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### Title

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Arthur Fry and Melvin Calvin  
November 26, 1951

Berkeley, California

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by

Arthur Fry<sup>3</sup> and Melvin Calvin

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ABSTRACT

A kinetic product study of the carbonate cleavage of malonic ester has been made, and it is shown that the formation of carbonate from malonic ester in alkaline solution involves the direct fission of the half acid ester.

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- (1) The work described in this paper was sponsored by the U.S. Atomic Energy Commission.
  - (2) This paper was abstracted from the thesis submitted by Arthur Fry to the Graduate Division of the University of California in partial fulfillment of the requirements for the Ph.D. degree, June, 1951.
  - (3) Present address: Department of Chemistry, University of Arkansas, Fayetteville, Arkansas.
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CARBONATE CLEAVAGE IN THE HYDROLYSIS OF DIETHYL  $\alpha$ -NAPHTHYLMALONATE<sup>1,2</sup>

by

Arthur Fry<sup>3</sup> and Melvin Calvin

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In conjunction with a study of the isotope effect in the decarboxylation of  $\alpha$ -naphthylmalonic acid<sup>4</sup>, a carbonate cleavage reaction was observed in the basic hydrolysis of the substituted malonic ester.

Such basic carbonate cleavage reactions of substituted malonic esters have been observed by a number of workers<sup>5</sup>, but no critical work has been done on the actual point during the hydrolysis at which this cleavage occurs. Wallingford, Homeyer and Jones<sup>6</sup> were able to prepare substituted malonic esters by an alkoxide catalyzed Claisen

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- (3) Present address: Department of Chemistry, University of Arkansas, Fayetteville, Arkansas.
- (4) A. Fry and M. Calvin, to be published.
- (5) H. Bickel, Ber., 22, 1537 (1889); M. Guyot and M. Esteva, Bull. soc. chim., [4] 3, 803 (1908); A.W. Dox and A. Thomas, J. Am. Chem. Soc., 45, 1811 (1923); E. Tassilly, A. Belot and M. Descombes, Compt. rend., 186, 149 (1928); A.C. Cope and S.M. McElvain, J. Am. Chem. Soc., 54, 4311, 4319 (1932); R. Conner, J. Am. Chem. Soc., 59, 132 (1937); F. Krollpfeiffer and A. Rosenberg, Ber., 69B, 465 (1936); T. Ando, J. Chem. Soc. Japan, 57, 1351 (1936).
- (6) V.H. Wallingford, Q.H. Homeyer and D.M. Jones, J. Am. Chem. Soc., 63, 2056 (1941).
-

type condensation between diethyl carbonate and the ester of the substituted acetic acid. They showed that the reaction was reversible in many cases and that good yields of the malonic esters could be obtained by using excess diethyl carbonate.

In the present work kinetic studies have been carried out in aqueous alcohol on the hydrolysis of diethyl  $\alpha$ -naphthylmalonate by sodium hydroxide. An individual sample was prepared for each point since the formation of a precipitate of sodium salts precluded representative sampling during the later stages of the hydrolysis. The experiments were carried out in a constant temperature bath maintained at  $25.00 \pm 0.05$  or  $36.95 \pm 0.05^\circ\text{C}$ . Weighed samples of the ester were dissolved in 95% alcohol, and a known excess of sodium hydroxide was added. The alcohol and base solutions were preheated to bath temperature before mixing. After standing for appropriate lengths of time in the constant temperature bath, the samples were washed into excess water, and the excess base immediately titrated with standard acid using a pH meter to determine the end point. When the samples were poured into the water, the hydrolysis of the diester was stopped for all practical purposes by its precipitation. The time required for titration was short compared to the rate of hydrolysis of the half acid ester. The shape of the titration curves varied considerably as the hydrolysis progressed, due to the changing buffer system, but the end point was always taken at the midpoint of the first break of the titration curve as shown in Figure 1. At this point the excess hydroxide ion is neutralized, and any carbonate present is in the form of bicarbonate. The kinetic data obtained are presented in Table I.

