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Heats of Polymerization. II. Some Esters of α-Methylacrylic Acid

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The details of an isothermal calorimeter of simplified design for determining the heats of polymerization of ethylenic unsaturates were given in an earlier paper. Investigations on methyl methacrylate were used to exemplify its operation.[1]

The present paper extends the investigation to include other esters of α-methylacrylic acid. These include the methyl (for comparison), *n*-butyl, cyclohexyl, benzyl and phenyl esters. The *n*-butyl, cyclohexyl, benzyl, phenyl and methyl (for comparison) esters were chosen to illustrate the effects of wide variation in the structure of the ester group. Certain modifications of the calorimeter are described.

Experimental

Apparatus.—The apparatus and experimental procedures employed include the following slight modifications of those described previously.[1]

Calorimeter.—A small Dewar tube instead of the plain glass tube is suspended in the calorimeter to contain the heat-exchange liquid and the reaction tube. This effectively reduces heat leakage through the walls, which can otherwise produce large errors when the reactions are slow. The Dewar tube has a 0.75-inch inside diameter, a 1.25-inch outside diameter, and a capacity of 45 cc., with a narrow unsilvered strip to permit observation of the liquid level. The heat-exchange liquid is preheated to its boiling point, then siphoned into the Dewar tube. This operation is conducted within the calorimeter.

Balance and Recorder.—The Dewar tube with its contents is suspended in the calorimeter from a hook on the left arm of a pulp balance which is situated on top of a case enclosing the calorimeter, as shown in Fig. 1. The suspension wire (A) runs through suitable openings. On the right arm of the balance is suspended an aluminum cylinder (B), partially submerged in motor oil contained in a 3-inch diameter brass cup (C). This arrangement has the effect of a damper and sensitivity regulator, since cylinders of various diameters can be interchanged to give the desired sensitivity to the balance. For samples of about 5 g. we have used a sensitivity such that a change of weight of one gram deflects the light beam about 0.9 cm. on the recording drum described below.

A small vertical mirror (D) is attached to the balance beam near the fulcrum to reflect a narrow beam of light which is finally focused on photographic paper wrapped around a rotating drum (E). The drum has its axis parallel to the direction of motion of the light beam and is driven at a speed of one-sixth revolution per hour by a synchronous motor. The recorder is properly shaded to permit operation without darkening the room. Prior to each polymerization experiment, the scale representing weight loss was recorded photographically on the paper by adding known weight increments to the right-hand balance arm and giving a short exposure after each addition, but with the drum stationary. The current to the light source is mechanically interrupted for one minute out of each five-minute period. This serves as a measure of the time scale.

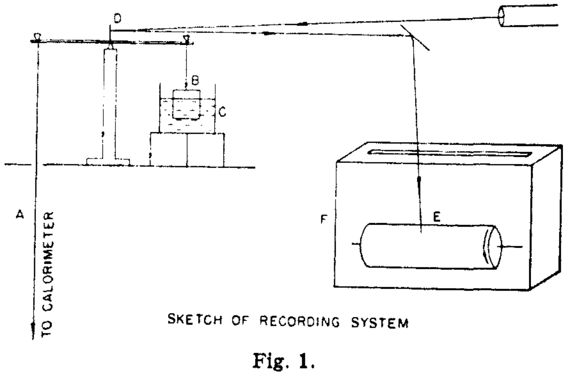

Fig. 1.

Materials

Methyl methacrylate was purified as previously described.[1]

***n*-Butyl methacrylate** of commercial grade was distilled under reduced pressure: $n^{20}\text{D}$ 1.4248 found; $n^{15}\text{D}$ 1.426 literature.[2]

Phenyl methacrylate was prepared by the reaction of methacrylyl chloride with phenol.[3] It was distilled under reduced pressure and crystallized by partial freezing in a Dry Ice-bath; m. p. 17.6°, $n^{20}\text{D}$ 1.5161.

