(without mercaptalation) at 0° was followed by optical rotation measurements.

4. A graphic analysis of the data yielded a value of 2.22×10^{-2} (hours^{-1}) for the specific rate constant of the rate of change of the degree of polymerization in concentrated hydrochloric acid at 0°.

5. By graphic analysis the minimum value of *ca.* 150 was obtained for the initial average degree of polymerization of the methylated starch.

6. The degree of polymerization of a starch product is highly dependent on the method of preparation of the product.

COLUMBUS, OHIO RECEIVED MARCH 12, 1941

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

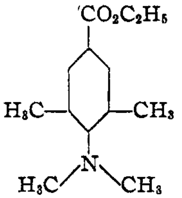
The Effect of Resonance on Reaction Velocity[1]

BY F. H. WESTHEIMER AND RICHARD P. METCALF

In previous publications,[2] one of us has computed that part of the effect of substituents on the velocity of saponification which can reasonably be considered electrostatic in origin. Many cases are explicable on an electrostatic basis; the extraordinarily slow rates of saponification of ethyl *p*-aminobenzoate[3] and ethyl *p*-dimethylaminobenzoate, however, cannot be ascribed exclusively to the effect of the dipole moment of the amino group. The assumption was therefore made that resonance interaction of the amino and carbethoxy groups stabilized the ester, and thereby caused a decrease in the rate of saponification. This assumption is consistent with the fact that ethyl *m*-aminobenzoate, where such resonance interaction is impossible, saponifies twenty times faster than the para isomer.

It was realized that this hypothesis could be subjected to a severe test. Birtles and Hampson[4] have shown that the introduction of alkyl substituents ortho to the dimethylamino group prevents that group from lying in the plane of the benzene ring, and thereby "damps" its resonance. It is a necessary condition imposed by our theory that elimination of the resonance involving the amino group should result in a rate of saponification approaching that of the unsubstituted ester. On the other hand, in those cases in which the effect of the substituent on the rate of saponification can be explained on an electrostatic basis alone, "damping" the resonance should have only a minor effect on the rate.

The theory was examined experimentally by measuring the rates of saponification of the following esters: ethyl 3,5-dimethylbenzoate, ethyl 3,5-dimethyl-4-nitrobenzoate, ethyl 3,5-dimethyl-4-aminobenzoate and ethyl 3,5-dimethyl-4-dimethylaminobenzoate. (I). To supplement Kindler's data the rate of saponification of ethyl *p*-dimethylaminobenzoate was also obtained.



I

All the compounds needed for the investigation with the exception of ethyl 3,5-dimethyl-4-dimethylaminobenzoate were known. The acid corresponding to this ester was synthesized by two methods. First 2,6-dimethylaniline was brominated, and the bromoamine methylated with dimethyl sulfate. The 3,5-dimethyl-4-dimethylaminobromobenzene was converted into the corresponding lithium compound, and carbonated to the acid. The second method of synthesis consisted of methylating the methyl ester of 3,5-dimethyl-4-aminobenzoic acid. The resultant crude ester was hydrolyzed to the desired acid.

Experimental

Materials.—3,5-Dimethylbenzoic acid was made both by the oxidation of mesitylene[5] and, probably for the first time, by a Grignard reaction from 3,5-dimethylbromobenzene. The latter reaction gave more than an 80% yield of recrystallized acid melting at 168°. The ester[6] boiled at 74–75° at 2 mm. Ester obtained from both samples of acid saponified at the same rate.

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[1] Presented on April 9, 1941, at the St. Louis meeting of the American Chemical Society.

[2] Westheimer and Shookhoff, This Journal, **62**, 269 (1940); Westheimer, *ibid.*, **62**, 1892 (1940).

[3] Kindler, *Ann.*, **450**, 1 (1926).

[4] Birtles and Hampson, *J. Chem. Soc.*, 10 (1937); Ingham and Hampson, *ibid.*, 981 (1939).

[5] Fittig, *Ann.*, **141**, 129 (1867).

