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PYROLYTIC DECOMPOSITION OF SOME EVEN CHAIN LENGTH COPPER(II) CARBOXYLATES

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The products of the pyrolytic decomposition of some even chain-length copper(II) carboxylates from decanoate to octadecanoate inclusive have been identified, using a flow system, to be copper, carbon dioxide, a carboxylic acid and an odd chain-mength alkene. These products are similar to those reported for the decomposition of mercury(II) carboxylates. The unexpectedly low (less than unity) CO_2/soap ratio was attributed to the reduction of the CO_2 to carbon monoxide. The carboxylic acid was characterised by wet chemical tests, determining the melting points of the acid and its amide derivative and matching its IR spectrum with that of the authentic acid. Elemental analysis and wet chemical tests were employed for the identification of the alkene.

The products of decomposition and mechanism proposed to account for the degradative route of the systems show that good quality thin solid copper oxide films may only be obtained from the decomposition of copper(II) carboxylates if the carrier gas is non-inert (e.g. oxygen).

Most of the previous studies in this laboratory [1–8] and elsewhere [9–11] on metal carboxylates (soaps) have focussed attention mainly on their physical properties in the molten phase. For example, in our laboratory, the electrical conductivity, viscosity and heat of phase changes of lead [1, 3, 6], zinc [1], cadmium [2], mercury [4] and copper(II) [8] carboxylates have been studied from the melting to just before the decomposition temperatures. However, the decomposition behaviour of copper(II) carboxylate was not investigated. A literature survey also shows that some other properties such as fluorescence [12] and magnetism [13–15] have attracted the attention of other workers. Jewar [16], Duval [17] and Judd [18] have extensively studied the decomposition kinetics of some metal acetates. Bass [19] and Alexandrov [20] have reported the decomposition kinetics of a few short chain metal carboxylates. For the long chain soaps, Kambe et al. [15] reported that

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a ketone was obtained with a metal oxide residue from the pyrolysis of cobalt(II) octadecanoate. Recently, Ellis [21] and Akanni [22] studied the decomposition products and decomposition kinetics of some long chain leadII) and mercury(II) carboxylates respectively. They confirmed the observation of Judd [18] that a metal oxide is the solid residue when a ketone is obtained as an intermediate product while an acid is obtained when the final product is the metal. A number of mechanisms have been proposed to account for the decomposition routes of these carboxylates [23–25]. The decomposition behaviour of some inorganic materials containing copper has also been studied. For example, a mixture of copper, copper(I) oxide and copper(II) oxide was reported to be among the products obtained from the kinetic decomposition of copper(II) trihydroxyl chloride [26]. Also, the decomposition products of copper carbonate [27] and copper hydroxide [28] have been determined.

These extensive studies carried out on the physical [1–8], chemical [21, 22, 29] and other properties [12–14] of metal carboxylates seem to be adequately justified by their wide application in commerce, industry and medicine [13, 14, 30, 31]. One vital area, however, where metal carboxylates do not seem to have gained appreciable ground is in applied physics and electronics where some other metal organic compounds provide versatile routes for the preparation of thin films for electronic devices [32–37]. Utilization of these metal organic compounds as starting materials in the production of thin solid films involves pyrolysis [32–34], a route currently preferred to others because it permits considerable lowering of the working temperatures [35] and has been shown to give good quality films as well [35–37].

Perhaps a new horizon for the production of thin solid films might be opened up if the products and mechanism of the decomposition of metal carboxylates are fully understood. This, in part, is the driving force behind the present study which reports the identification of the products of the thermal decomposition of the even chain length copper(II) carboxylates from decanoate to octadecanoate inclusive. A mechanism is suggested to explain the degradative routes of the systems.

Experimental

Materials

The fatty acids used for preparing copper(II) tetradecanoate and copper(II) hexadecanoate were of B.D.H. grade and were stated to be "specially pure" with a minimum 99% purity by GLC assay. They were used without further purification. The copper nitrate used was of "Analar" grade. These two soaps were prepared by metathesis in alcohol solution as described elsewhere [8, 38–40]. The IR spectra showed them to be free of excess acid and water. Their melting points were in agreement with the literature values (see Table 1). All the other soaps used had previously been prepared and characterized in our laboratory [8].

