Preparation of Brassylic Acid

Rapeseed oil (420 g.) was converted to methyl esters by treating with boiling methanol (500 ml.) containing 0.75% of caustic soda. The reaction mixture was diluted with water and the fatty esters extracted with petroleum ether and distilled from a Claisen flask. The fraction boiling 170–200° (2 mm.) deposited crystals of methyl arachidate which were filtered off. The liquid esters were saponified with alcoholic caustic potash and, upon cooling, the crystalline potassium salt of erucic acid which separated was filtered off and recrystallized from hot absolute ethanol. The purified potassium salt upon decomposition gave erucic acid which once crystallized from acetone melted at 33°; yield 32% on the rapeseed oil.

13,14-Dihydroxybehenic acid was prepared in theoretical yield by treating 9.0 g. of erucic acid with peracetic acid (6.5 ml. of 30% hydrogen peroxide in 20 ml. of acetic acid) at 92° and standing overnight at 40°. The reaction mixture was poured into water and the solid acid filtered off. Crystallized from ethylene dichloride, it melted at 99°.

The above acid was oxidized by treating 4.0 g. in 500 ml. of ethanol with 3.1 g. of periodic acid for forty minutes. Excess sodium bicarbonate was added and excess periodic acid destroyed with normal sodium arsenite solution. Insoluble sodium salts were filtered off, most of the alcohol removed by distillation, and the residue diluted with water and extracted with ether. The brassylic acid half-aldehyde was separated from pelargonic aldehyde by washing the ether solution with 2% sodium carbonate solution.

Acidification of the sodium carbonate solution yielded 2.8 g. of brassylic half-aldehyde which was oxidized to brassylic acid by peracetic acid in the usual manner. After twice crystallizing from ethylene dichloride, the brassylic acid melted at 113°; yield theoretical.

Quantitative Semi-micro Determination of α,β-Dihydroxy Compounds.—An accurately weighed sample of about 0.1 millimole of dihydroxy compound is dissolved in 5 ml. of 95% pure ethanol in a 200-ml. erlenmeyer flask and 5.0 ml. of periodic acid solution (0.5 g. of periodic acid in 28 ml. of 95% ethanol) is pipetted into the flask, mixed and allowed to stand at room temperature for fifteen to forty-five minutes, the time varying with the compound.

The solution is diluted with 100 ml. of water and approximately 0.5 g. of sodium bicarbonate and 0.5 g. of potassium iodide added in that order. The liberated iodine is titrated with $N/10$ potassium arsenite solution. Titrate similarly a 5.0-ml. sample of the periodic acid solution as a blank. The difference between the two titrations represents the equivalent periodic acid consumed in the oxidation, one atom of oxygen being used per mole of dihydroxy compound oxidized according to the equation

$$\mathrm{RCH(OH)CH(OH)R'} + \mathrm{HIO_4} \longrightarrow \mathrm{RCHO} + \mathrm{R'CHO} + \mathrm{HIO_3} + \mathrm{H_2O}$$

Summary

1. The thermal polymerization of undecylenic acid and methyl undecylenate has been examined.

2. Linear polymerization has been shown to occur and as evidence the presence of the dimethyl ester of 8-eicosene-1,20-dicarboxylate was shown in the dimeric fraction.

3. Other dimeric esters and higher polymers were shown to be formed but their structure was not elucidated.

JERSEY CITY, NEW JERSEY RECEIVED APRIL 18, 1945

[COMMUNICATION NO. 1025 FROM THE KODAK RESEARCH LABORATORIES]

Heats of Polymerization. I. An Isothermal Calorimeter and its Application to Methyl Methacrylate

BY L. K. J. TONG AND W. O. KENYON

A knowledge of heats of polymerization is important to a fundamental understanding of the mechanism of polymer-forming processes, but few published quantitative data are available on the subject. Flory[1] has discussed heats of polymerization in his consideration of the mechanism of vinyl polymerizations, but the values used were obtained indirectly. The few direct measurements of heats of polymerization include those of Goldfinger, Josefowitz and Mark,[2] and of Evans and Polanyi.[3] These investigators are not in agreement on the results for methyl methacrylate, giving ΔH values of -7.9 and -11.6 kcal./mole, respectively. Houwink[4] has published values for heats of polymerization for several unsaturates, calculated from experimental data on heats of combustion, but a value for methyl methacrylate was not included.