[6] Fittig and Brueckner, *ibid.*, **147**, 42 (1868).

Ethyl *p*-dimethylaminobenzoate was prepared by the esterification of acid melting at 238° (uncor.).[7] The acid was recrystallized several times, and had been synthesized from dimethylaniline[7] freed from monomethylaniline with acetic anhydride. The ester melted sharply at 63–63.5° after many recrystallizations from ligroin. It is believed that the ester was pure, although this melting point is several degrees below that reported in the literature.

Ethyl 3,5-dimethyl-4-nitrobenzoate melted at 72°.[8] Ethyl 3,5-dimethyl-4-aminobenzoate melted at 67°.[9]

3,5-Dimethyl-4-dimethylaminobromobenzene.—3,5-Dimethyl-4-aminobromobenzene[10] was heated to 160° for half an hour with three times its weight of dimethyl sulfate. The solution was cooled, and decomposed with dilute aqueous ammonia. The aqueous layer was extracted with ether, and the ether dried with potassium carbonate. After evaporation of the ether, the partially methylated amine was treated with dimethyl sulfate as before. The resultant solution was decomposed with ammonia, and the amine dissolved in excess cold 3 *N* hydrochloric acid. The solution was treated at 0° for an hour with excess sodium nitrite. Then the excess nitrous acid was destroyed with urea, and the precipitated nitrosamine removed by filtration. The solution was made alkaline, and the 3,5-dimethyl-4-dimethylaminobromobenzene separated. It is a white solid, melting at 33°, which rapidly turns yellow in air. It can conveniently be purified by vacuum or molecular distillation.

Anal. Calcd. for $C_{10}H_{14}NBr$: C, 52.63; H, 6.19. Found: C, 52.83; H, 6.10.

The nitrosoamine crystallizes easily from methanol, and melts at 69°.

Anal. Calcd. for $C_9H_{11}N_2OBr$: C, 44.44; H, 4.53; N, 11.52. Found: C, 44.90; H, 4.85; N, 11.49.

3,5-Dimethyl-4-dimethylaminobenzoic Acid.—0.64 grams of lithium metal was cut into small pieces, and placed in 30 cc. of dry ether in a three-necked flask; 9.0 grams of bromoamine dissolved in 30 cc. of dry ether was added slowly with stirring, while nitrogen was passed over the solution. The technique was the usual one,[11] and the reaction proceeded smoothly to completion. The lithium compound was carbonated by pouring it into a five-fold excess of dry-ice and ether. After acidification, the ether layer was extracted with aqueous carbonate solution. On acidification of this carbonate solution, a 35% yield of 3,5-dimethyl-4-dimethylaminobenzoic acid was obtained. The acid can be crystallized from ligroin and melts at 188°.

Anal. Calcd. for $C_{11}H_{15}NO_2$: C, 68.36; H, 7.81. Found: C, 68.34; H, 7.91.

The ether layer contained 2.5 g. of a neutral compound which, after recrystallization from methanol, melted at 145°. It is probably 3,5,3′,5′-tetramethyl-4,4′-tetramethyldiaminobenzophenone. It was not further investigated.

Anal. Calcd. for $C_{21}H_{28}N_2O_2$: C, 77.73; H, 8.69; N, 8.65. Found: C, 78.28; H, 8.88; N, 8.93.

Attempts to methylate 3,5-dimethyl-4-aminobenzoic acid met with difficulty, but the methyl ester[12] reacts easily. Three grams of methyl 3,5-dimethyl-4-aminobenzoate and ten cc. of dimethyl sulfate were heated under a reflux condenser at 110–120° for an hour. The solution was cooled and decomposed by stirring for an hour with a solution containing 12 g. of sodium carbonate in 75 cc. of water. The water was extracted with ether, the ether dried with sodium sulfate, and evaporated. The residue was treated with dimethyl sulfate and decomposed with carbonate solution as before. The amino ester was taken up in ether and the ether extracted with 3 *N* hydrochloric acid. The acid solution was treated with sodium nitrite, extracted with ether and then made alkaline. The liberated ester was taken up in ether, the ether evaporated. The crude liquid ester was saponified by refluxing for half an hour with 30 cc. of 5% sodium hydroxide in 50% alcohol. On acidification, a 50% yield of acid was obtained. It had the same melting point as the 3,5-dimethyl-4-dimethylamino acid prepared through the lithium compound, and the melting point was not lowered by admixture with the latter.

