[CONTRIBUTION FROM THE SCHOOL OF MINES AND METALLURGY, UNIVERSITY OF MISSOURI]

THE CATALYTIC ACTION OF NEUTRAL SALTS. THE EFFECT OF NORMAL ALKALI SULFATES ON ALKALI ACID SULFATES IN THE KETONIC SPLITTING OF ETHYL ACETOACETATE

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RECEIVED FEBRUARY 2, 1928 PUBLISHED JULY 6, 1928

In this work the action of normal potassium and sodium sulfates has been investigated with two concentrations of their corresponding acid salts. The compound used for studying this effect is ethyl acetoacetate, which gives carbon dioxide upon its ketonic splitting in an acid solution, thus serving as a means for carefully following the course of the reaction. Also, this reaction is irreversible, as one of the products of the reaction is removed as a gas.

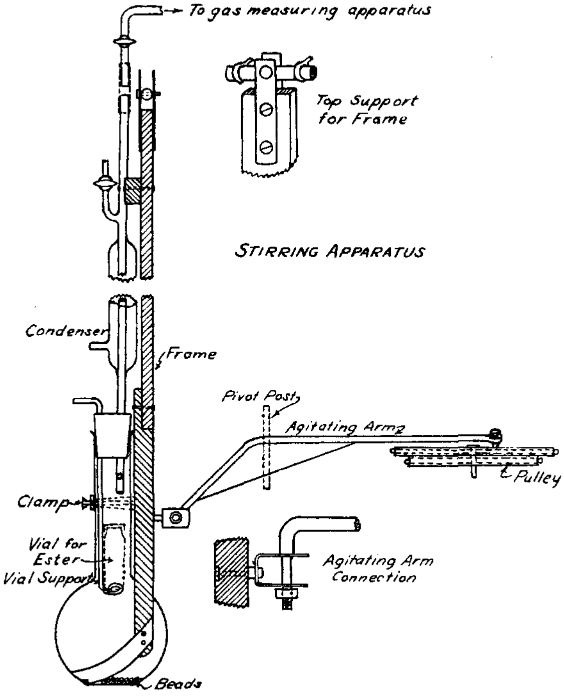

Fig. 1.

Bürki[1] used ethyl acetoacetate in his study of the hydrolysis reactions with sulfuric, hydrochloric and nitric acids and found that this ester was completely decomposed above 40°. The advantage in using this ester

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[1] Bürki, *Helv. Chim. Acta*, **1**, 231 (1918).

is that the carbon dioxide evolved can be easily measured to follow the course of the reaction over a long period of time. The classical method[2] of halting the reaction, if this is possible, and determining by titration the amount of ester hydrolyzed at intervals, is subject to considerable error.

Experimental Part

Materials.—The best grade of ethyl acetoacetate was redistilled under reduced pressure and the middle half of the distillate used. This was stored in amber colored bottles, each containing enough for a few determinations, in order not to expose the ester to air over too long a period. The ethyl alcohol was dehydrated over lime and anhydrous copper sulfate in the usual manner.

The best grades of sodium and potassium sulfates and acid sulfates were each recrystallized from water several times, dried to constant weight and analyzed for their sulfate content. The various stock solutions of these salts were analyzed for their sulfate content to make sure that all solutions were of known concentrations. Aliquot parts of these stock solutions were taken for dilution to their required normalities.

