THE γ-IRRADIATION OF AQUEOUS ACETIC ACID-CLAY SUSPENSIONS

ALICIA NEGRÓN-MENDOZA and RAFAEL NAVARRO-GONZÁLEZ*

Instituto de Ciencias Nucleares, U.N.A.M. Circuito Exterior, C.U., A. Postal 70-543, México D.F. 04510, México

Abstract. γ-radiolysis of 0.8 mol dm^{-3} aqueous, oxygen-free acetic acid solutions was investigated in the presence or absence of Na-montmorillonite (1–3 g per 10 cm^{-3}). The systems were irradiated at their natural pH (3.5), and 25 °C in a dose range from 0.01 to 500 kGy. H_2, CH_4, CO, CO_2, and a variety of polycarboxylic acids were formed in all systems. The major features of the radiolysis in the presence of clays were: (1) More solute molecules were decomposed; (2) Carbon dioxide was produced in higher yield; (3) The yield of methane was unaffected; and (4) 44% less polycarboxylic acids were formed. Three possible mechanisms that could account for the observed changes are suggested. The results are important in understanding heterogeneous processes in radiation catalysis and might be significant to prebiotic chemistry.

1. Introduction

Clay minerals are important constituents of the Earth's crust not only because of their abundance but merely because of their chemical activity. They are formed by igneous activity as an alteration product of silicate minerals and also during diagenesis of sediments. They probably accumulated on the Earth surface and became suspended in the primitive oceans. The importance of clay minerals in prebiotic chemistry was suggested by Bernal (1951). More recently, Ponnamperuma *et al.* (1982) have reviewed a number of experiments testing Bernal's ideas, and they extended his hypothesis of the role of clay minerals during the stages of origins of life as follows:

(1) Clay minerals catalyzed the reactions of biomonomer synthesis from gaseous constituents of the primordial atmosphere.

(2) Clay minerals adsorbed biomonomers on their surfaces, providing a highly concentrated system in which the monomers had a specific orientation.

(3) Clay minerals facilitated condensation reactions between adsorbed monomers in which biopolymers were formed.

Clay minerals are characterized by a high specific surface area and the presence of exposed cations on their surface such as potassium ions (Fripiat and Cruz-Cumplido, 1974). Four billion years ago the abundance of ^{40}K on the Earth's lithosphere was probably four times higher. ^{40}K decays with a half-life of 1.3×10^9 y giving off γ-rays and β-particles. Ionizing radiation must have played a role, therefore, in promoting prebiotic reactions in clay minerals. In addition to ^{40}K,

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* To whom correspondence should be addressed.

other sources of ionizing radiations are likely to have contributed to the synthesis of organic compounds in the ocean-lithosphere interphase (Draganić and Draganić, 1980).

We were prompted to investigate the γ-radiolysis of aqueous acetic acid in the presence of Na-montmorillonite because simple carboxylic acids could have been important raw materials for prebiotic syntheses (Negrón-Mendoza and Ponnamperuma, 1976, 1982). Carboxylic acids are important in prebiotic chemistry studies due to the versatility of the CO_2H group. They can be converted into more complex molecules. The synthesis of di- and tricarboxylic acids is, however, limited to some acids.

2. Experimental Procedures

2.1. CHEMICALS AND GLASSWARE

The purification of water and cleaning of glassware were carried out by standard procedures used in radiation chemistry (Draganić and Draganić, 1971). The chemicals used were of the highest purity commercially available. Acetic acid was further purified by distillation.

Na-montmorillonite of Wyoming Bentonite was obtained from the Source Clay Minerals Repository of the Clay Minerals Society at the University of Missouri-Columbia.

