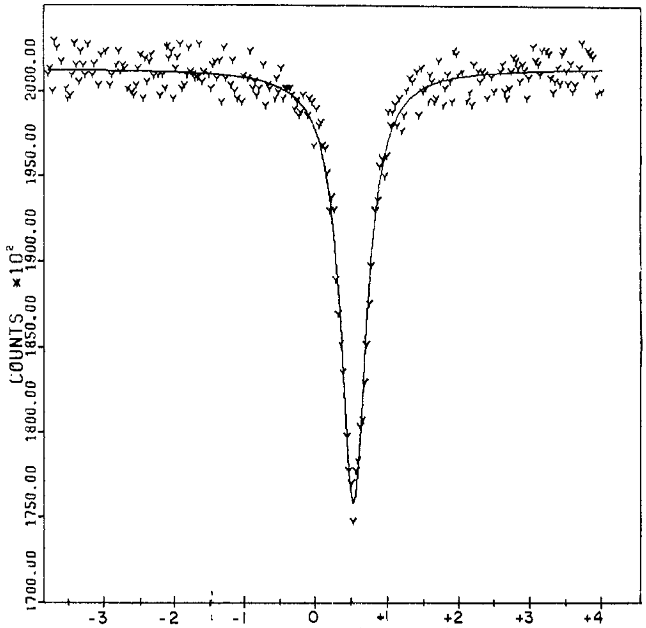

Figure 2.—Mössbauer spectra of $[(C_2H_5)_4N][FeCl_3Br]$.

quadrupole splitting in the spectra or at least a broadening of the absorption line which would be indicative of an unresolved quardupole splitting. The absence of either one of these effects in the mixed-halide anions indicates that the difference in bonding between a bromide and a chloride ligand in the tetrahaloferrates is not enough to distort the tetrahedral charge distribution.

The isomer shift values obtained for $FeCl_4^-$ and $FeBr_4^-$ as shown in Table V are in excellent agreement with those reported by Edwards, *et al.*[2] The decrease in the positive isomer shift (δ) in the tetrahaloferrates as the number of chlorides in the coordination sphere increases indicates an increase in the s-electron density at the iron nucleus. This decrease in δ with an increase in the number of chlorides is just opposite from what one would predict based upon covalency considerations. As the degree of covalency in the metal–ligand bond increases, an increasing fraction of σ-electron density is transferred to the iron, causing a decrease in δ. Edwards, *et al.*,[2] have shown that the Fe–Br bond is more covalent than the Fe–Cl bond, and thus one would expect that the isomer shift for $FeCl_4^-$ should be more positive than that for $FeBr_4^-$. The smaller amount of s-electron density at the iron nucleus in $FeBr_4^-$ as compared to $FeCl_4^-$ can be accounted for if the π-bond formation in these complexes is considered in addition to the σ-bond formation. Based upon the crystal structure determination for $[(C_6H_5)_4As][FeCl_4]$, Zaslow, *et al.*,[11] postulated the existence of π-bond formation to account for the short Fe–Cl bond distance. The π bond would result from the overlap of lone pairs of p electrons on the halides with partially filled $3d_{xz}$, $3d_{xy}$, and $3d_{yz}$ orbitals of iron which are of the same symmetry. Since the capability of this type of bond formation has been shown to be greater for bromides than for chlorides,[12] the 3d orbital electron density would be greater in $FeBr_4^-$ than in $FeCl_4^-$. This 3d orbital electron density partially shields the 4s-electron density from the nucleus, thus accounting for the reduction in s-electron density at the iron nucleus in $FeBr_4^-$ relative to $FeCl_4^-$. This enhanced shielding effect from (p → d) π-bond formation accounts for the increase in isomer shift with an increase in the number of bromides as is observed in Table V.

[11] B. Zaslow and R. E. Rundle, *J. Phys. Chem.*, **61**, 490 (1957).

