IRON ALKOXIDE OBTAINED BY REACTING IRON OXIDES WITH GLYCEROL

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Abstract — Goethite, lepidocrocite and hematite were reacted with glycerol and reaction products were studied at various steps of the reaction. After a treatment of 16 hr at 245°C the final form of the reaction product, a deep green soft solid, was obtained whatever the starting material. According to hydrolysis and chemical analysis, the reaction product can be identified as iron alkoxide. Hydrolysis of the solid by boiling water yielded glycerol and a strongly magnetic material characterized by a spinel structure like maghemite and magnetite.

The iron alkoxide is seen by electron microscope as large well-formed hexagonal platelets. The similarity between a and b parameters of this compound and those of brucite suggests that the iron alkoxide structure is based on an iron (II and III) octahedral layer. The glycerol chains should be located between the sheets. Two models were proposed in which iron and oxygen, linked to the chain of glycerol, could be accommodated in octahedral layers giving a basal distance of 8·1 Å.

At least two steps are involved in the formation of the iron alkoxide: (1) a rearrangement of the structure of the starting material with accomodation of carbon in the structure and (2) a reduction of ferric iron.

INTRODUCTION

THE INTERCALATION of glycerol within sheet structures (Mac Ewan, 1944; Walker, 1948) has been studied extensively mainly because of the changes that occur in their basal spacings. This change is a valuable tool in the identification by X-ray of expanding lattices in mixtures of clay minerals (Brown, 1961). R. M. Taylor has shown (1969)§ that glycerol reacts with hematite, lepidocrocite and goethite at relatively high temperatures. This reaction could be useful for the identification of different forms of amorphous iron oxides and hydroxides in soils.

An investigation was therefore carried out in which goethite, lepidocrocite and hematite were subjected to reaction with glycerol. Reaction products at various stages during the reactions were studied by electron microscopy, electron

diffraction, X-ray diffraction, differential thermal analysis, nuclear magnetic resonance, i.r. spectroscopy and specific surface area measurements. The reduction of ferric iron was followed during the reaction and a complete chemical analysis of the final reaction products was carried out. Amorphous ferric hydroxide gel was also reacted with glycerol, but only the final product was studied by X-ray diffraction and i.r. analysis. It became rapidly evident that the reaction of glycerol with ferric oxides and hydroxides involves more than the intercalation of glycerol within sheet structures.

EXPERIMENTAL

Preparation of starting materials

Hematite was a commercial product obtained from Kaliechemie (surface area = 39·4 m²/g). Goethite was prepared by aging of ferric hydroxide gel (obtained by the addition of ammonia to $FeCl_3$ solution) in boiling 2N KOH for 2 hr according to the method of Glemser (1937). Lepidocrocite was prepared by the oxidation of $FeSO_4$ (in solution with NH_4Cl and $Na_2S_2O_3$) by KIO_3 (Fricke and Zerrweck, 1937). Ferric hydroxide gel was obtained by the addition of N NaOH to N/10 $FeCl_3$ solution until a pH 8 was reached. The preparations of goethite,

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lepidocrocite and ferric hydroxide gel were subjected to dialysis against distilled water until no positive Cl^- and SO_4^{2-} tests occurred and were separated from the liquid by centrifugation. Goethite (surface area = $71·0 \, m^2/g$) and lepidocrocite (surface area = $136·4 \, m^2/g$) were dried at 110°C for 24 hr and ground. Ferric hydroxide gel was reacted with glycerol without prior drying.

Reaction with glycerol

1 g starting material was reacted with 7 ml glycerol in an open glass tube fitted with a condenser. A treatment during 16 hr at 245°C was sufficient to give the final form of the reaction product. Intermediate reaction products were studied at various stages during the reaction. The moment that the reaction temperature of 245°C was reached (after 40 min) was taken as the beginning of the reaction and the "0 hr" reaction product was obtained at this stage.

The reaction products were washed 3–4 times with approximately 30 ml portions distilled water in order to extract excess glycerol and water soluble products. They were then dried at room temperature for 24 hr, ground and finally dried for 24 hr at 110°C. The colour of the starting materials changed to green as the reaction proceeded. After 16 hr, a very dark green soft solid was obtained from all starting materials. The product obtained from the 16 hr treatment was analyzed for Fe^{2+} and total Fe content and the remaining liquid, which contained the excess glycerol and water soluble products, was analyzed by i.r. spectroscopy after evaporation of water.

Hydrolysis of the reaction product

Hydrolysis of the reaction products obtained during different stages of the reaction was accomplished by treatment with boiling water. Although only several minutes were required to destroy the greatest part of the reaction product, the hydrolysis was continued for 20–30 min. The dark coloured magnetic iron oxide obtained by hydrolysis was separated from the solution by a magnet and subsequent filtration. Then it was dried at room temperature and examined by X-ray diffraction. The hydrolysis solution of the 16 hr treatment was analyzed by i.r. spectroscopy after evaporation of water.

Instrumentation

X-ray examination was carried out on a Philips diffractometer using Co–Kα radiation (12 mA, 28 kV). I.R. absorption spectra were obtained on a Beckman IR-4 spectrometer fitted with NaCl optics. Powder spectra were recorded by the usual KBr pellet technique using a concentration of

$0·81 \, mg/cm^2$. Spectra of liquids were recorded by using AgCl windows. A AEI EM6G electron microscope was used for electron-optical and diffraction studies. An accelerating potential of 60 kV was used for bright field transmission microscopy and 100 kV for selected area diffraction. In the latter case, an aperture of $50 \, \mu$ was used which selected a domain of $1·23 \, \mu$ diameter. A drop of suspension of the sample was dried out on the carbon support film after ultrasonic dispersion. Some of the grids were shadowed with an alloy 40% Pd/Au ($\alpha = 26·5°$) and others were coated with a thin film of TlCl for diffraction work. B.E.T. surface area measurements were carried out according to the Nelsen-Eggertsen method (Nelsen and Eggertsen, 1958). For the differential thermal analysis a Netzsch apparatus fitted with a platinum-platinum/rhodium thermocouple was used. Al_2O_3 was used as reference. The rate of temperature increase was 10°/min.