Apparatus.—The apparatus used in the work was developed by Dr. C. E. Boord and H. L. Dunlap in an unpublished work on the study of alkali and alkaline earth chlorides with hydrochloric acid on the hydrolysis of this same ester. The thermostat was electrically heated and the temperature controlled to a tenth of a degree. The flasks were made specially for this work, having a capacity of two hundred cc. and with necks five inches in length. These were connected to a condenser (Fig. 1) by means of a two-holed rubber stopper, one for the condenser and the other for the stiff platinum wire which held the vial containing the ester. The flask and condenser were firmly fastened to a frame which was suspended at the top, the lower part being connected to a pivoted arm from a pulley. In operation, this gave the flask a circular motion in the bath and thus agitated its contents. The neck of the flask extended three inches above the thermostat liquid and thus permitted the watching of the

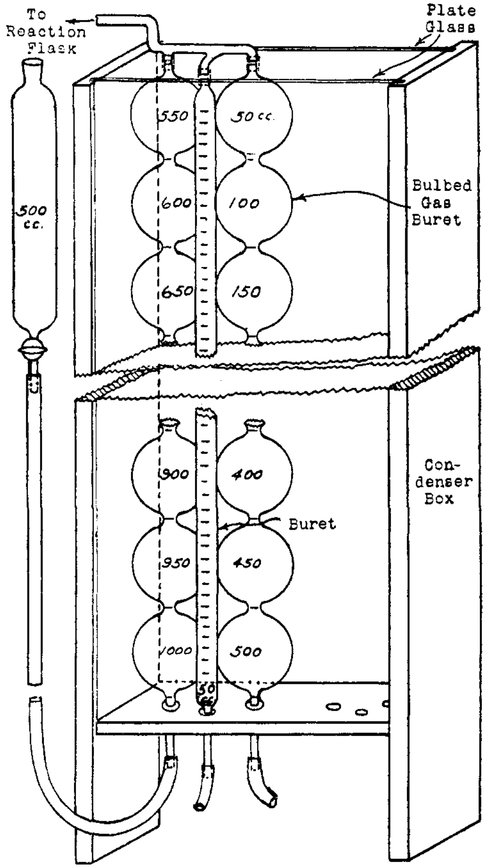

Fig. 2.—Gas measuring apparatus.

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[2] Ostwald, *J. prakt. Chem.*, **28**, 449 (1883).

vial before its release. The side arm at the top of the condenser permitted the adjusting of the pressure within the apparatus before tripping the ester into the solution for starting the reaction.

The gas measuring apparatus (Fig. 2) is a modified Blier-White chain of bulbs type. A three-way manifold connects all compartments of the condenser and leveling bulbs. These gas measuring compartments were all carefully calibrated and the volume of gas at any time could be read to one-tenth of a cc. The whole gas train was immersed in a water-filled box which had two opposite sides of glass. The temperature of the surrounding water was recorded with each reading for correcting the volume of the gas to standard conditions. Two sets of flasks were used in the thermostat, thus permitting of two determinations at the same time. Readings were taken at five-minute intervals.

