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Kinetic and thermodynamic studies of the nonisothermal decomposition of anhydrous copper(II) formate in different gas atmospheres

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Abstract

The thermal decomposition of anhydrous (orthorhombic) copper(II) formate was studied by programmed rising-temperature methods (TG, DTG, DTA and DSC) to about 250 °C in flowing gas atmospheres of nitrogen (inert), hydrogen (reducing) and air (oxidizing). The degradation reaction, anion breakdown, proceeded to completion in two distinct, but partially overlapping, rate processes and apparent Arrhenius parameters, calculated by the Ozawa nonisothermal kinetic method, agreed satisfactorily with the literature results. It was concluded that the two consecutive processes, contributing to the overall reaction, involved stepwise cation reduction: $Cu^{2+} \rightarrow Cu^{+} \rightarrow Cu^{0}$, with copper(I) formate as intermediate. This mechanism is similar to that proposed in previous studies of the decompositions of copper(II) oxalate, malonate, maleate, fumarate, mellitate and squarate. For all of these reactants, the Cu^{+} salt has been identified as an intermediate, exhibiting a (slightly) lower relative reactivity than the corresponding Cu^{2+} salt. For copper(II) formate the response curves in the three different gaseous atmospheres were generally similar, showing that neither oxidizing nor reducing conditions caused a marked change in reactivity. The temperature of reaction initiation in H_2 was slightly diminished and the temperature of the second stage of reaction in O_2 was raised appreciably. It is believed that electron transfer contributed to the control of reactivity and that the gases present appreciably influence the rates of the contributory reactions occurring.

Keywords: Copper formate; Crystolysis reaction; Decomposition kinetics; Reaction mechanism

1. Introduction

Investigations have been reported for the thermal decompositions of a number of copper(II) carboxylates and other copper(II) salts of organic acids, including copper oxalate [1], copper malonate [2], copper maleate and copper fumarate [3], copper mellitate [4], copper itaconate [5] and copper squarate [6]. Some [1–4,6] were based on kinetic measurements of the accumulated pressure of gas evolved from isothermal salt breakdown into an evacuated glass apparatus at suitable time intervals, whereas a nonisothermal technique was used in [5].

A common mechanistic feature in this group of isothermal investigations of copper(II) salts [1–4,6], characterized by analytical measurements, was stepwise cation reduction, $Cu^{2+} \rightarrow Cu^{+} \rightarrow Cu^{0}$ [2,4]. The copper(I) salt of each anion was appreciably more stable than the copper(II) reactant. It was shown by direct observation of partially reacted copper(II) salts using the scanning electron microscope that some of these processes involved at least partial melting, for example: copper malonate [2]. Residual (solid) products remaining on completion of these reactions were identified by microscopic and analytical measurements as metallic copper dispersed on a carbonaceous matrix.

The present study of the nonisothermal decomposition of copper(II) formate was undertaken to complement and to extend an earlier isothermal study [7] of the breakdown of this reactant. Thermoanalytical techniques are used here to determine the influence of the gas atmosphere (flowing hydrogen, nitrogen or air) on the kinetics of reaction. These results are discussed in the context of conclusions reached in previous studies of the thermal properties of the other copper(II) salts mentioned [1–6].

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2. Experimental

2.1. Salt preparation

The 0.1 M (13.4 g) anhydrous $CuCl_2$ (AnalaR) in 100 ml distilled water, was mixed slowly, with stirring, to 0.2 M (12.6 g) ammonium formate (NH_4OOCH, analytical grade) in ethanol at 50 °C. The solution was extracted with excess diethyl ether, the light-blue precipitate was filtered and dried at 100 °C. Carbon and hydrogen contents of this salt were determined by standard combustion techniques and copper by the inductively coupled plasma (ICP) method using a Model OES ARL instrument (Switzerland).

2.2. Apparatus and experimental methods

2.2.1. Thermal analysis

Thermal analyses (TG, DTG, DTA, and DSC) were carried out by a Shimadzu "Stand Alone" thermal analyzer (TGA-50H, DTA-50 and DSC-50, Japan) using the associated data acquisition and handling system, TA-50WSI.

