TABLE II
ANALYSES

No.	Formula	Carbon		Hydrogen		Sulfur		Metal	
		Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.
1	$C_{16}H_{14}S_4Zn$	48.03	48.08	3.53	3.66	32.08	32.14	16.36	16.22
2	$C_{16}H_{14}S_4Pb$	35.45	35.80	2.60	2.70	23.68	23.94	38.26	38.18
3	C_8H_9NS	63.51	63.95	6.00	6.13	21.21	21.17		
4	$C_{15}H_{15}NS$	74.62	74.73	6.26	6.37	13.29	13.39		
5	$C_{15}H_{13}O_2NS_2$	59.35	59.61	4.32	4.46	21.14	20.99		
6	$C_9H_{10}S_2$	59.27	58.75	5.53	5.65	35.19	35.14		
7	$C_{10}H_{12}S_2$	61.15	60.64	6.16	6.16	32.68	32.65		
8	$C_{12}H_{16}S_2$	64.21	63.60	7.19	7.37	28.59	28.71		

Summary

1. Tolyl-4-carbithioic acid was prepared by the action of carbon disulfide on tolyl-4-magnesium bromide.

2. The acid readily forms salts and esters.

3. A thio amide and the p-toluide were prepared.

4. The acid is very sensitive to oxidizing agents.

5. Attempts to prepare the acid chloride were negative.

CHAPEL HILL, NORTH CAROLINA

THE EFFECT OF HEAT UPON CROTONIC ACID

BY EVALD L. SKAU[1] AND BLAIR SAXTON

In the course of a study of the mutual solubility relations of geometrical isomers, an unsuccessful attempt was made to prepare isocrotonic acid by a method based upon the work of Michael[2] and Schulthess and of Morrell and Hanson.[3]   According to these investigators the product obtained upon heating crotonic acid or isocrotonic acid to a temperature above 100° is a binary mixture of these two acids.   The latter authors made a more extensive study of the system and came to the conclusion that it afforded an example of "unstable" or "false equilibrium."   Since there is considerable doubt whether such cases actually exist,[4] the system promised to be interesting from this point of view also.

Morrell and Hanson obtained their "equilibrium" values by heating a sample of each acid for successive six-hour periods at various temperatures and determining the primary freezing points of the solutions obtained at each temperature.   (Their data are included in Table I.)   The composition

[1] Du Pont Fellow, 1924–1925.

[2] Michael and Schulthess, *J. prakt. Chem.*, [2] **46**, 236 (1892).

[3] Morrell and Hanson, *Chem. News*, **90**, 166 (1904); *J. Chem. Soc.*, **85**, 1520 (1904).

[4] See Roozeboom, "Die Heterogenen Gleichgewichte," **1918**, Vol. II, Part 3, p. 13; Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, **1923**, p. 17.

in each case was then read from the freezing point–composition diagram of the binary system crotonic acid–isocrotonic acid (a system of the simple eutectic type) on the assumption that only these two acids were present. Their "equilibrium curves meet at 172°" at a composition corresponding to 24% isocrotonic acid and 76% crotonic acid.[5]

On the basis of their work we proposed to prepare a quantity of isocrotonic acid for use in another investigation. By heating a sample of crotonic acid at 172° a mixture freezing at about 50° should be obtained, from which we hoped to get a 34% yield of liquid having the eutectic composition (70% isocrotonic acid) by filtering the crotonic acid separated just above the eutectic temperature, $-3°$. It seemed probable that the isocrotonic acid could be isolated from this solution since Wislicenus[6] was able to obtain it from Kahlbaum "Isocrotonic acid" which was found by him to be only 33% pure.

Upon carrying out this procedure, the heating being at various temperatures ranging from 125 to 175°, a liquid was obtained by filtering at 0° which did not solidify completely at $-3°$, nor could isocrotonic acid be isolated from it by Wislicenus' method.

A study of the equilibrium mixtures showed that they are not simple binary but at least ternary mixtures containing crotonic acid, probably some isocrotonic acid and a third substance which has been isolated in 90–95% purity. The evidence seems to show that this third substance is a double molecule having one free carboxyl group and one double bond, the suggested formula being $CH_3CH{=}CHCOOCH(CH_3)CH_2COOH$.

It has also been shown that above 110° the system does not exhibit the phenomenon of "false equilibrium" as Morrell and Hanson stated.

Effect of Heating Upon Certain Properties of Crotonic Acid

Materials.—The first part of the work was carried out on a sample of Kahlbaum crotonic acid obtained through the courtesy of the Bureau of Chemistry; later, samples were purchased from the Sylco Laboratories of Chicago. In all cases the acid was repeatedly crystallized from petroleum ether, the purified product giving a flat on its time–temperature curve at 71.4°.[7] Successive vacuum sublimation also proved to be an effective method of purification.