Chemical methods

Ferrous iron and total iron were determined colorimetrically by the o-phenanthroline (Charlot, 1961) and sulphosalicilic acid methods (Voinovitch, Debras-Guedon and Louvrier, 1962) respectively. Iron determinations on liquids were carried out directly on the sample, but solids were dissolved in hot 1 : 1 HCl prior to the determination. Carbon and hydrogen were analyzed by an outside laboratory using a combustion method. The oxygen content was calculated by difference.
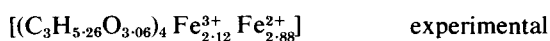
RESULTS

Chemical analysis

A chemical analysis of the solid reaction product obtained when glycerol was reacted with goethite, lepidocrocite and hematite at 245°C for 16 hr, followed by extraction of the excess glycerol and water soluble reaction products, is given in Table 1. The extracted reaction products contained less than 2 per cent of the total iron present in the reaction medium and consisted, according to i.r. analysis, mainly of glycerol. The presence, however, of a compound containing a carbonyl function was indicated by a low intensity CO stretching vibrational band at $5·75 \, \mu$ (see Fig. 4A). Qualitative tests carried out to establish the character of the CO function proved negative for aldehydes and ketones.

Hydrolysis of the solid reaction product yielded, according to i.r. analysis, glycerol and magnetic iron oxides. It is therefore reasonable to assume that the carbon chain of glycerol does not change during the reaction and that carbon is linked to iron through an oxygen atom. The reaction
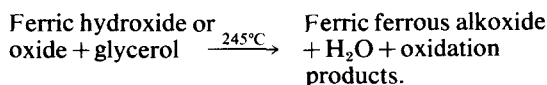
Table 1. Chemical analysis of the reaction products

Starting material	C	H	Percentage O	Fe^{2+}	Fe^{3+}
Goethite	22·52	3·26	31·38	23·74	19·10
Lepidocrocite	22·82	3·72	29·34	26·26	17·50
Hematite	22·07	2·95	30·86	25·79	18·33
Average	22·47	3·31	30·53	25·38	18·31

Table 2. Specific surface area (m^2/g) of the reaction products at different reaction times

Reaction time	Goethite	Lepidocrocite	Hematite
Starting material	71·0	136·4	39·4
0 hr*	67·8	28·9	37·3
1 hr	9·4	24·8	38·1
3 hr	9·1	14·7	12·5
16 hr	8·1	6·6	4·0

*About 40 min were required to reach the reaction temperature of 245°C.

product can therefore be identified according to the chemical analysis, as iron alkoxide with a chemical formula as follows:

$$[(C_3H_{5·26}O_{3·06})_4 \; Fe^{3+}_{2·12} \; Fe^{2+}_{2·88}] \qquad \text{experimental}$$

$$[(C_3H_5O_3)_4 \; Fe^{3+}_2 \; Fe^{2+}_3] \qquad \text{calculated.}$$

The reaction involves basically a dehydration and oxidation-reduction reaction and can be summarized as follows:

Ferric hydroxide or oxide + glycerol $\xrightarrow{245°C}$ Ferric ferrous alkoxide + H_2O + oxidation products.

Hydrolysis of the iron alkoxide, which was found to be retarded by the presence of free glycerol, produced glycerol and dark brown to black, strongly magnetic material with a spinel structure like maghemite and magnetite. The magnetic hydrolysis product was transformed into the original iron alkoxide when it was subjected to reaction with glycerol at 245°C. The hydrolysis reaction is thus reversible.

Electron microscopy

Electron-optical studies show the iron alkoxide as large well-formed hexagonal platelets (Fig. 1(a)), with a small amount present as small irregular platelets, especially in preparations obtained from goethite and lepidocrocite. The occurrence of the small platelets partly explains the difference in the values of the specific surface area (Table 2) of iron alkoxides prepared from goethite, lepidocrocite and hematite which have surface area values of 8·1, 6·6 and 4·0 m^2/g respectively.

A difference in the rate of iron alkoxide formation was observed with the electron microscope for different starting materials. This difference is also evident from the changes in the surface area values with time (Table 2). A value of 136·4 m^2/g for the original lepidocrocite declines to 28·9 m^2/g before the reaction temperature of 245°C is reached. The surface area values for hematite and goethite show at this stage no marked change.

The larger particles have the appearance of agglomerates of single crystals. Shadowing of the particles indicates a height of 0·3 μ for thick particles (A in Fig. 1(b)) and a height of 300 and 400 Å for thin ones (Particles B and C in Fig. 1(b) respectively). The electron diffraction patterns are not easy to record because of the high sensitivity of the iron alkoxide structure to heating by the electron beam. Two characteristic patterns obtained with a low beam intensity are shown in Fig. 1(d) and (e): they are diffraction patterns of thin particles. On the pattern of Fig. 1(e) the ring pattern of polycrystalline thallous chloride has been superimposed for calibration purposes. From these patterns it is possible to determine two in-plane spacings $d(hkl)$ i.e. 5·32 Å and 9·36 Å which probably correspond to the a and b parameters respectively. The angle between the two corresponding reciprocal axes is 84°. The diffraction pattern in Fig. 1(f) was obtained from the thick particle shown in Fig. 1(c) and may correspond to a structure damaged by the heat of the electron beam.

The electronmicrograph of the hydrolysis product (Fig. 1(g)) shows opaque particles which are usually linked in chains. This orientation is probably due to their magnetic properties.