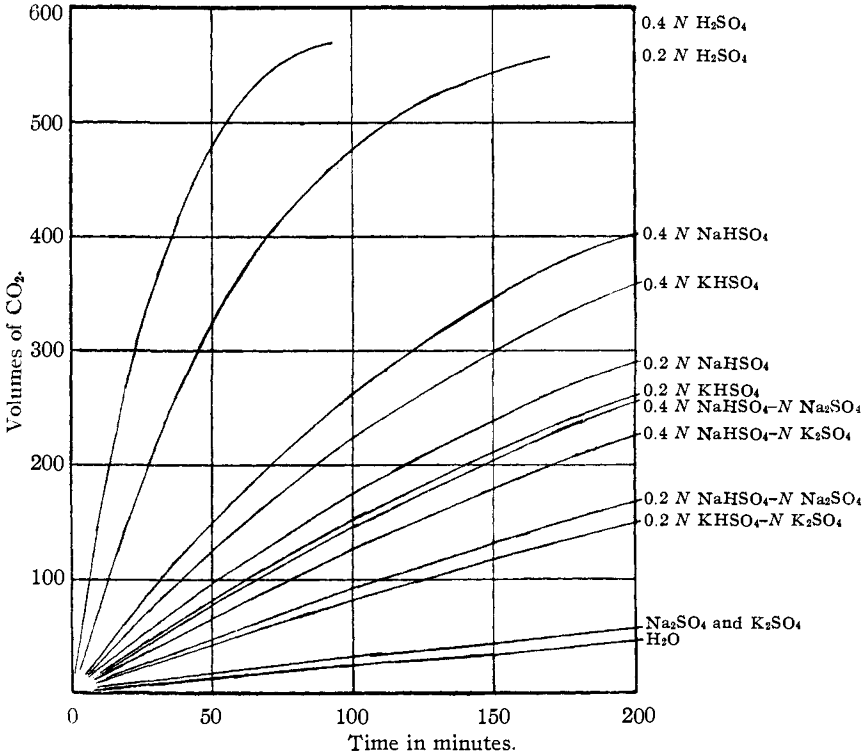

Fig. 3.—Hydrolysis of $N/2$ ester at 90°.

Experimental Procedure.—The desired concentration of salts was placed in the flasks along with one cc. of alcohol and water to make 46.8 cc. and when the ester (3.2527 g.) was introduced, this made 50 cc. of a half molar solution of ester. The capped vials containing the ester were held in place until the temperature of the flask and contents became that of the bath. After adjusting the measuring bulbs and starting agitation, the outside connection was closed, the vial dropped and the zero reading taken. As soon as 50 cc. of gas is collected in the burets, this is simply transferred to one of the 50-cc. bulbs. Checks were run in all cases with an allowable variation of three-fourths of one per cent. Vapor pressure corrections were made in all cases as that of pure water, which is in slight error but it is the same for all determinations.

The volume of carbon dioxide was reduced to standard conditions and graphs were plotted for the five minute intervals. The data are condensed in Tables I to VII. The reaction constant is calculated according to the formula

$$K = \frac{1}{t}\log_{10}\frac{560.3}{560.3 - V_t}$$

where V_t represents the corrected volume of carbon dioxide collected in time "t" and 560.3 is the volume of the gas which could be obtained by complete decomposition of the ester. The third column gives the various values for "k," the constant for a first order reaction.

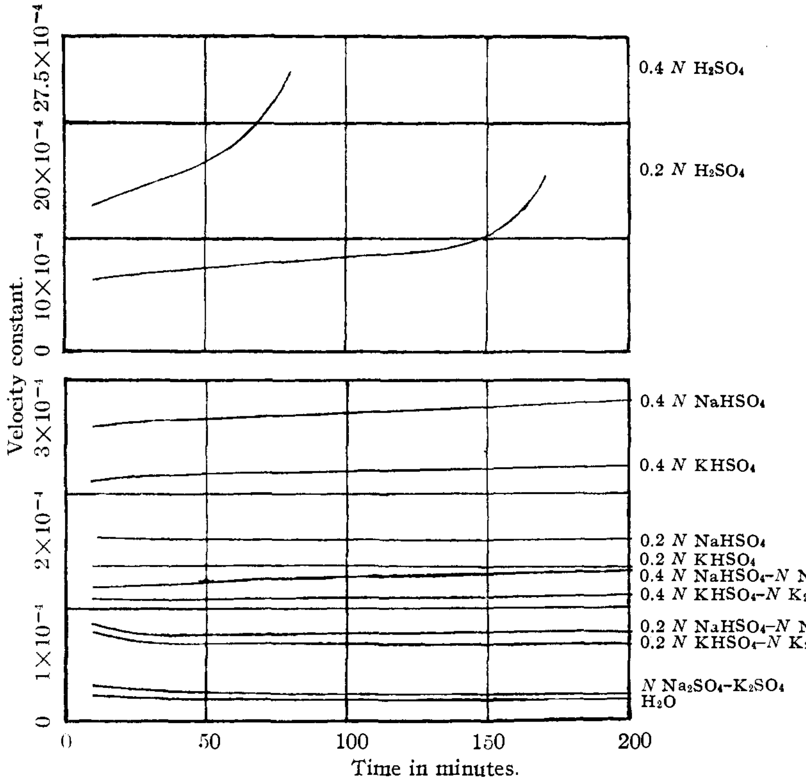

Fig. 4.—Reaction constants for hydrolysis of esters at 90°.