Salt decompositions were studied in dynamic atmospheres of dry nitrogen, hydrogen or air, flowing at 40 ml min^{-1}. Constant sample masses, between 10 and 15 mg, were used to minimize any possible influences of sample mass on instrumental responses (peak shape and temperatures of maxima) [8]. Highly sintered α-Al_2O_3 powder (Shimadzu) was used as the DTA and DSC reference material. Each thermal analysis experiment was repeated three times and all mass losses reported were average measurements. Reproducibility was better than ±1%. DTA and DSC peak temperatures similarly showed acceptable reproducibility, values agreeing within ±1 °C. Calibrations of both DTA and DSC instruments, in the different atmospheres, for temperature and enthalpy measurements were carried out at selected heating rates from 2 to 20 °C min^{-1} using Specpure metals, Johnson Matthey, melting points: indium, 156.3 °C, and zinc, 419.6 °C, with ΔH: 28.24 and 101.50 J g^{-1}, respectively [9]. Nitrogen gas was 99.0% pure, from Egyptian Company of Industrial Gases (El-Hawamdya, Giza).

2.2.2. X-ray diffraction

X-ray powder diffraction was used to characterize the original reactant, the decomposition products of reaction in N_2, H_2 and in air, and also the prepared (reference) metal oxides. A model D5000 Siemens diffractometer (Germany) used Ni-filtered Cu Kα radiation ($\lambda = 1.5406$ Å), with an on-line data acquisition and handling system. This included an automatic JCPDS [10] library search and match facility (Diffrac AT software, Siemens) for phase identification.

2.2.3. Infrared spectroscopy

Infrared spectra for the reactant as prepared, after partial decompositions at selected temperatures in different atmospheres and residual (final) products were obtained using KBr discs on a Magna-FTIR 560 (USA) instrument with Nicolet Omnic softwear.

2.2.4. Gas chromatography

The volatile reaction products were analysed by a Shimadzu computer-controlled gas chromatograph, Model GC-14A (Japan), at atmospheric pressure with N_2 or H_2 carrier gas (160 ml min^{-1}). Products were separated on a SUS column PEG 6000 10% on Shimalite TPA, 60–80 mesh, 3 mm i.d. × 2 mm at 80 °C with a thermal conductivity detector. Automatic sampling used a heated gas-sampling valve, Type HGS-2.

2.2.5. Copper(II) ion determination

As previously [1–4,6], progressive changes in Cu^{2+} ion contents in samples of partially decomposed copper(II) salt reactant, after various known times and temperatures of reaction, were measured by iodometric titration, as described in [2]. Weighed (constant amounts) of reactant were heated to appropriate temperatures in the different gas atmospheres under conditions similar to those of the kinetic studies. Each sample was removed, cooled and immediately dissolved in an acid iodide solution and the iodine released was, at once, titrated with standard (0.05 N) sodium thiosulphate, using starch indicator.

2.2.6. Kinetic analysis

Kinetic parameters: E, activation energy (kJ mol^{-1}) and A, frequency factor (min^{-1}) were calculated by the Ozawa equation [11–13], for the decomposition reactions studied, from

$$\ln\left(\frac{\phi}{T_m^2}\right) = -\left(\frac{E/R}{T_m}\right) + \ln\left(\frac{R}{\theta E}\right) \qquad (1)$$

where ϕ is the constant heating rate (°C min^{-1}), T_m the DTG peak maximum temperature, R the gas constant and $\theta = A^{-1}$. DSC measurements were used to calculate enthalpy changes, ΔH, for the decompositions [14].

3. Results and discussion

3.1. Copper(II) formate reactant characterization

The results of elemental analysis of the reactant were as follows, the theoretical values (bracketed) refer to the anhydrous preparation investigated—$CuC_2H_2O_4$: Cu, 40.95% (41.36); C, 15.4% (15.65); H, 1.45% (1.30); O (by difference), 42.2% (41.69).