Table 1 Data for the formation of CO_2 from the decomposition of copper(II) carboxylates

Soap	M.P., K	Literature M.P., K	Weight of soap decomposed, g	Weight of CO_2 produced, g	CO_2/soap mole ratio
Copper(II) decanoate (CuC_{10})	—	379–381 (Ref. 8) 376–377 (Ref. 30)	1.0050	0.0333	0.31 : 1
Copper(II) dodecanoate (CuC_{12})	—	385–386 (Ref. 8) 384–386 (Ref. 30)	1.0100	0.0183	0.29 : 1
Copper(II) tetradecanoate (CuC_{14})	386–388	389	1.0150	0.0154	0.18 : 1
Copper(II) hexadecanoate (CuC_{16})	388–390	387–388 (Ref. 8) 388–393 (Ref. 30)	1.0001	0.0477	0.62 : 1
Copper(II) octadecanoate (CuC_{18})	—	383–385 (Ref. 8) 398 (Ref. 30)	1.0047	0.0238	0.34 : 1

Errors from three runs in the values of CO_2 for each soap are within ±3%.

Decomposition of the soaps

Figure 1 shows the diagram of the set-up employed for the decomposition of the soaps. It was constructed at the University of Ife glass workshop and the component parts are shown in *A* to *M*.

The weighed soap samples were put into the decomposition tube and heated up to and slightly above the decomposition temperatures (325–400°) [41]. The temperature was monitored by attaching a thermometer to the heating element of the heating mantle and the glasswool used to insulate the lower part of the decomposition tube ensures that heat dissipation to the surrounding is minimal. The whole system was continuously flushed with nitrogen (or argon) gas at a flow rate of about 1.0 dm^3/min. The CO_2 produced was trapped by a previously weighed tube containing sodalime. Except for the decanoate, a white fluffy material was found to deposit in small quantities at *G*, *L* and *K* (see Fig. 1). A dark brown material mixed with tiny black particles was left as a residue at the bottom of the

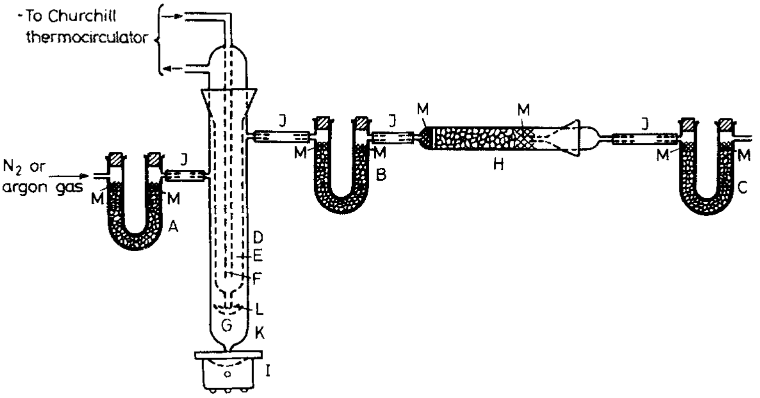

Fig. 1 Diagram of the set-up for decomposition A. U-tube containing silica gel to dry incoming carrier gas (N_2 or Argon). B. U-tube containing fused $CaCl_2$ to dry CO_2 and carrier gas. C. U-tube containing silica gel to absorb water vapour from the air. D. Long decomposition tube. E. Outer jacket of condenser. F. Inner jacket of condenser. G. Cup attached to lower part of condenser. H. Tube containing soda lime to absorb evolved CO_2. I. Heat source (Mantle). J. Connecting rubber tubing. K. Bottom of decomposition tube (sample position). L. Inner wall of decomposition tube. M. Cotton wool

decomposition tube. The dark brown material was found to envelope the solid copper metal.

The decomposition was repeated at least three times for each soap.

Results

The decomposition products of each of the copper(II) carboxylates are carbon dioxide, metallic copper, an acid and an alkene. The gaseous product of decomposition gave a white precipitate (milky) upon bubbling it into a saturated solution of barium hydroxide suggesting qualitatively that the evolved gas is carbon dioxide.

$$Ba(OH)_2 + CO_2 \rightarrow BaCO_3 + H_2O \qquad (1)$$

Quantitatively, the weight of CO_2 produced was obtained from the difference in the weights of the sodalime tube before and after the absorption of CO_2. The results are presented in Table 1 together with the melting points of our soaps and the literature melting points [8, 30].