2.2. SAMPLE PREPARATION AND IRRADIATION

The syringe technique was used for the preparation of deaerated solutions of acetic acid and for the irradiation of the samples (Draganić and Draganić, 1971). One gram of degassed Na-montmorillonite was suspended into 10 cm^3 of deaerated solutions of acetic acid. In additional studies, the amount of clay added was varied from one to three grams. The systems were irradiated at their natural pH (3.5), and 25 °C in a dose range from 0.01 to 500 kGy. The concentration of acetic acid was selected as 0.8 mol dm^{-3}. Under this condition, the amount of radiolytic products is suitable for fast routine analysis (Negrón-Mendoza and Ponnamperuma, 1976). From what is known of the influence of solute concentration on the radiolysis of dilute solutions, the observations made under these conditions are essentially valid also for smaller concentrations, down to one or more orders of magnitude (Josimović and Draganić, 1973).

Irradiations were performed in two cobalt-60 units located at I.C.N., U.N.A.M. The dose rates determined by Fricke dosimetry (G(Fe^{3+})=15.6) were 0.7 and 20 kGy h^{-1}, respectively.

2.3. ANALYSIS

Sorption of Acetic Acid and Extraction of Carboxylic Acids from the Clay

The concentration of acetic acid in solution before and after the addition of clay

was practically unchanged; it was not possible to determine the extent of sorbed acetic acid in the clay in the presence of a 0.8 mol dm^{-3} CH$_3$CO$_2$H solution. The infrared spectra of the dried clay after contact with the acetic acid solution did indicate that it was sorbed even after complete drying the clay at 45 °C under reduced pressure.

The clay-carboxyylic acid suspensions were centrifuged after irradiation. The supernatant containing the carboxylic acids was collected. The residue was washed with distilled water and recentrifuged. These steps were repeated 3 times. The supernatants were evaporated to dryness at 45 °C under reduce pressure, and then redissolved in a methanol/BCl$_3$ solution and heated for 1 h at about 80 °C to methylate the carboxylic acids. The carboxylic acids methyl esters were collected in benzene by extraction with a benzene-water mixture. This procedure was followed using acetic and aconitic acids in order to determine the efficiency of extraction. The recovery for both acids was determined to be within 96%.

Gas Products

H$_2$, CH$_4$, CO$_2$ and CO were analyzed by gas chromatography. The irradiated sample was injected into an evacuated chamber and the gases were extracted and introduced by a Töepler pump into a gas chromatograph equipped with a thermal conductivity detector (Negrón-Mendoza *et al.*, 1984).

Analysis of gases in blank samples showed the presence of a high initial concentration of carbon dioxide. Its background concentration increased from 10^{-6} mol dm^{-3} in acetic acid solutions to 10^{-4} mol dm^{-3} in acetic acid-clay suspensions. The origin of this CO$_2$ is attributed to the spontaneous decarboxylation of acetic acid catalyzed by clays (Shimoyama and Johns, 1971) and/or to CO$_2$ originally adsorbed in the clay. We used blanks therefore, to correct for the yield of CO$_2$ in irradiated samples.

Carboxylic Acids

Acetic acid was analyzed by direct injection of the centrifuged solution into a Varian Aerograph (Series 2400) gas chromatograph (Castillo *et al.*, 1985). It was also determined by titration with NaOH using phenophthalein as indicator. Nonvolatile carboxylic acids were analyzed by gas chromatography (Negrón-Mendoza *et al.*, 1983) and gas chromatography-mass spectometry. In the latter case, the analysis was performed in a Hewlett Packard System 5992. A 50 m long capillary column with SE-30 was used with helium as the carrier gas (12 cm^3 min^{-1}). The column programmed temperature was from 80 to 270 °C by increments of 4 °C min^{-1}. An isothermal regime was kept at 80 and 270 °C for 4 and 20 min. respectively.

Identification and Determination of Carboxylic Acids

These were identified by their retention times, coinjections with standards and by their fragmentation patterns by mass spectrometry. Calibration curves of carboxylic acids were obtained for quantitative analysis of the radiolytic products.