The X-ray powder diffraction pattern for the reactant agreed with JCPDS Card no. 32-0332 [10], identifying this as the orthorhombic form of anhydrous copper(II) formate. This is concluded from the peaks at $2\theta = 18.42^\circ$, 15.94° and 3.30° ($d = 4.81$, 5.55 and 27.03 Å) and relative intensities, $I/I_0 = 100$, 22.7 and 11.4%, respectively. Infrared spectra confirmed the presence of the characteristic absorption

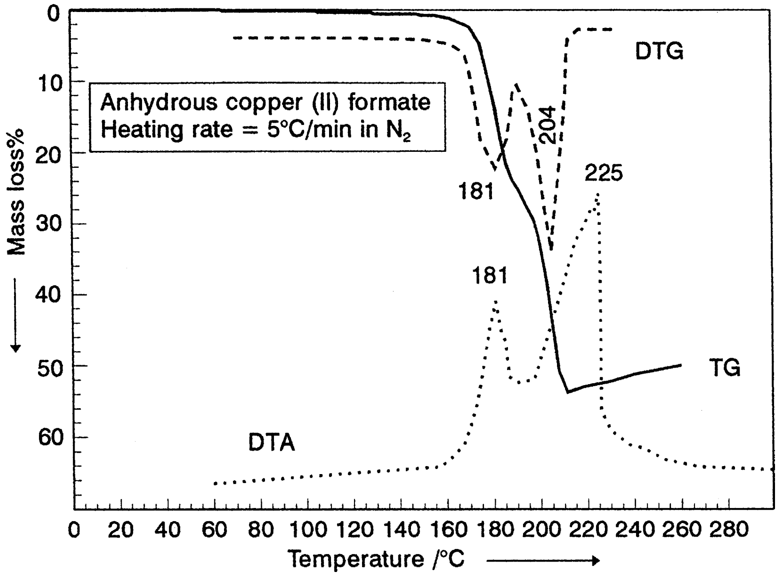

Fig. 1. TG, DTG and DTA curves for the decomposition of anhydrous copper(II) formate in nitrogen (flow 40 ml min^{-1}) with temperature increase of 5 °C min^{-1}.

peaks of the formate ion at 1551, 1405, 1362 and 832 cm^{-1} [15]. The absence of absorption peaks characteristic of water confirmed the absence of water of crystallization in this prepared anhydrous reactant (which, therefore, differed from the prepared salts in the earlier study [7]).

3.2. Thermal analysis results

3.2.1. In nitrogen

TG, DTG and DTA response curves observed during heating (5 °C min^{-1}) anhydrous copper(II) formate in a nitrogen flow (40 ml min^{-1}) are shown in Fig. 1. Reaction became detectable above 110 °C and at higher temperatures two distinct, but partially overlapping, mass-loss rate processes were observed. Reactions between 110–190 and 190–213 °C were estimated to result in mass losses of 24.8 and 30.7%, respectively, giving an overall mass diminution of 55.5%. Above 215 °C there was a slow, small increase in mass. DTG curves identified peak maxima at 181 and 204 °C and, for the same reactions, the DTA curves gave exothermic responses with maxima at 181 and 225 °C.

The mass loss corresponding to the completed reaction, 55.5%, is somewhat less than expected for the formation of metallic copper as the only residual product (58.6%) but greater than values corresponding to the formation of Cu_2O (53.4%) or CuO (48.2%). The later slow mass-gain detected by TG is the evidence of residual product metal oxidation following completion of reaction, attributable to reaction with traces of oxygen in the flowing nitrogen atmosphere used [16]. This 3.1% difference represents oxide formed and the rate observed after completion of decomposition is comparable with that attributed to late mass-gain occurring following salt breakdown in air (described in Section 3.2.3). It is concluded, therefore, that copper metal is the dominant, possibly exclusive, primary solid product, as previously reported for the decomposition of copper(II) formate [7].

3.2.2. In hydrogen

TG, DTG and DTA response curves for salt decomposition during heating (5 °C min^{-1}) in flowing hydrogen (40 ml min^{-1}) are shown in Fig. 2. The onset of reaction becomes detectable at a slightly lower temperature (around 100 °C) than in the inert atmosphere (N_2). Again the main decomposition occurs as two overlapping mass-loss processes estimated as 25.1 and 33.2%, between 143–196 and 196–220 °C, and with DTG peak maxima at 184 and 213 °C. The sum of both mass losses, 58.3%, is close to expectation (58.6%) for reactant decomposition to copper metal as the only residual product. The DTA curve for the same reaction conditions is significantly different, in that the first peak was endothermic (maximum at 179 °C) which contrasts with the exothermic responses detected in nitrogen and in air. The second exothermic peak maximum occurred at 226 °C.