[12] M. S. Whitehead and H. H. Jaffé, *Theoret. Chim. Acta*, **1**, 209 (1963).

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A Mössbauer Study of the Thermal Decomposition of Potassium Tris(oxalato)ferrate(III)

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Mössbauer spectroscopy has been used to follow the thermal decomposition of $K_3Fe^{III}(C_2O_4)_3 \cdot 3H_2O$ in air and *in vacuo*. After dehydration at about 120°, a binuclear complex containing the anion $(C_2O_4)_2Fe^{II}OxFe^{II}(C_2O_4)_2^{6-}$ (Ox = quadridentate oxalate group) is formed. This complex then decomposes above 380° *via* Fe_3O_4 to either Fe_2O_3 (in air) or Fe (*in vacuo*).

Introduction

Several workers have recently studied the thermal decomposition of potassium tris(oxalato)ferrate(III) and the analogous tris-oxalate complexes of chromium, manganese, and cobalt.[1-4] For the iron complex,[3] infrared spectra have been recorded at the plateaus of the thermogravimetric analysis (tga) curve, but the decomposition products have not been conclusively identified, nor has the mechanism of decomposition been discussed.

[1] W. W. Wendlandt, T. D. George, and K. V. Krishnamurthy, *J. Inorg. Nucl. Chem.*, **21**, 69 (1961).

[2] W. W. Wendlandt and E. L. Simmons, *ibid.*, **27**, 2317, 2325 (1965).

[3] N. Tanaka and M. Nanjo, *Bull. Chem. Soc. Japan*, **40**, 330 (1967).

[4] L. A. Funes and W. W. Wendlandt, *Arch. Bioquim. Quim. Farm. Tucuman*, **12**, 113 (1965).