Differential thermal analysis

Figure 2A gives the differential thermal analysis pattern for iron alkoxide prepared from hematite as recorded in nitrogen. A sharp exothermic peak is observed at 270°C. Preparations obtained from goethite and lepidocrocite gave the exothermic peak at 300 and 315°C respectively. The exothermic peak may be due to the rearrangement of the organic residue whilst the endothermic peak at 715°C, in the same diagram, may be assigned to volatilization of carbon compounds. Figure 2B was obtained from the same iron alkoxide in presence of oxygen. The same general pattern was also observed for iron alkoxides prepared from goethite and lepidocrocite, but the temperature at which the exothermic effects were evident varied
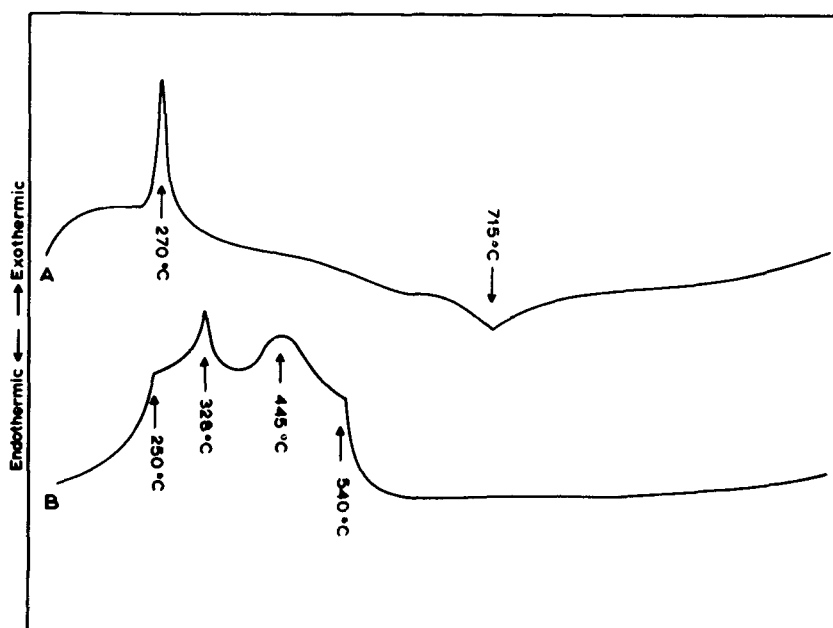
Fig. 2. Differential thermographs of iron alkoxide prepared from hematite (A was recorded in nitrogen and B in air).

considerably. The exothermic effects may be due to several changes in the material. X-ray analysis of brown material obtained after heating the iron alkoxides to 380°C in the air for 1 hr gave a spectrum of a spinel structure, probably maghemite, which changed into turkey-red hematite after additional heating for one hour at 800°C. More than 50 per cent of the iron in the iron alkoxide is present as ferrous iron. The exothermic effect can therefore be explained by the following changes in the material: (1) Break up of the iron alkoxide to give magnetite and an organic residue (shoulder at 250°C); (2) Oxidation of the magnetite to maghemite (sharp peak at 328°C) (Mackenzie, 1957); (3) Oxidation of carbon (broad peak around 445°C); (4) A change of maghemite into hematite (probably indicated by the shoulder at 540°C).

X-ray diffraction spectra

The X-ray spectrum of the final iron alkoxide (Fig. 3A) is well developed and contains a number of sharp reflections of which the 8·1 Å line is the most prominent. The X-ray data are contained in Table 3. Since the first reflection has a very strong intensity, probably because of preferential orientation, it is taken as the basal reflection. The general appearance of the spectrum is the same when starting from lepidocrocite, hematite, ferric hydroxide gel and the hydrolysis product. The goethite derivative shows the same positions of the reflec-

Table 3. X-ray diffraction data for iron alkoxide

2θ	d(Å)	Relative intensity	hkl
12·67	8·112	100·0	001
13·78	7·461	4·5	
19·29	5·343	2·2	
20·72	4·978	3·4	
23·75	4·350	7·6	
24·45	4·227	4·5	
25·54	4·050	2·3	002
27·88	3·716	1·8	
28·48	3·639	3·0	
31·50	3·298	2·1	
33·46	3·110	3·3	
35·97	2·899	1·8	
36·92	2·827	3·4	
37·80	2·763	1·2	
38·40	2·722	2·1	
38·75	2·698	2·7	003
40·58	2·581	7·5	
42·02	2·498	6·9	
44·30	2·374	4·5	
47·80	2·209	2·4	
49·18	2·151	3·9	
51·38	2·065	3·0	

tions, but the intensity and sharpness of the peaks are less.