Ethyl 3,5-Dimethyl-4-dimethylaminobenzoate.—The ester was prepared from the purified acid by refluxing for four hours with twenty times its weight of absolute alcohol, saturated with hydrogen chloride. Most of the alcohol was removed by distillation, and then the solution was poured into iced carbonate solution. The ester, purified by vacuum distillation, melts at 15°.

Anal. Calcd. for $C_{13}H_{19}NO_2$: C, 70.52; H, 8.57; N, 6.34. Found: C, 70.60; H, 8.58; N, 6.66.

The alcohol used in the kinetic investigation was dried with barium oxide and distilled. The desired alcohol–water mixtures were prepared by measuring the calculated volume of water from a buret into a volumetric flask, and filling to the mark with absolute alcohol. The mixtures were then refluxed for a short time to remove carbon dioxide and kept in flasks protected by soda-lime tubes.

The alkali solutions were prepared by the addition of metallic sodium to the alcohol immediately after the refluxing. The solutions were protected by soda-lime tubes. They were standardized from time to time by titration with standard acid.

Method.—The rates of saponification of the esters were determined by titrating the alkali present at various times during the reaction. The alkali solution, and additional alcohol if necessary, were measured from burets into a 125-cc. Erlenmeyer flask. The flask was placed in a thermostat controlled to ±0.01°, and allowed to come to temperature. Then an open glass capsule containing a weighed quantity of ester was introduced, and the solution thoroughly shaken. After temperature equilibrium had again been established, from time to time solution was forced into a calibrated pipet of 10-cc. capacity by air pumped through a soda-lime tube. In this way, no carbon dioxide came in contact with the solution except while it was being drawn from the buret, and momentarily when the ester was introduced. On some occasions, nitrogen rather than air was used, and the solutions protected from oxygen as well as carbon dioxide.

The samples removed from the Erlenmeyer flasks were

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(7) Rivier and Schneider, *Helv. Chim. Acta*, **2**, 717 (1919).

(8) Emerson, *Am. Chem. J.*, **8**, 268 (1886).

(9) Wheeler and Hoffman, *ibid.*, **44**, 113 (1910).

(10) Fischer and Windaus, *Ber.*, **33**, 1967 (1900).

(11) Gilman, Zoellner and Selby, THIS JOURNAL, **54**, 1957 (1932).

(12) Meyer, *Monatsh.*, **25**, 1201 (1904).

discharged from the pipet into excess standard acid. The entire operation of rinsing out, filling, and draining the pipet required about a minute. The cooling of the sample during this time introduced an error which is due chiefly to the change in volume.

The danger from carbon dioxide was negligible for the nitro ester, since it reacted quite rapidly. The solution was therefore withdrawn by suction with a transfer pipet which emptied in a few seconds. Successive samples could be taken only a minute apart.

The samples were analyzed by back-titrating the excess acid with 0.01 *N* alkali, using phenolphthalein as indicator. The titrations were corrected for the amount of alkali required to give the end-point color in a solution of equal volume containing no acid.

The rates of saponification of ethyl benzoate and ethyl *p*-dimethylaminobenzoate were measured at 30.1° in 87.83% alcohol by weight, so that the results might be comparable to Kindler's. In order to speed the work, the other measurements were made at 55.0° and in 70.0% alcohol by weight.

The authors are indebted to Dr. T. S. Ma for the microanalyses reported in this paper.