The hydrolysis of the ester might be represented by the following equations:

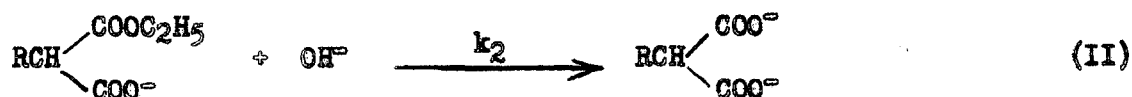
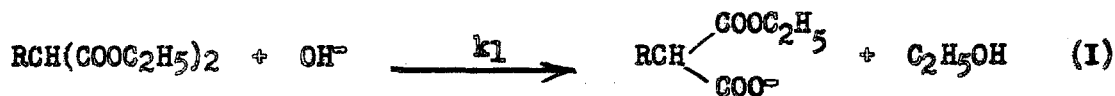


TABLE I

Kinetic Data on the Hydrolysis of Diethyl  $\alpha$ -Naphthylmalonate

Temp. 25.00°C			Temp. 36.95°C		
Time hr.	mmoles excess base	% of ester hydrolyzed*	Time hr.	mmoles excess base	% of ester hydrolyzed*
0	1.500	0	0	2.981	0
0.12	1.308	19.1	0.27	1.976	50.1
0.27	1.187	31.2	0.32	1.954	51.2
0.52	1.060	43.8	0.48	1.766	60.6
1.02	0.949	54.9	0.70	1.634	67.2
2.00	0.834	66.3	1.00	1.474	75.2
3.50	0.740	75.7	1.90	1.262	85.7
5.38	0.662	83.5	3.03	1.126	92.6
7.67	0.613	88.3	4.42	1.049	96.4
24.40	0.524	97.2	(∞)	(0.977)	(100.0)
(∞)	(0.496)	(100.0)			

\*This column is determined by the ratio of the equivalents of base used up to the equivalents of ester initially present.

If these reactions follow the usual second order ester hydrolysis kinetics, the values of the specific rate constants,  $k_1$  and  $k_2$ , calculated from the integrated rate law remain constant. By inspection of the data in Table I and Figure 2, it can be seen that  $k_1 \gg k_2$ , so at short times equation (II) will not enter into the calculations as a first approximation, and at long times reaction (I) will have gone to completion. In making the calculations for  $k_2$  by this method, a zero time value must

be assumed for reaction (II), at which time reaction (I) is assumed to be complete. These values have been chosen somewhat arbitrarily as 0.5 hr. and 0.25 hr. after mixing at 25.00°C and 36.95°C, respectively. The actual value is of small consequence for most of the points, since it is small compared to the total time. The values of  $k_1$  and  $k_2$  calculated in this manner are given in Table II.

TABLE II

Second Order Rate Constants Calculated from the Integrated Rate Equation  
at Various Points

$k_1, 25.00^\circ\text{C}$		$k_2, 25.00^\circ\text{C}$		$k_2, 36.95^\circ\text{C}$	
t	$k_1 \frac{1}{\text{mole hr.}}$	t	$k_2 \frac{1}{\text{mole hr.}}$	t	$k_2 \frac{1}{\text{mole hr.}}$
0.12	33.2	1.02	2.23	0.48	12.1
0.27	31.7	2.00	3.27	0.70	11.7
0.52	38.3	3.50	3.21	1.00	12.5
		5.38	3.28	1.90	11.3
		7.67	3.10	3.03	11.2
		15.75	2.40	4.42	11.2
		24.20	2.14	8.50	10.3

The values of  $k_1$  and  $k_2$  at both temperatures remain quite constant, thus confirming our assumption of second order kinetics. The values of  $k_1$  at the longer times and  $k_2$  at shorter times are probably somewhat inaccurate due to neglecting equations (II) and (I) respectively. The values of  $k_2$  at longer times are probably somewhat inaccurate since the reaction is very near completion and we are dealing with small differences between large numbers. This method of obtaining data was not deemed sufficiently sensitive to calculate  $k_1$  at the higher temperature.



