptions of the same molecule (vs = very strong, s = strong, m = moderate, w = weak, vw = very weak). From Puchert (1981).

Group	Molecule	%	N—H stretch position (μm)	FWHM (μm)	rel. str.	O—H stretch position (μm)	FWHM (μm)	rel. str.	C—H stretch position (μm)	FWHM (μm)	rel. str.	C=O stretch position (μm)	FWHM (μm)	rel. str.	C—N stretch position (μm)	FWHM (μm)	rel. str.	C—O stretch position (μm)	FWHM (μm)	rel. str.	Undentified position (μm)	FWHM (μm)	rel. str.
	ethylene glycol	2				3.00	0.4	s	3.40	0.15	M							9.22 } 9.63	0.8	s s			
alcohols	glycerol	4				3.00	0.4	s	3.40	0.14	W							9.02 9.60	0.45 0.45	M s			
	hydroxy acetamide[1]	7																					
	glyceramide[1]	8																					
	oxamide	14	2.96 } 3.14	0.4	s s							6.05	0.8	s	7.42	0.3	s				9.07 8.72	0.3 0.5	M M
amides	urea	2	2.90 } 2.99	0.4	s s							6.28	1.3	s									
	biuret		2.92 } 3.10	0.4	s s							5.90	0.8	s	7.51	0.45	s						
	oxamic acid	6	2.97 } 3.07	0.3	M M							5.99	0.5	s	7.24	0.10	w						
carboxylic acids	glycolic acid	47				3.11 3.5	0.25 1.10	M W				5.85	0.25	s				8.00 9.20	0.3 0.2	VS VS			
alcohols	lactic acid	2				2.95	0.9	W	3.33	0.15	VW	5.81	0.3	s				8.21 8.89	0.45 0.25	s s			

[1] Absorption spectra for these molecules were not available.

oxamide ($H_2NCOCONH_2$), oxamic acid ($H_2NCOCOOH$), hydroxyacetamide ($HOCH_2CONH_2$), biuret ($H_2CONHCONH_2$), and glyceramide ($HOCH_2$— $HOCHCONH_2$). The characteristic amide absorptions are the double peaked N—H stretch absorption around 3.0 μm, the C=O stretch absorption around 6.0 μm and the C—N stretch absorption around 7.4 μm. The N—H stretch absorption consists of a shorter wavelength asymmetric and a longer wavelength symmetric stretch absorption. This band probably gives an important contribution to the 2.93 μm feature in the residue spectrum because it is about as strong in amides as the CO stretch feature which is presumed to produce the deep absorption in the residue spectrum at 6 μm (see below). It seems possible that the position of the band shortward of the 3.0 μm alcohol feature results from a blending of the alcohol with the amide feature. This blending can also explain the relative shallowness of the 3.4 μm absorption compared to the 3 μm absorption in the residue spectrum, because the amides, with the exception of hydroxy acetamide and glyceramide, do not contribute to the 3.4 μm feature. However, no clear double peak structure can be seen in the residue absorption. This can be the result of the interactions of the amides with the neighboring molecules in the complex organic refractory mixture. The C=O stretch absorption agrees quite well both in position and full width half maximum (FWHM) with the residue 6.0 μm band. An identification of this band with the blended bands of the detected amides is therefore plausible. The C—N stretch absorption seems to be a good candidate for the identification of the residue 7.2 μm as compared with the position in pure samples, but the position of the C—N stretch absorption of two of the detected amides is not available. Some other rather weak bands are present in the spectra of some of the detected amides. No counterparts of these bands can be seen in the residue spectrum, so they are probably 'blended out' by the absorptions of other molecules.