X-ray diffraction patterns obtained from reaction products at different stages during the reaction
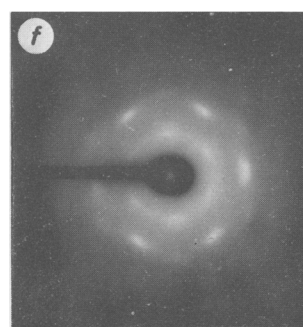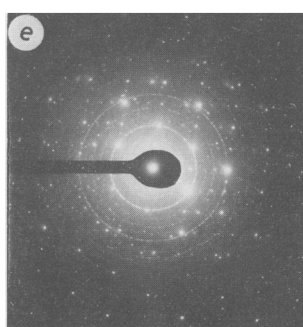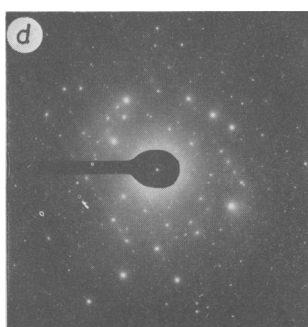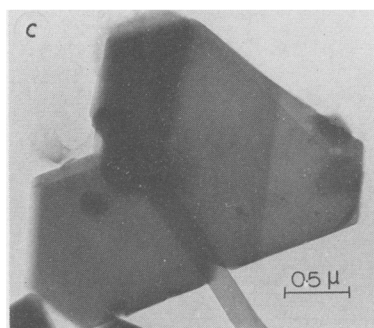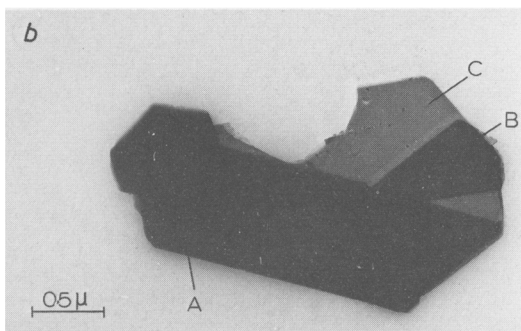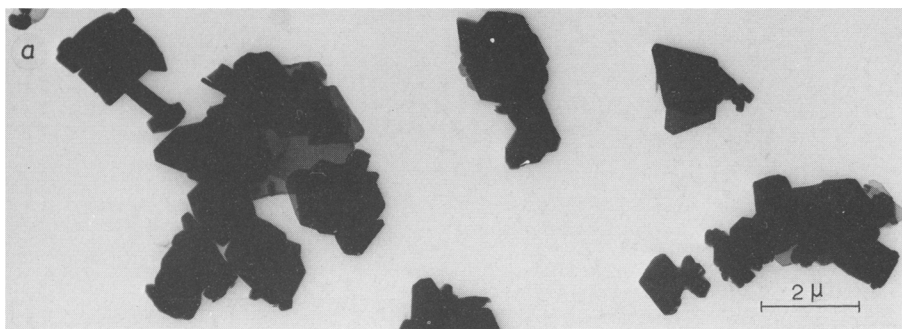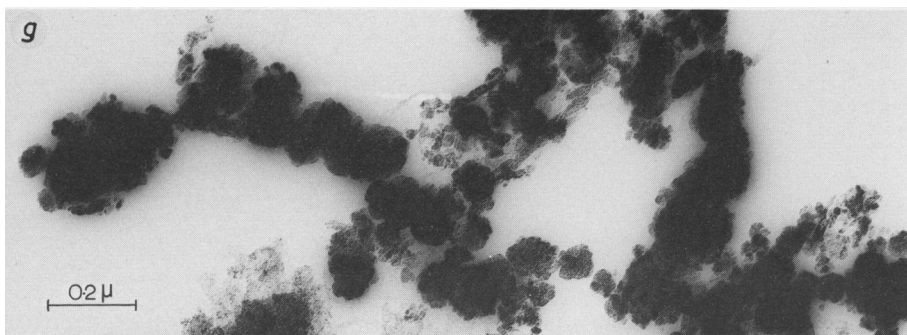
Fig. 1(a–f).

Fig. 1. (a) Iron alkoxide prepared from hematite (× 6400); (b) Shadowed particles of iron alkoxide (× 18,850); (c) and (f) Iron alkoxide particle (× 16,500) and corresponding selected area diffraction (S-A-D) diagram; (d) and (e) S-A-D diagrams of thin iron alkoxide particles; (g) Hydrolysis product of iron alkoxide prepared from goethite (× 58,500).
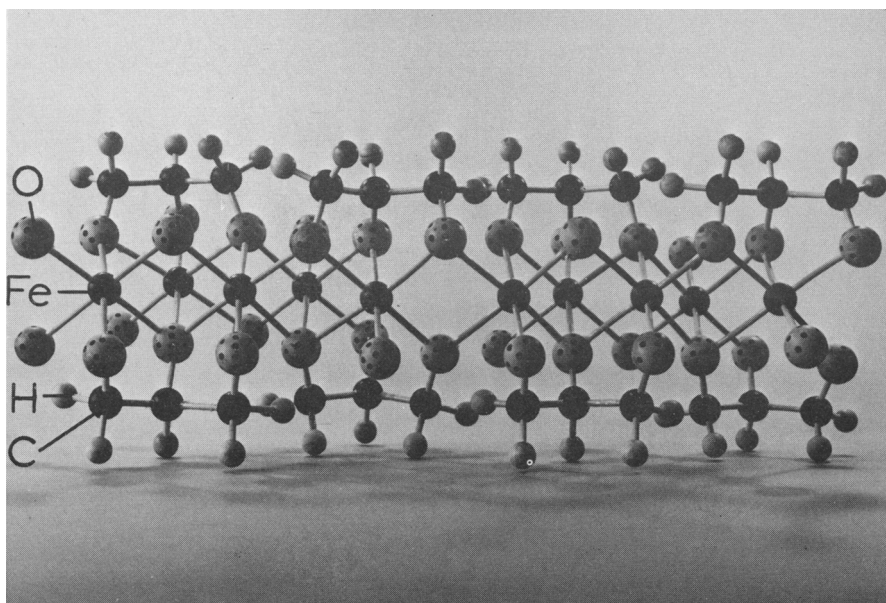

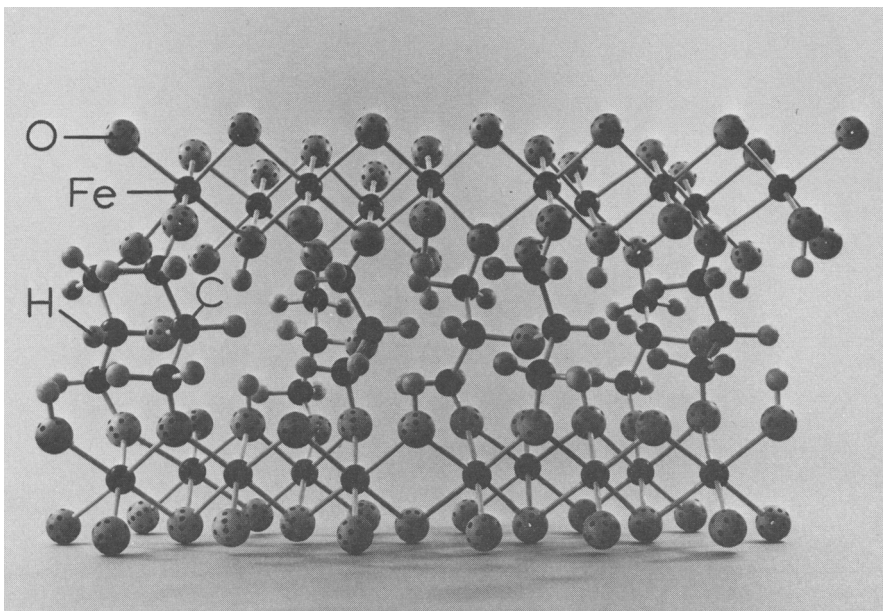Fig. 6. Model structure of iron alkoxide in which the octahedral layers are not linked.