3.2.3. In air

TG, DTG and DTA response curves during heating of the reactant in air under the same conditions (5 °C min^{-1} and 40 ml min^{-1}) are shown in Fig. 3. Again two DTG peaks were identified between 140–187 and 187–229 °C, maxima at 175 and 224 °C. The first represented a relatively smaller mass loss, 11.7%, than the second, 40.6% and the sum, 52.3%, is evidence of significant oxide product formation. The continued mass increase after decomposition (TG) was ascribed to maintained slow oxidation of metallic Cu or Cu_2O present in the residual products, confirmed by XRD examination of products from reaction in air at 245 °C. The

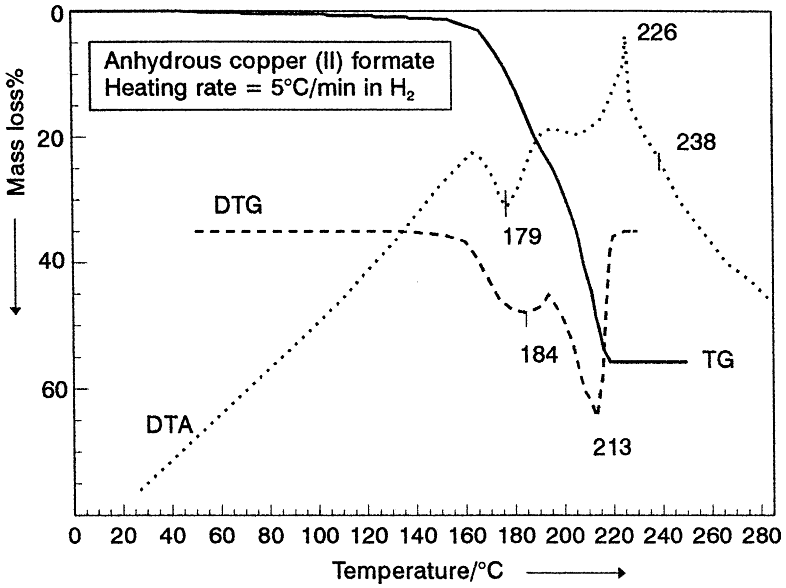

Fig. 2. TG, DTG and DTA curves for the decomposition of anhydrous copper(II) formate in hydrogen (flow 40 ml min^{-1}) with temperature increase of 5 °C min^{-1}.

DTA response trace identified two exothermic peaks, maxima at 184 and 219 °C, together with a minor shoulder at 238 °C.

3.2.4. Thermogravimetric results

Comparisons of the TG traces for decompositions in the three atmospheres, Figs. 1–3, show that in N_2 and in H_2 reactions proceeded within comparable temperature intervals, but with slightly higher rates and earlier completion in nitrogen. This similarity may be a consequence of reaction in a reducing atmosphere: with nitrogen some hydrogen is present as a result of formate anion breakdown [7]. The reaction onset temperature varied little between the three gases compared, initiation and reactivity being marginally greatest in hydrogen. The most significant result was the appreciable diminution of reactivity (represented, after 10% mass loss, by a temperature increase of 20–22 °C) during decomposition in air, presumably due to (re)oxidation of cation ($Cu^{+} \rightarrow Cu^{2+}$) or of the copper metal product. The (post-decomposition) increase of mass is attributed to residual metal oxidation in air and is ascribed to the presence of oxygen impurity [16] in the nitrogen gas: these rates are similar during subsequent product heating. In the reducing hydrogen atmosphere there can be no oxidation and the residue