Data obtained with hydrolysis of the ester at 90° are shown graphically in Fig. 3 and the variation of the velocity constants with time is shown in Fig. 4. Similar curves are obtainable at other temperatures.

Discussion of Data.—It might be expected in the hydrolysis of the ester with pure acid that the reaction constant would increase with time as the more active hydrogen would be affected by the increasing concentration of the alcohol and acetone from the decomposition of the ester.

TABLE I

HYDROLYSIS OF $N/2$ ETHYL ACETOACETATE

Time, min.	At 80° with				Time, min.	At 90° with			
	0.2 N H_2SO_4		0.4 N H_2SO_4			0.2 N H_2SO_4		0.4 N H_2SO_4	
	CO_2	$k \times 10^3$	CO_2	$k \times 10^3$		CO_2	$k \times 10^3$	CO_2	$k \times 10^3$
25	94.0	31.90	173.6	64.42	10	75.7	6.304	142.1	12.70
50	179.1	33.45	309.0	69.65	30	213.2	6.932	358.1	14.75
100	311.0	35.17	466.7	77.71	50	316.6	7.231	478.8	16.74
150	401.9	36.56	530.8	85.24	70	395.9	7.607	540.3	20.68
200	461.0	37.57	561.0	...	90	454.7	8.053	...	...

Time, min.	At 95° with				Time, min.	At 95° with			
	0.2 N H_2SO_4		0.4 N H_2SO_4			Water alone		N Na_2SO_4	
	CO_2	$k \times 10^3$	CO_2	$k \times 10^3$		CO_2	$k \times 10^3$	CO_2	$k \times 10^3$
20	191.3	9.069	310.1	17.51	50	20.9	0.333	24.4	0.387
40	318.4	9.119	455.7	18.22	100	39.2	.315	46.9	.380
60	404.5	9.264	522.5	19.52	200	72.2	.300	85.0	.357
80	460.6	9.371	555.8	26.19	300	100.6	.287	114.2	.330
100	496.2	9.417	...	...	400	125.9	.276	139.9	.314

TABLE II

NEUTRAL SALT EFFECT ON ACID SULFATE IN HYDROLYSIS OF $N/2$ ETHYL ACETOACETATE

Time, min.	At 80° with							
	0.2 N $KHSO_4$		0.2 N $KHSO_4$ N K_2SO_4		0.2 N $NaHSO_4$		0.2 N $NaHSO_4$ N Na_2SO_4	
	CO_2	$k \times 10^3$	CO_2	$k \times 10^3$	CO_2	$k \times 10^3$	CO_2	$k \times 10^3$
25	24.1	0.764	11.8	0.370	27.3	0.868	12.5	0.395
50	48.1	.780	23.0	.364	54.6	.890	25.4	.403
100	93.6	.794	44.3	.358	105.2	.903	51.0	.410
150	133.6	.796	66.3	.364	150.5	.906	75.6	.420
200	172.5	.798	86.5	.365	191.7	.909	98.9	.421

TABLE III

Time, min.	At 80° with							
	0.4 N $KHSO_4$		0.4 N $KHSO_4$ N K_2SO_4		0.4 N $NaHSO_4$		0.4 N $NaHSO_4$ N Na_2SO_4	
	CO_2	$k \times 10^3$	CO_2	$k \times 10^3$	CO_2	$k \times 10^3$	CO_2	$k \times 10^3$
25	37.0	1.195	17.6	0.554	44.4	1.434	20.7	0.657
50	74.1	1.232	35.5	.569	88.1	1.485	41.7	.672
100	141.5	1.264	69.2	.573	165.6	1.521	82.7	.694
150	200.3	1.278	100.9	.574	230.8	1.538	121.6	.708
200	250.0	1.285	132.6	.586	286.5	1.555	158.4	.721