Fig. 7. Model structure of iron alkoxide in which the octahedral layers are linked by the carbon chain.
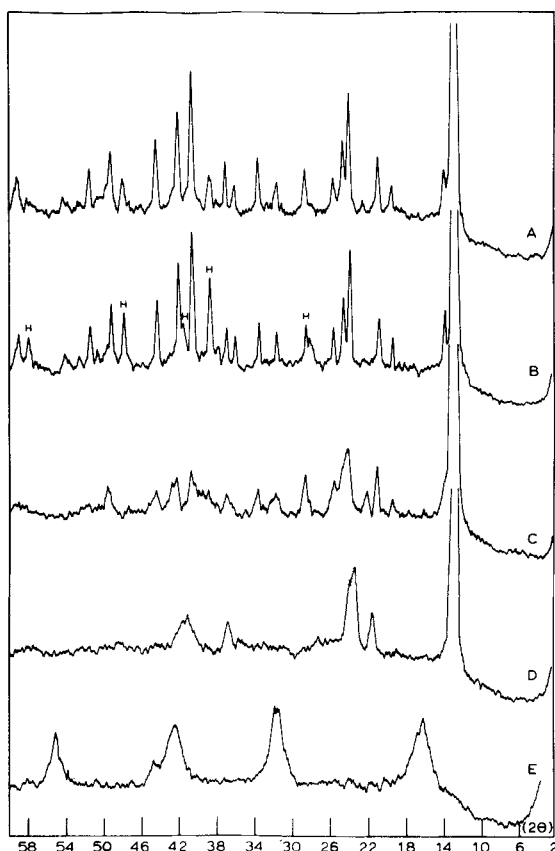
Fig. 3. X-ray diffractometer traces of iron alkoxides (A, B, C and D) and original lepidocrocite (E). A, C and D were obtained from lepidocrocite after a reaction time of 16, 3 and 0 hr respectively and B was obtained from hematite after 3 hr.

indicate that the evolution of the spectrum with time is different for the three starting materials. The diffraction pattern obtained from the lepidocrocite derivative (Fig. 3(D)) shows that the 8·1 Å line occurs the moment that the reaction temperature is reached and that no reflections of the original lepidocrocite (Fig. 3(E)) are visible at this or any further stage during the reaction. A gradual increase in the intensity of the 8·1 Å line, however, occurs with time but the position remains constant within 0·1 Å (Fig. 3(C)). The gradual increase in the sharpness and in the intensity of the reflections of a rather ill-defined spectrum (except for the 8·1 Å line) with time in the lepidocrocite reaction, was not observed in the reaction with hematite, where only sharp reflections of the final iron alkoxide were evident (Fig. 3(B)) together with unreacted hematite reflections, after 3 hr. The diffraction spectra of the solids obtained

from goethite followed the same general pattern as those recorded during the lepidocrocite reaction, except that goethite reacted at a slower rate and was still present after 1 hr reaction time.

I.R. analysis

The i.r. spectrum of the final iron alkoxide (Fig. 4(C)) shows a number of sharp bands (Table 4). No bands of the original iron compounds are present. CH_2 and CH stretching vibrational bands at about $3·5\,\mu$ and CH_2 bending vibrational bands at about 7·0 and $11\,\mu$ can be distinguished. A number of sharp bands occur in the region where, in glycerol (Fig. 4(b)), the secondary CO vibrational stretching ($8·8$–$9·6\,\mu$) and the primary CO vibrational stretching ($9·6$–$10·0\,\mu$) occur. A group of 3 distinct bands which are not present in the glycerol spectrum appear in the region between 12 and $13\,\mu$. Only a very low intensity OH stretching vibrational band can be recognized in the spectrum. The same spectrum is obtained for iron alkoxides prepared from the different starting materials. The band intensities of preparations obtained from goethite are, however, less.

The evolution of the spectrum follows a different pattern when starting from goethite and lepidocrocite, than when starting from hematite. Figure 4(E) gives the spectrum of the reaction product obtained when lepidocrocite is reacted with glycerol during a short period. It represents the reaction product
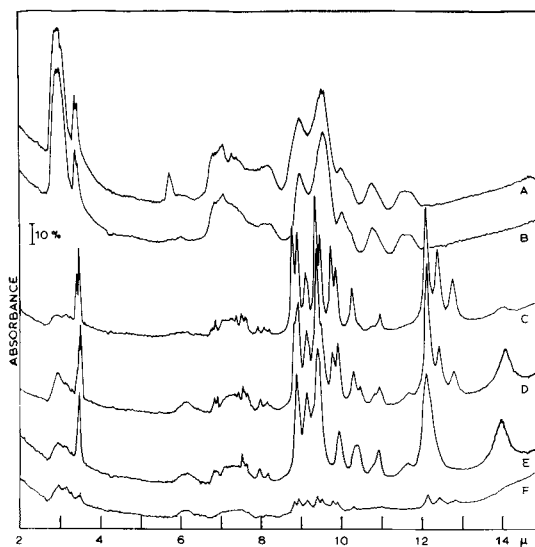

Fig. 4. Infrared spectra of excess glycerol (A), glycerol (B) and iron alkoxides (C, D, E and F). C, D and E were obtained from lepidocrocite after a reaction time of 16, 3 and 0 hr respectively and F was obtained from hematite after 1 hr.

