

PICRATES OF CHALCONES AS ORGANIC
MOLECULAR COMPOUNDS.⁽¹⁾

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It is well known that unsaturated ketones as chalcones form various molecular compounds,⁽²⁾ among which some picrates were reported by D. Vorländer.⁽³⁾ He classified them as salt-like compounds between α , β -unsaturated ketones and acids, and the following picrates were enumerated by him ;

(1) Read before the ordinary meeting of the Chemical Society of Japan, June 14th, 1930.

(2) P. Pfeiffer, "Organische Molekülverbindungen," (1927) 66-85.

(3) *Ann.*, **341** (1905), 32.

Benzalacetophenone picrate	1:2 ⁽⁴⁾
Anisalacetophenone picrate	1:2
Piperonilideneacetophenone picrate	1:2
Cinnamilideneacetophenone picrate	1:2
Anisalpinacoline picrate	1:2
Dipiperonilideneacetone picrate	1:1

These picrates are formed in combining each molecule of chalcone with two molecules of picric acid, but it is not quite certain whether chalcones other than those mentioned above also combine with picric acid always in this proportion of 1:2. Further it is somewhat uncertain whether these picrates are formed just in the same way as chalcones combine with inorganic acids, as was mentioned by Vorländer.

The cause of formation of a molecular compounds, as a component of which nitrophenols are concerning, may perhaps be considered in various ways; i.e., we may attribute the point of the molecular linkage of a nitrophenol either to its phenol group, nitro group or to NOOH-radical, which is considered usually in a nitrophenol molecule.

The present study was then undertaken, in order to elucidate these questions.

The method of investigation employed by the author is similar to that proposed by H. Rheinboldt,⁽⁵⁾ only slight modification being done in the shape of the stirring rod. Rheinboldt used a slender glass rod for this purpose, but it occurs creeping-up of the molten material along the wall of observing capillary and some errors are often caused, while the pin-head shaped stirrer devised by the author may avoid this difficulty (compare A and B in Fig. 1).

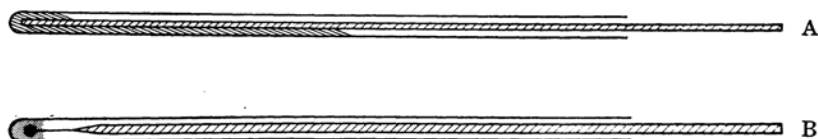


Fig. 1.

The molecular compounds of the chalcones studied by the author were in the following molecular proportions, namely they are not exclusively 1:2;

(4) The figures show the molecular proportions.

(5) *J. prakt. Chem.*, [2] **111** (1925), 242; **112** (1926), 187; **113** (1926), 199.

Piperonilideneacetophenone picrate	1 : 2
2'-Oxybenzalacetophenone picrate	2 : 3
4'-Oxybenzalacetophenone picrate	1 : 1
4'-Ethoxybenzalacetophenone picrate	1 : 1

As β -naphthol gave no molecular compound with piperonilideneacetophenone, it seems that phenols have no affinity with chalcones to form molecular compounds.

Experimental.

3.4-Methylenedioxybenzalacetophenone⁽⁶⁾ was prepared by the condensation of piperonal and acetophenone: 10 gr. of piperonal and 8 gr. of acetophenone were dissolved in 200 c.c. of spirit, and to this solution was added some 5% caustic soda. The separated crystals of feebly yellow colour were recrystallized twice from alcohol: m.p. 121.0°C.

2'-Oxybenzalacetophenone⁽⁷⁾ was prepared by dissolving 2 gr. of *o*-oxyacetophenone and 2 gr. of benzaldehyde in 20 gr. of alcohol and by adding 4 gr. of 50% caustic potash. Evolving a little heat, the solution turned to yellow and then became orange-red and at the same time muddy. After standing overnight it was poured into dilute hydrochloric acid, and then separated chalcone was recrystallized from alcohol: m.p. 88.0–89.0°C.

4'-Oxybenzalacetophenone⁽⁸⁾ was prepared by dissolving one part of *p*-oxyacetophenone and one part of benzaldehyde in 10 parts of alcohol and by adding 2 parts of 50% caustic potash, warming the mixture for half an hour on the water-bath, then pouring it into water and acidifying. The separated chalcone was recrystallized from spirit: m.p. 174.5–175.5°C.