When the completely hydrolyzed samples were made strongly acid, carbon dioxide was rapidly evolved. This carbon dioxide did not come from the decarboxylation of the malonic acid as is shown by the data in Table III. A sample which had been completely hydrolyzed was acidified and the carbon dioxide evolved was collected as a function of time. After carbon dioxide evolution was complete at one temperature, the temperature was increased and the experiment continued.

TABLE III

Carbon Dioxide Evolution from the Hydrolysis Product of Diethyl  $\alpha$ -Naphthylmalonate

Time hr.	Temp. °C	BaCO <sub>3</sub> obtained mg.	Accumulated yield, %	Time hr.	Temp. °C	BaCO <sub>3</sub> obtained mg.	Accumulated yield, %
0.5	22±2	81.1	41.1	4.5	23±2	0.6	56.9
1.0		17.1	49.8	5.0	75±2	18.4	66.2
1.5		7.2	53.4	5.5		12.4	72.5
2.0		0.0	53.4	6.0		20.7	83.0
2.5		0.5	53.7	6.5		14.3	90.2
3.0	53±2	1.5	54.5	7.0		12.6	96.6
3.5		2.9	56.0	7.5		1.0	97.1
4.0		1.2	56.6	8.0		2.3	98.3

From these data it is obvious that the initial carbon dioxide evolution has a different source from that evolved after heating the solution. The final carbon dioxide evolution is undoubtedly from the decarboxylation of the malonic acid, while the initial rapid carbon dioxide evolution arises from carbonate as such.

In order to determine the amount of carbonate obtained as a function of the amount of hydrolysis, the samples in the above 36.95°C kinetic run and in an earlier kinetic

run at room temperature were acidified in a sweep system and the carbon dioxide evolved in two and one-half hours at room temperature was collected. This was sufficient time to insure complete collection of the carbon dioxide, as shown by the data in Table III. The results of these measurements are shown in Table IV. The percentages are calculated on the basis of the hydrolysis of the diester to the diacid, and the decarboxylation of the diacid to the mono-acid and carbon dioxide.

TABLE IV

Amount of Carbonate Cleavage as a Function of the Amount of Hydrolysis of  
Diethyl  $\alpha$ -Naphthylmalonate

Room Temperature, 25°C				36.95°C			
Time hr.	% Hyd.	% CO <sub>3</sub> <sup>=</sup> cleavage <sup>1</sup>	$\frac{\% \text{CO}_3^=}{\% \text{Hyd.} = 50}$	Time hr.	% Hyd.	% CO <sub>3</sub> <sup>=</sup> cleavage <sup>1</sup>	$\frac{\% \text{CO}_3^=}{\% \text{Hyd.} = 50}$
0*	0	0	--	0*	0	0	--
0.5	29.0	0.0	--	0.27	50.1	0.0	--
1.0	50.0	0.0	--	0.32	51.2	0.0	--
2.0	60.6	7.8	0.74	0.48	60.6	11.3	1.07
17.0	88.0	33.9	1.03	0.70	67.2	11.6	0.67
45.0	102.4	54.4	1.04	1.00	75.2	30.2	1.20
88.5	108.3**	52.1	0.90	1.90	85.7	48.1	1.35
				3.03	92.6	55.8	1.31
				4.42	96.4	58.2	1.25
				8.50	99.5	65.1	1.32
				22.67	99.9	61.8	1.24

\* Blank run

\*\* This high value may be due to an error in titration.

<sup>1</sup> This column is the ratio of CO<sub>3</sub><sup>=</sup> formed to moles of ester initially present.

From the data presented in Table IV, three definite conclusions can be drawn. First, the carbonate is not coming from the decarboxylation of the di-ion of the acid, since at both temperatures the amount of carbonate does not increase upon long standing in base after the hydrolysis is complete, even though in each case 40-50% of the original ester is present as the di-ion of the malonic acid. Second, the carbonate is not being formed during the hydrolysis of the diester to the ion of the half-ester acid. At 50% hydrolysis at the end of one hour at room temperature (corresponding approximately to complete hydrolysis to the ion of the half-ester acid) no carbonate has been formed, while at the end of the second hour 7.8% of the carbonate cleavage has occurred while an additional 10.6% hydrolysis has occurred. The higher temperature case is equally clear cut. Third, the rate of production of carbonate is roughly proportional to the rate of hydrolysis of the ion of the half-ester acid to the di-ion of the diacid, as is shown by the constancy of the ratio in the final columns at the two temperatures in Table IV. These three observations lead to the conclusion that the carbonate is being produced from the ion of the half-ester acid, either during the hydrolysis or by a path parallel with the hydrolysis with a nearly equal activation energy.