Table 4. Infrared absorption bands of the well crystallized iron alkoxide. Intensities are given by the ratio of the weight of the absorbance band to the weight of the band at $9.4\,\mu$

λ (μ)	ν (cm^{-1})	Relative intensity (%)	Provisional assignment
2·9	3455	19·0	Residual OH
3·41	2935	23	
3·45	2900	39	CH$_2$ and CH stretching
3·505	2355	61	
6·79	1473	6	
6·85	1460	7	
6·91	1447	12	CH$_2$ deformation
7·43	1346	15	
7·55	1325	16	
7·59	1318	15	
7·65	1307	12	
7·70	1299	12	
7·97	1255	6	
8·12	1232	6	
8·15	1227	6	
8·25	1212	3	
8·82	1133	83	
8·95	1118	82	
9·14	1093	45	
9·19	1090	41	
9·40	1063	100	C—O stretching
9·51	1051	77	
9·79	1021	70	
9·92	1008	52	
10·32	967	34	
10·78	928	3	
11·02	906	13	CH$_2$ deformation
12·16	823	89	
12·43	804	61	
12·82	779	36	
14·07	711	4	

obtained the moment that the reaction temperature of 245°C (after 40 min) was reached and is typical of an intermediate product also observed in the reaction with goethite. The reaction of glycerol with hematite does not show any sign of this intermediate product and only the evolution of the spectrum typical of the final iron alkoxide can be observed (Fig. 4(F)).

The i.r. spectrum of the intermediate product contains also, as the final product, the CH$_2$ and CH stretching vibrational bands at $3.5\,\mu$, the CH$_2$ bending vibrational bands at about 7 and $11\,\mu$ and virtually no OH stretching vibrational bands. The rest of the spectrum shows some distinct differences from the spectrum of the final iron alkoxide, especially in the region between 8·8 and $10.0\,\mu$, and between 12 and $13\,\mu$, where only single bands, instead of multiple bands occur. The intensity of the band at $14\,\mu$ is also considerably higher than in the final Fe alkoxide.

Figure 4D gives the spectrum of lepidocrocite after 3 hr which shows the development of a doubling of the bands between 8·8 and $10.0\,\mu$ and the evolution of the three bands between 12 and $13\,\mu$. A similar evolution takes place during the glycerol–goethite reaction, but not during the glycerol–hematite reaction.

Reduction of ferric iron

The change in the ferrous iron content of the solid (Fig. 5) during the reaction with glycerol indicates a fast reduction of ferric iron during the first hour when starting from goethite and lepidocrocite. When starting however, from hematite most of the reduction occurs between 1 and 3 hr. The presence of unchanged starting material will, of course, influence the relative ferrous content. According to X-ray diffraction no lepidocrocite and goethite are present in the reaction product after 0 hr and 1 hr reaction time respectively, but hematite is still present after 3 hr. This result indicates, therefore, that the intermediate products observed in the reaction with goethite and lepidocrocite, by means of i.r. analysis, are rich in ferric iron and are gradually reduced during the reaction.

DISCUSSION

The form of the platelets as shown by the electron-optical studies, suggests the presence of a pseudo hexagonal basal plane which may, of course, be due to the presence of an octahedral layer in the structure of the iron alkoxide of glycerol. According to the X-ray and electron diffraction data and allowing that the unknown direct angles are close to 90°, a, b and c parameters of 5·3 Å, 9·4 Å and 8·1 Å respectively are suggested. The cell is monoclinic or triclinic. Comparison of the a and b parameters with those of octahedral hydroxides shows a reasonable fit with the corresponding distances in brucite, where $a = a_0\sqrt{3} = 5.38$ Å and $b = 3a_0 = 9.36$ Å. Since the ionic radius of Mg^{2+} is 0·65 Å and those of Fe^{2+} and Fe^{3+} are 0·76 Å and 0·64 Å respectively, the similarity of the observed a and b distances with those of octahedral hydroxides suggests that the iron alkoxide structure is patterned by an iron (II and III) octahedral layer. The glycerol chains should then be located between the sheets. The number n of molecular weight formulas in the unit cell may be roughly estimated, assuming an orthorhombic structure:

$$n = \frac{243\ \text{cm}^3 \times \dfrac{2.52\ \text{g}}{\text{cm}^3}}{640.41\ \text{g}} = 0.96$$
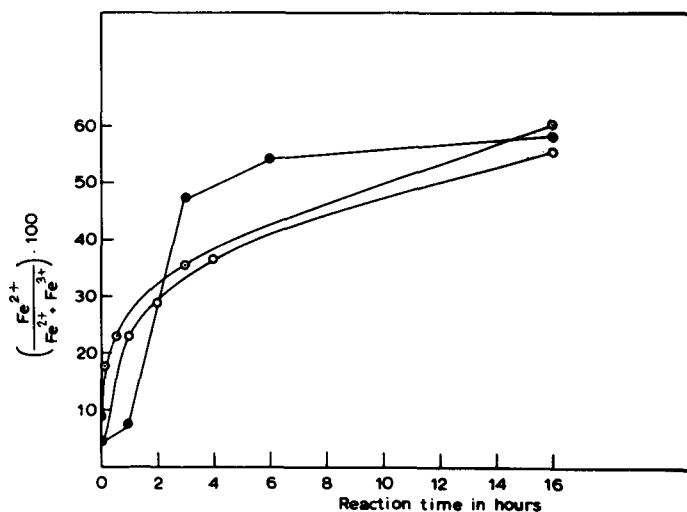
Fig. 5. Percentage of ferrous iron present in the solid phase during the reaction of glycerol with goethite (-○-) lepidocrocite (-◉-) and hematite (-●-).

where $2·52$ g/cm^3 is the density. The density was obtained by using a Berman balance fitted with toluene. The powdered sample was compressed under 300 kg per cm^2 prior to the determination. 243 cm^3 is the molar unit cell volume and $640·41$ g the molecular weight. There is thus one molecular weight unit per unit cell.

With the aid of models, an attempt was made to construct an iron alkoxide structure in which iron and oxygen, linked to the chain of glycerol, could be accommodated in octahedral layers spaced at distances of $8·1$ Å. One way in which this could be accomplished, without changing the aliphatic chain and without having OH groups present in the structure, was by linking the glycerol molecules to three adjacent oxygens on the same octahedral layer as shown in Fig. 6 and by removing the water molecules obtained in this process. Therefore, no chemical link between the octahedral layers is formed. In order to accommodate a ratio of 3 Fe^{2+} to 2 Fe^{3+} one out of 6 octahedras must remain vacant. The model is in agreement with the requirements set down by the chemical analysis, basal spacing and absence of hydroxyl groups. Since no direct linking occurs between octahedral sheets this structure may explain the stacking disorder suggested by some of the electron diffraction patterns, since the basal plane is a cleavage plane. The multiplicity of the CO stretching band may be assigned to linkages with either Fe^{2+} or Fe^{3+}.