4'-Ethoxybenzalacetophenone⁽⁸⁾ was prepared by ethylation of 4'-oxybenzalacetophenone in the ordinary way with ethyl iodide and caustic alkali: m.p. 73.5–74.5°C.

The *o*- and *p*-oxyacetophenone used in the preceding preparations, were obtained by heating for five hours at 120°C. the mixture of one part of phenol acetate and two parts of anhydrous aluminium chloride, treating the mixture with cold water and then separating the two acetophenones by steam distillation.⁽⁹⁾ The picric acid and the naphthol were purified from the commercial products by repeated recrystallization from water.

(6) St. v. Kostanecki u. M. Schneider, *Ber.*, **29** (1896), 1892.

(7) W. Feuerstein u. St. v. Kostanecki, *Ber.*, **31** (1898), 715.

(8) Kostanecki u. J. Tambor, *Ber.*, **32** (1899), 1924.

(9) K. Freudenberg u. L. Orthner, *Ber.*, **55** (1922), 148.

The system : 3,4-Methylenedioxybenzal-
acetophenone—picric acid (See Fig. 2)

Molecular percentages of		Temperatures of	
Chalcone	Picric acid	Thawing	Complete fusion
0.0	100.0	—	122.0
2.5	97.5	113.5	120.0
4.4	95.6	113.5	116.5
9.2	90.8	113.5	119.8
13.1	86.9	113.5	123.0
19.8	80.2	113.5	126.5
23.0	77.0	113.5	127.2
23.2	76.8	113.0	127.3
32.0	68.0	114.5	128.5
38.3	61.7	104.5	128.0
50.2	49.8	105.0	125.3
61.8	38.2	104.0	117.5
68.0	32.0	104.0	111.0
78.4	21.6	104.3	110.0
83.8	16.2	103.5	113.5
89.8	10.9	104.0	116.5
94.5	5.5	104.5	119.0
100.0	0.0	—	121.0

Eutectic points :

{ 113.5°C. picric acid
 94.5 mol %
 { 104.0°C. picric acid
 27.0 mol %

Distectic point :

128.5°C. { picric acid
 2 mols
 chalcone
 1 mol

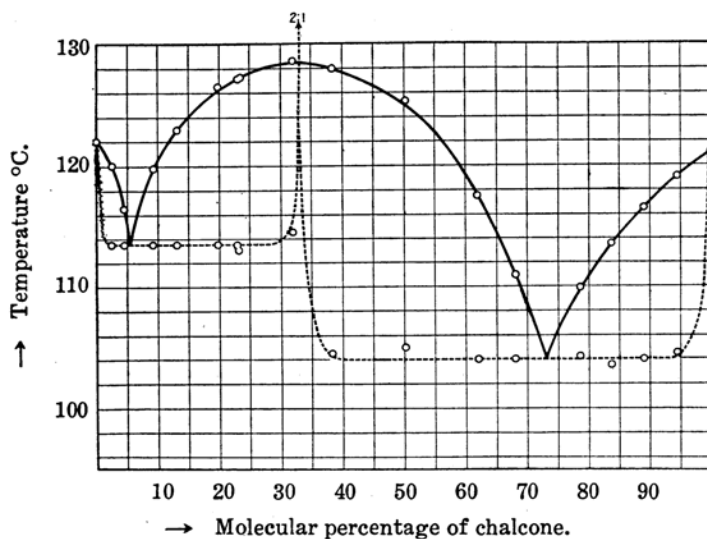


Fig. 2.

The system : 2'-Oxybenzalacetophenone—
picric acid (See Fig. 3)

Molecular percentages of		Temperatures of	
Chalcone	Picric acid	Thawing	Complete fusion
0.0	100.0	—	122.0
5.1	94.9	113.0	118.0
10.2	89.8	113.0	120.5
20.4	79.6	113.0	128.4
24.5	75.5	113.0	129.3
30.5	69.5	113.0	129.5
35.5	64.5	112.0	130.0
38.0	62.0	120.0	130.5
40.6	59.4	110.0	131.0
45.5	54.5	82.5	129.0
50.6	49.4	82.0	127.5
55.6	44.4	82.0	125.8
60.0	40.0	82.0	—
65.4	34.6	82.0	120.0
71.0	29.0	82.0	115.0
80.4	19.7	82.0	103.5
89.8	10.2	82.3	85.0
94.2	5.8	82.5	85.8
100.0	0.0	88.0	89.0

Eutectic points :