Three carboxylic acid molecules were detected in the residue: oxamic acid ($HOOCCONH_2$), which also has an amide group, glycolic acid ($HOCH_2COOH$) and lactic acid ($CH_3CHOHCO_2H$). The typical carboxylic acid absorptions of the molecules occur around 3.0 μm (the O—H stretch absorption), 5.8 μm (the C=O stretch absorption) and 8.1 μm (the C—O stretch absorption). Furthermore, there is the C—H stretch absorption around 3.4 μm. Lactic acid and glycolic acid also have O—H and C—O stretch absorptions around 3.0 and 9.0 μm due to the hydroxyl group. The 3 μm O—H stretch band of the carboxyl group is blended with the O—H stretch absorption from the hydroxyl group in lactic and glycolic acid and with the N—H stretch band in oxamic acid. In lactic acid and oxamic acid, the two absorptions can not be seen separately. It is likely that the contribution of the weak C—H stretch absorption of glycolic acid to the residue 3.4 μm feature is small. The 5.8 μm band probably shows up as a shoulder at the short wavelength side of the 6.0 μm absorption in the residue spectrum. The 8.1 μm bands from different carboxylic acids are probably responsible for the small double absorption peak in the residue spectrum at 8 μm. The C—O stretch around 9.2 μm may contribute to the residue absorption at 9.35 μm.

The identification of the IR spectral features of the $H_2O:CO:NH_3 = 5:5:1$ residue may be summarized as follows: The 3 μm feature is considered to be made up primarily

of the blended N—H and O—H stretch vibration absorption features of amides and alcohols respectively. The 3.4 µm feature results from the blended C—H stretch absorptions of all molecules present in the residue that contain this group. The 6 µm feature can be identified with the C=O stretch absorption of the amide (—CONH$_2$) group. The 5.8 µm shoulder is ascribed to the C=O stretch of carboxylic acids. The 7.2 µm absorption can probably be identified with the C—N stretch of the amide group. The double absorption peak at 8 µm can probably be ascribed to the C—O stretch vibration of the carboxylic acid (—COOH) group of different carboxylic acid molecules. Finally, the two C—O stretching bands of alcohols are reasonable assignments for the residue absorptions at 9.35 and 9.80 µm.

4.4. ASTRONOMICAL RELEVANCE OF THE RESIDUE INFRARED SPECTRUM

In Figure 3 we show the spectrum of the galactic center source IRS 7 (Greenberg *et al.*, 1985) as obtained between 2.95 and 3.7 µm and the spectrum of Sqr AW (IRS 7) from 2.7 to 8 µm.

The 3.4 µm region encompasses the C—H stretch absorption in organic compounds. While it is hardly likely that the particular residue we have produced is exactly what is formed in the wide variety of conditions in interstellar space it is clear from Figure 4 that its 3.4 µm feature is rather close to that seen towards IRS 7. The amount of interstellar dust which is required to obtain an adequate 3.4 µm absorption is quite large. For example the dust observed toward the galactic center is distributed over 10 kiloparsecs
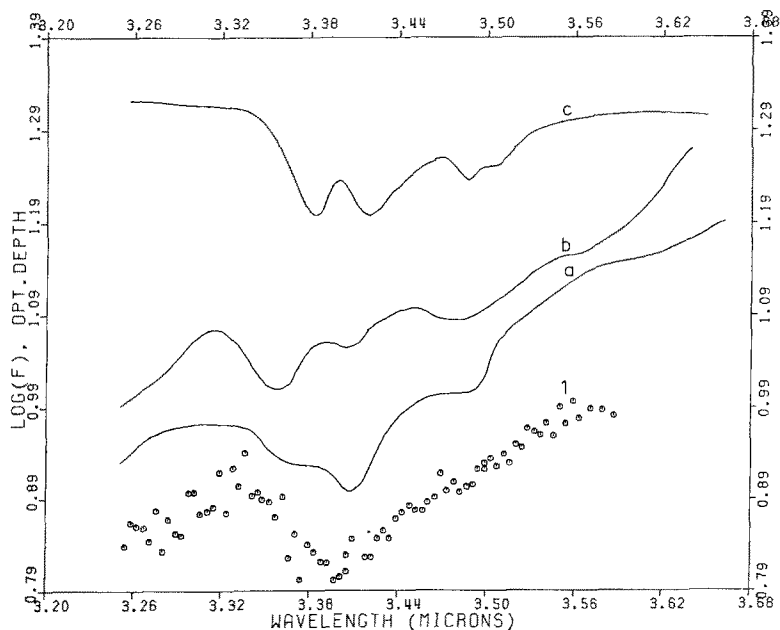