Benzyl methacrylate was prepared by ester exchange between methyl methacrylate and benzyl alcohol using sodium methoxide catalyst and removal of methyl alcohol by benzene distillation.[4] The product was fractionated at reduced pressure; $n^{20}\text{D}$ 1.5148. *Anal.* Calcd.: C, 74.97; H, 6.87. Found: C, 75.28; H, 7.15.

Cyclohexyl methacrylate was prepared by the method used for the benzyl esfer: $n^{20}\text{D}$ 1.4585. *Anal.* Calcd.: C, 71.42; H, 9.52. Found: C, 71.56; H, 9.63.

Carbon tetrachloride was purified as previously described.[1]

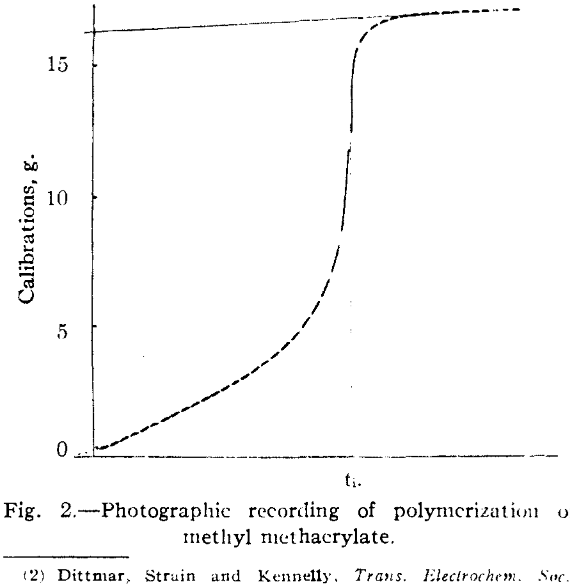

Fig. 2.—Photographic recording of polymerization of methyl methacrylate.

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[1] Tong and Kenyon, THIS JOURNAL, **67**, 1278–1281 (1945).

[2] Dittmar, Strain and Kennelly, *Trans. Electrochem. Soc.*, 159–169 (1938).

[3] Graves, U. S. Patent 2,129,685, September 13, 1938.

[4] Barrett and Strain, U. S. Patent 2,129,665, September 13, 1938.

[5] We wish to thank Mr. T. M. Laakso for the preparation of the benzyl and cyclohexyl esters, Dr. G. P. Waugh for the phenyl ester, and Dr. P. T. Newsome for the refractive index values.

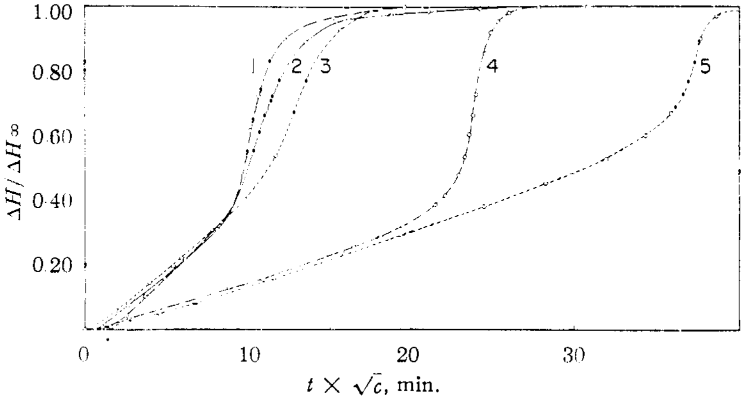

Fig. 3.—Per cent. of polymerization *vs.* $t\ \sqrt{\text{Cat.}}$: 1, phenyl methacrylate; 2, cyclohexyl methacrylate; 3, benzyl methacrylate; 4, methyl methacrylate; 5, butyl methacrylate.

Benzoyl peroxide of Eastman Kodak Co. white label grade was used directly.[5]

Results and Discussion

Figure 2 shows a photographic recording of the weight loss (grams) of heat-exchange liquid with polymerization time. This curve was chosen to illustrate the correction by extrapolation for drift. In most experiments such correction is unnecessary. The inflection point (t_i) is indicated. Each segment of the curve is a four-minute interval. The abrupt lengthening of the segments, indicating rapid polymerization, is quite marked. For brevity, we have not included the complete experimental curves but have condensed the final results in Table I.