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[5] They suggested the possibility of compound formation within the range 138–145° inasmuch as the sample of isocrotonic acids after being heated at 145° failed to solidify completely at $-19°$, whereas the eutectic temperature for the crotonic–isocrotonic acid system is $-3°$ as determined by themselves. They state that with the possible exception of this temperature range, preliminary experiments on the equilibrium in the liquid phase seemed to indicate the absence of compound formation below 170°.

[6] Wislicenus, *Vierteljahrsschrift der naturforschenden gesellschaft in Zurich*, **41**, 270 (1896); *Verh. d. Vers. deutsch. Ntf. u. Arzte*, (II) **1**, 78 (1895).

[7] It may be noted that this is 0.5° below the value given by Morrell and Hanson. On the basis of purity of material and accuracy of temperature measurement, we believe our value to be the more accurate. By means of heat content curves, Lynn, in this Laboratory, estimated that the impurity was less than 0.03 mole per cent.

Method of Heating.—Samples sealed in evacuated tubes were heated at different temperatures between 97 and 170° for various periods of time. The resulting mixtures, in some cases after the crotonic acid which separated on cooling had been removed by filtration, were examined with reference to the following properties.

Freezing Point.—The apparatus used has already been described.[8] Since it is difficult to control the supercooling of crotonic acid mixtures, it was impossible to use Andrews, Kohman and Johnston's[9] method of correction for the amount of solvent which separated. Instead, the surroundings (the copper shield) were set at various temperatures below the freezing point and the highest maximum after crystallization was taken as the freezing point. The values are, therefore, accurate for pure crotonic acid and the error increases with the increase in concentration of the other components up to probably 1.5° for the most concentrated solutions.[10]

We confirm the finding of Morrell and Hanson that the freezing point is lowered by previous heating and our results show fairly good agreement with theirs for equal periods of heating (see Table I). That these are not the equilibrium values at the respective temperatures, as these investigators evidently assumed, is shown by the fact that further heating at the same temperature caused additional lowering, as can be seen from this table. In fact, by heating a sample of crotonic acid for 165 days at 110° ($\pm 1°$), a freezing point of 41° was attained, a value which was decidedly lower than any of theirs, even though in some cases they heated to 168°.

TABLE I

THE CHANGE IN FREEZING POINT UPON HEATING THE CROTONIC ACIDS

	Morrell and Hanson				Skau and Saxton	
Duration of heating,[a] hours	Temp. of heating, °C.	Freezing point, Tube I (isocrotonic), °C.	Freezing point, Tube II (crotonic), °C.	Heating, hours	Temp. of heating ($\pm 1°$), °C.	Freezing point, (crotonic), °C.
0	...	14.96	71.96	0	...	71.4
6	100	13.6	70.5	6	100	70.8
6[a] more	126	10.8	68.4	6.5 more	125	68.7
6 more	138	3.1	64.8	10 more	127	66.9
6 more	145	−3.1	60.3	56 more	123	52
6 more	152	21	55.8			
6[a] more	160	37.6	52.8			
6[a] more	168	46	51			

[a] The time of heating is not specifically stated, but it is to be implied that each period was six hours.

Acid Value and Bromination Value.—The acid value is taken as the number of grams of crotonic acid equivalent to the amount of standard alkali used per gram of sample. It was determined by direct titration in dilute alcohol solution using phenolphthalein as an indicator. The bromination value is taken as the number of grams of crotonic acid equivalent to the amount of bromine absorbed by one gram of sample. It was obtained by the method of Gaebel,[11] extending the time for absorption to exactly four hours.

The acid value and the bromination value were always numerically equal within

[8] Skau and Saxton, THIS JOURNAL, **50**, 2693 (1928).

[9] Andrews, Kohman and Johnston, *J. Phys. Chem.*, **29**, 914 (1925).

[10] For a discussion of the error due to this procedure see Andrews, Kohman and Johnston, Ref. 9.

[11] Gaebel, *Arch. Pharm.*, **250**, 72 (1912).

experimental accuracy and were always less than unity. For example, sixty-five hours at 110° gave 0.934; one hundred and twenty hours at 127° gave 0.816; and seven hours at 175° gave 0.891. Since the values for crotonic acid and isocrotonic acid are both unity, these results prove that there is some other substance or substances present in the heated product.

Saponification Value.—This seems to be unchanged by previous heating.

The Reversibility of the Reaction.—To test whether we were dealing with a case of true equilibrium, the final state was approached from two sides in the following manner. A sample of crotonic acid was heated at 160° for thirty-five hours and, after cooling to room temperature, the solid crotonic acid was removed by filtration. The remaining liquid gave a primary freezing point of 18.9° and an acid value of 0.750. Samples of this liquid, "Mixture I," and of pure crotonic acid were sealed in separate evacuated tubes and heated at constant temperature for a number of months. Their freezing points and acid values were then determined, as recorded in Table II.