This preliminary paper describes a calorimeter and technique which have been found to be well adapted to the determination of heats of polymerization. Data on methyl methacrylate are presented to illustrate the method. Investigations of other polymerizable systems are expected to be the subjects of future publications.

The present method utilizes the heat evolved from the polymerization reaction to evaporate a liquid which is in equilibrium with its own vapor at its boiling point. Thus the heat given off by the reaction is directly proportional to the amount of material evaporated. The heat of polymerization is calculated from the amount of liquid evaporated and its heat of vaporization. The system is kept at constant temperature by being completely immersed in the boiling vapor. A

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(1) Flory, THIS JOURNAL, **59**, 241–253 (1937).

(2) Goldfinger, Josefowitz and Mark, *ibid.*, **65**, 1432 (1943).

(3) Evans and Polanyi, *Nature*, **152**, 738 (1943).

(4) Houwink, "Chemie und Technologie der Kunststoffe," Vol. I, Leipzig, 1940, p. 60.

similar arrangement has been used by Mathews and Fehlandt[5] in their direct determination of heat of vaporization. In their experiments the heat was obtained from the known amounts of electrical energy applied.

This calorimeter has several advantages over the conventional type when used for measuring heat of polymerization as follows: (1) No complicated electrical and mechanical devices are necessary for temperature controls and measurements. (2) Very few manipulations or adjustments are required between experiments, thus enabling consecutive runs to be made quickly. (3) The course of the reaction can be followed continuously, thus providing a very convenient method for measuring the rate of reaction.

We have measured the heat of polymerization of methyl methacrylate at three temperatures, using as heat-exchange media, toluene, benzene, and carbon tetrachloride at their boiling points of 110, 80.2, and 76.8°, respectively. The heats of vaporization of these substances are taken as 86.5 cal./g. for toluene, 94.3 for benzene, and 46.4 for carbon tetrachloride. No correction was made for buoyance, since it is within our experimental error.

Experimental

Apparatus.—The calorimeter, shown in Fig. 1, is essentially an all-glass refluxing apparatus. The inner jacket has a one-fourth-inch hole (K) at the bottom to permit passage of vapor. Inside of the jacket is a tube (E) suspended freely from a scale by means of no. 40 nichrome wires tied on two glass hooks sealed on the outside of the tube (E) as shown. The wires must not touch the lip of the tube, so that any condensate flows down the outside of the tube. During a run, the tube is loosely covered with a hollow glass plug (G) to prevent spraying when the liquid boils. A small dent is made on the lip of the tube to allow the vapor to escape freely.

The reaction tubes (H) are totally submerged in the boiling liquid. They have an average length of 2.5 inches and are made from 18-mm. Pyrex tubing. The sides softened in a flame were pushed in with capillary tubes to increase the surface for better heat transference and at the same time to provide capillaries which promote smooth boiling. These details are illustrated in Fig. 1. When filled, the tubes stand submerged in the boiling liquid and when necessary are weighted by wrapping with copper wire.

The level of the heat-exchange liquid is about one inch below the lip of tube (E) at the beginning of the run and should remain above the top of the reaction tube at the end of the run. During a run, the saturated vapor rises to the level h-h′. The condensate from the upper part of the jacket is caught in the trap (C) and returned through the outlet. After the experiments were completed it was found that the calorimeter showed less tendency to exhibit drifts when the outlet is closed. The glass plates (P) minimize the disturbance due to outside air currents. The scale is a Cenco triple-beam type with sensitivity of 0.01 g. This was found to be sufficiently sensitive because more than 10 g. of material was evaporated in each run.

Materials

Methyl methacrylate of commercial grade was distilled under reduced pressure and recrystallized three times according to the procedure described by Mayo and Lewis.[6]

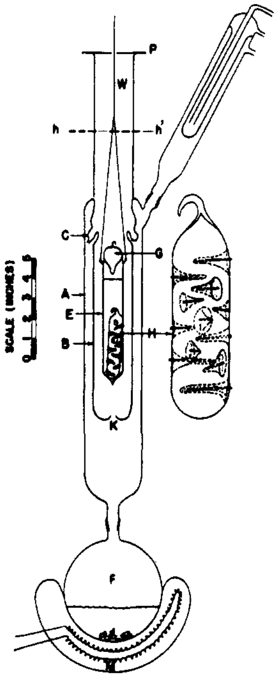

Fig. 1.