Fig. 4.   The 3.4 µm feature of: (1) Galactic Centre Source IRS 7. (a) Residue of CO:H$_2$O:NH$_3$ = 5 : 5 : 1.
(b) Residue of CO:H$_2$O:CH$_4$:NH$_3$ = 2 : 2 : 1 : 2. (c) Residue of CH$_4$.

distance – about one third the distance across the milky way. We are therefore sampling grains which are representative of all stages in their evolution and it would be surprising if any first generation space or laboratory residue provided a perfect match to the observation. To give an idea of the possible variability, 3.4 μm spectra of several residues are presented in Figure 4.

The upper spectrum in Figure 4 is that of a laboratory obtained residue resulting from ultraviolet photolysis of an initial pure CH_4 ice. We see that in this compound the C—H stretches identified with the –CH_3 group occur at 3.38, 3.48 μm and those from the —CH_2— group are at 3.42 and 3.52 μm (Bellamy, 1975). Substantial shifts from these positions are produced in molecules which have a number of functional groups different from those in hydrocarbons. The examples shown are residues of initial composition $CO:H_2O:CH_4:NH_3 = 2:2:1:2$ (residue 2) and $CO:H_2O:NH_3 = 5:5:1$ (residue 3, the one reported on here). The latter residue shows, as is confirmed by the chemical analysis, that CH groups are created whether or not the initial molecules contained them. For residue 2 all features are shifted to shorter wavelength relative to hydrocarbons, the —CH_3 ones being at 3.36, 3.4 μm and the longer wavelength —CH_2— feature (one feature is not clearly defined) is at 3.4 μm. For the other organic refractory we again see shifts in relative strengths and positions. It seems quite reasonable to conclude that, given the wide ranges in ages and chemical stages of the astronomically observed grains, the 3.4 μm feature(s) should degrade by averaging into a rather featureless band at around 3.4 μm. This indeed is what is observed with the best available spectrometer. Using the cooled grating spectrometer at the United Kingdom Infrared Telescope in Hawaii we have obtained the feature designated 1 in Figure 4.

Referring back to Figure 3, we see that a very broad feature around 3 μm shows up in the galactic center as well as in the various residues. Although this feature is characteristic of organic molecules containing OH and NH groups we do not believe we can yet make a definitive identification. The peak absorption of the $CO:H_2O:NH_3 = 5:5:1$ residue occurs at 2.93 μm which, while it is close to the IRS 7 peak at about 2.95 μm exhibits a serious discrepancy between its depth and that of the galactic center when compared with their respective 3.4 μm absorptions. This discrepancy may be explained in terms of long term photochemical evolution of grains as discussed in Section 2; i.e., we expect that continued photoprocessing of organic residues leads to enhancement of the number of CH bonds while decreasing the number of CO bonds.

The absorption spectrum from 5–8 μm is impossible to observe from the ground because of atmospheric absorption so that although the residues have a number of features in this region the number of relevant comparison spectra is scant. However, the spectra of the galactic center Sqr AW (IRS 7) taken with the Kupier airplane observatory (Willner et al., 1979) contains one broad feature at about 6 μm which is suggestively similar to that of our yellow stuff. We believe that this is produced by a C=O group.

To establish the relevance of the grain model of a core with organic refractory mantle

to the dust between us and the galactic center, it is necessary to provide not only spectroscopic correspondence, but also to establish a quantitative comparison in absorption strengths. For this we limit ourselves to the 3.4 μm strength.