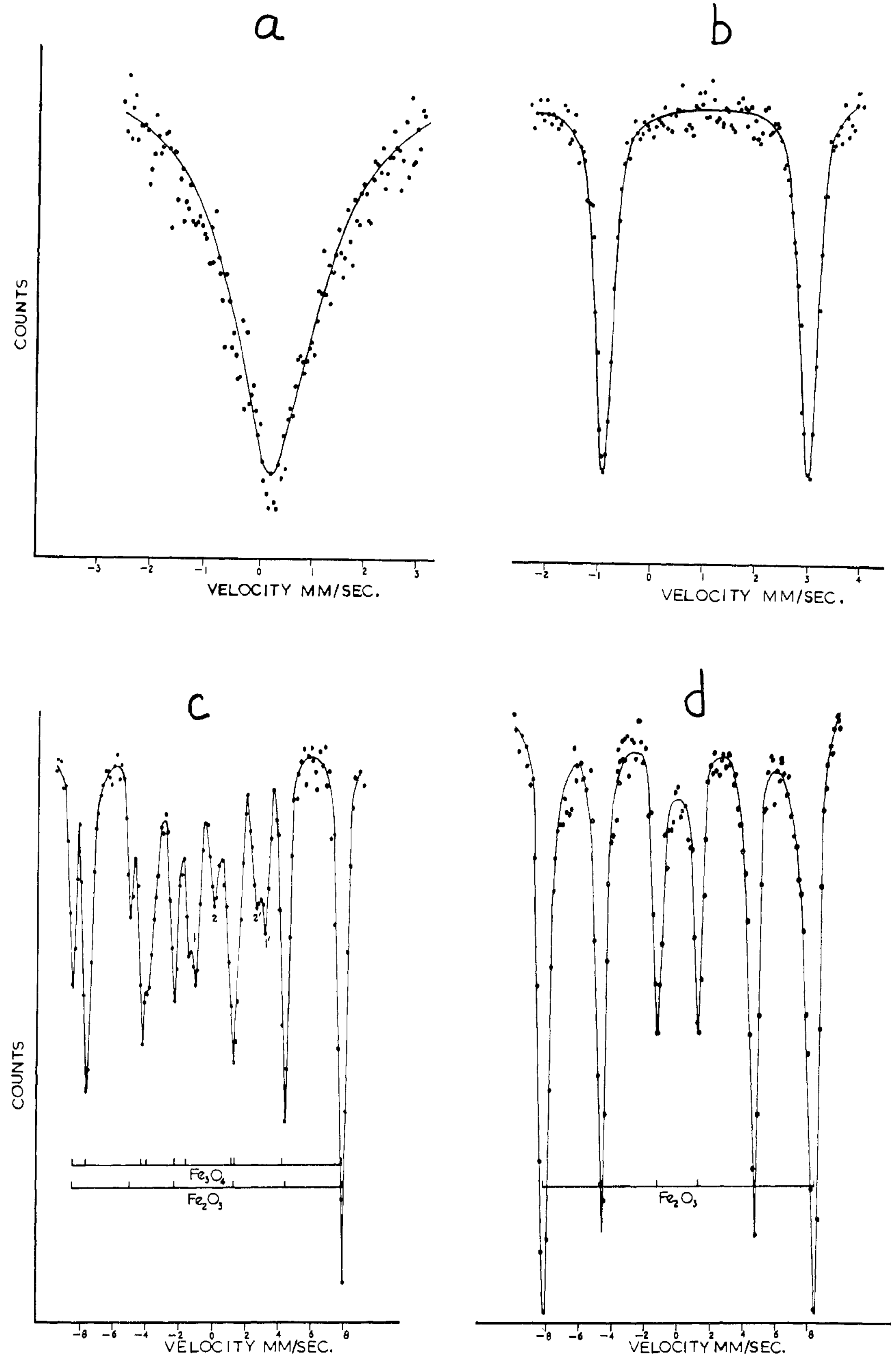

Figure 1.—Mössbauer spectra at various stages of the thermal decomposition of $K_3Fe(C_2O_4)_3 \cdot 3H_2O$ in air: (a) unheated $K_3Fe(C_2O_4)_3 \cdot 3H_2O$; (b) sample heated at 260° for 15 min [$K_6Fe^{II}_2(C_2O_4)_5$]; (c) sample heated at 380° for 20 min [mainly Fe_3O_4]; (d) sample heated at 400° for 10 hr [Fe_2O_3].

We have repeated the thermogravimetric analysis of $K_3Fe(C_2O_4)_3 \cdot 3H_2O$ and have used Mössbauer spectroscopy to follow the structural changes in the solid. Gallagher and Kurkjian[5] used Mössbauer spectra to follow the thermal decomposition of strontium and barium ferrioxalates. The mechanism and products of decomposition of $K_3Fe(C_2O_4)_3 \cdot 3H_2O$ are entirely different from those formed from the strontium and barium complexes.

Experimental Section

$K_3Fe(C_2O_4)_3 \cdot 3H_2O$ was prepared by a method described in the literature[6] and recrystallized from water–alcohol mixtures. Analysis of this compound gave an oxalate to iron ratio of 2.9. Mössbauer spectra were taken at room temperature using methods and techniques previously described.[7]

The center shift values are reported relative to a ^{57}Co in Pd source. (Add 0.44 mm/sec to convert to sodium nitroprusside as standard.)

The infrared spectra were obtained in hexachlorobutadiene and Nujol mulls using a Perkin-Elmer Model 257 spectrometer. Thermogravimetric analyses were performed in air using a Stanton automatic thermorecording balance.

Results and Discussion

A. Air Decomposition.—We obtained a thermogravimetric curve similar to that reported previously.[3] There are two plateaus in the curve—beginning at about 110 and 260°, respectively. There is also an inflection in the curve at about 420°.

