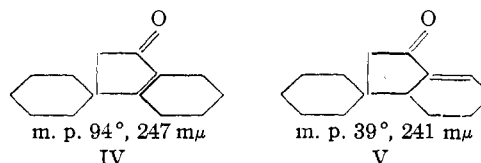


m. p. 39°, is not entirely certain,<sup>7</sup> the carbon skeleton of that part of the molecule containing the chromophoric group may be regarded as established. The observed values of  $\lambda_{\max}$  are in excellent agreement with the assignment to the two ketones of the structures IV [ $\lambda_{\max}$ . (calcd.) = 247  $m\mu$ ] and V [ $\lambda_{\max}$ . (calcd.) = 240  $m\mu$ ].

The new position is summarized in Table I, which is an adaptation of Table V in the earlier communication.<sup>2</sup>

(7) Professor R. P. Linstead in private conversation has informed me that recent work has shown that the previous formulation of these substances as hydrophenanthrene derivatives is untenable, and has suggested, on the basis of the work of Levitz, Perlman and Bogert, *J. Org. Chem.*, **6**, 105 (1941), that the ketones are spirane derivatives.



### Summary

The effect of exocyclic double bonds in determining the position of the band maxima for the intense band in the absorption spectra of  $\alpha,\beta$ -unsaturated ketones is demonstrated.

The recognition of the new effect permits certain refinements in the classification system previously proposed.

CAMBRIDGE, MASS.

RECEIVED SEPTEMBER 18, 1941

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

## The Saponification of Acetylsalicylic Acid at 35°<sup>1</sup>

BY JULIAN M. STURTEVANT

LaMer and Greenspan<sup>2</sup> studied the rates of saponification of several acetylated hydroxy acids at 25° by titration of the remaining alkali, and found that the reactions were sufficiently clean-cut to be susceptible to precise velocity measurements. Reactions of this type appeared to offer promising material for study by the calorimetric method developed by the author,<sup>3</sup> and some experiments were therefore performed with acetylsalicylic acid at 35°. The results of these experiments have shown, however, that it would be very difficult to get accurate heat data on these reactions, and it has therefore not been considered worthwhile to carry the measurements any further. The present paper reports the data obtained; even though significant thermal data were not obtained, the velocity constants observed in the range  $\mu = 0.0032$  to 0.021 follow the Brönsted theory better than would be expected from the work of LaMer and Greenspan at 25°.

### Experimental

Acetylsalicylic acid (of unknown source) was recrystallized four times from chloroform, once from dilute alcohol, and twice more from chloroform. Neutralization equivalent: observed 180.24, 179.97; calculated 180.15. The stock so-

dium hydroxide solution was prepared, analyzed, and handled by the methods described in an earlier communication.<sup>4</sup> The measurements were carried out in the apparatus described elsewhere.<sup>5b</sup>

In the calorimetric determination of reaction velocities it is impossible to obtain a value for the temperature at the start of the reaction, because of the heat of mixing the reactants, or for the final temperature, because of calorimetric difficulties. It is therefore necessary to use some method of calculation which does not involve these two temperatures. The present reaction follows the second order law

$$kt = \frac{1}{A - B} \ln \frac{B(A - Y)}{A(B - Y)} \quad (1)$$

where  $A < B$  are the initial concentrations of sodium acetylsalicylate and sodium hydroxide, and  $Y$  is the concentration of sodium salicylate at time  $t$ . Application of the method of calculation described in a previous paper<sup>5</sup> gives the following results

$$\frac{B}{A} = \frac{\alpha(\mu_3 - \mu_2) - (\mu_2 - \mu_1)}{(\mu_3 - \mu_2) - \alpha(\mu_2 - \mu_1)} \alpha^{(t + \Delta t)/\Delta t} \quad (2)$$

$$\mu_\infty = \frac{\mu_3(\mu_2 - \mu_1) - \alpha\mu_1(\mu_3 - \mu_2)}{(\mu_2 - \mu_1) - \alpha(\mu_3 - \mu_2)} \quad (3)$$

$$\mu_\infty - \mu_0 = \frac{A}{A - B} \left[ \mu_\infty - \frac{\mu_1(\mu_3 - \mu_2) - \alpha\mu_3(\mu_2 - \mu_1)}{(\mu_3 - \mu_2) - \alpha(\mu_2 - \mu_1)} \right] \quad (4)$$

$$k = \frac{1}{(A - B)\Delta t} \ln \alpha \quad (5)$$

(1) Part of the material in this paper was presented before the Division of Physical and Inorganic Chemistry at the Atlantic City meeting of the American Chemical Society, September, 1941.