Visual observation showed that the dark brown material recovered at the bottom of the decomposition tube consisted of an amorphous substance that floated on top of another solid. The amorphous substance was carefully scraped off to reveal a red solid with metallic lustre. Brown copious fumes were observed when a little portion of the metallic solid was treated with conc. nitric acid in a test tube. The colour of the resulting solution was light green. The only compound of copper (apart from copper metal itself) that gives brown fumes with conc. HNO_3 is the copper(I) oxide [42]. Even then the Cu_2O first undergoes disproportionation into copper(II) oxide and copper metal. The metal then reacts with the acid to produce the brown fumes.

$$Cu_2O \rightarrow CuO + Cu \tag{2}$$

$$Cu + 4HNO_3 \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O \tag{3}$$

It should be noted that the red non-lustrous colour of Cu_2O is quite distinct from the lustrous metallic solid we obtained. On the strength of the above discussion, the solid residue was inferred to be copper metal. Thus a quantitative method of determining copper contents in matrices was employed. The method was said to be suitable for copper determination in ores, slags and related systems [43]. The estimation of copper from the decomposition of copper(II) dodecanoate will be discussed as an example of this method. The residue left after decomposition (red solid plus amorphous substance) was weighed to be 0.377 g. This was dissolved in 7.5 cm^3 of conc. HNO_3 (70% w/w). About 9.4 cm^3 of water was added to the solution with boiling to ensure complete dissolution of copper and to expel oxides of nitrogen. The undissolved material (dark brown) was filtered off, washed with 1% hot HNO_3 and labelled B_m. The filtrate was concentrated to about 9.4 cm^3 and then allowed to cool. Ammonia solution was added dropwise to the filtrate to bring the pH to 3.3–4.0 and about 2.752 g of ammonium sulphate added to serve as a buffer. 1.131 g of potassium iodide was then added. The liberated iodine was at once titrated with 0.119 moles/dm^3 sodium thiosulphate solution, adding 0.1% starch solution near the end-point as indicator. The colour change is from blue to yellowish white. Each sample was analysed in triplicate and the same procedure was adopted for the analysis of the residues of the other soaps. The results are shown in Table 2.

The white fluffy material which settled at G, L and K was collected and labelled A_{12} in the case of decomposition of copper(II) dodecanoate. A_{12} and B_m were subjected to solubility tests. Both were insoluble in water but soluble in 0.2 M NaOH and a saturated solution of $NaHCO_3$ with the attendant effervescence in the latter. This thus suggests that A_{12} and B_m might contain an acidic functional group.

A_{12} was put on a silica gel based thin layer chromatography (TLC) bed (kieselgutor G, purified and incorporating 13% $CaSO_4$, 80–100 mesh ASTM) and developed in three different solvent mixtures of petroleum ether (60–80°) benzene in

Table 2 Copper contents from the decomposition of copper(II) carboxylates

Soap	Weight of soap decomposed, g	Weight of Cu produced, g	%Cu found	%Cu expected
Copper(II) decanoate (CuC_{10})	1.0050	0.1682	16.74	15.65
Copper(II) dodecanoate (CuC_{12})	1.0100	0.1477	14.62	13.75
Copper(II) tetradecanoate (CuC_{14})	1.0150	0.1378	13.58	12.27
Copper(II) hexadecanoate (CuC_{16})	1.0001	0.1182	11.81	11.06
Copper(II) octadecanoate (CuC_{18})	1.0047	0.1115	11.14	10.09

Errors of determination of the weight of the copper from three titrations are within ±2%.

the ratios 4 : 1, 2 : 1, 1 : 1. The result showed only one compound when viewed in a jar of iodine. Thus A_{12} was recrystallised from hot ethanol/water mixture. The melting points of A_n* and their amide derivatives are presented in Table 3 with literature melting points [44] for comparison.

B_m like A_{12}, was put on TLC and found to be a mixture of two compounds. The mixture was separated by dissolving in dilute NaOH (0.2 M) and extracting with ether. The ethereal extract was dried over anhydrous sodium sulphate, filtered and evaporated to dryness. The brown oily liquid obtained was labelled B_{11} and was found to decolourize bromine water. The percentage carbon and hydrogen in the sample was determined and the result is shown in Table 4.