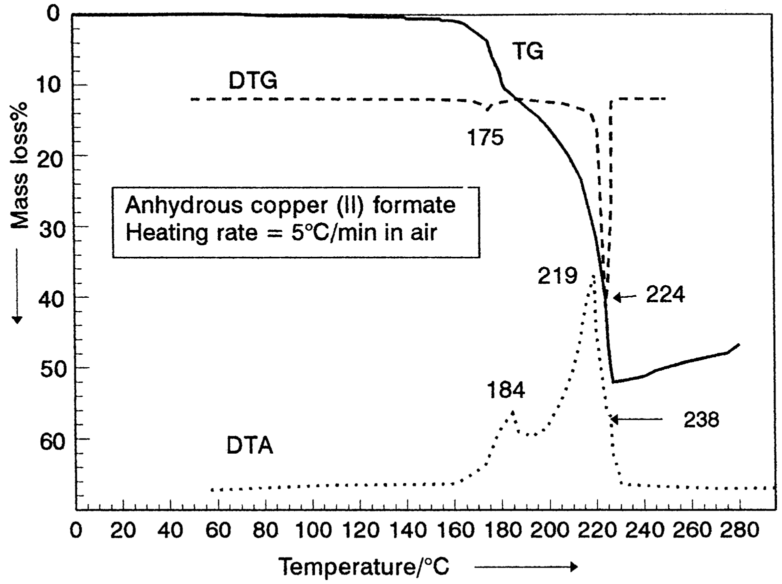

Fig. 3. TG, DTG and DTA curves for the decomposition of anhydrous copper(II) formate in air (flow 40 ml min^{-1}) with temperature increase of 5 °C min^{-1}.

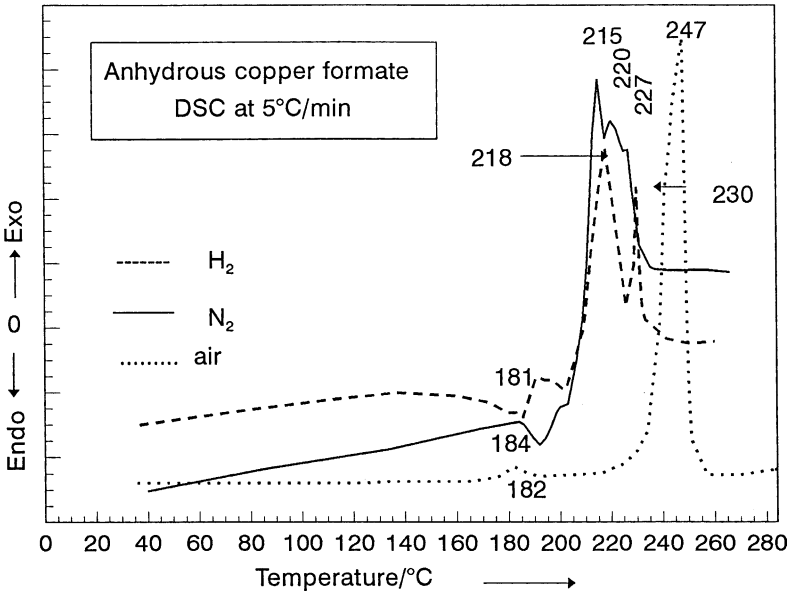

Fig. 4. DSC curves for the decomposition of anhydrous copper(II) formate in nitrogen, hydrogen and air (flow 40 ml min^{-1}) with temperature increase of 5 °C min^{-1}.

mass corresponds with expectation for copper metal and remains constant.

Minor DTA response peaks, at the limits of detection, were noted at 238 °C, for reactions in H_2 and air. The effects were too small to characterize, but may be due to product metal sintering or to removal of carbonaceous residues on the copper surfaces.

3.2.5. *Differential thermal analysis and differential scanning calorimetry*

The differential thermal responses associated with reactions in the different gas atmospheres are given in Figs. 1–3 (DTA curves) and DSC curves are compared in Fig. 4. ΔH values for decompositions in the three atmospheres were measured from the DSC curves and are reported in Table 1. In hydrogen, the first peak is endothermic.

The values in Table 1 are generally consistent with the stoichiometry of decomposition given in [7] (for which ΔH is estimated to be about -45 kJ mol^{-1}, taking the enthalpy of formation of the reactant as -743 kJ mol^{-1} (NIST data base)):

$$(HCOO)_2Cu \rightarrow Cu + H_2 + 2CO_2$$

The higher value for reaction in air is believed to be due to some copper oxidation. The relatively smaller enthalpy changes under reducing conditions (H_2 and N_2) may arise from incomplete oxidation yielding small amounts of CO, not detected by gas chromatography, and/or formic acid.

3.2.6. *Gas chromatography*

The volatile products of copper(II) formate decomposition in N_2 and in H_2 atmospheres were identified using gas chromatography. In nitrogen. the only product detected from reaction between 140 and 150 °C was formic acid. At 160 °C, CO_2 began to appear, together with HCOOH. On further heating, in N_2, the amounts of CO_2 increased at the expense of HCOOH up to 195 °C where CO_2 became the only volatile product detected. The disappearance of formic acid from the higher temperature products is attributed [7] to its catalytic breakdown on the copper metal product. Some of the CO_2 may have been formed through oxidation of CO (a probable product of thermal breakdown of HCOOH) by traces of oxygen in the nitrogen carrier gas. The hypothesis of CO formation was not supported by experimental evidence because the small amounts were undetected by the gas chromatograph.

