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Cosmic Rays and Chemical Evolution

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The role of cosmic rays in the processes of chemical evolution on Earth and on other bodies of the Solar System has been examined.

All bodies in the Universe are influenced constantly by rays from outer space: both galactic and solar. Cosmic rays consist mainly of atomic nuclei, moving at almost the speed of light. The main components of cosmic rays are protons and He nuclei.

Secondary cosmic rays (SCR) arise as a result of the influence of galactic and solar cosmic rays on gas molecules in the upper atmosphere. These SCR contain protons, neutrons and mesons. Nuclei of carbon-14 are created after exposure of atmospheric nitrogen to the neutron irradiation. These carbon-14 nuclei react with atmospheric oxygen within a few hours, to give $^{14}CO_2$ or ^{14}CO.[1] The newly formed carbon oxides react like their non-radioactive analogues containing the stable carbon isotopes ^{12}C and ^{13}C. Radioactive carbon-14 nuclei are thus inculcated into the carbohydrate products of photosynthesis [eqn. (1)].

$$^{14}CO_2 + 5CO_2 + 6H_2O \rightarrow {}^{14}CC_5H_{12}O_6 + 6O_2 \qquad (1)$$

Compounds such as CH_4, $MeCH(OH)CO_2H$, EtOH and $MeCO_2H$ are formed by the degradation of carbohydrates. Various nitrogen-containing compounds may be formed as a result of the radioactive decay of ^{14}C ($^{14}C \rightarrow {}^{14}N + e^-$) and the stable nitrogen-14 isotope is formed. In the case of β-decay, the major nuclear transitions do not lead to the destruction of the daughter molecular systems,[2] and the nitrogen-containing compounds are formed as a result of deprotonisation reactions.

Depending on the location of the radioactive carbon atoms within the molecule, a large range of nitrogen-containing compounds may be formed: amino acids, amino alcohols, amines, amides, nitriles, nitro- and nitroso-compounds [eqns. (2)–(11)]. From this point of view, it is interesting to examine the results of a study of the atmosphere of Titan, Saturn's largest satellite.[3]

$$^{14}CH_4 \rightarrow {}^{+}NH_4 \rightarrow NH_3 + H^+ \qquad (2)$$

$$^{14}CH_3CHOHCO_2H \rightarrow {}^{+}NH_3CHOHCO_2H \rightarrow NH_2CHOHCO_2H + H^+ \qquad (3)$$

$$^{14}CH_3CH_2OH \rightarrow {}^{+}NH_3CH_2OH \rightarrow NH_2CH_2OH + H^+ \qquad (4)$$

$$^{14}CH_3CH_2CO_2H \rightarrow {}^{+}NH_3CH_2CO_2H \rightarrow NH_2CH_2CO_2H + H^+ \qquad (5)$$

$$^{14}CH_3CH_2Me \rightarrow {}^{+}NH_3CH_2Me \rightarrow NH_2CH_2MeH^+ \qquad (6)$$

$$Me^{14}CH_2Me \rightarrow Me\overset{+}{N}H_2Me \rightarrow MeNHMe + H^+ \qquad (7)$$

$$MeCH_2{}^{14}CO_2H \rightarrow MeCH_2\overset{+}{N}O_2H \rightarrow MeCH_2NO_2 + H^+ \qquad (8)$$

$$MeCH_2{}^{14}CHO \rightarrow MeCH_2\overset{+}{N}HO \rightarrow MeCH_2N{=}O + H^+ \qquad (9)$$

$$MeCO^{14}CH_3 \rightarrow MeCO\overset{+}{N}H_3 \rightarrow MeCONH_2 + H^+ \qquad (10)$$

$$Me^{14}C{\equiv}CH \rightarrow MeC{\equiv}\overset{+}{N}H \rightarrow MeC{\equiv}N + H^+ \qquad (11)$$

The atmosphere of Titan is made up of nitrogen (90%), methane (1–10%) and ethane. Small amounts of propane, ethylene, acetylene, propyne and buta-1,3-diene are also present, together with C_2N_2, HCN, CH≡CCN and CO. Nitrogen-containing organic compounds as EtCN, $CH_2{=}C(Me)CN$, $CH_2{=}CHCN$ and MeCH=CHCN have also been discovered on the surface of Titan, plus pyrimidine and adenine. These results were obtained by the American automatic space station 'Voyager-1'.[3]

The formation of these compounds may be connected with the reaction of 'hot' atoms, formed by neutron irradiation (by SCR) on nitrogen molecules in Titan's atmosphere [eqns. (12) and (13)].