TABLE I

Radiation chemical yields (G) in the radiolysis of aqueous solutions of acetic acid and aqueous acetic acid-clay suspensions

Compound	Conditions	Acetic acid				Acetic acid-clay
	$[CH_3CO_2H]$ (mol dm^{-3})	0.25	1.0	0.1	0.8	0.8
	pH	1.0	1.0	1–3	3.5	3.5
	Type of radiation	He ions	X-ray	γ-ray	γ-ray	γ-ray
	Dose range (kGy)	6; 168		≤ 0.5	≤ 500	≤ 500
	Reference	1; 2	3	4	This work	This work
CH_3CO_2H					−4.12	−8.01
H_2		1.20	3.3	3.75	2.94	2.94
H_2O_2		0.38	0.6	0.79	NA*	NA*
CO					Trace	Trace
CO_2		0.14	1.0	0.20	0.29	6.61
CH_4		0.04	0.4		0.015	0.015
Succinic acid		0.30; 0.14		3.22	0.60	0.33
β-hydroxy-β-methyl-glutaric acid					0.012	0.003
Tricarballylic acid		0.02			0.25	0.047
Citric acid					0.023	0.007
Polycarboxylic acids (total)					0.89	0.39

* NA: Not analyzed.
1. Garrison *et al.*, 1955; 2. Garrison *et al.*, 1953; 3. Hayon and Weiss, 1960; and 4. Josimović and Draganić, 1973.

3. Results and Discussion

Table I summarizes the initial radiation chemical yields* for the decomposition of acetic acid and the formation of several products from the radiolysis of aqueous solutions of acetic acid and acetic acid-clay suspensions. Table I also compares our G values for the case of acetic acid solutions with some values reported in the literature. The differences observed between these values are due to different experimental conditions. G values depend on the radiation type, pH, dose, and concentration (Draganić and Draganić, 1971).

3.1. GAS PRODUCTS

H_2, CH_4, CO and CO_2 were formed in the irradiated solutions. The concentrations of hydrogen and methane linearly increased with dose, and were not affected by the presence or absence of clay in the irradiated sample. Figure 1a shows this effect for the case of methane. The initial radiation chemical yields of formation of hydrogen and methane were 2.94 and 0.015, respectively. CO was formed in very low yield to be followed quantitatively. CO_2 was the major radiolytic product,

* Initial radiation chemical yields (G) are expressed as the number of molecules formed or destroyed per 100 eV, and were calculated from extrapolation to initial conditions from G *vs* dose plots.
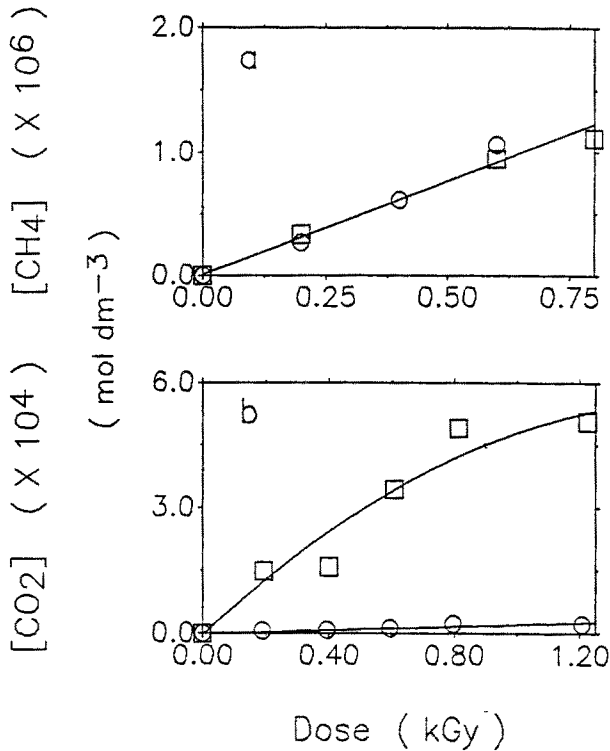
Fig. 1. Dose dependence of formation of methane (a) and of carbon dioxide (b) in the presence (□) and absence (○) of Na-montmorillonite.

particularly in the presence of clay (Figure 1b). The G values for CO_2 were 0.29 and 6.61 in the absence and presence of clays, respectively.