Results

The saponification measurements were made with equal concentrations of alkali and ester, and the constants determined graphically by plotting $1/x$ against t, where x is the concentration of hydroxide ion at time t. The average rate of saponification of ethyl benzoate at 30° and in 87.83% alcohol by weight was found to be 0.052 min.$^{-1}$ (m./l.)$^{-1}$, as compared with the value of 0.049 given by Kindler.[3]

The graphs of the velocity constants were in all cases linear, except those for the saponification of ethyl 3,5-dimethyl-4-aminobenzoate. For this compound there was a decided upward drift of the constant. This drift was traced to the action of the hot alkali on the glass. This complication was unimportant for the compounds which saponify much more rapidly than ethyl 3,5-dimethyl-4-aminobenzoate. (The velocity constants for ethyl *p*-dimethylaminobenzoate, determined at 30°, showed a just noticeable drift which was neglected.)

Blanks showed that, at 55°, the action of the alkali on the glass accounted for a change in hydroxide ion concentration of about 0.4% an hour. No hydrolysis of the ester was apparent in the absence of alkali, and the possibility that the alcohol was being oxidized by the air was eliminated, at least as a major factor, by determinations made under nitrogen.

The values of the velocity constants for ethyl 3,5-dimethyl-4-aminobenzoate were obtained by taking the limiting slope of the plot of $1/x$ against t, and also by applying approximate corrections, according to the method previously developed.[1]

The ester concentration, x_0, was obtained from the alkali concentration by graphical integration, and the results fitted into the equation

$$1/x_0 = kt(1 - pt/2) + C \qquad (1)$$

where p is the fraction change of hydroxide ion concentration per minute due to action of alkali on the glass, and C is a constant of integration. This method somewhat overcorrects for the action on the glass, and suffers from the fact that the surface–volume relationship in an Erlenmeyer does not remain constant as samples are withdrawn. It is sufficiently accurate, however, to show that the action of alkali on the glass was at least the major cause of the curvature of the plots.

The magnitude of the difficulty can be seen from the fact that, for a particular rate determination, the value of the constant, in min.$^{-1}$ (m./l.)$^{-1}$, determined from the limiting slope, was

TABLE I

Compound	T, °C.	Initial concn.	k in min.$^{-1}$ (m./l.)$^{-1}$
Ethyl benzoate	30	0.0395	0.052
		.0395	.052
		.0200	.051
		Average	.052
Ethyl *p*-dimethylaminobenzoate	30	.0395	.00151
		.0395	.00150
		.0197	.00164
		.0197	.00143
		Average	.00152
Ethyl 3,5-dimethylbenzoate	55	.0398	.355
		.0398	.376
		.0398	.386
		.0200	.375
		Average	.373
Ethyl 3,5-dimethyl-4-nitrobenzoate	55	.0146	15.0
		.0100	13.6
		Average	14.8
Ethyl 3,5-dimethyl-4-aminobenzoate	55	.0200	0.019 (0.020)[b]
		.0200	.018 (.016)[b]
		.0200[a]	.017 (.018)[b]
		.0350[a]	.020 (.019)[b]
		.0400	.020 (.024)[b]
		Average	.019
Ethyl 3,5-dimethyl-4-dimethylaminobenzoate	55	.0400	.202
		.0200	.207
		.0150	.209
		Average	.206

[a] Determination made under nitrogen. [b] Computed using equation (1).

0.019, the corrected value 0.020, while the value obtained from the initial point and one at 50% reaction was 0.030.

The results of the velocity determinations are given in Table I.

In Table II are tabulated the values of Δ log k, or log k_s/k. Here k_s is the velocity constant of saponification of an ester containing a particular substituent, while k refers to the saponification rate of ethyl 3,5-dimethylbenzoate for substituted derivatives of this ester, and to the saponification rate of ethyl benzoate for its substitution products.

TABLE II

	Δ log k	
Substituent	Ethyl benzoates	Ethyl 3,5-dimethyl benzoates
H	0.00	0.00
NO_2	2.02[a]	1.60
NH_2	−1.63[a]	−1.29
$N(CH_3)_2$	−1.53	−0.26

[a] From Kindler's data.