Although the above data on the carbonate cleavage are not very quantitative, we may choose reasonable average values for the ratios of carbonate cleavage to hydrolysis of the ion of the half-ester acid, and by combining these values with the values of  $k_2$  from Table III, we can calculate the energy and entropy of activation for each reaction from the theory of absolute rates<sup>7</sup>.

The values of  $k_2$  given in Table II are actually the sums of the second order rate constants for the hydrolysis reaction ( $k_h$ ) and the carbonate cleavage reaction ( $k_c$ ). The values given in the fourth column of Table IV at each temperature are the ratios of  $k_c$  to  $k_h$ .

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(7) S. Glasstone, K.J. Laidler and H. Eyring, "The Theory of Rate Processes," 1st. Ed., McGraw-Hill Book Company, Inc., New York, New York (1941).

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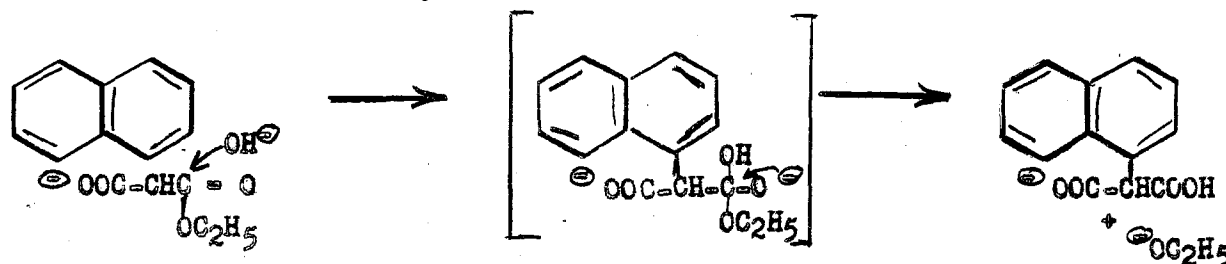
1.0 and 1.25 were chosen as the best values for this ratio at 25.00°C and 36.95°C, respectively, while 3.2 and 11.5 were chosen as the best values of  $k_2$  at these temperatures.

Using these values for  $k_2$  and for the ratio of  $k_c$  to  $k_h$ , the values for the entropy and energy of activation for the two reactions were calculated. The results are shown in Table V. The values are probably not too accurate since the original data scattered somewhat, but they are certainly of the correct order of magnitude.

TABLE V  
Energy and Entropy of Activation for the Hydrolysis and Basic Carbonate Cleavage of Monoethyl  $\alpha$ -Naphthylmalonate

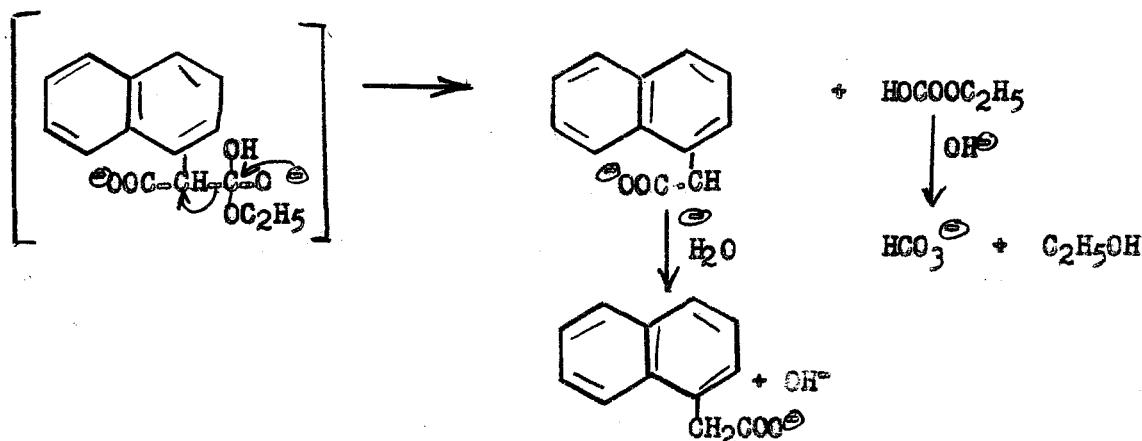
$T, ^\circ\text{C}$	$k_2$	$k_c$	$k_h$	$\Delta H_c^\ddagger$	$\Delta S_c^\ddagger$	$\Delta H_h^\ddagger$	$\Delta S_h^\ddagger$
	$\frac{1}{\text{mole hr.}}$	$\frac{1}{\text{mole hr.}}$	$\frac{1}{\text{mole hr.}}$	kcal/mole	e.u.	kcal/mole	e.u.
25.00	3.2	1.6	1.6	21	-3.4	18	-13.6
36.95	11.5	6.4	5.1				