The values of column 4 of the table show that those methacrylic esters investigated exhibit substantially similar heats of polymerization. This may be expected as the structural variations of the ester groups are well removed from the double bond, therefore they should have little effect on the bond energies involved in polymerization. Nevertheless, cyclohexyl and phenyl esters show definitely lower and remarkably similar values, which may result from greater rigidity of the polymer chains; here, the carbon atom bonded to the carboxyl group is contained in a ring structure. Further data dealing with rigidity effects of substituents are expected to be shown in a subsequent paper of this series.

Sub-column (B) of column 4 ($-\ \Delta H$) were obtained with the older-style plain glass suspension tube. With high catalyst concentrations the values of 13.0 kcal./mole are apparently valid and in agreement with later values of sub-column (A) using the Dewar-type tube. At lower catalyst concentrations the extended reaction periods may have involved heat loss to produce the lower $-\ \Delta H$ values.

Data of column 6 show that the product of the square root of the catalyst concentration and the time of inflection (t_i) on the ΔH *vs.* t curve is, to the first approximation, a constant for each ester studied. If the reciprocal of this product is used as a convenient index for the over-all speed of polymerization, it indicates that those monomers containing rings in the ester group have similar rates and for these esters the rates are appreciably larger than the rates for the alkyl esters. In Figure 3, the fraction of heat evolved $\Delta H/\Delta H_\infty$ is plotted against $t\sqrt{(\text{Cat.})}$, where t is in minutes and the catalyst concentration is in terms of mole per cent. In a previous paper we showed that the rate of polymerization of methyl methacrylate is a function of the square root of the concentration of the catalyst. This method

Table I

Values for Heat and Relative Speed of Polymerization

Substance, methacrylate	Expt.	Cat., mole %	$-\Delta$H, kcal./mole (A)	(B)	Time at inflection, min.	$\frac{100}{t_i\sqrt{\text{Cat.}}}$
Methyl	1a	0.413		13.0[a,b]	41	3.8
	1b	.206		13.0[a,b]	53	4.2
	1c	.082		12.9[a,b]	81	4.3
	1d	.021	13.0	12.4[b]	128	5.4[c]
	1e	.0041	12.9	11.7[b]	262	6.0[c]
			13.0 ± 0.2 av.			
n-Butyl	2a	1.17	13.8		34	2.7
	2b	1.17	13.3			
	2c	0.59	13.2		45	2.9
	2d	.59	13.4			
	2e	.59	13.5			
	2f	.59	13.3			
	2g	.29	13.8		70	2.6
	2h	.29	13.5			
	2i	.29	13.4			
			13.5 ± 0.2 av.			
Cyclohexyl	3a	0.46	12.1			
	3b	.29	12.2		19	9.8
	3c	.21	12.3			
	3d	.104	12.1			
			12.2 ± 0.2 av.			
Benzyl	4a	.334	13.2			
	4b	.27	13.5			
	4c	.153	13.2		32	8.0
	4d	.073	13.6			
	4e	.037	13.4			
			13.4 ± 0.2 av.			
Phenyl	5a	.68	12.4		11	11
	5b	.34	12.2		17	10
			12.3 ± 0.2 av.			

[a] Data from ref. 1. [b] Plain glass tube used instead of Dewar tube to hold heat-exchange liquid. [c] Calculated from new results using Dewar tube.

of expressing the results serves to bring the experiments with the various esters to a common basis for comparison of polymerization rates. Each curve of Fig. 3 represents a single typical run. If we assume the chain mechanism described by Norrish and Smith[6] and applied by them to methyl methacrylate, the similarity of the shapes and position of the curves for phenyl, benzyl, and cyclohexyl methacrylate indicates that all the steps involved in these chain reactions have similar rate constants. Methyl and butyl esters have similar initial slopes, but the curve for the methyl ester has an earlier inflection time. This would indicate either that in the case of methyl compound the chain terminating step is more sensitive to viscosity change or that the viscosity increases more rapidly than in the case of the butyl compound, or possibly both factors are pertinent. It is believed that the present data are insufficient to warrant further speculation concerning the causes of such variations.