TABLE IV

Time, min.	At 90° with							
	0.2 N $KHSO_4$		0.2 N $KHSO_4$ N K_2SO_4		0.2 N $NaHSO_4$		0.2 N $NaHSO_4$ N Na_2SO_4	
	CO_2	$k \times 10^3$	CO_2	$k \times 10^3$	CO_2	$k \times 10^3$	CO_2	$k \times 10^3$
25	42.2	1.360	22.4	0.709	49.8	1.617	24.5	0.777
50	81.6	1.367	42.5	.685	94.6	1.606	47.0	.761
100	150.4	1.357	80.4	.673	171.9	1.591	90.4	.764
150	209.0	1.358	115.0	.665	237.3	1.595	130.5	.767
200	260.7	1.359	149.1	.667	(292.8)[a]	(1.605)[a]	(167.3)[a]	(.770)[a]

[a] Extrapolated from graphs.

TABLE V

NEUTRAL SALT EFFECT ON ACID SULFATE IN HYDROLYSIS OF $N/2$ ETHYL ACETOACETATE

At 90° with

Time, min.	0.4 *N* $KHSO_4$		0.4 *N* $KHSO_4$ *N* K_2SO_4		0.4 *N* $NaHSO_4$		0.4 *N* $NaHSO_4$ *N* Na_2SO_4	
	CO_2	$k \times 10^3$	CO_2	$k \times 10^3$	CO_2	$k \times 10^3$	CO_2	$k \times 10^3$
25	65.0	2.142	33.5	1.071	78.8	2.633	37.3	1.197
50	123.6	2.164	65.4	1.078	148.0	2.664	74.1	1.230
100	222.6	2.198	124.3	1.089	260.4	2.714	141.3	1.262
150	299.7	2.210	176.7	1.097	345.6	2.777	202.1	1.295
200	359.2	2.225	225.0	1.112	(405.3)[a]	(2.791)[a]	(256.8)[a]	(1.331)[a]

[a] Extrapolated from graphs.

TABLE VI

At 95° with

Time, min.	0.2 *N* $KHSO_4$		0.2 *N* $KHSO_4$ *N* K_2SO_4		0.2 *N* $NaHSO_4$		0.2 *N* $NaHSO_4$ *N* Na_2SO_4	
	CO_2	$k \times 10^3$	CO_2	$k \times 10^3$	CO_2	$k \times 10^3$	CO_2	$k \times 10^3$
25	55.8	1.822	32.8	1.048	62.9	2.068	34.9	1.117
50	103.0	1.764	52.8	0.963	116.1	2.017	63.5	1.045
100	181.3	1.698	101.9	.872	199.5	1.912	111.2	0.961
150	243.8	1.654	139.0	.826	264.9	1.853	152.5	.919
200	(296.4)[a]	(1.634)[a]	(173.0)[a]	(.809)[a]	316.0	1.803	(189.0)[a]	(.894)[a]

[a] Extrapolated from graphs.

TABLE VII

At 95° with

Time, min.	0.4 *N* $KHSO_4$		0.4 *N* $KHSO_4$ *N* K_2SO_4		0.4 *N* $NaHSO_4$		0.4 *N* $NaHSO_4$ *N* Na_2SO_4	
	CO_2	$k \times 10^3$	CO_2	$k \times 10^3$	CO_2	$k \times 10^3$	CO_2	$k \times 10^3$
25	82.7	2.774	46.5	1.505	95.5	3.250	48.3	1.566
50	148.2	2.668	83.1	1.394	171.6	3.176	89.5	1.512
100	250.6	2.575	147.5	1.328	284.5	3.078	161.6	1.478
150	322.8	2.485	202.2	1.295	359.3	2.968	220.3	1.446
200	(379.2)[a]	(2.455)[a]	248.1	1.270	(408.0)[a]	(2.829)[a]	(266.0)[a]	(1.399)[a]

[a] Extrapolated from graphs.