It may be shown (Greenberg, 1982; Van de Bult and Greenberg, 1984) that the strength of our absorption band in a grain mantle relative to the extinction of visual light ($V \simeq 5500\,\text{Å}$) is given by

$$\frac{\tau_{\text{abs}}(\lambda)}{\tau(V)} = \frac{16\varPi}{\lambda}\,\frac{a_m^3 - a_c^3}{a_m^2}\,\frac{\varepsilon_2(\lambda)}{[\varepsilon_1(\lambda) + 2]^2 + \varepsilon_2^2(\lambda)}, \tag{1}$$

where a_m = mantle radius, a_c = core radius, λ = band absorption wavelength, $\varepsilon(\lambda) = \varepsilon_1(\lambda) - i\varepsilon_2(\lambda)$ is the complex dielectric coefficient of the mantle, and $\varepsilon_1 = m'^2 - m''^2$, $\varepsilon_2 = 2\,m'm''$ with m', m'' being the real and imaginary parts of the index of refraction $m = m' - im''$.

We define the 3.4 μm index of refraction as that relative to a baseline drawn between its full width limits whether in the observed or the laboratory spectrum. Adopting the grain model in which $a_c = 0.05\,\mu\text{m}$, $a_m = 0.12\,\mu\text{m}$, and letting $m' = 1.45$ be the real index of refraction of the organic refractory mantle we may approximate Equation (1) by:

$$\frac{\tau(\lambda)}{\tau(V)} = 0.285\,m''.$$

For the yellow stuff (5 : 5 : 1) in Figure 4 we have measured $m'' \simeq 0.015$ by making a KBr pellet of the residue. Thus Equation (2) gives

$$\left[\frac{\tau(3.4)}{\tau(V)}\right]_{\text{model}} \simeq 0.0045.$$

The optical depth deduced from Figure 4 for the IRS 7 3.4 μm feature is $\tau = \ln(I_0/I) = 0.28$. Using an optical depth to the galactic center of $\tau(V) = 30$ (Becklin et al., 1978) gives

$$\left[\frac{\tau(3.4)}{\tau(V)}\right]_{\text{astronomical}} \simeq 0.01.$$

This is encouragingly similar to this model result which is just a factor of two lower. As already pointed out further photoprocessing of the organic refractory should tend to enhance the 3.4 μm absorption per unit mass (or volume) of the mantle. In any case, there are a number of uncertainties which must be settled not only in the laboratory strength but also in the parameter defining the observed strength. For example, the visual extinction to the galactic center is estimated by various observers as being as high as $\tau_V = 70$ (Aitken and Jones, 1973; Roche and Aitken, 1984).

5. Significance

5.1. INTERSTELLAR DUST AND MOLECULES

The present research identified some of the compounds (Table I) that may be present in the non-volatile mantle of organics which coat interstellar dust particles. The listing in Table I is by no means complete because minor photoproducts form $CO:NH_3:H_2O$ remain to be identified and because other non-volatile organics are probably generated from the more complex mixtures of starting materials on dust grains. The compounds in Table I will form very slowly at 10 K from the photochemically generated radicals on the dust grain or more rapidly if the particle is warmed by the heat evolved by the combination of the photochemically generated radicals (Greenberg, 1984). Molecules will be injected into the interstellar medium if the grain is warmed sufficiently to volatize the photoproducts.

Many of the same photoproducts were obtained at 10 K and 298 K. If this finding is corroborated in future experiments, it will then be possible to use the large body of knowledge obtained in gas phase photochemical experiments to predict some of products formed at 10 K on dust grains. For example, one would expect, on the basis of gas phase results, that one route for the formation of interstellar CH_4, CH_3OH, CH_2O, CH_3CH_2OH, HNCO, HCN and formamide is by the photolysis of mixtures of $CO:NH_3:H_2O$ (Bar-Nun and Chang, 1983; Hubbard *et al.*, 1975). It should be emphasized that our results do show some significant differences in product composition as the temperature is varied. It will still be necessary to perform an experimental study of the photolysis at 10 K to gain a clearer insight into the processing of organic compounds on interstellar grains.

