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Laser-induced Chemical Reactions. III. The Decomposition of Metal Salts of Carboxylic Acid and Selective Decomposition

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Various copper metal salts of organic acid were decomposed by laser heating and conventional heating methods. The product distributions were reasonably explained in terms of the expected reaction of the decarboxylated intermediates. Generally the yield percentage of products is higher in laser decomposition than in thermal decomposition. However, in maleate and fumarate the product distribution is quite different in thermal and laser decompositions. The main product is ethylene in the thermal decomposition, but acetylene in the laser decomposition. This difference may be the result of the heating rate. Since rapid heating and quenching are characteristic of laser heating, the formation of acetylene may be brought about by the simultaneous decarboxylation of two carboxyl groups, while the formation of ethylene may be brought about by successive decarboxylation. Selective decomposition by laser heating will also be discussed in binary systems, such as maleate and ethylene.

The chemical reaction induced by a laser beam (ruby laser) has been investigated previously. The reaction mechanism[1] has been considered to be: (1) photodissociation,[2,3] (2) direct heating of the solid, causing vaporization,[3,4] and (3) breakdown of gases.[5] The reaction of carbon vapor produced by the ruby laser and that caused by the breakdown of gases have been previously

1) J. F. Verdieck and A. W. H. Mau, *Chem. Commun.*, **1969**, 226.

2) I. Tanaka, Y. Mori, Y. Minagawa and E. Okutsu, *J. Phys. Chem.*, **72**, 2684 (1968).

3) W. B. Tiffany, *J. Chem. Phys.*, **48**, 3019 (1968).

4) R. Schaeffer and R. K. Pearson, *J. Amer. Chem. Soc.*, **91**, 2153 (1969).

5) A. H. Adelman, *J. Chem. Phys.*, **45**, 3152 (1966).

reported by the present authors.[6,7] As the ruby laser (photon energy: 1.8 eV) does not have enough energy to dissociate organic molecules, any photochemistry by the ruby laser is restricted and some of the reaction must be performed by multiphoton absorption processes. Therefore, the ruby laser may be most useful for the pyrolysis.

Organic carboxylic acids are well known to be decomposed by heating, resulting in decarboxylation in the presence of a copper catalyst.[8,9] Metal salts of carboxylic acid are also decomposed to produce organic radicals and ketones[10] under decarboxylation.[11] Acetic acid is decomposed at 530—762°C to give methane and ketene.[12]

By the absorption of the pulse ruby laser beam, the target surface is heated rapidly to about 600—800°C,*1 resulting in heat decomposition. As the copper salts of organic acids are blue and green, these salts may absorb the ruby laser beam efficiently and themselves be decomposed.

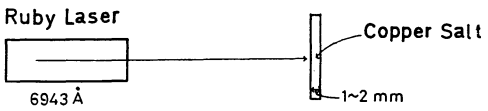
Among the copper salts of organic acids decomposed by laser heating (laser decomposition) and conventional heating (thermal decomposition), both maleate and fumarate give quite different results between the laser and thermal decompositions.

In this experiment the mechanism of laser decomposition has been studied; this paper will also discuss another possibility of the use of a laser beam.

Experimental

Copper maleate and fumarate were prepared by the reaction of maleic acid and copper carbonate, and of fumaric acid sodium salt and a copper sulfate solution, respectively. Each of them has crystal water,*2 and the decomposition temperature was checked by differential thermal analysis and thermal gravimetrical analysis.

The laser used was a pulse ruby laser, the output energy and pulse duration of which were about 3 J and 0.5 msec respectively. The sample target in the cell



output energy 3 J
pulse duration 0.5 msec

Fig. 1. Experimental block diagram.

was irradiated by the laser beam as is shown in Fig. 1; after 2—7 pulse irradiations the gaseous products were analysed by gaschromatography using silica-gel, activated-charcoal, and squalane columns. Quantitative analysis was performed by the internal standard system.

The thermal decomposition (0.1 g salt) was carried out in a metal bath for 30—60 sec at various temperatures.

Results and Discussion

1) Decomposition of Metal Salt. Various copper salts (acetate, propionate, *n*-butyrate, isobutyrate, acrylate, malonate, benzoate, phthalate, succinate, adipate, maleate, and fumarate) were decomposed by both the thermal and laser decomposition methods. The results for several salts are shown in Table 1. Generally, the product distributions are almost the same in the two decomposition methods, but maleate and fumarate are exceptions. The gaseous products can be reasonably explained in terms of the expected reaction of the decarboxylated fragments. The amount of carbon dioxide may be considered to represent the fraction of the decomposed copper salt. For convenience, the product yield may be represented as per cent of carbon dioxide.