It is possible to link octahedral layers of the same composition, but not within the requirements set by the chemical analysis and absence of

hydroxyl groups. One of the possibilities giving the required spacing involves units of two glycerol molecules linked by an ether linkage as shown in Fig. 7. The chemical formula $C_{12}H_{24}O_{14}Fe_2^{3+}Fe_3^{2+}$ differs not too much from the experimental value of $C_{12}H_{21·04}O_{12·24}Fe_{2·12}^{3+}Fe_{2·88}^{2+}$, but it becomes difficult to explain the low intensity of the OH stretching band and to explain the hydrolysis of the ether linkage by water.

However, a slightly different structure, in which the glycerol units are not all oriented in the same direction and in which oxygens not bonded to the carbon chain do not bear hydrogen, is possible. In this case the space requirements between the organic chains are not easily met. The structure contains no OH groups and the chemical formula agrees with the chemical analysis. In this case all the octahedral positions are occupied.

The first derivative of the nuclear magnetic resonance spectrum of the iron alkoxide is shown in Fig. 8. Due to the high content in paramagnetic nuclei (Fe^{2+} and Fe^{3+}) the second moment is, as may be expected, very large. It was found to be 112 G^2. The proton contribution to the average mean square width is probably less than 20 G^2 for the structure models proposed above. Consequently the contribution of the paramagnetic nuclei is of the order of 90 G^2. For a paramagnetic dipole interacting with spins of quantum number $\frac{1}{2}$, this contribution is expressed by (Andrew, 1958):

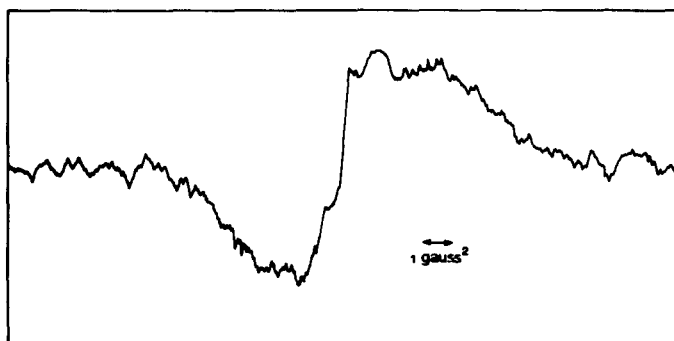$$\frac{2}{15} \langle \mu_p^2 \rangle \sum r_{if}^{-6}$$

Fig. 8. Nuclear magnetic resonance line shape of iron alkoxide prepared
from goethite.

where the maximum value of $\langle \mu_p{}^2 \rangle$ is $\frac{1}{3}\mu^2$. μ being the paramagnetic dipole moment (for Fe^{2+}, $\mu = 5\cdot9$ Bohr magnetons). It follows that if r_{if} is in Å units:

$$\sum r_{if}^{-6} \geqslant 0\cdot675\ 10^{-6}$$

and $(\sum r_{if}^{-6})^{-1/6} \leqslant 10\cdot7$ Å. This result is again compatible with the proposed models.

The existence of an iron alkoxide of glycerol has not been reported in the literature. But the synthesis of several other Fe(III) alkoxides, $Fe(OR)_3$, from $FeCl_3$ or ferric ethoxide has been reported by Bradley, Multani and Wardlaw (1958, a and b). They have been found to be mono-, di- or tri-meric with presumably alkoxide oxygen bridges between Fe atoms. Recently Blyholder and Neff (1966) found by i.r. study that the stable structure of a number of C_xH_yO compounds on evaporated-into-oil Fe at 25°C also gave an alkoxide structure.

The proposed linkage of Fe atoms through alkoxide oxygen bridges is in agreement with the structure containing an octahedral layer, as proposed by us. The octahedral layer can accommodate different ratios of ferric and ferrous iron without a change in the overall oxygen and carbon structure. This may explain the same basal spacing as observed by X-ray diffraction for both the intermediate product and the final alkoxide.

The i.r. spectrum is, however, influenced by changes in the electron distribution between atoms.

Infrared data on alkoxides are rather scarce and the comparison of the spectrum described in Table 4 with other references is almost impossible. Guertin et al. (1956) pointed out that, in Al alkoxide, the C—O—Al stretching occurs between 1033 and 1070 cm^{-1} according to the nature of the derivative. Moreover two strong bands appeared at 850 and 834 cm^{-1} which were absent in the

corresponding alcohols. Miyake (1959) observed the splitting of the C—O bands between 1000 and 1100 cm^{-1} into more numerous components in nickel and cobalt complexes of ethylene- or diethyleneglycols.

A change in the ratio of ferric and ferrous iron probably influences the i.r. spectrum. Differences between the i.r. spectrum of the intermediate product and the final alkoxide are, therefore, probably related to the ratio of Fe^{3+} and Fe^{2+} in the reaction products. The doubling of bands, as compared with the intermediate product, especially between $8\cdot8$ and $10\cdot0\mu$ and the appearance of the three bands between 12 and 13μ in the i.r. spectrum of the final iron alkoxide may be due to interactions caused by both ferrous and ferric ions. The bands between $8\cdot8$ and $10\cdot0\mu$ are probably primary and secondary CO vibrational stretching bands, but no definite assignment could be proposed for the three bands around 12μ. It is interesting to mention in this connection that Stubican and Roy (1961) established that the vibration bands in layer structure silicates are very sensitive to ionic substitution of ions of different charge and that the ionic substitution in certain coordinations will strongly affect absorption bands which appear to be associated with the ions present in that same coordination.