{ 113.0°C. picric acid
 92.5 mol %
 { 82.0°C. picric acid
 9.5 mol %

Distectic point :

132°C. { picric acid
 3 mols
 chalcone 2 mols

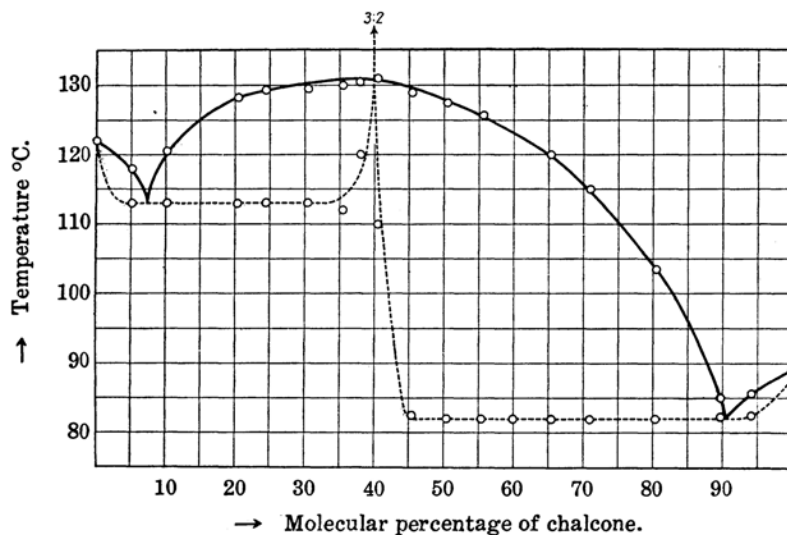


Fig. 3.

The system : 4'-Oxybenzalacetophenone—
picric acid (See Fig. 4)

Molecular percentages of		Temperatures of	
Chalcone	Picric acid	Thawing	Complete fusion
0.0	100.0	—	122.0
2.5	97.5	119.0	119.5
6.5	93.5	119.0	134.3
10.2	89.8	118.0	139.5
16.6	83.4	119.0	145.3
21.0	79.0	119.0	148.0
25.4	74.6	119.5	151.3
30.5	69.5	118.5	153.0
33.0	67.0	120.0	154.0
35.5	64.5	125.0	155.0
40.5	59.5	135.0	156.8
45.5	54.5	141.0	157.0
50.0	50.0	150.0	157.5
55.3	44.7	149.0	156.4
60.5	39.5	150.0	156.2
64.3	35.7	148.0	155.0
68.0	32.0	150.0	158.0
70.1	29.9	149.0	159.5
74.5	25.5	149.0	164.5
88.1	11.9	148.0	170.8
100.0	0.0	174.5	175.5

Eutectic points :

{ 119.0°C. picric acid
 97.5 mol %
 { 149.5°C. picric acid
 37.5 mol %

Distectic point :

157.5°C. { picric acid
 1 mol
 chalcone
 1 mol

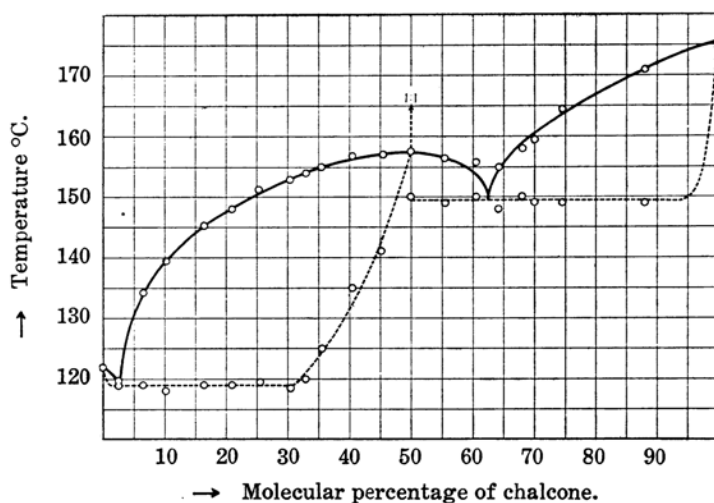


Fig. 4.