It is interesting to speculate on the mechanism of the reaction of the ion half of the half-ester acid with base. The hydrolysis may be represented by the commonly accepted mechanism<sup>8</sup> of the attack of the hydroxide ion on the carbonyl carbon of the ester, followed by elimination of the ethoxide ion.



(8) L.P. Hammett, "Physical Organic Chemistry", McGraw-Hill Book Company, Inc., New York, New York (1940), p. 355.

This same intermediate complex may also decompose by the rupture of the carbon-carbon bond instead of the carbon-oxygen bond, giving the half-ester of carbonic acid and a di-ion of  $\alpha$ -naphthylacetic acid.



The carbon-carbon bond in the above complex is undoubtedly weakened by the repulsion between the two negatively charged ends of the molecule, thus facilitating the carbonate cleavage. This weakening effect is not present in the hydrolysis of the diester, and is perhaps the reason why we do not get this cleavage during this first hydrolysis step.

Examination of the above mechanism reveals that it is simply a Claisen ester condensation in reverse, where hydroxyl ion is the base. This type of condensation is known to be reversible<sup>9,10</sup>, and, as mentioned above, Wallingford, Homeyer and Jones<sup>6</sup> have demonstrated the specific reversibility using diethyl carbonate as one of the esters. Undoubtedly this reverse Claisen condensation takes place in the hydrolysis of all malonic esters, but with most, it is so much slower than the normal hydrolysis that it is never observed.

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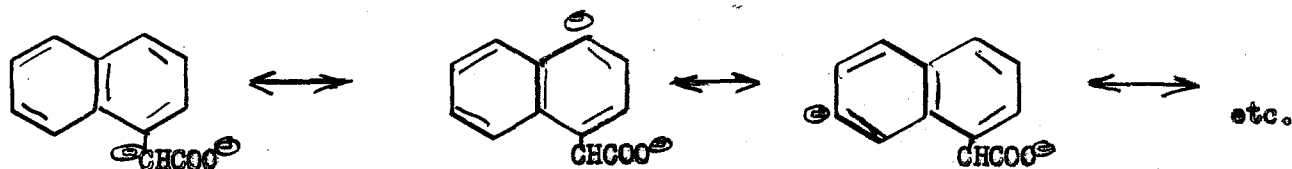
(9) E.R. Alexander, "Principles of Ionic Organic Reactions", John Wiley and Sons, Inc., New York, New York (1950), p. 185.

(10) C.R. Hauser and B.E. Hudson, Jr., in R. Adams, "Organic Reactions", Vol. I, John Wiley and Sons, Inc., New York, New York (1943), p. 267.