3.2. CARBOXYLIC ACIDS

Figure 2a shows the decomposition of acetic acid as a function of dose. The G values were 4.12 and 8.01 in the absence and presence of clays, respectively. More acetic acid molecules were decomposed during the radiolysis in the presence of clays.

A variety of polycarboxylic acids were formed in the irradiated solutions. The most abundant was succinic acid; among other acids formed were oxalic, malonic, β-hydroxy-β-methyl-glutaric, tricarballylic, aconitic, citric, isocitric, 1,2,4-butanetricarboxylic and 1,2,3,4-butanetetracarboxylic acids. Figures 2b and 3 show the effect of clay on the yields of these acids. The G values for all polycarboxylic acids were 0.89 and 0.39 in the absence and presence of clays, respectively.

44% less polycarboxylic acids were produced in the presence of clays in spite of the fact that twice more acetic acid molecules were decomposed. These results are important since they demonstrate that polymerization of free radicals is inhibited by clays and decarboxylation of acetic acid is the major process. The extent of decomposition of acetic acid is linearly related with the amount of clay present
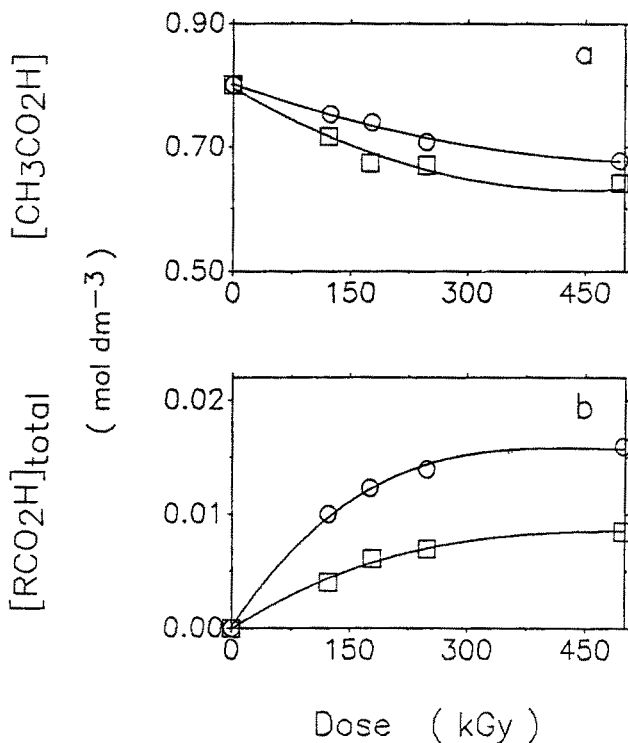
Fig. 2. Decomposition of acetic acid (a) and formation of total polycarboxylic acids (b) as a function of dose in the presence (□) and absence (○) of Na-montmorillonite.
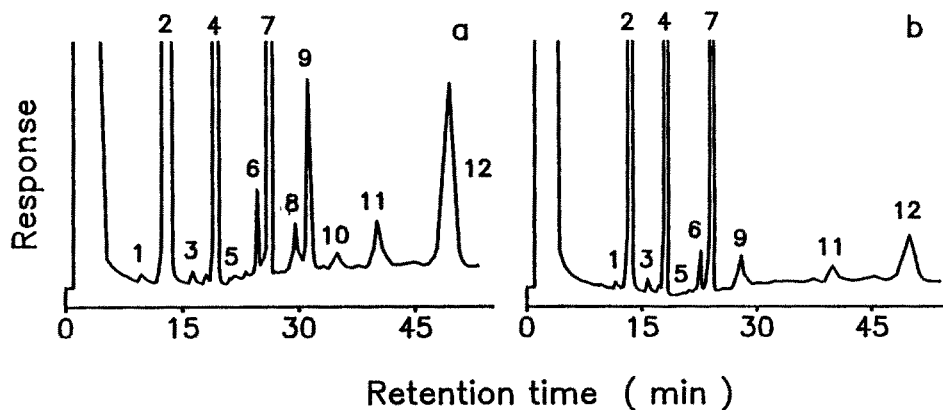