(2) LaMer and Greenspan, *THIS JOURNAL*, **56**, 1492 (1934).

(3) (a) Sturtevant, *ibid.*, **59**, 1528 (1937); (b) *J. Phys. Chem.*, **45**, 127 (1941).

(4) Sturtevant, *ibid.*, **62**, 2276 (1940).

(5) Sturtevant, *ibid.*, **59**, 699 (1937).

In these equations  $\mu_1, \mu_2, \mu_3$  are temperature readings (conveniently expressed in microvolts, since temperatures were measured thermoelectrically) taken at times  $t, t + \Delta t$ , and  $t + 2 \Delta t$  after starting the reaction, and  $\mu_0, \mu_\infty$  are respectively the hypothetical initial and final temperatures. Since  $A, B$  are known accurately from the make-up of the reacting solution, eq. (2) can be used to obtain  $\alpha$  by successive approximations. This value of  $\alpha$  is utilized to calculate  $\mu_\infty, (\mu_\infty - \mu_0)$  and  $k$  by eqs. (3), (4) and (5).

### Results

Table I has the data for one of the faster runs. It is seen that rather good velocity constants are obtained, though a slight trend downward and then upward is evident. Similar trends appear in the values of  $\mu_\infty$  and  $(\mu_\infty - \mu_0)$ . The quantity  $(\mu_\infty - \mu_0)$  is proportional to the heat of reac-

TABLE I

THE SAPONIFICATION OF ACETYSALICYLIC ACID AT 35.06°  
 $A = 0.005083$  mole per 1000 g. H<sub>2</sub>O,  $\sqrt{\mu} = 0.1450$ ;  
 $B = 0.01594$  mole per 1000 g. H<sub>2</sub>O,  $\Delta t = 8$  minutes.  
 Half-time = 3.09 minutes. Observations extend from 43 to 99% conversion.

$t$ , min.	Temperatures (corrected for stirring and non- adiabaticity), microvolts,			0.4343 $k$	$\mu_\infty$	$\mu_\infty - \mu_0$
	$\mu_1$	$\mu_2$	$\mu_3$			
2.5	66.45	116.05	126.39	6.737	129.82	112.14
3.5	78.32	118.30	127.01	6.705	129.95	112.15
4.5	87.75	120.19	127.49	6.697	129.98	112.07
5.5	95.19	121.73	127.86	6.691	129.97	111.76
6.5	101.19	123.05	128.18	6.718	129.94	112.27
7.5	106.10	124.13	128.44	6.712	129.93	112.18
8.5	110.07	125.06	128.67	6.749	129.91	112.96
			Mean	6.724	129.93	112.22 = 0.0939°
			Average deviation	±0.4%	±0.03	±0.2%

tion; determination of the total heat capacity after the reaction is complete gives the necessary proportionality constant. However, the data for this comparatively rapid reaction illustrate clearly one of the difficulties in obtaining reliable heat values in the present experiments. In this run the dilution cup contained 2.6915 molal sodium hydroxide, and the calorimeter contained 0.1059 g. of acetylsalicylic acid in 114.72 g. of water. The time of starting the reaction was taken as ten seconds after opening the dilution cup. There is no way of verifying this estimate of the time required for mixing; as a matter of fact, if the acetylsalicylic acid was not all dissolved, a considerably longer time may have been required. Calculations were carried through taking  $t_0 = 40$  seconds after opening the dilution cup; in this case  $0.4343 k = 6.651, \mu_\infty = 129.92, (\mu_\infty - \mu_0) =$

100.6. Thus  $k$  is relatively insensitive to errors in  $t_0, \mu_\infty$  is very insensitive, while  $(\mu_\infty - \mu_0)$ , actually  $\mu_0$ , is very sensitive.