According to our results at least two steps are involved in the formation of the final iron alkoxide: (1) a rearrangement of the structure of the starting material with accommodation of carbon in the structure (2) a reduction of ferric iron.

The occurrence of the intermediate product in the reaction with lepidocrocite and goethite may be related to the structure of these materials and especially to the fast rate at which the structures of goethite and lepidocrocite are rearranged to accommodate glycerol. The reduction of ferric iron may be the limiting step and this could explain

the formation of a ferric-rich intermediate product. The hematite structure, however, being more compact, breaks up at a relatively slow rate and may cause a relative rate of reduction fast enough to favour the formation of the stable ferrous-rich iron alkoxide directly.

The exact role of organic molecules in the transformations of iron compounds should be an interesting field of study. We obtained the same end product when starting from hematite, amorphous ferric hydroxide gel, lepidocrocite, goethite and a spinel structure. The stable structure of hematite, for instance, could be converted into the less stable structure of maghemite. A strong influence of organic matter on transformations of iron oxides was also found by Van der Marel (1951). He found that heating to 600°C of lepidocrocite, limonite and goethite in the presence of organic compounds always resulted in the formation of the spinel structure of maghemite. In the absence of organic compounds hematite was formed.

The main reason for this study was to obtain knowledge about the reaction of glycerol with iron oxides and hydroxides in order to determine the possibility of the reaction as a tool for distinguishing between different forms of iron oxides and hydroxides in soils. Since the same iron alkoxide is obtained from different oxides and hydroxides however, the reaction does not offer a direct possibility for the determination of the different forms of iron compounds in soils. The studied reaction may however, be interesting for removing iron oxides from clay surfaces and for preparing magnetic iron oxides.

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Résumé— La goethite, la lépidocrocite, et l'hématite ont été soumis à une réaction avec du glycérol et les produits de réaction ont été étudies à des étapes diverses de la réaction. Après un traitement de 16 hr à une température de 245°C la forme finale de produit de réacton, un solide mou de couleur vert foncé, a été obtenue, à partir du matériau de départ quelconque. D'après l'analyse d'hydrolyse et chimique, le produit de réaction peut être identifié comme un alkoxide de fer. L'hydrolyse du solide avec de l'eau bouillante, produit du glycérol et un matériau fortement magnétique caractérisé par une structure spinel comme le maghémite et la magnétite. L'alkoxide de fer apparaît au microscope électronique sous le forme de plaquettes hexagonales bien dessinées. La similarité entre les paramètres a et b de ce composé et ceux de brucite. suggère que la structure de l'alkoxide de fer est basée sur une couche octahédral de fer (II et III). Les chaînes de glycérol devraient être situées entre les feuilles. Deux modèles ont été proposés dans lesquels le fer et l'oxygène, rattachés à la chaîne de glycérol, pouvaient être accommodés dans des couches octahédrales, donnant une périodicité basale de 8·1Å. Au moint deux étapes sont impliquées dans la formation de l'alkoxide de fer: (1) un réarrangement de la structure du matériaux de départ avec une accommodation de carbone dans la structure et (2) une réduction de fer ferrique.

Kurzreferat—Goethit. Lepidokrokit und Hämatit wurden mit Glyzerin reagiert und die Reaktions-produkte wurden in den verschiedenen Stufen der Reaktion studiert. Nach 16-stündiger Behandlung bei 245°C wurde die schliessliche Form des Reaktionsproduktes, ein tiefgrüner, weicher, Feststoff erhalten, und zwar unabhängig vom Ausgangsmaterial. Gemäss Hydrolyse und chemischer Analyse handelt es sich bei dem Reaktionsprodukt um Eisen-Alkoxyd. Die Hydrolyse des Feststoffes in kochendem Wasser ergab Glyzerin und ein stark magnetisches Material gekennzeichnet durch Spinellstruktur wie Maghämit und Magnetit. Das Eisen-Alkoxyd erscheint im Elektronenmikroskop in der Form von grossen. wohlgeformten, hexagonalen Plättchen. Die Ähnlichkeit zwischen *a* und *b* Parametern dieser Verbindung und denjenigen des Brucits deutet darauf hin, dass das Eisen-Alkoxyd Gefüge auf einer Eisen (II und III) oktaedrischen Schicht beruht. Die Glyzerinketten würden sich zwischen den Platten befinden. Es wurden zwei Modelle vorgeschlagen, in welchen die an die Glyzerinkette gebundenen Eisen- und Sauerstoffatome in oktaedrischen Schichten mit einer Basalabstand von 8,1 Å untergebracht werden könnten. An der Bildung von Eisenalkoxyd sind zum mindesten zwei Stufen beteiligt: (1) Umlagerung des Gefüges des Ausgangsmaterials mit Unterbringung von Kohlenstoff in Gefüge und (2) eine Reduktion des Ferri-Eisens.

Резюме—Гётит, лепидокрокит и гематит были подвергнуты реакции с глицерином; изучались протукты различных стади й реакыии. После обработки в течение 16 часов при 245⁰ С была получена конечная форма продукта реакции, представляющая собой, независимо от исходного материала, мягкое вещество темно зеленого цвета. Согласно данным гидролиза и химического анализа продукт реакции может быть идентифицирован как алко-окисел железа. При гидролизе в кипящей воде были получены глицерин и сильно магнитное веще-ство, характеризующееся, подобно магемиту и магнетиту, шпинелевой структурой.

Согласно данным электронной микроскопии алко-окисел состоит из хорошо оформлен-ных гексагональных пластинок. Близость *a* и *b* параметров этого соединения и брусита указы-вает, что структура алко-окисла железа основывается на железистом (II и III) октаэдри-ческом слое. Глицериновые цепи должны располагаться между слоями. Предложены две модели, в которых атомы железа, соединенные с цепью глицерина, могут размещатся в октаэ-дрические слои, обуславливая базальное межплоскостное расстояние 8,1 А.

Образование алко-окисла железа осуществляется по меньшей мере в две стадии: (1) перестройки структуры исходного вещества с размещением в нем атомов углерода и (2) уменьшения количества окисного железа.