The Mössbauer spectrum of $K_3Fe(C_2O_4)_3 \cdot 3H_2O$ (Figure 1a) consists of one broad peak having a center shift of 0.15 mm/sec. The first stage of decomposition, beginning at 110°, corresponds to the loss of the three crystal waters. The observed weight loss of 11% is identical with the theoretical value. The Mössbauer spectrum of anhydrous $K_3Fe(C_2O_4)_3$ is very similar to that of the hydrate.

The infrared and Mössbauer spectra of the orange-yellow product obtained when a sample was heated at 260° for 15 min are shown in Figures 2a and 1b, respectively. Both infrared and Mössbauer spectra [center shift 1.05 ± 0.05 mm/sec and quadrupole splitting 3.90 ± 0.05 mm/sec] correspond to the compound assigned as the dinuclear species $K_6Fe^{II}_2(C_2O_4)_5$ in the previous study[7] of the γ radiolysis of $K_3Fe(C_2O_4)_3 \cdot 3H_2O$. The observed weight loss of 19.9% is identical with the theoretical value and corresponds to the loss of one CO_2 group and three crystal waters per iron atom, *i.e.*, $K_3Fe^{III}(C_2O_4)_3 \cdot 3H_2O \rightarrow 0.5K_6Fe^{II}_2(C_2O_4)_5 + 3H_2O + CO_2$. Thus two iron atoms are reduced by one oxalate group *via* charge transfer from the oxalate.

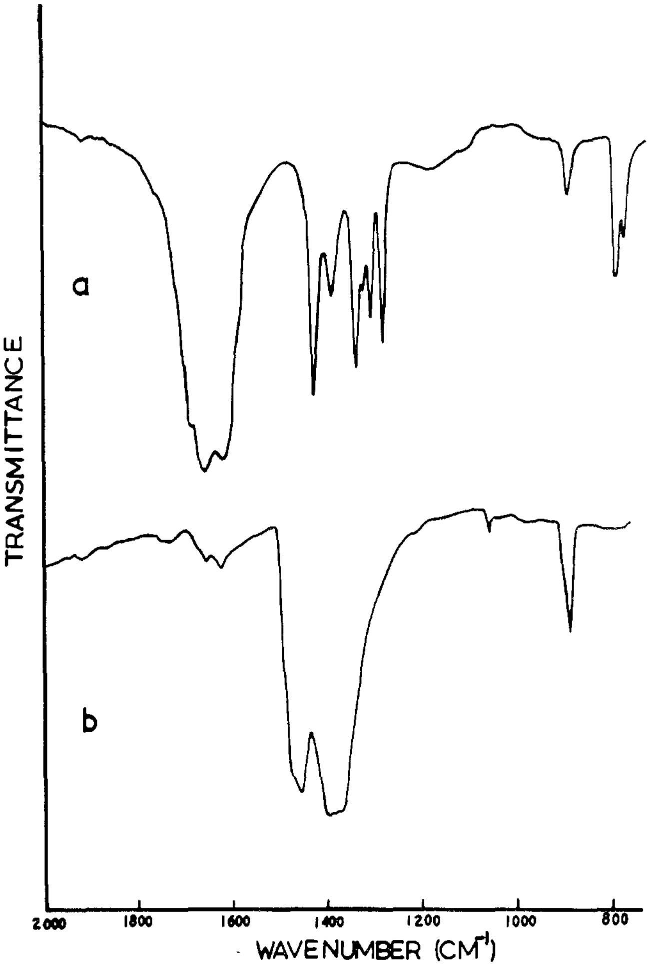

Figure 2.—Infrared spectra of : (a) $K_6Fe^{II}_2(C_2O_4)_5$; (b) sample heated at 380° for 20 min [mainly K_2CO_3].