The data for the velocity experiments are collected in Table II. The velocity constants have been corrected to 35° using a temperature coefficient estimated from the present data and those of LaMer and Greenspan<sup>2</sup> at 25°. The values of  $\log k$  are found to be a linear function of the square root of the ionic strength (Fig. 1); the average deviation of the individual values from the least-squared equation

$$\log k = 1.0521 + 0.937\sqrt{\mu} \quad (6)$$

is  $\pm 1.3\%$  in  $k$ . At 35° in aqueous solution Brønsted's<sup>6</sup> equation for a bimolecular ionic reaction between ions having charges  $z_1 = z_2 = -1$  is

$$\log k = \log k_0 + 1.032\sqrt{\mu} \quad (7)$$

Equation (7) can, of course, be expected to hold only in solutions so dilute that the Debye-Hückel limiting expression for activity coefficients is valid. The results of LaMer and Greenspan<sup>2</sup> for this reaction at 25° seem to deviate considerably from the theoretical expression in a concentration range which, they recognized, may be too high for safe application of the Debye-Hückel limiting law.

The next to the last column of Table II gives the values for the heat of the saponification reaction, per mole of ester, obtained from the observed total heat capacity ( $C$ ), the number of moles of ester ( $n_2$ ), and the values, listed in the seventh column, of  $(\mu_\infty - \mu_0)$  obtained by application of eq. (4). Part of the large deviations shown in these heats is to be attributed to the fact that the fractions of the acetic and salicylic acids formed which are neutralized by sodium hydroxide depend on the concentrations of the various substances and the respective ionization constants. In the absence of reliable values for the heats of ionization, one cannot make allowance for these effects. However, it is probable that the larger part of the deviations is the result of inaccuracies in the estimate of the time required for mixing the reagents.

Three runs of type 4 were made in which acetylsalicylic acid and sodium hydroxide were used in approximately equivalent amounts. These data are summarized in Table III. In obtaining the corrected heat effects listed in column 5, sodium hydroxide dilution heats were employed which were calculated from results at 25°,<sup>7</sup> using the

(6) Brønsted, *Z. physik. Chem.*, **102**, 169 (1922); **115**, 337 (1925).  
 (7) Sturtevant, ref. 4; also *THIS JOURNAL*, **64**, in press (1942).

TABLE II

## THE SAPONIFICATION OF ACETYLSALICYLIC ACID AT 35°

All concentrations in moles per 1000 g. water;  $k$  calculated using natural logarithms; time in minutes

Run	$A \times 10^3$	$B \times 10^3$	$\sqrt{\mu}$	Time of half conversion, min.	$k \pm$ av. dev.	$\mu_\infty - \mu_0$		$\frac{C}{H_2}(\mu_\infty - \mu_0)_{\text{obs.}}$	Type of experiment <sup>a</sup>
						obs.	calc.	joules (int.) per mole	
1	1.350	1.913	0.0571	36.08	12.66 $\pm$ 0.10	26.29	26.84	-73,540	4
2	1.376	5.082	.0803	10.85	13.55 $\pm$ .12	26.73	25.97	-72,520	4
3	2.586	5.068	.0875	11.16	14.35 $\pm$ .06	52.33	53.72	-75,970	2
4	3.404	12.11	.1245	4.20	14.77 $\pm$ .04	84.85	...	-93,170	1
5	3.308	16.95	.1423	2.84	15.22 $\pm$ .14	68.04	64.66	-77,330	3
6	5.083	15.94	.1450	3.09	15.42 $\pm$ .06	112.22	44.88	-83,600	2

<sup>a</sup> Type 1, solid acetylsalicylic acid in dilution cup; type 2, concn. sodium hydroxide in cup, acetylsalicylic acid solution (?) in calorimeter; type 3, dilute sodium hydroxide in cup, acetylsalicylic acid solution (?) in calorimeter; type 4, dilute sodium hydroxide in cup, acetylsalicylic acid dissolved in water before being placed in calorimeter.