Fig. 3. Gas chromatograms of methyl esters of polycarboxylic acids formed in irradiated aqueous solutions of acetic acid in the absence (a) and presence (b) of Na-montmorillonite at 500 kGy. 1. Malonic; 2. Succinic and Fumaric; 3. Citraconic; 4. β-Hydroxy-β-methyl-glutaric; 5. Carboxysuccinic; 6. Methyl tricarballylic; 7. Tricarballylic and aconitic; 8. 1,2,4-Butanetricarboxylic; 9. Citric; 10. Isocitric; 11. 1,2,3,4-Isobutanetetracarboxylic; and 12. 1,2,3,4-Butanetetracarboxylic acids.
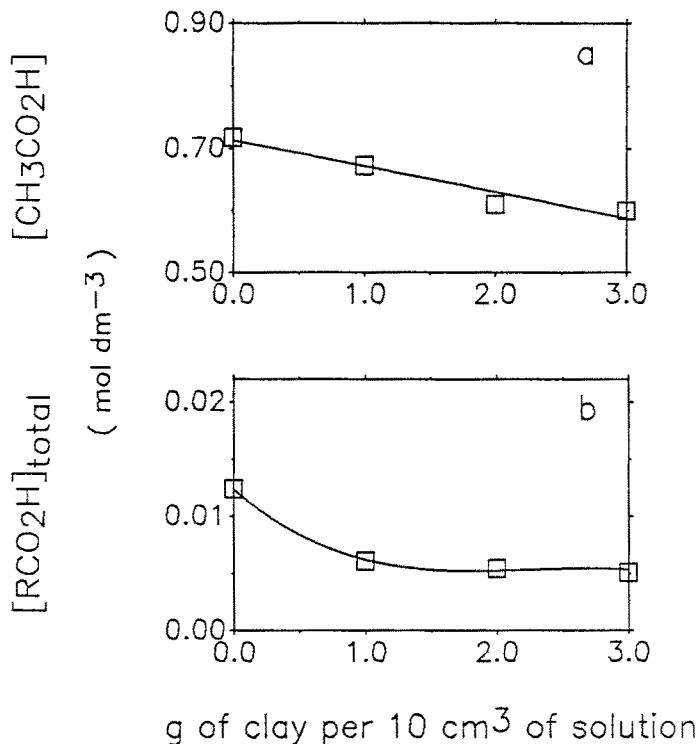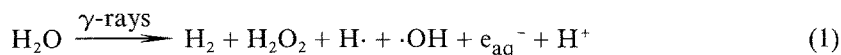
Fig. 4. Effect of the amount of clay on the radiolysis of 0.8 mol dm^{-3} acetic acid suspensions at 180 kGy. a. Decomposition of acetic acid; b. Formation of total polycarboxylic acids.
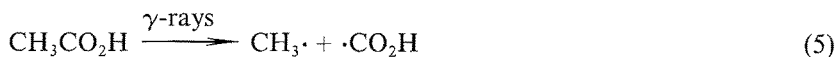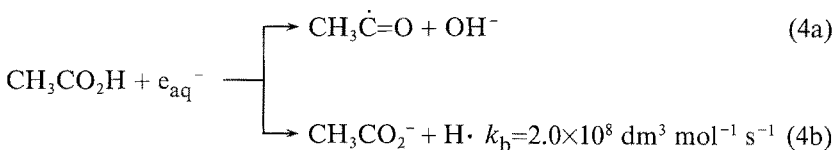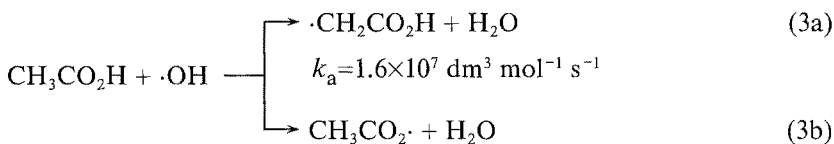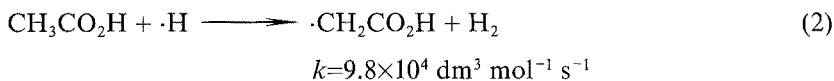
in the solution (Figure 4a); whereas the production of polycarboxylic acids is unaffected by changing the amount of clay from 1 to 3 g per 10 cm^3 of solution (Figure 4b).