Discussion of Results

These results show clearly that the nitro group is approximately as effective in increasing the rate of saponification of the methylated as of the unmethylated ester. Electrostatic theory predicts that the small changes in effectiveness of the nitro substituent, due to higher temperature, higher dielectric constant and larger molecular volume, would be expected to cancel among themselves.[2] The decrease in the effect of the nitro group can probably be ascribed to the change in its dipole moment due to the damping of resonance. While the magnitude of this decrease in moment is not accurately known, it is probably in the neighborhood of 15%.[4] The decrease in the logarithm of the relative rate constant (which is proportional to the moment[2]) is 20%.

The effect of the amino substituent in the methylated ester is smaller than its effect on ethyl benzoate, and it is possible that this small change can also be ascribed to damping of resonance.[4] But the large and significant effect was found, as expected, in a consideration of the rate of saponification of ethyl 3,5-dimethyl-4-dimethylaminobenzoate. While the rate of saponification of ethyl *p*-dimethylaminobenzoate is only 3% of that of its parent compound, the hindered ester saponifies more than half as fast as ethyl 3,5-dimethylbenzoate. Further, the dimethylamino ester saponifies eleven times as fast as 3,5-dimethyl-4-aminobenzoate.

The predictions which served as a basis for this investigation have, then, been verified by experiment. This does not constitute unambiguous proof that the hypotheses involved are correct; it does, however, strongly support the idea that the slow rates of saponification of ethyl *p*-amino- and ethyl *p*-dimethylaminobenzoate are largely due to the resonance interaction of the amino and carbethoxy groups.

It will prove convenient for further discussion to restate the facts in terms of the theory of the activated complex.[13,2] Resonance interaction of the groups in para position occurs in the unhindered ester; the addition of a hydroxide ion prevents this resonance in the activated complex. Since the stabilization of the ester relative to its activated complex is increased by the presence of the amino substituent, the rate of reaction is diminished.

It is interesting to note that the present work deals with a case in which "steric hindrance" has resulted in an increase in reaction velocity. Had resonance stabilized the activated complex rather than the starting material, then eliminating the resonance would have resulted in a decrease in rate.[14]

It is also of interest to inquire as to the extent to which resonance has been "damped." For this purpose it is necessary to establish the rate of saponification which would obtain in the absence of resonance involving the amino or dimethylamino group. It is possible to estimate an upper limit for this rate, on the assumption that the effect of the substituent would then be largely electrostatic. The moment would probably be of the order of 1.0 Debye unit.[15] The direction is unknown; to obtain the maximum electrostatic effect, it may be assumed that the dipole is parallel to the para axis of the ring, and with its positive end toward the ring. A computation similar to those made previously[2] shows that the rate could be two and a half times that of ethyl benzoate, or Δ log k = +0.40. It must be stressed that this value of Δ log k is almost certainly too large, since it is extremely unlikely that the dipole would actually be parallel to the para axis of the ring.

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(13) Eyring, *J. Chem. Phys.*, **3**, 107 (1935).

(14) For an example of this sort, see Spitzer and Wheland, THIS JOURNAL, **62**, 2995 (1940).

(15) The moment of dimethylaminodurene[4] is 1.03, that of triethylamine in the neighborhood of 0.8 Debye unit (*Trans. Faraday Soc.*, **30**, i–lxxxvi (1934)).

In actual fact, and with resonance present, the value of $\Delta \log k$ for the dimethylamino ester is -1.53. The maximum increase in the free energy of activation ($2.303\ RT\ \Delta \log k$) which can be ascribed to the resonance of the dimethylamino group, then, is 2700 cal. The actual decrease in the free energy of activation caused by damping the resonance is about 1800 cal. It is clear that the major portion of the stabilization has been eliminated by damping the resonance.

A more significant calculation, which would permit an estimate of the effect of damping on the interaction of the dimethylamino group with the carbethoxy group alone, and free from electrostatic effects, must await the determination of the direction of the moment of the hindered dimethylamino group.