TABLE III

## NEUTRALIZATION OF ACETYLSALICYLIC ACID BY SODIUM HYDROXIDE AT 35°

Mole of sodium hydroxide	Mole of acetylsalicylic acid	$\sqrt{\mu}$	Heat of diln. of sodium hydroxide, joules (int.)	$\Delta q$ (cor.), joules (int.)	Heat of formation of water, joules (int.)	Moles ionized	$\Delta H_A$ , heat of ionization, joules (int.) per mole	Deviation from mean, microvolts
0.001040	0.001040	0.0888	-0.62	-59.10	-56.02	0.0008570	-3590	-0.17
.0007256	.0006389	.0692	-.38	-36.03	-34.41	.0004875	-3329	+ .16
.0001627	.0001557	.0336	-.08	- 8.69	- 8.38	.0000916	-3361	+ .02
Weighted mean							-3493	$\pm$ .12

temperature coefficient derived from the data of Gucker and Schminke,<sup>8</sup> also at 25°. Some error may be introduced here because of the long temperature extrapolation involved. All acetylsalicylic acid dilution heats were assumed to be negligible. In calculating the moles of acid ionized (column 7) and the heat effect resulting from the formation of water (column 6), all activity coefficients were set equal to unity. Since  $K_A$ , the ionization constant of acetylsalicylic acid, is much larger than  $10^{-14}$ , hydrolysis of the salt formed can be neglected. Roth and Reyer<sup>9</sup> report that  $K_A(25^\circ) = 3.27 \times 10^{-4}$ . Using this to obtain an approximate value of  $\Delta H_A$ , which is in turn used to compute the temperature coefficient of  $K_A$ , one obtains  $K_A(35^\circ) = 3.12 \times 10^{-4}$ . Calculation according to the empirical equation of Pitzer<sup>10</sup> gives  $K_A(35^\circ) = 3.03 \times 10^{-4}$ . The heat of formation of water, -53,850 joules (int.) per mole, given by Pitzer,<sup>10</sup> was used. In computing the mean of the heats of ionization given in the next to the last column, the individual quantities were weighted in proportion to the observed heat effect after deducting the heat of formation of the water.

The mean value of the heat of ionization, together with the heat of formation of water and the appropriate heats of dilution of sodium hydroxide,

(8) Gucker and Schminke, *THIS JOURNAL*, **55**, 1013 (1933).

(9) Landolt-Börnstein "Tabellen," 5th edition, Vol. II, p. 1136.

(10) Pitzer, *THIS JOURNAL*, **59**, 2365 (1937).

were used to calculate the heat effect to be expected from neutralization of the acetylsalicylic acid in the runs in Table II (excluding run 4).

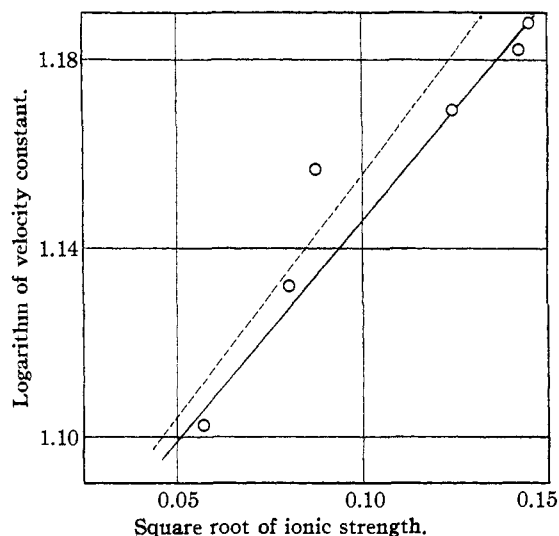


Fig. 1.—Plot of  $\log k$  vs.  $\sqrt{\mu}$ . The dotted line is the theoretical slope.

These expected heat effects were deducted from the total temperature changes ( $\mu_\infty$  minus the reading before mixing the reactants) to obtain the values of  $\mu_\infty - \mu_0$  listed in column 8 of Table II. The poor agreement between observed and calculated values even in runs 1 and 2, in which the acetylsalicylic acid was certainly all in solution,

is further indication that the time of mixing was poorly defined.