$$N_2 + n \rightarrow {}^{14}C + N + p \qquad (12)$$

$$N_2 + n \rightarrow {}^{12}C + N + {}^{3}H \qquad (13)$$

The mechanism of formation of some of the organic nitrogen compounds discovered on Titan, for example HCN, C_2N_2 and $CH_2{=}CHCN$, may be rationalised as shown in eqns. (14)–(23).

$$N_2 + {}^{12}C^{\cdot\cdot\cdot\cdot} \rightarrow {}^{12}\dot{C}N + N^{\cdot\cdot\cdot} \qquad (14)$$

$$N_2 + {}^{14}C^{\cdot\cdot\cdot\cdot} \rightarrow {}^{14}\dot{C}N + N^{\cdot\cdot\cdot} \qquad (15)$$

$$^{12}CH_4 + N^{\cdot\cdot\cdot} \rightarrow {}^{12}\dot{C}H_3 + {}^{\cdot\cdot}NH \qquad (16)$$

$$^{12}CH_2{=}{}^{12}CH_2 + {}^{12}\dot{C}N \rightarrow {}^{12}CH_2{=}{}^{12}\dot{C}H + H^{12}CN \qquad (17)$$

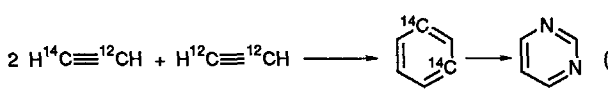
$$^{12}CH_2{=}{}^{12}\dot{C}H + {}^{12}\dot{C}N \rightarrow {}^{12}CH_2{=}{}^{12}CH^{12}CN \qquad (17)$$

$$^{12}\dot{C}N + {}^{12}\dot{C}N \rightarrow {}^{12}C_2N_2 \qquad (19)$$

$$^{12}CH_4 + {}^{14}C^{\cdot\cdot\cdot\cdot} \rightarrow {}^{12}\dot{C}H_3 + {}^{14}\dddot{C}H \qquad (20)$$

$$^{12}CH_4 + {}^{12}C^{\cdot\cdot\cdot\cdot} \rightarrow {}^{12}\dot{C}H_3 + {}^{12}\dddot{C}H \qquad (21)$$

$$^{14}\dddot{C}H + {}^{12}\dddot{C}H \rightarrow {}^{14}CH{\equiv}{}^{12}CH \qquad (22)$$



(23)

The formation of acetylene and hydrogen cyanide also occurs by means of an 'insertion' reaction,[4] which is common during the interaction of 'hot' atoms with hydrocarbons [eqns. (24)–(26)].

$$CH_4 + {}^{14}C^{\cdot\cdot\cdot\cdot} \rightarrow {}^{14}CH{\equiv}CH + H_2 \qquad (24)$$

$$C_2H_6 + {}^{14}C^{\cdot\cdot\cdot\cdot} \rightarrow {}^{14}CH{\equiv}CH + CH_4 \qquad (25)$$

$$^{14}CH{\equiv}CH \rightarrow \overset{+}{N}H{\equiv}CH \rightarrow HCN + H^+ \qquad (26)$$

According to some estimates, 40% of the carbon on Earth is of extra-terrestrial origin (meteorites, comets, space dust and solar wind).[5] As a comet passes close to the sun, its surface is exposed to strong solar cosmic rays, which may also cause the formation of carbon-14 from the stable carbon isotopes ^{12}C and ^{13}C [eqns. (27) and (28)].

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$$^{12}C + {}^{3}T \rightarrow {}^{14}C + p \quad (27)$$

$$^{13}C + {}^{2}D \rightarrow {}^{14}C + p \quad (28)$$

All the data presented here indicate that cosmic rays may contribute to the chemical evolution of molecules both on Earth and on other bodies of the Solar System.

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Iron(III) Chloride Catalysed Photooxygenation of Alcohol Solutions of Alkanes by Atmospheric Oxygen

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Alkanes (cyclohexane, pentane, hexane, heptane, 3-methylhexane) have been oxidised to the corresponding alcohols, together with minor amounts of ketones (aldehydes) by irradiation of solutions of the alkanes in aliphatic alcohols in air in the presence of catalytic amounts of $FeCl_3$: unusual selectivity in the reaction is revealed.

Liquid phase oxidation of saturated hydrocarbons by dioxygen catalysed by transition metal complexes under mild conditions, which requires activation of an inert C—H bond, is an area of continuing interest (reviews[1] and recent original papers[2]). Functionalisation of alkanes and arylalkanes under visible irradiation in the presence of high-valent metal complexes as catalysts is one of the most intriguing problems.[3]

Previously, we have found that alkanes can be oxygenated when irradiated in air in the presence of catalytic amounts of transition metal chlorides ($FeCl_3$, $CuCl_2$, $PtCl_6^{2-}$, $AuCl_4^-$, $CrCl_3$ *etc.*).[4] Relatively inert solvents ($MeCO_2H$, MeCN, CH_2Cl_2, Me_2CO) were used in these oxidations.