On heating above 360°, a black mixture is obtained. The Mössbauer and infrared spectra of a sample heated at 380° for 20 min are shown in Figures 1c and 2b, respectively. The infrared spectrum shows intense bands at about 1380 and 1460 cm^{-1}, characteristic of K_2CO_3.[8] The Mössbauer spectrum shows that Fe_3O_4 is the main iron-containing constituent, with smaller amounts of Fe_2O_3 and two paramagnetic substances (lines 1 and 1′ and 2 and 2′). The lines for Fe_2O_3 and Fe_3O_4 have been assigned using the known positions[9] from previous studies. Lines 1 and 1′ are due to undecomposed $K_6Fe_2(C_2O_4)_5$ while lines 2 and 2′ have a center shift and quadrupole splitting of 1.14 ± 0.10 and 2.35 ± 0.10 mm/sec, respectively. These parameters are similar to those attributed to $K_4Fe(C_2O_4)_3$ in the previous study. The presence of free carbon in this sample has been confirmed by analysis, but no attempt has been made to analyze for amounts of C or the proportions of CO or CO_2 in the evolved gases.

On heating above 500° in the tga experiments, or at 400° for 10 hr, the resulting product gives a Mössbauer spectrum (Figure 1d) characteristic of almost pure Fe_2O_3. The presence of K_2CO_3 in this example was again confirmed from the infrared spectrum. The final products are thus K_2CO_3 and Fe_2O_3—as has been noted by previous workers.[4]

The aerial decomposition can thus be written in full as

$$K_3Fe^{III}(C_2O_4)_3 \cdot 3H_2O \xrightarrow{110^\circ} K_3Fe^{III}(C_2O_4)_3 + 3H_2O \qquad (1)$$

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[5] P. K. Gallagher and C. R. Kurkjian, *Inorg. Chem.*, **5**, 214 (1966).

[6] H. S. Booth, *Inorg. Syn.*, **1**, 36 (1939).

[7] G. M. Bancroft, K. G. Dharmawardena, and A. G. Maddock, *J. Chem. Soc., A*, in press.

[8] C. J. H. Schutte and K. Buijs, *Spectrochim. Acta*, **17**, 921 (1961).

[9] (a) A. H. Muir and H. Wiedersich, *Bull. Am. Phys. Soc.*, **11**, 770 (1966); see also A. Muir, K. J. Ando, and H. M. Coogan, Ed., "Mössbauer Effect Data Index," John Wiley & Sons, Inc., New York, N. Y., 1966, p 26; (b) G. M. Bancroft, A. G. Maddock, and J. Ward, *Chem. Ind.* (London), 423 (1966).

