less fully developed than in the ionic intermediate. For this reason and because of the assumption of a dielectric constant of unity, the tabulated electrostatic energies represent maximum values in excess of those actually contributing to the reaction rates. Furthermore, the difference between the change in activation energy and the change in energy of the intermediate ion will be a function of the endothermicity of the process of its formation. The more endothermic the process, the more nearly will the change in activation energy approximate the change in energy of formation. As the process becomes more exothermic, the activation energy will decrease and changes in the energy of formation will have continuously smaller influence on the activation energy.[10]

[10] This relationship was pointed out to the author in a discussion with Professor Herbert C. Brown of Purdue University. The author is indebted to Professor Brown for permission to present this interpretation here. It will be discussed in detail by him in papers with his students reporting their work on directive effects.

NOTRE DAME, INDIANA RECEIVED MARCH 22, 1950

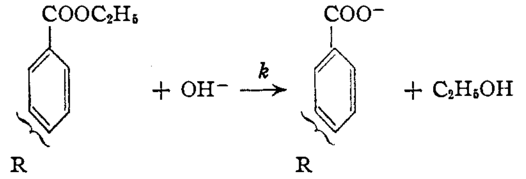
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Rates of Saponification of Ethyl *m*- and *p*-Toluate and *m*- and *p*-*t*-Butylbenzoate

BY CHARLES C. PRICE AND DWIGHT C. LINCOLN[1,2]

The effect of *t*-butyl groups in the meta and para position on the saponification of ethyl benzoate has been determined. Analyzed in terms of an "apparent" electrical effect, the influence seems anomalous. It has been suggested that the anomaly is due to the bulk effect of the large alkyl group decreasing solvation stabilization of the charged transition complex.

The nature of the influence of alkyl groups on reactivities of aromatic compounds has been the subject of a great deal of experiment and much controversial interpretation. It was the purpose of the investigation reported herein to obtain data on the difference between the influence of the methyl and *t*-butyl groups on a simple, well understood reaction, the saponification of an ester. We have therefore studied the rates of saponification of ethyl *m*- and *p*-toluate and *m*- and *p*-*t*-butylbenzoate in 56% by weight aqueous acetone at 25 and 40°.



R = Me or *t*-Bu

Experimental[3,4]

The *m*- and *p*-toluic acids were obtained from Monroe Scientific Service, Hilton, New York, and melted at 111–112° and 178–179°, respectively.

***m*-*t*-Butylbenzoic Acid.**—*t*-Butylbenzene was converted to *m*-bromo-*t*-butylbenzene by nitration, reduction, acetylation, bromination, hydrolysis, diazotization and treatment with hypophosphorous acid. The *m*-bromo-*t*-butylbenzene so obtained boiled at 116.5° at 27 mm., n^{20}_D 1.5343–1.5351 (lit.[5] b.p. 103–106° (17 mm.), n^{20}_D 1.5337).

The Grignard reagent from 95 g. of this *m*-bromo-*t*-butylbenzene and 12 g. of magnesium in 500 ml. of ether was treated with carbon dioxide at −5 to 0°. After acidification with 6 *N* hydrochloric acid, the ether was extracted with portions of 10% sodium bicarbonate. Acidification of the combined extracts precipitated 60 g. of crude acid, purified by crystallization from "Skellysolve L" to yield 25 g. (32%), m.p. 127.2–127.6° (lit.[6] m.p. 127.0–127.6°).

***p*-*t*-Butylbenzoic Acid.**—*t*-Butylbenzene was converted in 85% yield to *p*-*t*-butylacetophenone, b.p. 137° (15 mm.) (lit.[7] b.p. 137–138° (16 mm.)). The acetyl group was converted to carboxyl in 96% yield by adding one mole of ketone to approximately 400 g. of potassium hypochlorite in 3.5 l. of water at 60° with stirring. The potassium hypochlorite solution was prepared by treating 500 g. of "H.T.H." (commercial 70% calcium hypochlorite) in 2 l. of warm water with 350 g. of potassium carbonate and 100 g. of potassium hydroxide in 1 l. of water. The precipitate of calcium carbonate was removed by filtration before use. The acid was precipitated by acidification and purified by crystallization from aqueous methanol, m.p. 166.0–166.3° (lit.[6] m.p. 165–165.6°).

Ethyl Esters.—All the esters were prepared by standard Fisher esterification with ethanolic hydrogen chloride and purified by distillation through a 90 × 1.2-cm. column with double glass spiral packing. A constant-boiling center fraction was taken for the samples employed in the rate experiments. Results are summarized in Table I.