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It is well known<sup>9,10</sup> that esters with only one alpha hydrogen give very poor results in the normal Claisen condensation unless a base stronger than ethoxide, such as sodium triphenylmethyl, is used. Since this is the case, we would expect a dialkyl acetic ester and ethyl carbonate to give a poor forward Claisen condensation, and correspondingly, the product, a dialkyl malonic ester, should give an improved reverse reaction, or carbonate cleavage. In view of this, we would expect  $\alpha$ -naphthylalkylmalonic esters to undergo this reverse Claisen condensation especially readily, and it may be that "hydrolysis" of these esters goes almost exclusively by the carbonate cleavage path. Blicke and Feldkamp<sup>11</sup> prepared a series of  $\alpha$ -naphthylalkylacetic acids by hydrolysis of the corresponding malonic esters and acidification of the resulting salts. They reported that the "malonic acids" so obtained spontaneously decarboxylated at room temperature. It seems very probable that the source of the carbon dioxide evolved in this case was not the decarboxylation of the malonic acid, but rather the reverse condensation in basic solution.

The question of why  $\alpha$ -naphthylmalonic ester (and other aryl malonic esters) undergoes this carbonate cleavage more readily than aliphatic malonic esters, is undoubtedly connected with the steric effect of the large bulky aryl groups as well as with the resonance stabilization of the intermediate ion.




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(11) F.F. Blicke and R.F. Feldkamp, J. Am. Chem. Soc., 66, 1087 (1944).

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In order to get kinetic data on the hydrolysis of the monoethyl  $\alpha$ -naphthylmalonate which would not be complicated by the hydrolysis of the diester, the preparation of the monoester was undertaken. A sample of the diester was hydrolyzed under the conditions shown in Table I to ~40% hydrolysis. The unreacted ester was extracted into ether, and after acidification of the aqueous phase, the monoester and any diacid were extracted into ether. Evaporation of the ether left an oil which has not yet been obtained in crystalline form. The oil gave very nearly the theoretical value for the equivalent weight of the monoester. Further work is in progress on this preparation, and on the reverse Claisen condensation of  $\alpha$ -naphthylalkylmalonic esters.

#### Experimental

Preparation of diethyl  $\alpha$ -naphthylmalonate. Diethyl  $\alpha$ -naphthylmalonate was prepared according to the procedure of Blicke and Feldkamp<sup>11</sup>. Ethyl  $\alpha$ -naphthylacetate was prepared by treating 41.03 g. of  $\alpha$ -naphthylacetic acid with 100 cc. of absolute alcohol and 5 cc. of concentrated sulfuric acid for 16 hours. The solution was poured onto ice, extracted into ether, washed with sodium carbonate solution, washed with water and dried. The ether was evaporated and the residue heated in vacuo to remove any traces of water. From the sodium carbonate solution 2.03 g. of  $\alpha$ -naphthaleneacetic acid was recovered. A solution of sodium ethoxide was prepared by dissolving 4.82 g. of freshly cut sodium in 100 cc. of magnesium dried absolute alcohol, and to this was added 30.60 g. of freshly distilled diethyl oxalate, followed by the ethyl  $\alpha$ -naphthylacetate prepared above. The solution was heated to reflux for a few minutes with stirring, and upon cooling the entire contents of the flask solidified. The mixture was filtered with the aid of ether and the precipitate suspended in water. The suspension was acidified and ether extracted. The ether solution was dried, the ether evaporated and the glyoxalate heated at 175-185°C at 15 mm. for one hour in the presence of 20 g. of ground glass. Most of the carbon monoxide came off in the first few minutes. The residual oil was dissolved in alcohol, filtered and allowed to

cool in the refrigerator overnight. The diethyl  $\alpha$ -naphthylmalonate weighed 39.49 g., 67.4% yield, m.p. 59-59.15°C. Recrystallization from alcohol gave material melting at 62-62.5°C, reported m.p. 62°C<sup>11</sup>. Alcohol is a much more satisfactory solvent for recrystallization than the petroleum ether used by Blicke and Feldkamp.

Attempted preparation of monoethyl  $\alpha$ -naphthylmalonate. From the kinetic data on the basic hydrolysis of  $\alpha$ -naphthylmalonic ester, conditions were chosen so that the ion of the half ester acid should be the major species in solution, and 2.87 g. of  $\alpha$ -naphthylmalonic ester dissolved in 200 cc. of alcohol was treated in this manner. At the end of the appropriate time, 300 cc. of water was added and the solution extracted with ether to remove any diester. The solution was made acid and extracted with ether. The ether solution was dried and the ether removed in vacuo at room temperature, leaving 2.16 g. of a very thick light yellow oil. All attempts to crystallize this oil have so far failed. After thorough drying in vacuo 0.0910 g. of the oil required 3.39 cc. of 0.100 N sodium hydroxide for neutralization, giving an equivalent weight of 268. Theoretical equivalent weight = 258.