In hydrogen, however, HCOOH was the only decomposition product detected and the yield increased with temperature rise. The formation of formic acid may be ascribed to the water gas-shift reaction between CO_2 (decomposition

Table 1
Enthalpy of decomposition, ΔH (kJ mol^{-1}) of copper(II) formate estimated from DSC response curves

Nitrogen		Hydrogen		Air	
Peak 1	Peak 2	Peak 1	Peak 2	Peak 1	Peak 2
−1.4 ± 0.1	−18.3 ± 1.2	0.92 ± 0.08	−27.8 ± 2.3	−5.7 ± 0.7	−62.8 ± 5.7

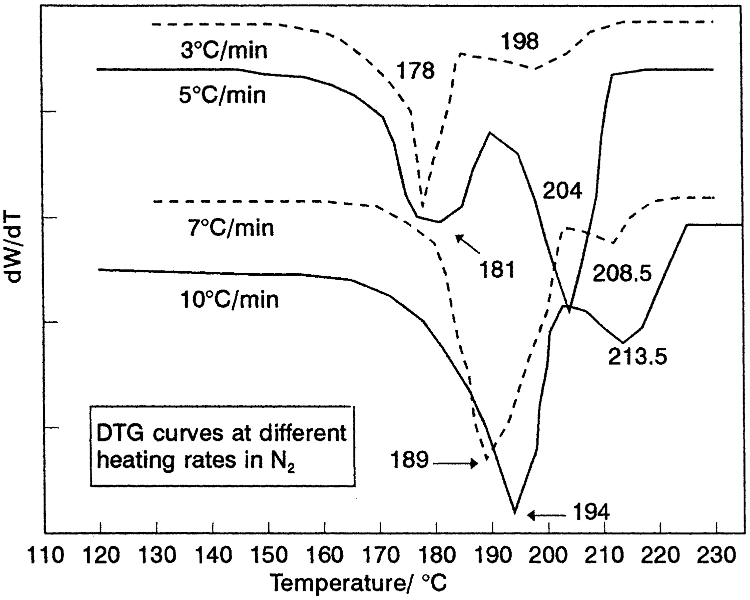

Fig. 5. DTG curve for the decomposition of anhydrous copper(II) formate in nitrogen at different heating rates.

product) and H_2 (carrier gas) over the metallic copper product surface [17]:

$$CO + H_2O \rightarrow CO_2 + H_2$$

3.3. Kinetic analysis of rate data

Fig. 5 shows DTG curves for the two-step decomposition of anhydrous copper(II) formate at different heating rates (3–10 °C min^{-1}) in which the separate maxima are easily distinguished. Ozawa plots [11–13] for these reactions are given in Fig. 6 and all kinetic parameters, calculated using the Ozawa equation (1), are reported in Table 2. Apparent values of E for the first step of the reactions in nitrogen and in air (109–110 kJ mol^{-1}) are close to and in satisfactory agreement with those for the accelerator period studied by isothermal methods during the decomposition in vacuum (115–120 kJ mol^{-1} [7]). For the second step, values measured nonisothermally were appreciably larger, 142 kJ mol^{-1} in nitrogen and 163 kJ mol^{-1} in air, and were qualitatively similar to two of the three isothermally determined values for the deceleratory period, which varied between 115 and 146 kJ mol^{-1} with the different crystal forms investigated [7].