In the laser decomposition on both copper maleate and fumarate, the gaseous products consisted of

Table 1. Product yield from copper salts in thermal* and laser decomposition based on CO_2 produced

Substrate	Product	Yield (%) Thermal decomp. (at 400°C)	Laser decomp. (6 pulses)
Copper acrylate	CH_4	0.011	0.39
	C_2H_6	0.0011	0
	C_2H_4	6.7	15
	Butadiene	0.023	3.2
Copper Succinate	CH_4	0.05	0.37
	C_2H_6	0.014	0.07
	C_2H_4	2.3	14
	Propane	0	0.26
	C_2H_2	0	1.7
Copper maleate	C_2H_4	2.2	1.2
	C_2H_2	trace	8—12
Copper fumarate	C_2H_4	2.4—4.7	5.0
	C_2H_2	trace	10—12

* The yield percents of CO_2 for salts used were 80—90% in maleate and 45—50% in fumarate.

6) K. Taki, P. H. Kim and S. Namba, This Bulletin, **42**, 823 (1969).
7) K. Taki, P. H. Kim and S. Namba, *ibid.*, **42**, 2377 (1969).
8) D. M. Burness, "Organic Syntheses," Coll. Vol. IV. p. 628 (1963).
9) R. H. Wiley and N. R. Smith *ibid.*, Coll. Vol. IV. p. 731 (1963).
10) L. Ruzicka, W. Brugger, M. Pfeiffer, H. Schinz and M. Stoll, *Helv. Chim. Acta*, **9**, 514 (1926).
11) E. Piers and R. K. Brown, *Can. J. Chem.*, **40**, 559 (1962).
12) P. G. Blake and G. E. Jackson, *J. Chem. Soc., B*, **1969**, 94.

*1 The surface temperature was estimated by the ignition point of amorphous carbon and the melamine polymer.

*2 Copper maleate dried at 80°C has 1 mol crystal water (Found: C, 24.5; H, 2.16%, ($C_4H_2O_4Cu+H_2O$)).

Table 2. Product yield from copper maleate and fumarate in laser decomposition based on CO_2 produced

Product	Substrate	
	Maleate	Fumarate
Methane	0.5 %	2.2 %
Ethane	0.05	0.2
Ethylene	1.2	5.0
Acetylene	8—12	10—12

10—15% noncondensable gases at the temperature of liquid nitrogen; the products were methane and carbon monoxide, hydrogen not being detected. 65% of the condensable gases consisted of carbon dioxide, and the rest were hydrocarbon and water. The hydrocarbon consisted of acetylene, ethylene, and a small amount of C_3 and C_4 compounds, as is listed in Table 2. Acetylene is the main product, but the yield is only about 10% of the carbon dioxide (10^{-5}—10^{-6} mol). The decomposition processes are considered to be as follows:

$$\text{Maleate or fumarate} \xrightarrow[\text{irradiation}]{\text{laser}} \text{Decarboxylated intermediate } (-CH{=}CH-) \longrightarrow \text{Acetylene, } C_4 \text{ compounds, and nonvolatile products}$$

On the other hand, the thermal decomposition gives not acetylene but ethylene at 350°C. The high-temperature decomposition gives acetylene, but ethylene is still obtained in a high yield, as is listed in Table 3. In the laser decomposition, the ethylene yield increases as the laser power is lowered by using a copper-sulfate-solution filter, but acetylene is still the main product, as is shown in Table 4. From the above results, the difference between the laser and the thermal decomposition does not seem to depend only on the decomposition temperature. In the laser heating, the temperature rises very rapidly to decompose the salt in a moment, and then two decarboxylations are brought about at the same time to produce an intermediate (–CH=CH–). This intermediate forms acetylene intramolecularly. Therefore, the formation of acetylene seems to depend on the heating rate.

Table 3. The ratio of acetylene to ethylene from copper maleate and fumarate in thermal decomposition at various temperatures

Substrate	C_2H_2/C_2H_4			
	350°C	500°C	570°C	670°C
Copper maleate	0.0015	0.22	—	1.3
Copper fumarate	0.009	0.12	0.15	—

— Detection was not carried out.

Table 4. The ratio of acetylene to ethylene from copper maleate and fumarate in laser decomposition at various transmissions of laser beam by using $CuSO_4$ solution filter

Substrate	C_2H_2/C_2H_4		
	100 % trans.	50% trans.	25% trans.
Copper maleate	6—10	5.8	4.9
Copper fumarate	2—2.4	2.0	1.3

In the thermal decomposition, the formation mechanism of ethylene and acetylene is not clear because the secondary decomposition may occur at a high temperature. However, on the basis of differential thermal analysis and thermal gravimetrical analysis data, the decomposition occurs over a wide temperature range in copper maleate (170—340°C) and fumarate (170—380°C). Therefore, it may be roughly presumed that the decarboxylation is brought about step by step, that the –CH=CH–COO–Cu– thus obtained may abstract hydrogen to produce an acrylic compound,[13] and that the secondary decarboxylation may give ethylene:

$$\text{Copper maleate or fumarate} \xrightarrow{\text{Decarboxylation}} -CH{=}CH-COOCu- \xrightarrow{\text{Hydrogen abstraction}} CH_2{=}CH-COOCu \xrightarrow{\text{Decarboxylation and hydrogen abstraction}} CH_2{=}CH_2$$

In fact, copper acrylate is decomposed to give ethylene in both the laser and thermal decompositions (Table 1).