3.3. REACTION MECHANISM

General

The mechanism of water radiolysis is well established (Draganić and Draganić, 1971). The energy absorbed in the solutions is mainly deposited in the water molecules, and the observed chemical changes are brought about indirectly via the radical products (Reactions 1–4). The percentage of energy of energy deposited directly into acetic acid molecules is unimportant in 0.8 mol dm^{-3} solutions, $\leq 1.4\%$ (Reaction 5). The rate constants giving here are from the data collected by Ross and Neta (1982) and Buxton *et al.* (1988).

$$H_2O \xrightarrow{\gamma\text{-rays}} H_2 + H_2O_2 + H\cdot + \cdot OH + e_{aq}^- + H^+ \qquad (1)$$

$$CH_3CO_2H + \cdot H \longrightarrow \cdot CH_2CO_2H + H_2 \tag{2}$$
$$k = 9.8 \times 10^4 \ dm^3 \ mol^{-1} \ s^{-1}$$

$$CH_3CO_2H + \cdot OH \longrightarrow \begin{cases} \cdot CH_2CO_2H + H_2O & (3a) \\ k_a = 1.6 \times 10^7 \ dm^3 \ mol^{-1} \ s^{-1} \\ CH_3CO_2 \cdot + H_2O & (3b) \end{cases}$$

$$CH_3CO_2H + e_{aq}^- \longrightarrow \begin{cases} CH_3\dot{C}{=}O + OH^- & (4a) \\ \\ CH_3CO_2^- + H\cdot \ k_b = 2.0 \times 10^8 \ dm^3 \ mol^{-1} \ s^{-1} & (4b) \end{cases}$$

$$CH_3CO_2H \xrightarrow{\gamma\text{-rays}} CH_3\cdot + \cdot CO_2H \tag{5}$$
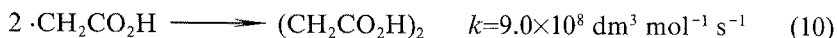
Methane originates almost exclusively by hydrogen abstraction reactions of the methyl radicals (Reactions 6 and 7) with solute molecules. Channel 7a is the main process (95%) as demonstrated by irradiation of deuterated acetic acid (Burr, 1951).
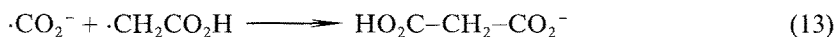
$$CH_3CO_2\cdot \longrightarrow CH_3\cdot + CO_2 \tag{6}$$

$$CH_3\cdot + CH_3CO_2H \longrightarrow \begin{cases} CH_4 + \cdot CH_2CO_2H & (7a) \\ k = 2.0 \times 10^2 \ dm^3 \ mol^{-1} \ s^{-1} \\ CH_4 + CH_3CO_2 \cdot & (7b) \end{cases}$$
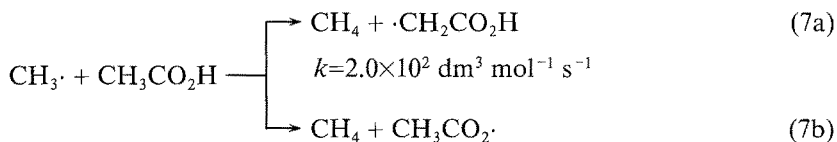
Carbon dioxide is formed by reactions 6 and 8. Carbon monoxide is a minor product of irradiation, and is formed by reaction 9.