TABLE I

PHYSICAL CONSTANTS FOR ETHYL ESTERS

Substituent	B.p. °C.	Mm.	$n^{20}D$
m-Methyl	105.6	11	1.5055
p-Methyl	102.6–102.8	8.5	1.5085
m-*t*-Butyl[a]	112.6–112.8	4.2	1.4994
p-*t*-Butyl[b]	117.0–117.8	5.0	1.5017

[a] *Anal.* Calcd. for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.32; H, 8.86. [b] Marvel, Johnston, Meier, Mastin, Whitson and Himel, THIS JOURNAL, 69, 914 (1947), report b.p. 120–120.5° (4 mm.).

Rate Measurements.—In general, the procedure was that described by Tommila and Hinshelwood[8] and extended by Tommila.[9] Equal volumes of 0.1 *M* ester and alkali dissolved in 56% by weight (60% by volume) aqueous acetone were mixed at the desired temperature. Samples were withdrawn at timed intervals by means of a volumetric pipet, discharged into an excess of standard hydrochloric acid and the excess back-titrated with standard sodium hydroxide, using phenolphthalein as an indicator.

The alkali solution was prepared by diluting exactly 0.01 mole of carbonate-free sodium hydroxide solution from the stock solution of approximately 0.275 *N* with enough water to make 40 ml., assuming the volumes to be additive. This was then diluted to 100 ml. with acetone in a 100-ml. volu-

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[1] Eastman Kodak Company Fellow, 1947–1948. Present address: Hercules Powder Company, Wilmington, Delaware.

[2] Abstracted from part of a Ph.D. thesis presented to the University of Notre Dame by Dwight C. Lincoln.

[3] All melting points were recorded with a modified Hershberg apparatus (Fieser "Experiments in Organic Chemistry," D. C. Heath Co., New York, N. Y., 2nd Ed., 1941, p. 327) and correspond to corrected values.

[4] Microanalysis by Microtech Laboratories, Skokie, Illinois.

[5] Marvel, Allen and Overberger, THIS JOURNAL, 68, 1088 (1946).

[6] Serijan, Hipsher and Gibbons, *ibid.*, 71, 873 (1949).

[7] Mowry, Renoll and Huber, *ibid.*, 68, 1105 (1946).

[8] Tommila and Hinshelwood, *J. Chem. Soc.*, 1801 (1938).

[9] Tommila, *Ann. Acad. Sci. Fennicae*, Ser. A57, No. 13, 3 (1941); *C. A.*, 38, 6171 (1944).

TABLE II

RATES OF SAPONIFICATION OF ETHYL ALKYLBENZOATES AT 25° AND 40° IN 56% AQUEOUS ACETONE

Substituent	$k_{25} \times 10^3$	$k_{40} \times 10^3$	ΔH_{act} kcal./mole	$\log_{10} PZ$	σ^b
m-Methyl[a]	1.686	....	14.87	8.17	−0.110
p-Methyl[a]	1.142	....	15.16	8.22	− .181
p-Isopropyl[a]	1.62	....	14.71	8.03	− .117
m-Methyl	1.75 ± 0.04	5.65 ± 0.17	14.46 ± 0.65	7.85 ± 0.47	− .102
p-Methyl	1.21 ± .01	3.96 ± .04	14.67 ± .25	7.84 ± .18	− .170
m-*t*-Butyl	1.00 ± .02	3.40 ± .10	15.12 ± .40	8.09 ± .29	− .205
p-*t*-Butyl	1.02 ± .02	3.30 ± .03	14.53 ± .26	7.67 ± .19	− .202

[a] From Tommila, ref. 9. [b] Calculated from Hammett's equation $\log k - \log k^\circ = \rho\sigma$, using $\log k^\circ = -2.513$. $\rho = 2.373$.

metric flask having a standard-taper stopper. The ester solution was prepared by diluting exactly 0.01 mole of the ester with 40 ml. of water and enough acetone to make 100 ml. in a standard-taper volumetric flask. The solutions were made up to volume at 25° and then placed in an electrically-controlled thermostat at 25° or at 40°. The thermostats were both held constant to 0.05°. After the solutions had come to the bath temperature, they were mixed through a "Y" adapter with standard-taper joints into a long-necked Pyrex flask, which was stoppered tightly and replaced in the thermostat. Mixing was complete in less than 15 seconds, both solutions flowing into the reaction flask at nearly the same rate and giving an initial concentration of 0.05 molar at 25° and of slightly less at 40° due to the expansion of the solvent.

In the cases of the *m*- and *p*-*t*-butylbenzoates, the solubilities were not sufficient to afford a 0.1 molar solution at 25°, but they did so at 40°. Hence, in the runs at 25° these solutions were prepared as usual. placed in the thermostat at 40° to effect solution, then returned to the 25° thermostat. Upon cooling at 25°, the esters separated from solution as very finely divided droplets which coalesced very slowly. When the solutions had attained the temperature of the thermostat, they were mixed in the usual fashion, giving an instantly clear solution of 0.05 molar concentration.