The difference between the two types of decomposition may depend on whether or not the two decarboxylations occur at the same time. Moreover, it may be also decided by the property of the one-decarboxylated intermediate. In fact, no difference was found in copper succinate (decomposition temperature range: 280—380°C). In this case, the decarboxylated intermediate, $-CH_2-$

Table 5. Product yield from mixture of benzoate and other salts in laser decomposition based on CO_2 produced

Substrate (Copper salt)	Yield(%)			
	Benzene	Toluene	Ethyl-benzene	Isopropyl-benzene
Benzoate and Acetate	7.2	0.9	—	—
Benzoate and Propionate	6.0	0.02	0.08	—
Benzoate and Isobutyrate	6.5	0.05	—	0.03

— Not detected.

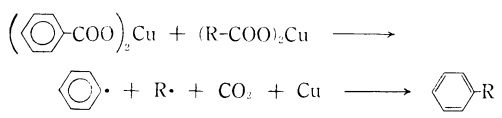
13) T. Voelker and H. Graefe, German 1195297. *Chem. Abstr.*, **63**, 8207f (1965).

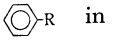
Table 6. Product yield in selective decomposition of binary system by laser heating based on CO_2 produced

Substrate	Yield (%) C_3 compounds	C_4 compounds	C_5 compounds	C_6 compounds
Copper maleate and 760 Torr nitrogen	0.2	0.6	0.17	0
Copper maleate and 730 Torr ethylene	0.35	3.9	—	—
Copper maleate and 730 Torr propylene	—	—	0.45	—
Copper maleate and 730 Torr 1-butene	—	—	—	0.67
Copper fumarate and 760 Torr nitrogen	0.24	0.3	0.12	0
Copper fumarate and 730 Torr ethylene	—	1.8	—	—
Copper fumarate and 730 Torr propylene	—	—	0.46	—
Copper fumarate and 730 Torr 1-butene	—	—	—	0.82

— Detection was not carried out.

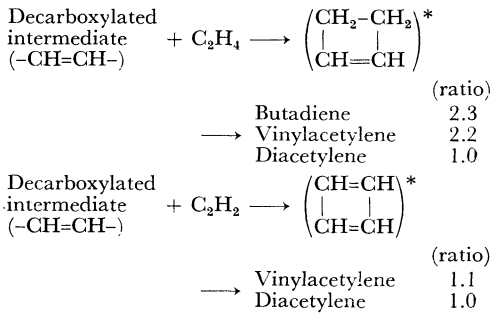
CH_2–COOCu–, may form ethylene intramolecularly in the thermal decomposition. The mechanism of decarboxylation in the laser decomposition may be supported by the following experimental fact. In the mixture of copper benzoate and acetate, benzoate and propionate, and benzoate and isobutyrate, the laser heating of the mixture gives toluene, ethylbenzene, and isopropylbenzene respectively, as is shown in Table 5. However, in the thermal decomposition at 400°C, toluene, ethylbenzene, and isopropylbenzene were not detected or were present in trace quantities only. The alkyl-substituted benzene may be formed by a recombination of the phenyl and alkyl radicals. Therefore, it is necessary for the decarboxylation of the two components to occur at the same time in a mixture of copper salts. The reaction mechanism may be considered to be as follows:



Each component is decomposed to produce R–R and biphenyl by both the laser and thermal decompositions. However, each component is decomposed in a different temperature range (acetate: 125—300°C; benzoate: 220—450°C; isobutyrate: 280—310°C, and propionate; 210—300°C). It is hard to obtain the product,  in thermal heating.

The above experimental results may be explained by the rapid heating and quenching by the laser heating. This type of pyrolysis is only possible in the laser heating.

2) Selective Decomposition. In a binary system, such as copper maleate and ethylene, the laser beam may decompose copper maleate only, and not ethylene, because the laser beam is absorbed on the copper maleate. If some intermediate in the decomposition of copper maleate is produced, the reaction with ethylene will be possible. Because copper maleate is decomposed by the laser heating to produce acetylene, the acetylene precursor, as has been mentioned before, may be the –CH=CH– intermediate. It is also dimerized to produce C_4 compounds. The determination of C_4 compounds was performed in the presence and in the absence of ethylene and acetylene. The data and the relative product yields in the binary system of copper salt and hydrocarbon gas are listed in Table 6. The (–CH=CH–) intermediate intramolecularly forms acetylene mainly, but a fraction reacts with ethylene and acetylene to produce C_4 compounds.



The decarboxylated intermediate (–CH=CH–) reacts with propylene and 1-butene to give C_5 and C_6 compounds respectively. Although C_5 compounds are produced in the laser decomposition of maleate itself, the yields of C_5 compounds in the mixture of maleate and propylene are higher than those in the decomposition of maleate itself.

It is worth noticing that the selective decom-

position and the above-mentioned reaction are only possible in the laser heating.

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