TABLE II

EQUILIBRIUM VALUES REACHED FROM OPPOSITE SIDES

No.	Sample	Original freezing point, °C.	Duration of heating, months	Temp. of heating ($\pm 1°$), °C.	Freezing point, °C.	Acid value
I	Crotonic	71.4	5.5	110	41.8	0.710
II	"Mixture I"	18.9	5.5	110	41.0	.703
III	Crotonic	71.4	6.5	125	48.2	.816[a]
IV	"Mixture I"	18.9	6.5	125	45.9	.772
V	"Mixture I"	18.9	5.0	(Room temp.)	19.1	.750

[a] Slight decomposition took place in this tube as was evidenced by the development of considerable pressure.

Besides indicating that above 110° we are dealing with a true and not a "false" equilibrium, these results afford evidence as to the effect of temperature on the equilibrium. This will be discussed more fully below. It should also be noted that while "Mixture I" showed substantially no change at room temperature during five months, heating at 110 and at 125° caused the freezing point to rise in both cases, whereas the acid value rose in one case and fell in the other. This points to the presence of at least three substances in the equilibrium mixtures.

Attempts to Isolate Isocrotonic Acid.—Michael's method was applied to a heated sample of crotonic acid from which considerable crotonic acid had been filtered at room temperature. Instead of isocrotonic acid, however, an oily liquid having an acid value of 0.608 was obtained.[12]

[12] Michael's method for the isolation of isocrotonic acid from the Kahlbaum "Isocrotonic acid" depends on the insolubility of the sodium salts of the foreign substances in alcohol. Wislicenus modified this by evaporating the alcoholic solution to a smaller volume and then precipitating a considerable amount of the remaining impurities by adding ether. He thus got a product which was nearly solid at 0°, whereas that obtained by Michael's method contained only a small amount of solid at that temperature.

The product obtained by the use of Wislicenus' modification on a similar sample had essentially the same properties, but undoubtedly contained less crotonic acid. It was a light brown liquid, not crystallizable at $-78°$, and was insoluble in water but very soluble in alcohol or ether. Its acid value was 0.535 and its bromination value approximately the same, 0.528. It appeared to be very readily hydrolyzed, for, after neutralizing, more acid seemed to be formed on heating, and if titrated back to neutrality occasionally the amount of alkali used approached a total corresponding to an acid value of unity. The saponification value was unity.[13]

From the depression of the freezing point of pure crotonic acid caused by the addition of various small amounts of this liquid, its apparent molecular weight was calculated[14] to be 144; that is, its molecular complexity was 1.67 times that of crotonic acid, thus corresponding to double molecules which are dissociated into single molecules to the extent of 20%.[15]

Distillation under diminished pressure of one of the samples of heated crotonic acid confirmed our conclusion that very little isocrotonic acid was present. We obtained a low-boiling fraction having an acid and a bromination value substantially of unity; a middle fraction rich in crotonic acid and, as the largest fraction, a high-boiling liquid (165–173° at 24 mm.)[16] which had an acid value of 0.679 and a bromination value of 0.671 and from which crotonic acid separated at room temperature.

Nature of the Products Formed.—All of the above data indicate that the system contains at least three substances: (1) crotonic acid; (2) a low-boiling constituent which comes over with the crotonic acid in a vacuum distillation; and (3) a high-boiling constituent which constitutes the major portion of the product obtained on applying the Michael–Wislicenus method for isolating isocrotonic acid.

[13] The low acid value, the high boiling point and the saponification value might be explained by the presence of an acid anhydride. To test this possibility, a sample from which the solid crotonic acid was filtered at 0° was treated in one case with a slight excess of alkali and in another with an excess of solid sodium carbonate in a small amount of water and then extracted thoroughly with ether. The ether extracts contained a slight amount of a brown resinous substance representing only a small fraction of a per cent. of the original heated mixture.

[14] From the ideal freezing point–solubility equation

$$\log N = \frac{-3100}{4.575(273.1 + 71.4)} \frac{\Delta t_F}{T_F} = -1.967 \frac{\Delta t_F}{T_F}$$

in which N is the mole fraction of crotonic acid, Δt_F the freezing point depression, T_F the freezing point of the solution on the absolute scale, 71.4 the freezing point of pure crotonic acid, and 3100 the molal heat of fusion of crotonic acid as determined by Lynn [Skau and Saxton, THIS JOURNAL, **50**, 2693 (1928)].

[15] From the relation $x = (2/1.67) - 1$.

[16] Wislicenus, Jr., ["Dissertation," Leipzig, **1892**; *Chem. Zentr.*, I, 413 (1893)] found that Kahlbaum's "Isocrotonic acid" distilled almost completely below 100° at this pressure, the impurity being essentially crotonic acid.