The velocity constants were calculated for each time interval from the simplified bimolecular equation[10] applicable for equal initial concentrations. In the runs made at 40°, correction is necessary for the change in initial concentration due to the expansion of the solvent and also for the sample volume taken with a pipet near 25° from a reaction mixture at 40°. This first correction is furnished by the data of Tommila[9] and amounts to 1.5% or an expansion from 100 ml. at 25° to 101.59 ml. at 40° giving an initial concentration of 0.04922 molar instead of 0.05 *M*. This corrected initial concentration was used in all the calculations at 40°. The second correction was arrived at by preparing a blank run in the identical manner used otherwise but containing no ester. Samples were withdrawn in the same manner employed in the normal runs, taking special care to standardize operations, and then titrated as usual. From the average amount of sodium hydroxide withdrawn, it was determined that 10 ml. withdrawn in this manner was equivalent to 10.033 ml. or 0.4938 milliequivalent measured at 40°. From this same blank run it was also possible to conclude that there was no error due to evaporation during the time the reaction flask was open for taking samples, since these samples showed no increase in sodium hydroxide titer.

The energy of activation and log *PZ* were calculated directly as parameters of the Arrhenius equation. The sigma constants were calculated from the rates at 25°, using the values of $\log k^\circ$ (−2.513) and rho ($\rho = 2.373$) given by Hammett.[10]

The results as presented in Table II give the mean values of rate constants for duplicate runs. The limits of accuracy recorded for the rate constants in Table II are those actually observed in duplicate determinations, except that a two per cent. variation has been assumed in all cases in which the observed variation was less than this. The errors in ΔE_{act} and log *PZ* were calculated by combining the lowest observed rate constant at 25° with the highest at 40° and *vice versa;* thus, these errors are maximum errors according to the data obtained.

Included in Table II for comparison are the results of Tommila[9] on saponification of ethyl *m*- and *p*-toluate and *p*-cumate.

Discussion of Results

The order of influence of alkyl groups on the saponification constants for substituted benzoate esters and on the dissociation constants of the corresponding acids, as summarized in terms of σ-constants in Table III, is quite different from the two generally accepted orders, the inductive effect in which electron donation increases regularly from methyl to ethyl to isopropyl to *t*-butyl and the Baker–Nathan[11] or hyperconjugation effect which places them in exactly the inverse order.

TABLE III

"ELECTRICAL EFFECTS" OF ALKYL GROUPS EXPRESSED AS σ-CONSTANTS FROM BENZOIC ACID DISSOCIATION CONSTANTS AND THE CORRESPONDING ESTER SAPONIFICATION RATE CONSTANTS

R	ArCOOH	ArCOOEt Tommila	ArCOOEt This invest.
p-Me	−0.170	−0.181	−0.170
p-Et	− .151	.....	.....
p-*i*-Pr	− .151	−0.117	.....
p-*t*-Bu	− .197	.....	−0.202
m-Me	− .069	−0.110	− .102
m-*t*-Bu	.....	.....	− .205

The increase in the σ-value from methyl to ethyl and isopropyl is in agreement with the Baker–Nathan order, which correctly predicts the influence of these groups in substitution[12] as well as in reactions of alkylbenzyl bromides.[12] It thus appears that we might consider the *t*-butyl group to be anomalous. This seems the more reasonable when the σ-values for this group in the meta and para positions are compared (Table III). Although the *t*-butyl group is clearly established as an ortho–para directing group, the σ-value in the meta position is slightly more negative than in the para.

In order to consider a possible explanation of the anomalous position of the *t*-butyl group, it is instructive to examine a theoretical derivation of Hammett's equation.[13]

$$k_0 = PZe^{-\Delta E^\circ/RT}$$

$$k_{\mathrm{R}} = PZe^{-(\Delta E^\circ - e_\sigma e_\rho/rD)/RT}$$

$$k_{\mathrm{R}}/k_0 = e^{e_\sigma e_\rho/rDRT}$$

$$\log k_{\mathrm{R}} - \log k_0 = [e_\sigma/2.303][e_\rho/rDRT]$$

$$e_\sigma/2.303 = \sigma; \; e_\rho/rDRT = \rho$$

For the particular case under consideration the

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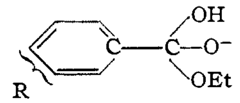
[10] Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 354.

[11] Baker and Nathan, *J. Chem. Soc.*, 1844 (1935).

[12] Berliner and Bondhus, THIS JOURNAL, 68, 2355 (1946); *ibid.*, 70, 854 (1948).

[13] Price, *Chem. Revs.*, 29, 37 (1941).

terms in the above equation can be defined from the structure of the intermediate ionic complex involved in the saponification.