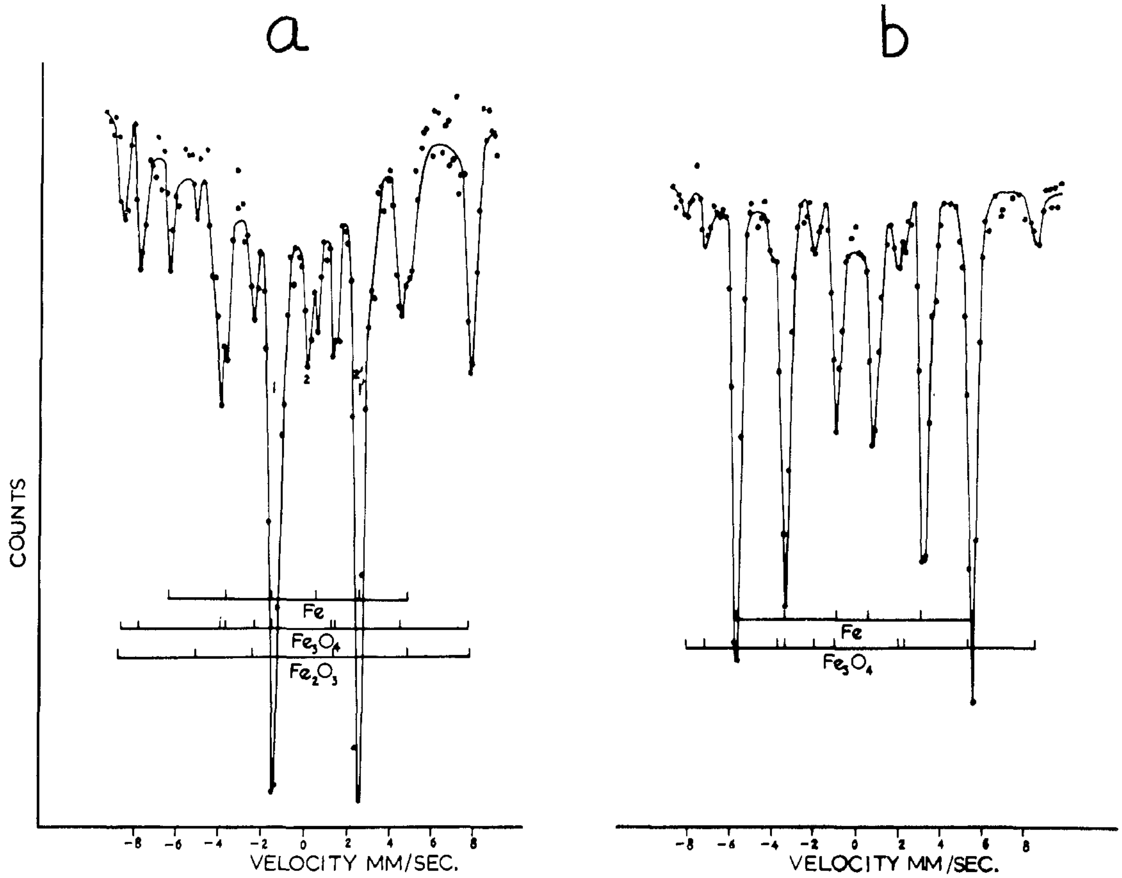

Figure 3.—Mössbauer spectra of $K_3Fe(C_2O_4)_3 \cdot 3H_2O$ heated *in vacuo:* (a) sample heated at 400° for 10 min; (b) sample heated at 400° for 20 min [mainly Fe].

$$K_3Fe^{III}(C_2O_4)_3 \xrightarrow{260^\circ} {}^1/_2K_6Fe^{II}_2(C_2O_4)_5 + CO_2 \qquad (2)$$

$$ {}^1/_2K_6Fe^{II}_2(C_2O_4)_5 \xrightarrow{380^\circ} {}^3/_2K_2CO_3 + {}^1/_3Fe_3O_4 + xC + (CO_2 + CO) \qquad (3)$$

$$ {}^3/_2K_2CO_3 + {}^1/_3Fe_3O_4 + xC \xrightarrow{400^\circ} {}^1/_2Fe_2O_3 + {}^3/_2K_2CO_3 + (CO_2 + CO) \qquad (4)$$

B. The Decomposition *in Vacuo.—In vacuo,* the first two steps of decomposition proceed as in air, but the H_2O begins to be lost at room temperature and the second step to the dinuclear compound begins at 230°. However, the final stages of decomposition are distinctive. The Mössbauer spectra of $K_3Fe(C_2O_4)_3 \cdot 3H_2O$ samples heated for 10 and 20 min at 400° *in vacuo* after dehydration at 110° are shown in Figures 3a and 3b. In Figure 3a the major decomposition products of $K_6Fe_2(C_2O_4)_5$ (lines 1 and 1′) are Fe_3O_4 with smaller amounts of Fe, Fe_2O_3, and the paramagnetic species $K_4Fe(C_2O_4)_3$ (lines 2 and 2′). On heating for 20 min (Figure 3b), the Mössbauer spectrum indicates that nearly pure Fe is formed. The analysis of these samples indicates the presence of K_2CO_3 and C and the ir spectrum is identical with that in the aerial decomposition (Figure 2b).

Thus, in the vacuum decomposition, the Fe_3O_4 formed is reduced by the carbon in the mixture on further heating, whereas in the aerial decomposition, both the Fe_3O_4 and carbon are oxidized.

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