The low-boiling constituent is probably isocrotonic acid, for in the mixture with crotonic acid, as it was obtained, the acid and bromination values were approximately equal to unity, and, therefore, its molecular weight (within 2%) is equal to that of crotonic acid. If the low-boiling fractions are thus assumed to be binary mixtures of crotonic and isocrotonic acids, their compositions can be estimated from their freezing points and Morrell and Hanson's freezing point–composition diagram. By such an estimation it was found that the amount of isocrotonic acid in the original heated mixture was in the neighborhood of 7%.

The high-boiling constituent appears to be a dimolecular polymer of crotonic or isocrotonic acid or an addition compound of the two acids having one free carboxyl group and one double bond. This would require acid and bromination values of 0.5. The formula $CH_3CH\!\!=\!\!CHCOOCH(CH_3)CH_2COOH$ seems to agree with the properties best. This was the structure attributed by Thackrah[17] to a compound distilling at 163° (24–25 mm.) from a mixture obtained by heating crotonic acid at 190–200° for a few hours. His proof for this structure was based on the fact that the compound neutralized only one-half as much alkali as the same weight of crotonic acid, and that it was readily hydrolyzed on boiling or on heating with an excess of alkali, giving crotonic acid and β-hydroxybutyric acid salts. He also claimed that crotonic acid was formed practically quantitatively[18] by heating this product for a long time at 200°.

Thackrah came to the conclusion that the liquid condensation product cannot be prepared free from crotonic acid and his lowest neutralization value corresponds to an acid value of 0.57. We have been able, however, by taking advantage of the difference in the solubility of the sodium salts in a mixture of alcohol and ether, to obtain a product having an acid value of 0.535 and have attempted to purify it further by various methods. (1) Petrol ether extraction resulted in a lowering of the acid value of the residue but the change was relatively small. (2) By using the principle of steam distillation with benzene as the carrier, the acid value of a sample was reduced from 0.634 to 0.561, but the procedure was very slow. (3) The product obtained by the last method was heated in a vacuum distilling apparatus for about six hours at 104° and 20 mm. The residual liquid, which was now a deep brown, had an acid value of 0.455 and its saponification value was unity. Due to the smallness of the sample the determination of the bromination value was omitted. The apparent molecular weight was still less than twice that of crotonic acid, the mean value of x being 0.11. The fact that the acid value was less than 0.5 might seem to

[17] Thackrah, "Dissertation," Leipzig, 1891. To the best of our knowledge this work has never been otherwise published, the only reference to it being in another Leipzig dissertation by Wislicenus, Jr., in 1892.

[18] This seems rather doubtful, considering his method of preparation of the compound.

indicate the presence of a trimolecular compound, but it could be equally well explained by assuming the presence of a dimolecular form having no free carboxyl groups.

Effect of Temperature on the Equilibrium.—An examination of the acid values of I to IV in Table II indicates that the percentage of double molecules in the equilibrium mixtures decreases as the temperature of heating increases.   This is to be expected since polymerization is, as a rule, exothermic.   We have also noted indications that the percentage of the low-boiling constituent does not change proportionately to that of the double molecule.   If it did, the separation of the crotonic acid at 0° would leave a liquid of the same acid value in all instances, but this was found not to be the case.

Summary

The effect of heating crotonic acid has been investigated.   It has been proved that the resulting mixture is not a binary mixture, as is stated in the literature, but contains at least three compounds: crotonic acid, a low-boiling constituent (probably isocrotonic acid) and a high-boiling liquid from the properties of which its probable structure has been deduced. It has further been proved that above 110° the system does not show the phenomenon of "false equilibrium" as was previously supposed.

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THE BROMINATION OF 2,4-DIMETHOXYCINNAMIC ACID

BY MARIE REIMER AND ELISE TOBIN

In the study, in this Laboratory, of unsaturated α-ketonic acids, certain substituted cinnamic acids have been needed for purposes of identification. This has led to the study of the bromination products of 2,4-dimethoxycinnamic acid which are described in this paper.   The acid was prepared by hydrolysis of ethyl 2,4-dimethoxycinnamate made by the Claisen condensation and was the stable form.

We have found that addition of bromine to 2,4-dimethoxycinnamic acid is invariably accompanied by bromination in the ring, the position of the nuclear bromine atom being established by oxidation of the tribromo acid thus formed to 2,4-dimethoxy-5-bromobenzoic acid.[1]   The behavior of the dimethoxycinnamic acid on bromination is, therefore, similar to that of the corresponding dimethoxybenzoylacrylic acid.[1]   It has not been possible to prepare an unsaturated acid by elimination of hydrogen bromide from the tribromo acid by the usual methods.   Invariably saturated alkoxy acids result which are probably formed by direct replacement of bromine by an

[1] Grace Potter Rice, THIS JOURNAL, **48**, 3125 (1926).