The system : 4'-Ethoxybenzalacetophenone—
picric acid (See Fig. 5)

Molecular percentages of		Temperatures of	
Chalcone	Picric acid	Thawing	Complete fusion
0.0	100.0	—	122.0
4.6	95.4	82.5	118.5
9.2	90.8	81.5	116.0
13.8	86.2	81.5	112.0
18.5	81.5	79.5	110.0
23.2	76.8	81.0	106.3
28.0	72.0	79.5	—
32.8	67.2	81.3	98.0
37.4	62.6	80.4	93.0
37.7	62.3	81.0	—
40.0	60.0	80.0	89.0
42.6	57.4	81.0	—
44.6	55.4	80.0	85.0
47.1	52.9	81.0	83.0
48.0	52.0	80.5	82.5
49.7	50.3	80.5	84.0
50.7	49.3	75.0	—
57.6	42.4	65.0	83.2
68.0	32.0	60.5	79.0
78.4	21.6	61.0	69.5
89.2	10.8	62.0	68.5
93.5	6.5	65.0	72.0
100.0	0.0	73.5	74.5

Eutectic points :

81.0°C. picric acid
53.5 mol %
60.5°C. picric acid
16.7 mol %

Distectic point :

84.5°C. { picric acid 1 mol
chalcone 1 mol

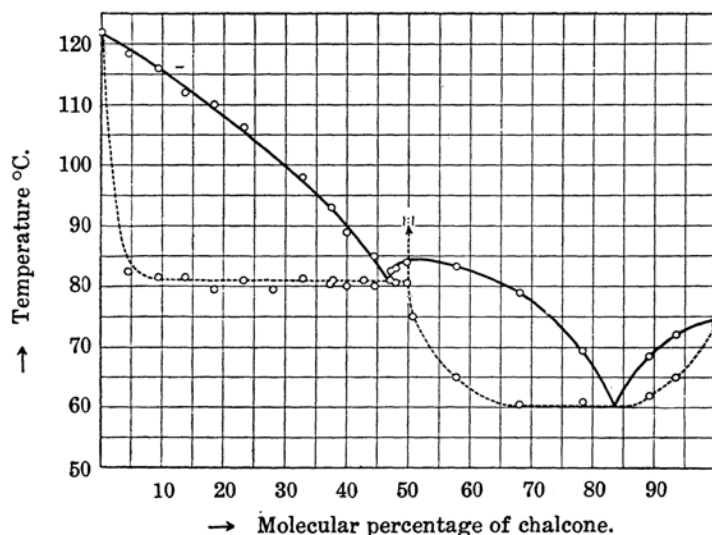


Fig. 5.

The system : 3,4-Methylenedioxybenzal-
acetophenone— β -naphthol (See Fig. 6)

Molecular percentages of		Temperatures of	
Chalcone	β -Naphthol	Thawing	Complete fusion
0.0	100.0	—	121.5
6.3	93.7	72.0	116.5
12.5	87.5	72.0	111.5
19.7	80.3	71.0	104.5
27.6	72.4	72.0	95.5
36.4	63.6	71.0	83.8
46.1	53.9	71.0	80.0
57.2	42.8	71.0	95.5
63.2	36.8	71.5	100.5
69.6	30.4	71.0	106.6
76.4	23.6	72.0	110.8
83.8	16.2	71.5	114.5
91.6	8.4	72.0	118.4
100.0	0.0	—	121.0

Eutectic point :
71.5°C. β -naphthol
58.2 mol %

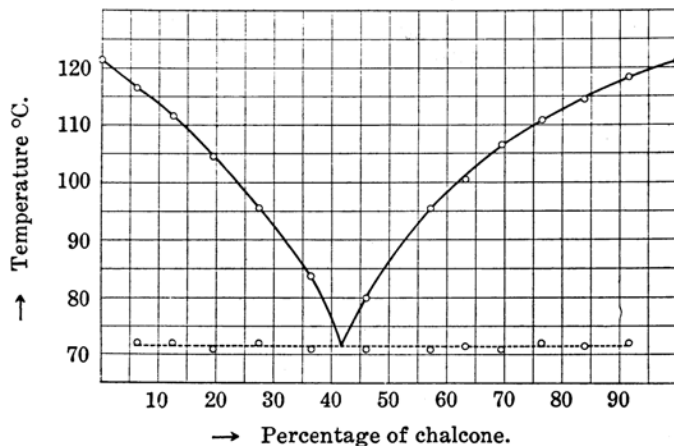


Fig. 6.

In conclusion, the author wishes to express his best gratitude to Prof. Y. Shibata for his kind and at the same time useful advises throughout this research.