The aqueous layer was treated with dilute HCl (1.0 M) and again extracted with ether. The ethereal solution was also dried over anhydrous Na_2SO_4, filtered and evaporated to dryness. The residue was recrystallized from hot water/ethanol mixture. The resulting white, fluffy solid was labelled B_{12} (see Table 3 for the M.pt). The % carbon and hydrogen are shown for A_{12} and B_{12} in Table 4. It should be mentioned that A_{10} expected from the decomposition of copper(II) decanoate was not found at G and L like for the other soaps. Instead, a viscous melt was found to cover the metallic residue at the bottom of the decomposition tube. This observation is likely to be correct as A_{10} is a liquid at temperatures above about 28° and hence probably drained to the bottom of the decomposition tube instead of crystallising out at G and L. Thus only the CO_2 and the metal content were analysed for the decomposition of copper(II) decanoate.

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* A_n is half the number of carbon atoms in the corresponding soaps.

Discussion

The decarboxylation of copper(II) carboxylates is expected to give a 1 : 1 CO_2/soap ratio by weight for a complete decomposition. However, the results presented in Table 1 show that the CO_2/soaps ratios are much less than unity for all the soaps. This result contrasts with that obtained for the decomposition of mercury(II) carboxylates where the decomposition products were similar to those obtained in the present work and where the CO_2/soap ratio was found to be 1 : 1 [22]. The reason for not obtaining a 1 : 1 ratio in the present case is not immediately clear. It is possible that one mole of CO_2 per mole of the soap was produced initially and part of it subsequently reduced to carbon monoxide by carbon produced as a result of charring.

$$CO_2 + C \rightarrow 2CO \tag{4}$$

This view is made attractive by the fact that the CO_2/soap ratio was lowest in the decomposition of copper(II) tetradecanoate for which charring was observed to be most pronounced. Such charring is not unexpected as carbon particles have been detected by Auger Electron Spectroscopy (AES) as impurities in some thin solid films obtained from the pyrolysis of metal organic compounds [45]. The reduction of CO_2 by carbon (equation 4) is feasible at the fairly high decomposition temperatures of the soaps. Such reduction features prominently in the extraction of metals from their ores [27]. In fact, Ellis and Okoh [29], indicated the presence of CO as one of the gaseous products of the decomposition of lead(II) carboxylates. In their case, however, a ketone was identified as an intermediate product.

The identification of A_n* and B_n* as acids was based on information obtained from a number of tests. Firstly, A_n and B_n were soluble in $NaHCO_3$ with effervescence. Since water-insoluble compounds containing acidic functional groups are generally soluble in alkalis, we speculated that A_n and B_n are probably acids. Secondly the melting points of A_n and B_n were found to be in good agreement with the literature melting points of the corresponding acids (Table 3). The melting points of the amide derivaties (Table 3) also agree very well with the literature values. Thirdly, the IR spectra of A_n and B_n together with that of the corresponding authentic acids were recorded as KBr pellets. Figure 2 shows the spectra of A_{12}, B_{12} and the authentic dodecanoic acid. It is clear from the figure that the series of absorption bands in the spectra of A_{12} and B_{12} match perfectly that of the spectrum of the authentic acid, suggesting that both A_{12} and B_{12} are dodecanoic acids. In the same manner IR spectra show A_n and B_n to be the acid decomposition products of the corresponding soaps. It is our belief that B_n is part of A_n which

* A_n and B_n represent half the number of carbon atoms in the soaps.

Table 3 Melting points (°C) of A_n, B_n, authentic acids and their amide derivatives 44

Copper(II)	Acid product expected	M.P. of A_n	M.P. of B_n	Literature M.P.'s of pure authentic acids	M.P. of amide derivative of A_n	Literature M.P.'s of amide derivatives of authentic acids
Decanoate	decanoic	—	—	31.5	—	—
Dodecanoate	dodecanoic	42–43	42–44	44	107–108	110
Tetradecanoate	tetradecanoic	54–55	54–56	58	103–105	105–107
Hexadecanoate	hexadecanoic	59–61	55–56	63	103–106	106
Octadecanoate	octadecanoic	66–68	—	71–72	—	109