Hydrolysis of diethyl  $\alpha$ -naphthylmalonate. The kinetic runs on the hydrolysis of diethyl  $\alpha$ -naphthylmalonate were carried out by dissolving weighed samples of 0.502 mmoles of the ester in 10 cc. of 95% ethanol and adding 1.5 cc. of 1.000 N carbonate-free sodium hydroxide. The alcohol and base solutions were preheated to the bath temperature before being used. After standing for appropriate lengths of time in the constant temperature bath the solutions were washed into excess water and immediately titrated with standard acid using a pH meter to determine the end point. After titration to pH = 7.5, the solutions were transferred to a sweep system, 10 cc. of 1 N hydrochloric acid was added, and the solution was swept for 2-1/2 hours with a stream of carbon dioxide-free air. The carbon dioxide was absorbed from the air stream in a spiral bubbler and precipitated and weighed as barium carbonate.



Preparation of  $\alpha$ -naphthylmalonic acid. The solutions remaining from the above kinetic runs were combined, made alkaline and ether extracted to remove any unreacted ester. The basic solution was then acidified and ether extracted again. Most of the ether was removed at room temperature to avoid decarboxylation of the free malonic acid, the solution was filtered, and a large excess of benzene was added. Upon standing, the  $\alpha$ -naphthylmalonic acid crystallized as fine white prisms, leaving any half-ester acid and the  $\alpha$ -naphthylacetic acid in solution. After purification by repeated solution in ether and precipitation by benzene,  $\alpha$ -naphthylmalonic acid m.p.  $162-5^{\circ}\text{d.}$ , equivalent weight  $\alpha$  115.5, calculated 115.1, was obtained. Ivanov and Pshenichnii<sup>12</sup> reported the melting point as "toward  $151^{\circ}\text{d.}$ "

#### Summary

A kinetic product study of the carbonate cleavage of malonic ester has been made, and it is shown that the formation of carbonate from malonic ester in alkaline solution involves the direct fission of the half acid ester.

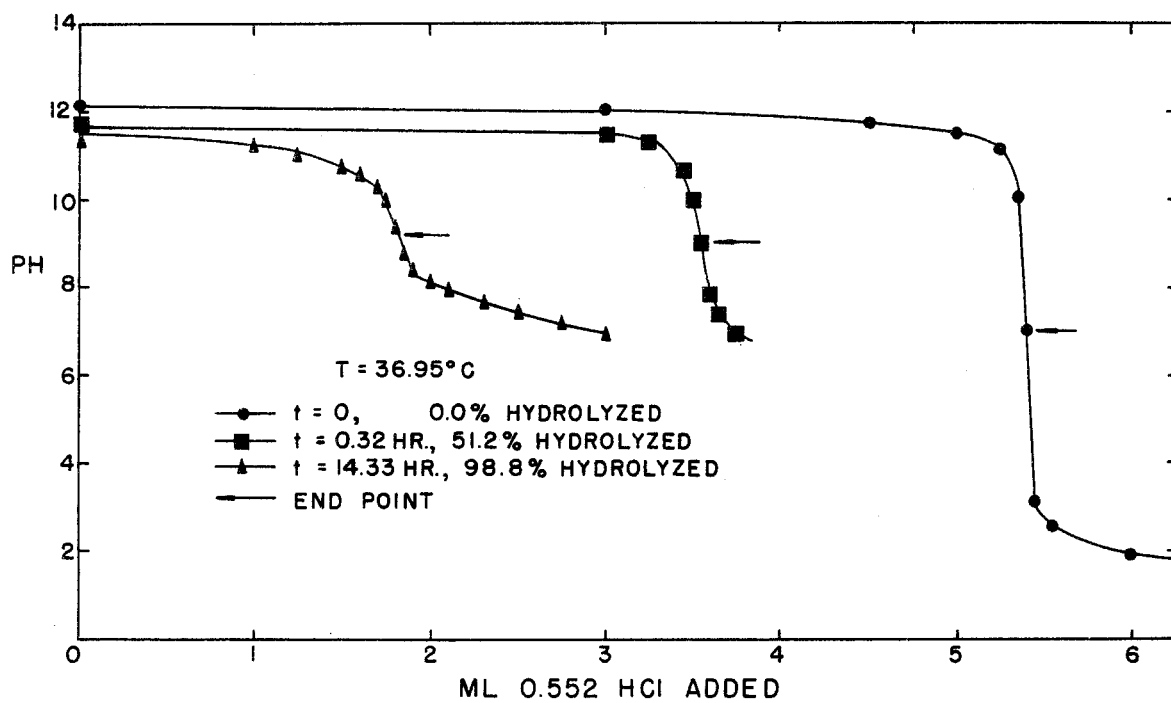
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(12) D. Ivanov and G. Pshenichnii, Ann. Univ. Sofia, II, Faculte phys-math., Livre 2, 33, 177-202 (in French 203-11) (1937); C.A. 32:33569.