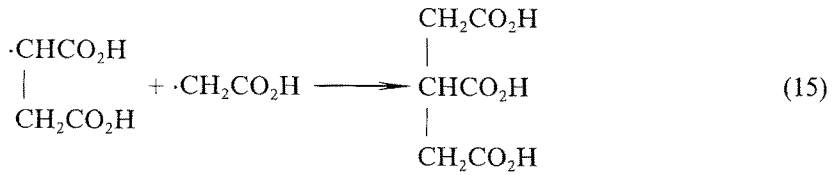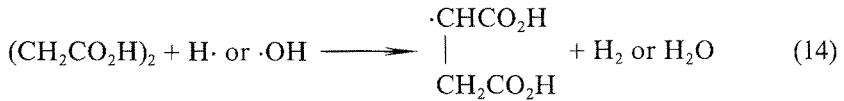$$\cdot CO_2H + H_2O_2 \longrightarrow CO_2 + \cdot OH + H_2O \tag{8}$$

$$CH_3\dot{C}{=}O \longrightarrow CH_3\cdot + CO \tag{9}$$
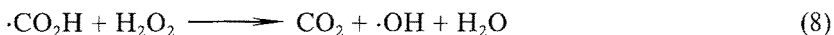
Other fates of radicals are through dimerization reactions such as 10 and 11:

$$2\cdot CH_2CO_2H \longrightarrow (CH_2CO_2H)_2 \quad k = 9.0 \times 10^8 \ dm^3 \ mol^{-1} \ s^{-1} \tag{10}$$

$$2\ CH_3\dot{C}{=}O \longrightarrow (CH_3C{=}O)_2 \tag{11}$$

The origin of other products is through secondary reactions involving carbon dioxide and succinic acid (Negrón-Mendoza and Ponnamperuma, 1976), for example reactions 12–15.

$$CO_2 + e_{aq}^- \longrightarrow \cdot CO_2^- \tag{12}$$

$$\cdot CO_2^- + \cdot CH_2CO_2H \longrightarrow HO_2C{-}CH_2{-}CO_2^- \tag{13}$$

$$(CH_2CO_2H)_2 + H\cdot \text{ or } \cdot OH \longrightarrow \begin{array}{c} \cdot CHCO_2H \\ | \\ CH_2CO_2H \end{array} + H_2 \text{ or } H_2O \qquad (14)$$

$$\begin{array}{c} \cdot CHCO_2H \\ | \\ CH_2CO_2H \end{array} + \cdot CH_2CO_2H \longrightarrow \begin{array}{c} CH_2CO_2H \\ | \\ CHCO_2H \\ | \\ CH_2CO_2H \end{array} \qquad (15)$$

On the Possible Effect of Clays in the Radiolysis

The presence of clays during the irradiation of acetic acid solutions led to the following major effects: (1) High yield of decomposition of acetic acid; (2) High yield of the formation of carbon dioxyde; (3) No effect on the yield of methane; and (4) Low yield of formation of polycarboxylic acids. Three possible mechanisms that might account for the observed effects are:

(1) The energy absorbed from the ionizing radiations by the clay minerals may be transferred to both, water and acetic acid molecules. Energy transfer to water molecules leads to the same products of water radiolysis (Allen, 1948). On the other hand, when this energy is transferred to the acetic acid, the net chemical effect might be similar as that of reaction 5. In fact, when acetic acid is irradiated at high concentrations, most of the energy is deposited directly into acetic acid and the same overall effects are also observed (Garrison et al., 1955; Josimović and Draganić, 1973).