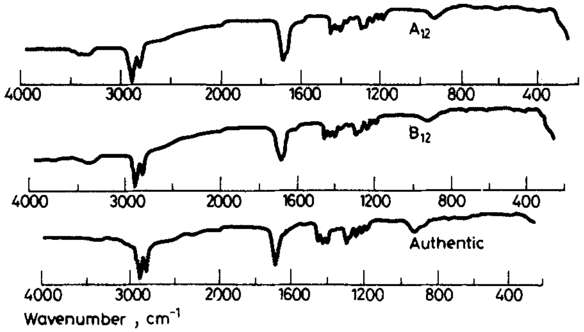

Fig. 2 IR spectra of A_{12}, B_{12} and authentic dodecanoic acid

recondensed at the bottom of the decomposition tube after the source of heat was withdrawn. The fourth evidence in support of A_n and B_n being acids is found in the closeness of the % composition of carbon and hydrogen (found) to the calculated values (Table 4).

Table 4 C and H analysis (%) of the organic products from the decomposition of copper(II) dodecanoate and the corresponding theoretical values in brackets

Element	A_{12}	B_{12}	B_{11}
C	71.49	70.23	83.98
	(71.95)		(85.63)
H	12.35	11.58	13.02
	(12.07)		(14.37)

The other organic product, B^*_{n-1}, was detected by its positive reaction with bromine water. The percentage of carbon and hydrogen in one of the products, B_{11}, was determined (Table 4). The values for C and H for B_{11} were close to the calculated values of 85.63 and 14.37% respectively, in an alkene of eleven carbon atoms. There was no visible reaction when a solution of B_{11} was added to a solution of silver nitrate in alcohol. This suggests that the decolourization of bromine water does not occur as a result of a triple (—C≡C—) bond in an alkyne with a terminal hydrogen. From the mechanism of decomposition proposed, and within the range of temperatures employed for this work, it is not likely that an alkyne other than one with a terminal hydrogen can be formed. Hence, we inferred that B_{11} is an alkene. Our inference was further strengthened by the same R_f value obtained when a solution of B_{11} and one available alkene, dodec-1-ene were placed on a TLC bed and developed separately in three different benzene/petroleum ether mixtures. We speculated that the R_f value of dodec-1-ene, an alkene with twelve carbon atoms will not be very different from that of an alkene with eleven carbon atoms and our result just confirmed this belief. The other B_{n-1} products for tetradecanoate and above were similarly identified and this procedure is the same as that used for the analysis of alkenes obtained in the decomposition of some mercury(II) carboxylates [22].

The percentage of copper, within the range of experimental error (Table 2) shows a good agreement with the expected values. This suggests that a complete decomposition was carried out in each case and it is satisfying to find that the value of 11.10% obtained for copper in copper(II) octadecanoate in this work is in agreement with that of 11.30% reported for the copper content in the same soap by Klare [30]. Thus the low CO_2/soap ratio obtained cannot be as a result of incomplete decomposition. This point lends further credence to our belief that some form of reduction may be taking place. It should be noted that charring that could bring about such a reduction is unavoidable even when decompositions are carried out at pre-determined optimum temperatures and times. If one takes all the results of the product analyses together, it follows logically to conclude that the decomposition of copper(II) carboxylates proceeds in the same way as that reported for mercury(II) soaps [22] where the initiation step for decomposition is the rupture of the oxygen-metal bond followed simultaneously by the abstraction of β-hydrogen by the carboxylate anion as shown below for copper(II) soaps.

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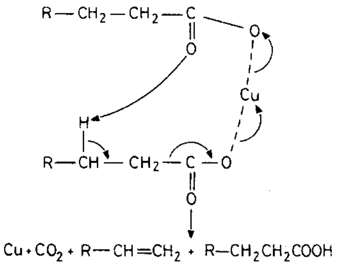
* B_{n-1} is one carbon atom less than B_n.



Thus the products of decomposition for copper(II) octadecanoate, for example, will be copper metal, CO_2, heptadec-1-ene and octadecanoic acid. This result agrees with our earlier reports [15, 21, 22] and the work of Judd [18] that a ketone was the usual intermediate product when the metal oxide was the solid residue while an acid was often obtained as the intermediate when the solid residue was a metal. However, it may still be possible to obtain a metal as the solid residue when a ketone is the intermediate product. This situation can be brought about by the subsequent reduction of the oxide to the metal in the presence of carbon or carbon monoxide.