We report here the oxygenation of alkanes by atmospheric oxygen, using aliphatic alcohols as solvents. Alcohols are easily oxidisable substrates and only a few examples of alkane oxygenation in the presence of alcohols are known[5] (catalytic photofunctionalisation of cyclooctane in the presence of butan-2-ol has also been reported[6]).

Irradiation of a solution of cyclohexane in an alcohol in the presence of a catalytic amount of $FeCl_3 \cdot 6H_2O$ in air affords cyclohexanol and a smaller amount of cyclohexanone. The reaction was carried out in a glass vessel (volume of reaction solution 5 ml) surrounded by a water-cooling jacket (15 °C) with stirring, and using the full spectrum of a 1000 W high-pressure mercury lamp ($\lambda > 310$ nm). The data are summarised in Table 1. It should be noted that both alcohol and ketone are accumulated linearly with time, a significant prevalence of cyclohexanol being observed. The reaction is first order in alkane concentration.

Table 1 Photooxygenation of cyclohexane catalysed by $FeCl_3$[a]

			Products	
Run	Solvent	Cyclohexane /mol dm^{-3}	Cyclohexanol /mmol dm^{-3}	Cyclohexanone /mmol dm^{-3}
1	MeOH	0.46	10.7	0.3
2	$MeCH_2OH$	0.46	3.0	1.1
3[b]	Me_2CHOH	0.46	11.3	1.7
4[b]	Me_2CHOH	2.76	30.6	5.9
5[c]	$MeCH(OH)CH_2Me$	0.46	5.2	0.9
6[c]	$MeCH(OH)CH_2Me$	2.76	30.3	9.5
7	Me_3COH	0.46	10.1	10.0
8[d]	MeCN	0.46	22.3	20.4

[a] Concentration of $FeCl_3$ 0.2 mmol dm^{-3}, 3 h irradiation. [b] Acetone was also formed: 26.0 (Run 3) and 6.3 mmol dm^{-3} (Run 4). [c] Methyl ethyl ketone was also formed: 66.4 (Run 5) and 23.1 mmol dm^{-3} (Run 6). [d] Cyclohexyl hydroperoxide was also formed: 32.0 mmol dm^{-3}.

The alcohol used as the solvent is also oxidised to afford a ketone or aldehyde (detected in Runs 3–6). The amount of the carbonyl compound formed from the solvent decreases with increasing initial concentration of cyclohexane. The turnover number in the $FeCl_3$-photocatalysed oxygenation of cyclohexane is *ca.* 60 h^{-1}. It is noteworthy that, in contrast to the reaction in acetonitrile, the oxygenation of cyclohexane in alcohols affords no cyclohexyl hydroperoxide. Similarly, when carried out in *tert*-butyl alcohol, which contains no active C—H bonds, the reaction produces no hydroperoxide, but in this case a large amount of cyclohexanone is formed (Run 7).

Linear alkanes can also be easily oxygenated in alcohols as solvents under the conditions described above. Heptane (2.76 mol dm^{-3}), for example, gives rise after 1 h irradiation to 10.8 mmol dm^{-3} of a mixture of isomeric alcohols (2.8 mmol dm^{-3} of heptan-1-ol) and 10.0 mmol dm^{-3} of carbonyl derivatives. The relative reactivities of the C—H bonds at the first, second, third and fourth carbon atoms of the hydrocarbon chains of pentane, hexane and heptane are given in Table 2. It can be seen that when propan-2-ol is used as a solvent the relative reactivity of the C—H bond at carbon atom C-1 is higher than that when acetonitrile is used as a solvent. However, the most striking feature of the reaction in alcohol solution is the enhanced reactivity of the C—H bonds at C-3 in comparison with those at C-2 in hexane. Similarly, the C—H bonds at C-4 in heptane are more reactive than those at C-2 and C-3. In the photo-oxygenation of 3-methylhexane, the distribution of isomeric alcohols formed by attack on primary, secondary and tertiary C—H bonds changes on passing from acetonitrile (1°:2°:3° = 1.0:3.8:16.9) to propan-2-ol (1°:2°:3° = 1.0:1.4:9.1) as solvents.

One may propose the following mechanism for the reaction under discussion. Photohomolysis of the Fe—Cl bonds[7] affords extremely reactive chlorine radicals[8] which abstract hydrogen atoms from alkane RH or alcohol R′R″CHOH to yield radicals R˙ or R′R″ĊOH respectively, the reactivities of alkane and alcohol in this process being approximately equal. Indeed, the reactivity of the CH_2 groups in ethylbenzene relative to that in