The charge on the reactive ester function is represented by e_ρ, the charge induced by the group R on the nuclear carbon holding the functional group by e_σ. The distance separating these two charges in the transition complex is r and the effective dielectric between them is D.

If the PZ factors for the rates with and without a substituent R are the same and if the only additional factor in the energy of activation is the simple coulombic interaction described in the added electrical potential term involving the charges e_σ and e_ρ, then Hammett's equation will be an accurate estimate of the charge e_σ. In fact, under these circumstances, Hammett's σ-value will be directly related to the magnitude of this charge.

However, if any other important energy factor differs in going from unsubstituted to substituted benzene reactant, then the σ-value calculated from Hammett's equation will not be an accurate representation of e_σ. It is suggested that this may be the explanation of the anomalous values for the *t*-butyl group. In the process whereby saponification occurs, a neutral ester molecule is converted to a negatively charged transition complex. In a polar solvent such as aqueous acetone, the charged transition complex will be appreciably stabilized by solvation and, to whatever extent this stabilization can occur, the activation energy will be decreased. Replacing a methyl group by a *t*-butyl group on the ring, *even in the para position*, will prevent solvent dipoles from orienting in this region and will thus, to a greater or lesser degree, decrease the solvation energy. This will in effect further increase the activation energy, already raised by the negative e_σ induced by the alkyl group, and will therefore give a σ-value disproportionately more negative than e_σ. As expected for such an effect, it is evidently of considerably greater magnitude in the meta position, closer to the polar reactive center. This is apparent from the much greater difference between methyl and *t*-butyl in the meta position as compared to the para (Tables II and III).

It is suggested that this sort of steric effect on solvation energy, which is quite distinct from the direct steric influences commonly recognized, be distinguished from these usual steric effects by the name "bulk effect."

It is perhaps appropriate to point out that the similar influence of *t*-butyl and neopentyl groups on the rates of bromination of alkyl benzenes, quite unexpected on the basis of hyperconjugation effects,[14] is not nearly so surprising if one of the important effects of varying alkyl groups is a "bulk effect" on the solvation stabilization of the polar transition complex for the bromination process.

NOTRE DAME, INDIANA RECEIVED MARCH 22, 1950

[14] Berliner and Berliner, THIS JOURNAL, **71**, 1195 (1949).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

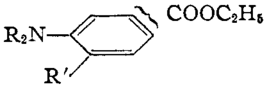
The Rates of Saponification of Some Ortho-substituted Ethyl *m*- and *p*-Aminobenzoates

BY CHARLES C. PRICE AND DWIGHT C. LINCOLN[1,2]

Steric inhibition of resonance between a dimethylamino group and a benzene ring has been measured by studying the rates of saponification of ethyl 3-dimethylamino-4-methylbenzoate and 4-dimethylamino-3-methylbenzoate. The inhibition of resonance by one ortho-methyl group markedly affects the electrical influence of the dimethylamino group in either the para or meta position to the reactive ester group, although quantitatively the influence is greater in the para position. A second order inductive or field effect is necessary to account for such a resonance influence on the meta position.

Westheimer and Metcalf[3] have shown that the influence of a dimethylamino group markedly decreasing the rate of saponification of an ethyl ester in the para position is almost completely damped by the presence of two methyl groups flanking the dimethylamino group. This evidence was interpreted as indicating a marked steric inhibition by the two *ortho*-methyl groups of resonance donation of electrons by the dimethylamino group to the para (and ortho) positions of the ring.

The purpose of the work reported herein was to use the same general experimental measurement, the rate of saponification, to estimate the effect of damped resonance on the position meta as well as para to the dimethylamino group. In order to avoid direct steric effects from a substituent ortho to the carbethoxyl group, it was possible to incorporate only one ortho-methyl group to hinder the amino group.



R and R′ = H or CH_3

Experimental[4]

m-Dimethylaminobenzoic acid was prepared through methylation of the amino acid to the hydriodide of trimethyl-*m*-benzobetaine, pyrolysis to the dimethylamino methyl ester followed by saponification, essentially according to the directions of Cumming.[5] The product melted at 150.5–151.3° (lit.[5] m.p. 151°).

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[1] Eastman Kodak Fellow, 1947–1948. Hercules Powder Company, Wilmington, Delaware.

[2] Abstracted from a portion of the Ph.D. dissertation submitted to the University of Notre Dame by Dwight C. Lincoln.

[3] Westheimer and Metcalf, THIS JOURNAL, **63**, 1339 (1941).

[4] Melting points are corrected. Analyses by Micro-Tech Laboratories, Skokie, Ill.

[5] Cumming, *Proc. Roy. Soc.* (*London*), **A78**, 103 (1906).