Summary

1. The heat of polymerization of several esters of methacrylic acid are compared using an improved isothermal calorimeter.

2. The $-\Delta H$ values obtained as kcal./mole are: methyl, 13.0; *n*-butyl, 13.5; cyclohexyl, 12.2; benzyl, 13.4; phenyl, 12.3. The average deviation was found to be about ±0.2.

3. These esters have generally similar $-\Delta H$ values, though the values for the cyclohexyl and phenyl esters are slightly the lower.

4. The rates of polymerization are similar for the esters having cyclic structures and greater than the rates for the alkyl esters.

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

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Dipole Moments and Structures of Ketene and of Several Polar Molecules Containing Conjugated Systems

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The striking results given by electron diffraction for the structure of ketene[1] made very desirable the measurement of the dipole moment of the molecule in order to obtain evidence of the contributions of the polar structures indicated by electron diffraction. The availability of samples of four aldehydes and nitriles and an ester with conjugated systems in their molecules made possible the extension of earlier work in this laboratory on similar molecules.[2]

Experimental Method

The dielectric constants of the vapors of these substances were measured with the apparatus and technique previously described,[3] and used to calculate the polarizations and dipole moments of the molecules.

Several of the substances showed a tendency to polymerize on the walls of the apparatus. As it was found that this could be largely prevented by warming the glass tubing, the whole vacuum system was wrapped with a coil of nichrome wire and electrically heated. Under these temperature conditions, the Apiezon stopcock grease ordinarily used had to be replaced by a special grease made of mannitol, dextrose and glycerol, which had a relatively high melting point.

Materials

Ketene.—The material was prepared by the pyrolysis of acetone, the vapor passing over the hot filament of the generator. A long reflux water condenser removed most of the acetone vapor, and all products condensing at −80° were collected. The ketene was purified by the method of Rice and his co-workers.[4] With the receiver at −80°, the condensate was warmed rapidly to 50°, a reflux water condenser being used. This was repeated twice with warming to 0° only. The fourth distillation was the same, but only the middle fraction was collected. This procedure, it was believed, would remove the last traces of dissolved ethylene from the ketene. The material was sealed on to the vacuum system of the dielectric cell in a side-arm and was measured by the two-point method, the ketene being maintained throughout the runs at about −50°, which was about 10° below its normal boiling point (−41°). Two samples of ketene were prepared and measured, the reproducibility of the moment obtained being taken as evidence of the purity of the substances used.

Acrolein, Methacrolein.—Pure samples given us by the Shell Development Company through the kindness of Dr. Otto Beeck were subjected only to the double distillation required to introduce the sample of vapor into the dielectric cell.

Ethyl Sorbate.—Material kindly furnished by the Carbide and Carbon Chemicals Corporation, containing possibly 0.2% sorbic acid, was subjected only to the double distillation required to introduce it into the cell.

Methacrylonitrile.—Material kindly furnished by the United States Rubber Company General Laboratories was believed to be quite pure but was fractionated to remove the hydroquinone inhibitor and any possible traces of polymer, the fraction boiling in the range 88.9–89.4° being used.

4-Cyanobutadiene-1,3.—A sample kindly given us by the du Pont Company contained 0.1% catechol as a stabilizer, which was removed in the usual double distillation carried out in the vacuum system.

Experimental Results

The results of individual runs at each absolute temperature, *T*, are given in Table I for the molar

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[1] Beach and Stevenson, *J. Chem. Phys.*, **6**, 75 (1938).

[2] Hurdis and Smyth, THIS JOURNAL, **65**, 89 (1943).

[3] McAlpine and Smyth, *ibid.*, **55**, 453 (1933); deBruyne and Smyth, *ibid.*, **57**, 1203 (1935); Wiswall and Smyth, *J. Chem. Phys.*, **9**, 352 (1941); Hurdis and Smyth, THIS JOURNAL, **64**, 2829 (1943).

[4] Rice, Greenberg, Waters and Vollrath, *ibid.*, **56**, 1760 (1934).