5.2. COMETS

Condensation of interstellar dust in the colder regions of the solar nebula far from the Sun or in an associated nebula led to the formation of comets (Whipple, 1978; Greenberg, 1982b). Water appears to be a major constituent of comets but there is also an appreciable amount of silicates and organics. It appears likely that the organic compounds present are the same ones that were present in the dust grains that condensed to form the comets 4.5 billion years ago (Greenberg, 1982b). Consequently, the present research makes some very specific predictions concerning the types of molecular species present in comets. Instrumentation utilized for molecular analysis of cometary material (Morrison *et al.*, 1983) should have the capability of detecting compounds of this type.

5.3. METEORITES

The organic matter in meteorites, unlike that in comets, has undergone subsequent transformations after its initial photochemical formation on dust grains. Current theory suggests that the parent bodies, from which meteorites formed, accreted from interstellar dust. In some instances the transformations appear to be very complex so it

may not be possible to reconstruct every one of the transformation leading to the organic structures found in meteorites from the compounds present in the dust particles. For example, the principal organic substance present in carbonaceous meteorites is a highly crosslinked polymer which can only be isolated by dissolving the associated silicates with HF and strong acids (Hayatsu *et al.*, 1977). The chemical route by which this polymer is formed will be difficult to unravel. On the other hand, there are some simple moleclar species in meteorites, the structures of which may reflect the original organic constituents of the dust. Of particular interest to the present study is the observation that glycolic and lactic acids are major acidic components of the Murchison meteorite (Peltzer and Bada, 1978; Peltzer *et al.*, 1984) and the present photochemical study. Oxalic acid was also detected in appreciable amounts in the Murchison meteorite by Peltzer and Bada (1978) while the amide derivatives of oxalic acid, oxamide and oxamic acid, are produced by photolysis of $CO:NH_3:H_2O$ mixtures. The correlation between the hydroxy acids in the Murchison meteorite and the products of our photochemical studies suggest that photochemical reactions may have been important for the formation of the components of meteorites. The observation of alternative pathways for the formation of hydroxy acids raises questions concerning the validity of the use of hydroxy acid: amino acid ratios for estimating concentrating of HCN and NH_3 on the parent body of the Murchison meteorite (Peltzer *et al.*, 1984).

5.4. ORIGINS OF LIFE

The current theory of the origins of life proposes that life arose spontaneously from the organic compounds present on the surface of the earth. Initially it was proposed that these organics were produced in Miller–Urey type syntheses from atmospheric constituents. The inhomogeneous accretion model for the formation of the earth (Walker, 1977) has led to a resurgence in interest in interstellar dust, comets and meteorites as the sources of preformed organic compounds. Dust and small planetis-mals would pass through the earth's atmosphere with little or no thermal alteration of their organic constituents. Larger planetismals would be subject to heating as they passed through the atmosphere and a portion of the organic constituents near the surface would be pyrolyzed. Separate arguments have been presented for carbonaceous meteorites (Anders and Owen, 1977) and comets (Schoemaker and Wolf, 1983; Greenberg, 1984) as the source of organic carbon on the early earth. The comet argument is especially intriguing. Schoemaker and Wolf (1983) note that if comets formed in the vicinity of the orbits of Uranus and Neptune and were ejected further away from the Sun (to Oorts Cloud) when Jupiter and Saturn formed then many comets would be deflected across the interior of the solar system and impact with the earth. They calculate that a primordial ocean of volume comparable to the present oceans was delivered to the earth by comets. If their estimate is correct, then a massive amount of organic material would also have been delivered to the surface of the earth with the water. If the theory connecting comet showers with the extinction of species on

the earth over the past 300 million years if correct (Davis *et al.*, 1984; Whitmore and Jackson, 1984), it could well be that a mass of organics comparable with the current biomass of the earth has been injected by comet impacts every 30 million years (Greenberg *et al.*, 1984). The molecular compositon of this organic material delivered to the earth would closely parallel that of the organics in interstellar grains (Greenberg, 1983) – the subject of the present research.

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