The purified product was analyzed by bromination.[7] The analytical sample was mixed with standard potassium bromate solution, excess potassium bromide, and hydrochloric acid solution and this mixture was irradiated by ultraviolet. After addition of solid potassium iodide and dilution, the excess bromine was determined by thiosulfate titration. Bromination periods of twenty and of thirty-five minutes gave values within 0.2% of that calculated for methyl methacrylate.

Carbon tetrachloride, benzene, and **toluene** were Eastman Kodak Co., white label grade. Prior to use they were again distilled, fractions of less than 0.05° boiling ranges being collected.

Benzoyl peroxide of Eastman white label grade was used directly.

Procedure.—Methyl methacrylate containing the desired amount of benzoyl peroxide catalyst was introduced into a dry reaction tube by means of a pipet. Air was displaced by introducing dry nitrogen through a fine capillary tube reaching to the liquid. After removal of the capillary, the opening was loosely plugged with cotton and sealed immediately. Before the reaction was started tube (E), containing a suitable amount of liquid, was lowered to rest vertically on the bottom of the jacket (B). It was brought to the equilibrium temperature by refluxing the liquid in (F) for one-half hour or longer. The reaction tube (H) was brought to temperature by lowering it into the jacket (B). It was held beside tube (E) for one and a half minutes, then lowered into (E) and covered with plug (G). This time was arbitrarily considered as zero time. The unit was then raised to the predetermined position by hooking the free end of the wire to the scale. This required an additional thirty seconds. The weight was determined as soon as possible and recorded. Subsequent measurements were taken at convenient intervals until no change or a constant drift was observed over a period equal to at least one-half the time required for the main part of the reaction to occur. This point will be discussed in a later section.

Results and Discussion

Preliminary control experiments using an inert material in the reaction tubes showed that by adjusting the position of tube (E) and the rate of heating, the weight of the heat-exchange liquid in the tube can be made to remain constant or have a very small constant drift either in the direction of gain or loss of weight. The position to obtain constant weight was empirically determined for each calorimeter and each heat-exchange liquid.

It was found that if drifts should occur corrections made by linear extrapolation to zero time are valid. Comparisons of extrapolated values of experiments having intentionally induced positive and negative drifts with those having no

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(5) Mathews and Fehlandt, THIS JOURNAL, **53**, 3212 (1931).

(6) Mayo and Lewis, *ibid.*, **66**, 1594 (1944).

(7) Lewis and Bradstreet, *Ind. Eng. Chem., Anal. Ed.*, **16**, 617 (1944).

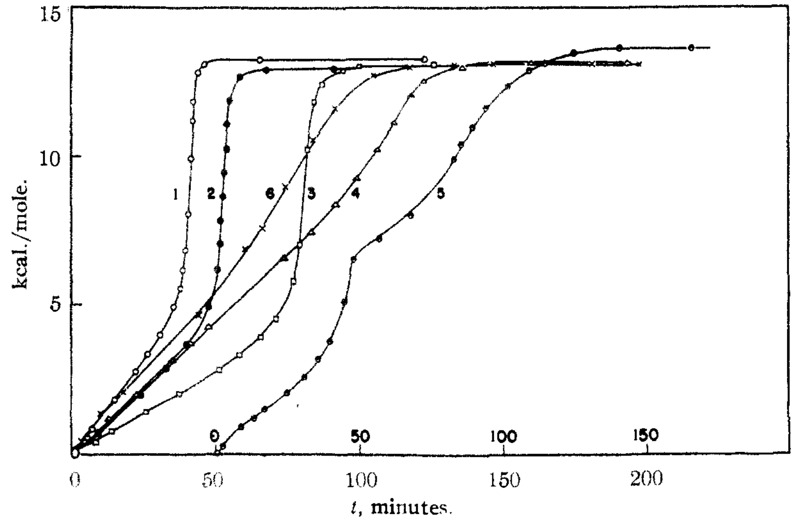

Fig. 2.—1 to 5 at boiling point of CCl_4 (76.8°): 1, 1.00% benzoyl peroxide; 2, 0.50% benzoyl peroxide; 3, 0.20% benzoyl peroxide; 4, 0.52% benzoyl peroxide + 51.4% methyl methacrylate + 48.0% CCl_4; 5, 36.3% methyl methacrylate + 0.36% benzoyl peroxide + 63.4% of 50% methanol; 6, 0.011% benzoyl peroxide at b. p. of toluene (110°).

drift gave ΔH values agreeing within the experimental error indicated.