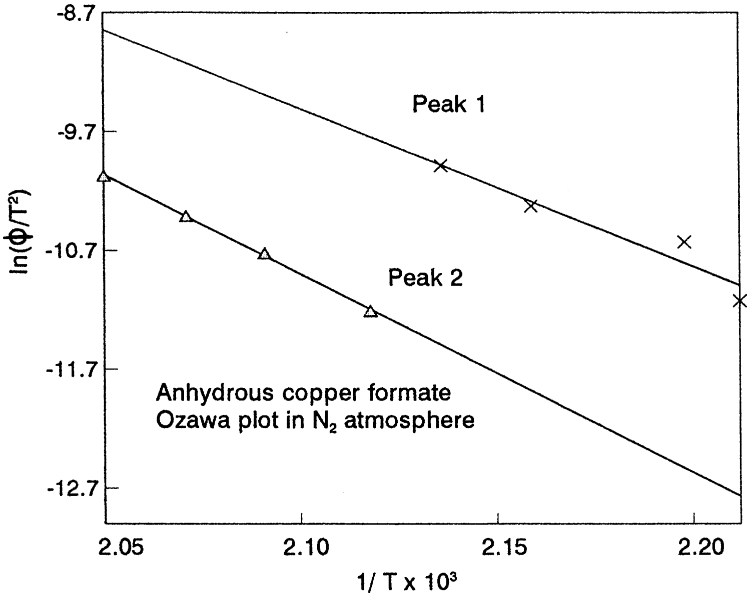

Fig. 6. Ozawa plots for the decomposition of anhydrous copper(II) formate in nitrogen at different heating rates.

Table 2
Kinetic parameters for the decomposition of anhydrous copper(II) formate in different atmospheres calculated by the Ozawa equation [11–13]

	Nitrogen		Hydrogen		Air	
	Peak 1	Peak 2	Peak 1	Peak 2	Peak 1	Peak 2
E/kJ mol^{-1} (apparent)	109.2 ± 3.1	142.4 ± 5.3	72.6 ± 2.1	176.3 ± 7.3	110.1 ± 5.8	162.7 ± 6.7
ln(A/min^{-1})	15.7 ± 0.9	20.0 ± 1.1	10.5 ± 0.7	35.9 ± 1.9	21.2 ± 1.3	32.3 ± 1.8
Correlation coefficient	0.985	0.988	0.982	0.966	0.997	0.991
Temperature (°C)	168–189	190–211	155–195	195–218	160–182	183–227

The significant influence of the gases present on the temperature coefficient of reaction rates (and the *apparent* activation energy values in Table 2) suggests that the decomposition process is not necessarily controlled by a single controlling step. Because decompositions in the different gases proceed in closely comparable temperature intervals, onset is identified as being determined by reactant stability but the gases present may exert some control over the course of subsequent breakdown processes and thus influence apparent magnitudes of E. The appreciable differences between apparent E values for reactions in hydrogen and in air or N_2 may be evidence that an oxidation or reduction step participates in salt breakdown, perhaps through electron transfer at an active salt/metal reaction interface. Magnitudes of apparent E values are not identified with any specific controlling bond redistribution step.

3.4. Copper(II) ion reduction during decomposition

3.4.1. Analytical measurements

The amounts of Cu^{2+} ion remaining in reactant samples, after partial decompositions under conditions identical with those used in the kinetic studies, were measured by titration of iodine released on dissolution in acid iodide solutions [2] and are reported in Fig. 7. On heating in all three atmospheres, the copper(II) present diminishes only marginally on heating below 170 °C. In all three atmospheres, the first significant reduction was detected between 170 and 180 °C. At higher temperatures the amount of Cu^{2+} remaining at 190 °C approaches zero on heating in nitrogen and in hydrogen, but increases in air. Comparison with the kinetic studies (Figs. 1–3 and Table 2) shows that copper reduction ($Cu^{2+} \rightarrow Cu^{+}$) is completed during the first reaction and the second reaction may, therefore, be identified as the decomposition of copper(I) formate. This mechanistic behaviour is identical with the two-step decompositions previously identified for the other copper(II) carboxylates [1–4,6]. We prefer this mechanism (because it is supported by analytical data) to the suggestion that a carbonate intermediate may be formed, as proposed to account for the two-step decomposition of copper(II) itaconate [5]. The contrasting behaviour in air is evidence that initial Cu^{2+} ion reduction is substantially reversed (Fig. 7) by the oxygen available. This is believed to represent oxide formation because there is no appreciable acceleration of reaction, which might have been expected because formate decomposition occurs at the