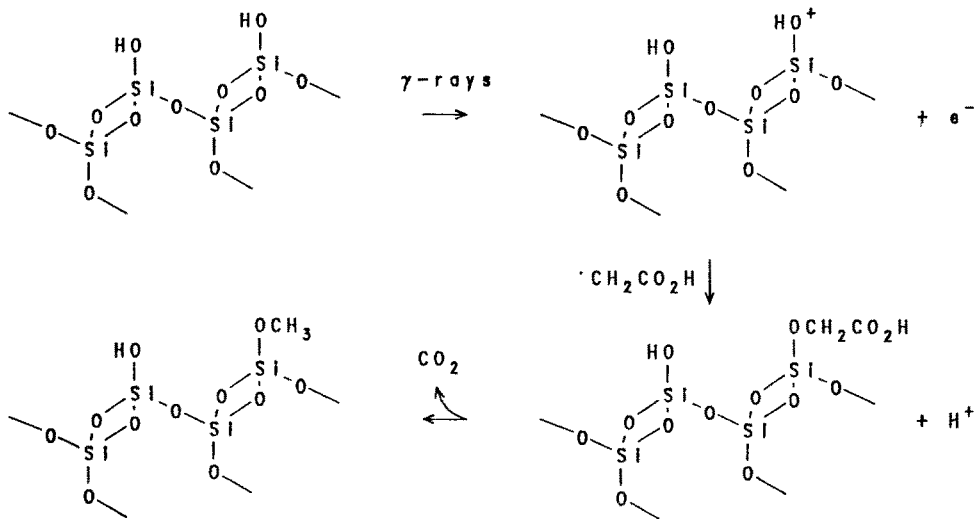(2) The deposition of energy on clay minerals may lead to the formation of

Fig. 5. Possible mechanism for the decarboxylation of the $\cdot CH_2CO_2H$ radical in the clay lattice.

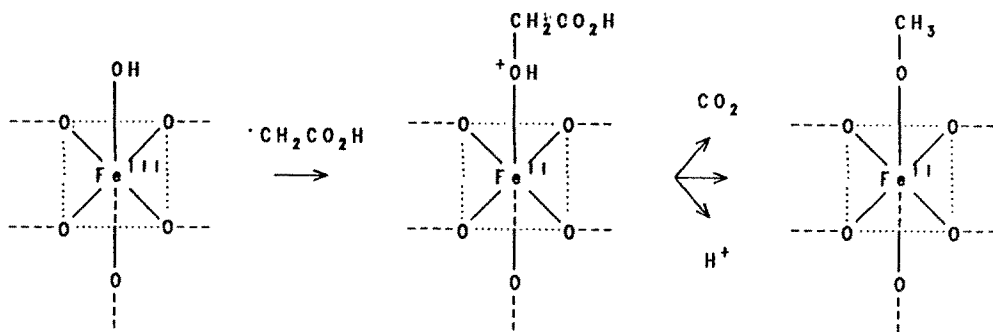Fig. 6. Possible mechanism for the oxidation of the ·CH₂CO₂H radical in the clay lattice.

positive sites probably in the oxygen atoms or hydroxyl groups which are the main surface constituents. They may play an important role by forming carbon-oxygen bonds with the radicals produced by the attack of the primary species of water radiolysis on the acetic acid. Figure 5 shows the steps leading to the decomposition of the ·CH₂CO₂H radical.

(3) Iron(III) oxide constitutes on the average 3.77% of the total mass of different montmorillonites from all over the world (Grim, 1968). Iron(III) ion or its complexes readily oxidizes free radicals. Figure 6 shows a possible channel for the oxidation of ·CH₂CO₂H by the iron(III) complex present in the clay lattice. Analog reactions are documented in aqueous solutions (Ross and Neta, 1982; Navarro-González et al., 1989).

Our current research is focussed on the elucidation of the relative contributions of the mechanisms by which clays catalyze free-radical reactions of prebiotic significance.

4. Conclusions

The present study established that the irradiation of acetic acid-clay suspensions led to a significant reduction in the oligomerization of acetic acid in spite of the fact that more solute molecules were decomposed. Decarboxylation, rather than condensation, was the major channel of clay-catalyzed decomposition of acetic acid under irradiation. Three possible mechanisms that could account for the observed changes were suggested. Contrary to the general idea of clays being good catalyzers for prebiotic syntheses (Ponnamperuma et al. 1982), this study indicates that clay minerals inhibit the free radical oligomerization. It is worth noticing that a different investigation has revealed that the ionic oligomerization of HCN is also inhibited by montmorillonite clays (Ferris et al., 1982). Since this is a pioneer work in radiation heterogeneous catalysis in prebiotic chemistry, further research is still needed with other systems before any conclusion can be reached regarding the possible catalytic role of clay minerals on free-radical reactions of prebiotic significance.

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