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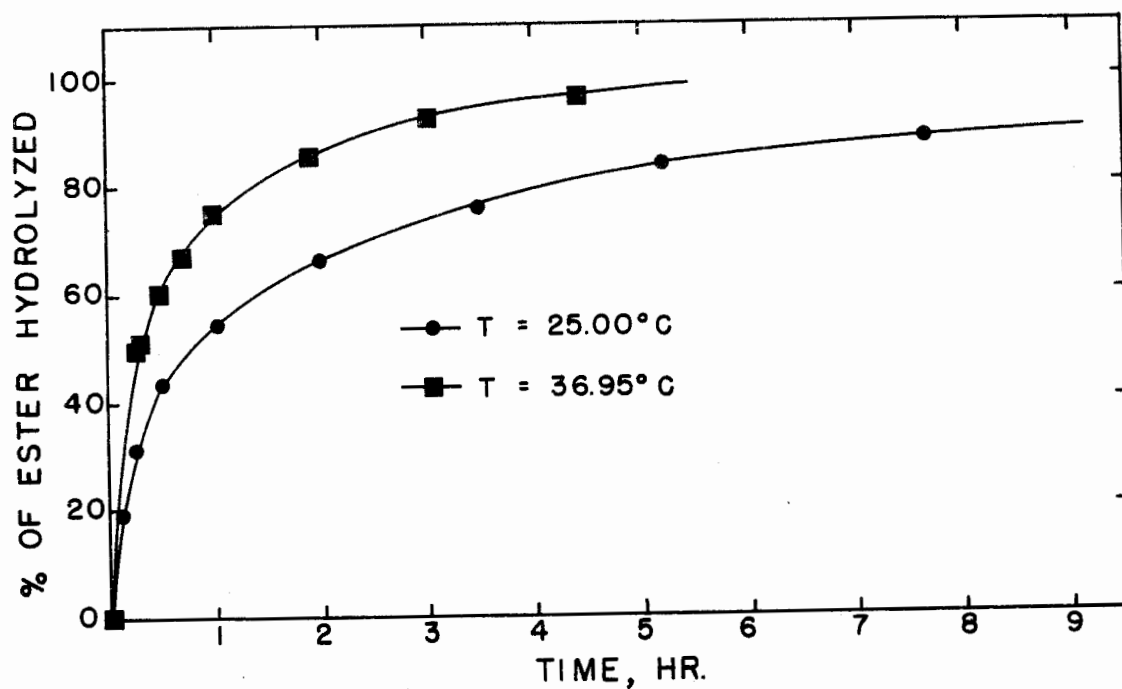
Figure 1 - Variation in Titration Curves with Amount of Hydrolysis of Diethyl  $\alpha$ -Naphthylmalonate.

Figure 2 - Hydrolysis of Diethyl  $\alpha$ -Naphthylmalonate as a Function of Time.



MU2813

Figure 1



MU 2814

Figure 2