The authors wish to acknowledge the valuable help and advice of Dr. G. W. Wheland.

Summary

1. Ethyl 3,5-dimethyl-4-dimethylaminobenzoate has been synthesized.

2. The rates of saponification of ethyl *p*-dimethylaminobenzoate, ethyl 3,5-dimethylbenzoate, ethyl 3,5-dimethyl-4-nitrobenzoate, ethyl 3,5-dimethyl-4-aminobenzoate and ethyl 3,5-dimethyl-4-dimethylaminobenzoate have been measured.

3. As predicted from the theory of damped resonance, the rate of saponification of ethyl 3,5-dimethyl-4-dimethylaminobenzoate greatly exceeds that of ethyl 3,5-dimethyl-4-aminobenzoate.

4. It is concluded that the low rate of saponification of ethyl *p*-aminobenzoate relative to that of ethyl benzoate is primarily caused by resonance interaction of the amino and carbethoxy groups.

CHICAGO, ILLINOIS RECEIVED JANUARY 15, 1941

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Heat Capacity of Organic Vapors. I. Methyl Alcohol

BY THOMAS DE VRIES AND BEN T. COLLINS

In order to calculate the potential of the barrier hindering the rotation of the methyl group in methyl alcohol, the heat capacity and fundamental vibration frequencies of the vapor must be known. In this paper are presented the experimental data for the heat capacity of the vapor from 75 to 170°. The continuous flow electric method of Callender and Barnes[1] was used with the improvements of Scheel and Heuse.[2]

The data in the literature are meager and questionable. Regnault[3] obtained an average value for the temperature interval 100–223° and Thibaut[4] obtained a value at 340°, both by calorimetric methods. The results obtained by Stevens[5] and by Dixon and Greenwood[6] with the velocity of sound method are too low because it is known that the conversion of translational or rotational energy into vibrational energy is too slow a process for the frequencies used in sound velocity measurements.

Apparatus and Method

Methyl Alcohol.—One of the best grades of commercially available methyl alcohol was dried with magnesium methylate and redistilled within 0.1° of its correct boiling point. The alcohol was vaporized in a Pyrex glass tube by means of controlled electrical heat. A uniform rate of flow of the vapor was obtained by surrounding the boiler with a Dewar flask and by insulating the exit tube to prevent refluxing. Before entering the calorimeter, the vapors were led through a long glass spiral to bring the vapors to the temperature of the thermostat. This equality of temperature was checked with a thermocouple. Both the rate of flow and the rate of heating were varied in order to obtain by extrapolation of the data a value corrected for heat losses. After leaving the calorimeter, the vapor was condensed and collected in a closed receiver.

Calorimeter.—The calorimeter was similar in general design and dimensions to that used by Scheel and Heuse[2] for their determination of the specific heat of gases. It was fabricated from Pyrex glass and was 25 cm. long and 4.6 cm. in diameter (Fig. 1). It was silvered and thoroughly evacuated. A tube with activated charcoal was sealed on which made it possible to compare the results of two series of determinations in one of which liquid air was used around the charcoal tube. There was not enough difference in the results to warrant the use of liquid air for the other determinations. The calorimeter was placed vertically in an oil filled thermostat, regulated to 0.01° with a mercury-in-glass regulator. The thermostat was 23 cm. in diameter and 54 cm. deep and a hydrogenated

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[1] Callender and Barnes, *Trans. Roy. Soc.* (London), **199A**, 55–263 (1902).

[2] Scheel and Heuse, *Ann. Physik*, (4) **37**, 79 (1912).

[3] Regnault, *Ann. chim. phys.*, **24**, 342 (1871).

[4] Thibaut, *Ann. Physik*, (4) **35**, 347 (1911).

[5] Stevens, *ibid.*, **7**, 285 (1902).

[6] Dixon and Greenwood, *Proc. Roy. Soc.* (London), **105A**, 199 (1924).