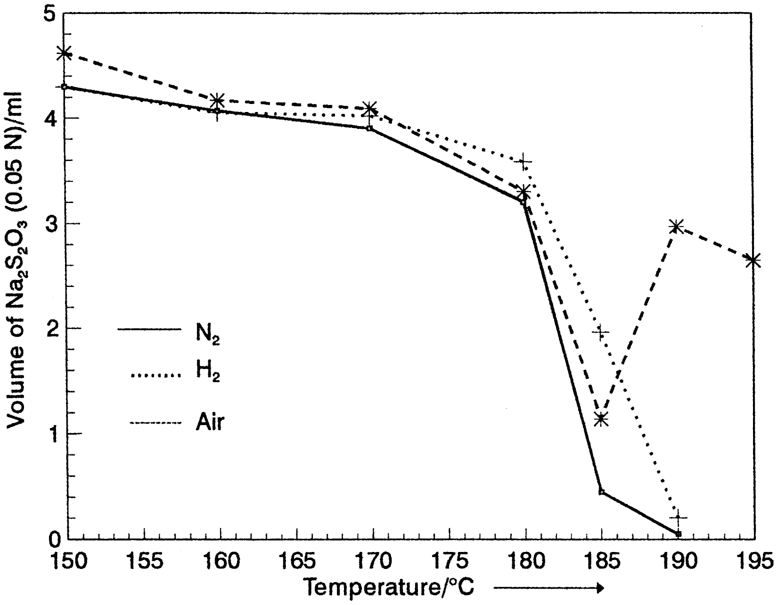

Fig. 7. Copper(II) formate decomposed (under similar conditions to those used in kinetic studies) and Cu^{2+} content measured as described in the text. Three sets of samples are compared for reactions in nitrogen, in hydrogen or in air.

lower temperature in the presence of cations in the higher oxidation state, Cu^{2+}.

3.4.2. *X-ray diffraction studies*

X-ray diffraction measurements for the residual products of decompositions completed at 220–230 °C detected copper metal as the only crystalline product phase. No evidence was obtained for the presence of either oxide expected, Cu_2O and/or CuO, suggesting that these were formed only as fine, poorly-crystallized material and/or as superficial layers on the finely-divided metallic particles formed by this reaction [7]. However, X-ray diffraction of the decomposition products from reaction in air at 250 °C gave clear evidence of CuO and Cu_2O (confirmed by a match with JCPDS Card nos. 5-0667 and 5-0661, respectively [10]). This could account for the small exothermic peaks at 238 and 247 °C in Figs. 3 and 4, respectively, attributable to recrystallization of the oxide products.

3.4.3. *Infrared spectra*

Infrared spectra for samples decomposed at 170, 180 and 190 °C showed strong absorption peaks characteristic of the formate ion. Residual products of reactant decomposed at 190, 230 and 300 °C in air showed absorptions at 500 and 610 cm^{-1}, which is evidence of the presence of CuO [18].

4. Conclusions

The most important conclusion from the present rising-temperature experiments is the demonstration that two distinct rate processes contribute to the overall decomposition of copper(II) formate. This is consistent with the previous research [7], which identified copper(I) formate as a (volatile) participant, and showed that two rate processes contributed to the overall anion breakdown reaction. Agreement between these two complementary kinetic studies (using different methods [7] and here) is very satisfactory. However, we can now extend the mechanistic interpretation by concluding that, as with other copper(II) organic salts, the formate breakdown similarly proceeds through stepwise cation reductions ($Cu^{2+} \rightarrow Cu^{+} \rightarrow Cu^{0}$), previously identified as occurring during the thermal reactions of copper(II) oxalate [1], malonate [2], maleate and fumarate [3], mellitate [4] and squarate [6].

The present observations show further that reducing conditions (H_2) only very slightly enhance decomposition rates though the apparent values of E are reduced for the first step and increased for the second. Moreover, the presence of oxygen appreciably decreases reactivity during the second process even though the lower temperature reaction is associated with the (slightly more reactive) original Cu^{2+} salt. Metal, which promotes the decomposition of the copper(I) salt [19,20], may be oxidized (perhaps superficially). We, therefore, identify the present decomposition as exhibiting mechanistic similarities with the heterogeneous catalytic breakdown of formic acid on metallic copper [19,20] which proceeds in the same temperature interval. The stepwise cation reduction is regarded as evidence of the participation of electron transfer during reaction: aspects of the controls of carboxylate decompositions have been discussed [21–24]. This conclusion is also consistent with the observation that reducing and/or oxidizing gases influence the magnitudes of apparent E values. The present observations identify one important control of reactivity as interface reactions, including electron transfer processes. Absolute reactivity is influenced to only a small extent by the atmosphere present, whether oxidizing, reducing or (nominally) inert.

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