Table I shows the observed heat of polymerization of methyl methacrylate at several temperatures with and without solvent. The heat of this reaction has a constant value of 13.0 ± 0.2 kcal./mole over the limit of temperature and catalyst concentrations studied. Our results are significantly higher than those reported by other investigators.[1,2] The fact that the use of carbon tetrachloride as a solvent did not alter the heat of reaction to any appreciable amount indicates that the heat of solution of the polymer is similar to that of the monomer—probably both are very small. However, in methanol–water mixture, the difference of 0.6 kcal./mole is believed due to the negative heat of solution of the monomer, since the polymer is insoluble under these circumstances.

Following other investigators[8,9] we may assume that the reaction proceeds according to the chain mechanism consisting of (1) a chain-initiating step, (2) a chain-propagating step, and (3) a chain-terminat-

TABLE I

HEAT OF POLYMERIZATION

Benzoyl peroxide, %	Methyl methacrylate, g.	$-\Delta H$ (kcal./mole)
(A) Heat-Exchange Medium, Toluene, b. p. 110°		
0.011	7.54	13.0 (Curve 6)
	7.45	12.9
(B) Heat-Exchange Medium, Benzene, b. p. 80.2°		
.50	5.67	13.0
	7.43	13.2
.20	3.69	13.0
	7.39	13.0
(C) Heat-Exchange Medium, Carbon Tetrachloride, b. p. 76.8°		
1.00	7.39	13.3 (Curve 1)
	3.68	12.8
.50	7.40	13.1
	5.68	13.0 (Curve 2)
	3.65	13.0
.20	7.37	13.0 (Curve 3)
	7.37	13.0
	3.72	12.7
	3.68	13.0
		13.0±0.1
51.4% Methyl Methacrylate, 48% Carbon Tetrachloride, 0.52% Benzoyl Peroxide	5.07	13.1 (Curve 4)
47.5% Methyl Methacrylate, 26% Water, 26% Methanol, 0.48% Benzoyl Peroxide	3.561	13.6
36.3% Methyl Methacrylate, 31.6% Water, 31.6% Methanol, 0.36% Benzoyl Peroxide	3.36	13.6 (Curve 5)

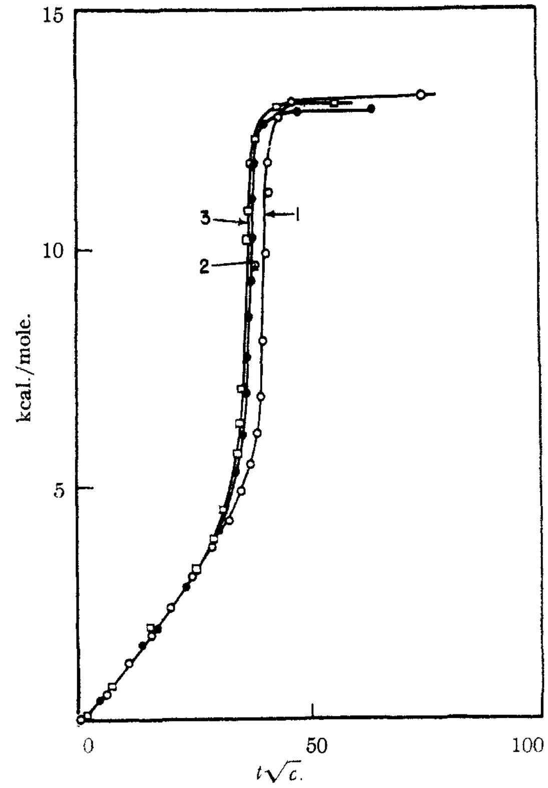

Fig. 3.—1, 1.00% benzoyl peroxide; 2, 0.50% benzoyl peroxide; 3, 0.20% benzoyl peroxide.

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[8] Norrish and Brookman, *Proc. Roy. Soc.*, **A171**, 147 (1939).

[9] Norrish and Smith, *Nature*, **150**, 336 (1942).

ing step. Since the chain length has been found to be long,[10] the groups at the ends of the chains can be neglected; likewise the heat contributed by reactions (1) and (3) is negligible compared to that of reaction (2).

If we further assume that the heat evolved in reaction (2) is independent of the chain length, then the percentage of heat evolution should be equal to the percentage of polymer formed. Consequently, the rates obtained by Norrish, *et al.*,[8,9] by measuring the percentage of polymer formation directly and those obtained in the present paper by measuring the percentage of heat evolved should be equal under the same experimental conditions.