TABLE VIII

TIME RATIO DATA FOR POTASSIUM SALTS

Temp., °C.	Concn.	Time to produce 75 cc. of CO_2, min.	Ratio	Time to produce 150 cc. of CO_2, min.	Ratio
80	0.2 *N* $KHSO_4$	80	0.465	...	...
	0.2 *N* $KHSO_4$, *N* K_2SO_4	172		...	...
	0.4 *N* $KHSO_4$	50	.459	...	...
	0.4 *N* $KHSO_4$, *N* K_4SO_2	109		...	...
90	0.2 *N* $KHSO_4$	46	.495	99	0.490
	0.2 *N* $KHSO_4$, *N* K_2SO_4	93		202	
	0.4 *N* $KHSO_4$	28	.483	63	.508
	0.4 *N* $KHSO_4$, *N* K_2SO_4	58		124	
95	0.2 *N* $KHSO_4$	34	.500	79	.476
	0.2 *N* $KHSO_4$, *N* K_2SO_4	68		166	
	0.4 *N* $KHSO_4$	22	.489	50	.490
	0.4 *N* $KHSO_4$, *N* K_2SO_4	45		102	
		Average 0.2 *N*	.487		.483
		Average 0.4 *N*	.477		.499

The greater the concentration of the acid, the greater we should expect the variation of this reaction constant. Data in Table I show this to be true.

The effect of the neutral salt on the rate of hydrolysis may be shown by calculating the ratio of the time required with the acid sulfate plus the neutral salt for producing 75 and 150 cc. of carbon dioxide, to the time required with the acid salt alone for producing the same quantity of carbon dioxide. In this manner the constituents in the solution will be the same at the time of comparison. These calculations are given in Table VIII for potassium salts and calculations for sodium salts give very similar results.

Summary

An apparatus has been devised for accurately measuring the velocity of reactions at higher temperatures and over a long period of time with substances evolving a gas.

The effects of normal sodium and potassium sulfates on their corresponding acid sulfates in the hydrolysis of ethyl acetoacetate have been studied at the temperatures of 80°, 90° and 95°.

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[Contribution from the Chemical Laboratory of Stanford University]

CARBONIC ACID AZIDES

By Charles Vinton Hart[1]

Received February 13, 1928 Published July 6, 1928

Accepting the view of Franklin and his collaborators to the effect that guanidine, cyanamide, dicyandiamide and melamine are ammono carbonic acids,[2] then the compounds named and formulated as follows: (1) guanylazide, $HNC(NH_2)N_3$, (2) cyanazide, NCN_3, (3) dicyanamidazide, $NCNC(NH_2)N_3$, (4) dicyandiazide, $NCNC(N_3)_2$, (5) cyanuramiddiazide, $C_3N_3(N_3)_2NH_2$ and (6) cyanurtriazide, $C_3N_3(N_3)_3$, are to be looked upon as carbonic acid azides.

Dicyandiazide, $NCNC(N_3)_2$, **and Dicyanamidazide,** $NCNC(NH_2)N_3$.—By the action of cyanogen bromide on sodium azide in water solution, Darzens[3] obtained a crystalline product, formed as he believed in accordance with the equation, $NCBr + NaN_3 = NCN_3 + NaBr$, to which he gave the name carbon pernitride.

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[1] An abstract of a thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy at Stanford University, 1927. Dr. Hart died at Berkeley, California, April 12, 1928. This paper, for the most part, is in the form written by the author. (E. C. Franklin.)

[2] Franklin, This Journal, **44**, 486 (1922); **46**, 2137 (1924); Burdick, *ibid.*, **47**, 1485 (1925); Blair, *ibid.*, **48**, 87, 96 (1926). See also Pinck and Blair, *ibid.*, **49**, 509 (1927).

[3] Darzens, *Compt. rend.*, **154**, 1232 (1912).