### Summary

The velocity of saponification of acetylsalicylic acid at 35° has been investigated by the calorimetric method. The results agree well with the

requirements of Brönsted's theory. The heat data obtained in these experiments are unsatisfactory.

Measurements of the heat of ionization of acetylsalicylic acid at 35° lead to the value  $\Delta H_A = -3500$  joules per mole.

NEW HAVEN, CONNECTICUT RECEIVED OCTOBER 16, 1941

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY, HARVARD UNIVERSITY]

## The Photochemical Decomposition of Cyclic Ketones

BY S. W. BENSON AND G. B. KISTIAKOWSKY

The work of Norrish, *et al.*,<sup>1,2</sup> on the photochemical decomposition of cyclic ketones has indicated the formation of free bi-radicals in the primary process. The results, however, were complicated and there are some objections to the experimental techniques employed. Furthermore, the reported identification of gaseous products can be questioned because of the use of incorrect physical constants from the literature. On these grounds it seemed desirable to repeat the work on cyclopentanone and cyclohexanone, and then to extend it to cyclobutanone, using modified techniques.

The results of this investigation are in general agreement with the results of Norrish, the main discrepancies existing in the identification of the gaseous hydrocarbons. Norrish's results can be summarized thus

- |                   |   |  |          |
|-------------------|---|--|----------|
| 1. Cyclohexanone  | ↗ | $C_5H_{10} + CO$                                       | (87-92%) |
|                   | ↘ | $C_2H_4 + C_3H_6 + CO$                                 | (8-13%)  |
| 2. Cyclopentanone | ↗ | $C_4H_8$ ( <i>cis</i> and <i>trans</i> -2-butene) + CO | (50%)    |
|                   | ↘ | $2C_2H_4 + CO$   | (50%)    |

In his first paper Norrish identified the  $C_5H_{10}$  as cyclopentane, but in his second paper he found a compound which boiled at 39° which was taken to be 1-pentene. However, the rather accurate work of Sherrill<sup>3</sup> gives the boiling point of 1-pentene as 29.0° and the boiling point of 2-pentene as 36°, this latter being in fact the highest boiling  $C_5H_{10}$  olefin. This would make it seem more likely that Norrish obtained a mixture of cyclopentane (b. p. 49°) and of one or more of the pentenes. In the present work the  $C_5H_{10}$  hydrocarbon was identified as a mixture of 75% cyclopentane and 25%

1-pentene. Except possibly for the proportions, this is probably the same mixture as obtained by Norrish.

Norrish identified the  $C_4H_8$  hydrocarbon obtained from the cyclopentanone as a mixture of *cis*- and *trans*-2-butenes, but the vapor pressure measurements he gives show the vapor pressure to be below the vapor pressure of the highest boiling butene,<sup>4</sup> and the melting point of -96° is higher than that of the highest melting butene, *cis*-2-butene (m. p. -107°). In the present work the  $C_4H_8$  hydrocarbon was positively identified as cyclobutane.

The experimental objection to the work of Norrish is that he refluxed the ketone past the source of light, and allowed the condensed vapors to flow back through the irradiated zone. This means that a considerable fraction of the light may have been absorbed by the *liquid*, and hence some of the reaction may have occurred in the liquid phase. This may contribute to the difference in the two sets of experimental results reported by Norrish, although he himself gives a different and plausible explanation of the discrepancy.

The decomposition of the cyclic ketones is important in that it provides a convenient method for studying the behavior of divalent free radicals and the mechanism of ring closure in the gaseous phase. The present work has been primarily concerned with the qualitative study of the products of photolysis, but future quantitative measurements will certainly provide interesting information on the above problems. An incidental consequence of the present work is that a convenient method of preparation of cyclobutane has

(1) Saltmarsh and Norrish, *J. Chem. Soc.*, 455 (1935).

(2) Bamford and Norrish, *ibid.*, 1421 (1938).

(3) Sherrill, *J. Chem. Phys.*, 4, 751 (1936).

(4) Kistiakowsky, Ruhoff, Smith and Vaughan, *THIS JOURNAL*, 67, 876 (1935).