In Fig. 2 we have shown the heat evolved in kcal./mole against the time of polymerization. Curves 1, 2, and 3 represent runs at 76.8° having catalyst concentrations of 1.0, 0.5, and 0.2%, respectively. The linearity of the initial slopes and their relationship to the square root of catalyst concentration is shown by graphing the thermal data against $t\sqrt{c}$, where c is the weight % of benzoyl peroxide (Figure 3). These observations are in agreement with the findings of Norrish and Brookman.[8] Quantitatively, our measurements obtained at the boiling point of benzene can be compared with theirs at 80°. Thus, using 0.20 weight % catalyst (0.0826 mole %), we obtained an initial slope,

$$\frac{d\left(\frac{\Delta Ht}{\Delta H_\infty} \times 100\right)}{dt} = 0.52.$$

At 80° and with 0.0082 mole % of catalyst, Norrish and Brookman obtained an initial slope of 0.15%/min. Extrapolation to 0.0826 mole % catalyst, using the square root relationship, gives 0.48%/min.

The characteristic upward turn of the curves was attributed by Norrish and Smith[9] to an increase of bulk viscosity which reduces the chain-terminating reaction. The use of carbon tetrachloride as a solvent (Curve 4) delayed this upward turn as these authors have previously observed. A two-step reaction was shown by Curve 5, which was measured in methanol–water mixture. This was due to the fact that the mixture separated into two phases during the reaction and probably the reaction in each phase proceeded at a different rate.

Summary

1. A simple isothermal calorimeter is described which is suitable for determination of heats of polymerization. Its operation using methyl methacrylate is illustrated.

2. The heat of polymerization of methyl methacrylate was found to be 13.0 ± 0.2 kcal./mole. This value did not change with temperature or catalyst concentration within the limits investigated.

3. The rate of polymerization as measured by heat evolution agrees with measurements of other investigators using other experimental methods.

ROCHESTER, NEW YORK RECEIVED APRIL 7, 1945

[10] Strain, *Ind. Eng. Chem.*, **30**, 345 (1938).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA, LOS ANGELES]

Cyclopropane Derivatives. I. Studies of the Photochemical and Thermal Chlorination of Cyclopropane

BY JOHN D. ROBERTS AND PHILIP H. DIRSTINE

Gustavson[1a] has reported that the photochemical chlorination of cyclopropane gave 1,1-dichlorocyclopropane and high-boiling compounds resulting from ring-opening reactions as the principal products. Small quantities of cyclopropyl chloride were isolated but the yields were unsatisfactory and attempts[1b] were made to prepare the monohalide by other methods. In beginning an investigation of the chemistry of cyclopropyl halides, we have studied the photochemical and thermal chlorination of cyclopropane in flow systems using conditions which were hoped to give useful yields of cyclopropyl chloride.

Experimental

The chlorination apparatus is shown in Fig. 1. U. S. P. cyclopropane (Ohio Chemical Company) was run from cylinder A through drying tube B (Anhydrone), gas-aspirator C and flowmeter D, mixed with chlorine (Dow) from cylinder E and flowmeter D′ and sent into the reactor G. The back pressure of the system was measured by the open tube manometer F. For the photochemical work, G was a 0.5 cm. i. d. × 250 cm. Pyrex tube shaped to form a grid about 6 cm. × 30 cm. Actinic energy was supplied by two No. 2 Photoflood bulbs at 7 cm. and a General Electric RS type sun-lamp at 8 cm. The grid was cooled by a strong air blast.

In the thermal runs G was a Pyrex tube (0.6 cm. i. d.) wound with Chromel A resistance wire and insulated with magnesite lagging. The tube was provided with several spaced take-offs so that the residence time could be varied without changing the flow rates. The take-offs were constructed of 1-mm. capillary tubing so that the transition time between reaction and quenching could be reduced to a negligible value. An exploring thermocouple was provided to measure the reaction temperature.

The hydrogen chloride in reaction products was removed by washing with water in tower H. The excess chlorine was absorbed in tower J with 5% sodium hydroxide solution. The gas stream was dried with calcium chloride (K) and Anhydrone (L). The cyclopropane was fractionated in column N and collected in Q. P and P′ were Dry Ice cooled condensers. The cyclopropane was refluxed rapidly in flask Q by means of an electric heater in

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[1] (a) Gustavson, *J. prakt. Chem.*, [2] **42**, 495 (1890); **43**, 396 (1891); (b) **46**, 157 (1892).