It should be recalled that a mixture of acid and acid anhydride was reported by Lawrence [46] to be among the decomposition products of some metal carboxylates (e.g. mercury(II) soap). This is in contrast to the result of the present work in which only the acid was detected. However, a case has earlier been made by us [22] that the presence of acid anhydride in Lawrence's soaps might have resulted from the conversion of excess acid in the soaps upon heating, according to the equation:

$$2RCOOH \rightarrow RCOOCOR + H_2O \qquad (5)$$

even before the onset of decomposition of the soaps. This argument is strengthened by the fact that the melting points observed by Lawrence were considerably lower than those obtained in our laboratory [4, 47]. The identification of an alkene as one of the decomposition products may, as already reported, provide a route for obtaining a more expensive odd-chain length carboxylic acid from the degradation of an even-chain length copper(II) carboxylate. This implies that the odd-chain alkene is first obtained and then converted into an alcohol, which could be oxidized to a carboxylic acid.

Some metal organic compounds have been successfully used to obtain good quality thin films [35–37]. It was envisaged that a good quality metal oxide film would be obtained from the pyrolysis of copper(II) carboxylates. However, the present result shows that copper metal is essentially the solid residue of the decomposition of copper(II) soaps. Thus for this system to be a suitable route for preparing thin oxide films, it is necessary to obtain a metal oxide in the first instance from the decomposition processes. The route will be adequate, for example, for preparing thin oxide films of lead and zinc since the carboxylates of these metals give the oxides upon decomposition. However, it may be possible to obtain good quality films from the degradation of copper(II) soaps by modifying our set-up [48] for preparing thin films via decomposition. For example, the use of oxygen instead of nitrogen or argon (inert) as a carrier gas could result in the production of oxide films by the conversion of the copper metal to the oxide at a fairly high working temperature.

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Zusammenfassung — Als Produkte der pyrolytischen, in einem Gasstrom vorgenommenen Zersetzung einiger Kupfer(II)-Karboxylate mit geradzahliger Kohlenstoffatomzahl der Kette (Dekanoat bis einschließlich Octadekanoat) wurden Kupfer, Kohlendioxid, eine Karbonsäure und ein Alken mit ungerader Kohlenstoffatomzahl identifiziert. Diese Produkte sind ähnlich denen, die bei der Zersetzung von Quecksilber(II)-Karboxylaten auftreten. Das unerwartet niedrige CO_2/Seife-Verhältnis (kleiner als 1) wurde der Reduktion von CO_2 zu Kohlenmonoxid zugeschrieben. Die Karbonsäure wurde durch naße chemische Tests, durch Bestimmung des Schmelzpunktes der Säure und dem des Amidderivats und durch Vergleich des IR-Spektrums mit dem der authentischen Säure identifiziert. Elementaranalyse und naße chemische Tests wurden zur Identifizierung der Alkene herangezogen. Die Zersetzungsprodukte und der zur Erklärung des Abbaus des Systems vorgeschlagene Mechanismus zeigen, daß dünne feste Kupferoxidschichten in guter Qualität nur bei der Zersetzung von Kupfer(II)-Karboxylaten in nicht-inertem Trägergas (z. B. in Sauerstoff) erhalten werden.

Резюме — Используя проточную систему, были идентифицированы продукты пиролиза карбоксилатов двухвалентной меди, начиная от деканоата и включая октадеканоат. Продуктами распада являются медь, двуокись углерода, карбоновая кислота и алкен с нечетным числом углеродных атомов. Эти продукты подобны тем, которые были получены при распаде карбоксилатов двухвалентной ртути. Необычное низкое (меньше единицы) отношение двуокись углерода — мыло было приписани восстановлению двуокиси углерода до моноокиси. Карбоновая кислота была идентифицирована влажным химическим анализом, определением

температуры плавления кислоты и ее амида, а также ИК спектром. Элементный анализ и влажный химический анализ были использованы для идентификации алкена. Продукты разложения и механизм, предложенный для объяснения пути распада системы, показали, что качественные тонкие пленки окиси меди могут быть получены только в том случае, если в качестве газа-носителя при разложении карбоксилатов меди использовать какой-либо не инертный газ, как например, кислород.