chloride. A total of 192.8 g. of hydrocarbon was recovered at this step.

Careful fractionation of this hydrocarbon gave 15.2% of benzene, 45.2% of *n*-butylbenzene, b.p. 96.5–97.5° at 50 mm. (99.4 mole % *n*-butylbenzene and 0.6 mole % *s*-butylbenzene by mass spectrometer analysis), 27.7% of dibutylbenzene, b.p. 160–162° at 50 mm. (at least 90 mole % *m*-di-*n*-butylbenzene), and 11.9% of a higher boiling residue.

Experiment B.—A mixture of 50.7 g. of the dibutylbenzene resulting from experiment A, 10.0 g. of aluminum chloride and 342 g. of benzene was heated at reflux, approx. 85° for 5 hours. The reaction mixture was worked up as in experiment A. Fractionation yielded, after removal of benzene, 65.4 g. of material consisting of 53.6 g. of monobutylbenzene and 11.8 g. of dibutylbenzene and residue. This represents a 75 mole % conversion of the dibutylbenzene to monobutylbenzene.

The monobutylbenzene was shown from mass spectrometer analysis to be 99.2 mole % *n*-butylbenzene and 0.8% *s*-butylbenzene.

The residue from experiment A, on heating with aluminum chloride and excess benzene, did not yield any monobutylbenzene. It is therefore believed not to be a polybutylbenzene.

PHILADELPHIA, PENNA.

[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Steric Effects. III. Alkaline Saponification of Methyl 4-x-2,6-Dimethylbenzoates[1]

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The rates of saponification for a series of methyl 4-substituted-2,6-dimethylbenzoates in 60% dioxane–40% water solution in the 82–174° temperature range have been measured. These results indicate that the reactions proceed mainly by alkyl–oxygen fission. An interpretation of the effect of ortho-methyl groups on the rho values for ionization of para substituted benzoic acids in water–dioxane and water–alcohol solutions is advanced. The density of 60% dioxane–40% water solutions in the range 25–160° has been determined.

It has long been known that the alkaline hydrolysis of 2,6-disubstituted benzoates is extremely slow. This has been ascribed to steric hindrance.[3] We thought it of interest to study the effect of various groups in the 4-position in such cases and report here on the alkaline hydrolysis of methyl 4-x-2,6-dimethylbenzoates where x is hydrogen, methyl, bromine, nitro and amino.

The hydrolyses were conveniently measured at temperatures ranging from 82 to 114° (for x = NO_2) to 120–174° (for x = NH_2) in stainless steel tubes. It was originally thought that the rates measured would be those of the typical carbonyl addition reaction. However, from the magnitudes of the Arrhenius log *PZ* terms obtained and from the value of the Hammett rho factor we are led to believe that these alkaline hydrolyses took place mainly if not completely by an SN2 type of displacement on the methyl carbon of the ester function. This type of ester cleavage has been observed previously in the reactions of methyl benzoate, mesitoate and 2,4,6-tribromobenzoate with methoxide ion[4] and in the alkaline hydrolysis of β-propiolactone.[5]

We attempted to verify this by O^{18} studies but owing to an error in procedure in two inportant cases involving benzoic esters which were used for checking purposes the results are not as clean cut as desired. Discussion of this phase will therefore be delayed until further experimental work is completed.

Experimental

Methyl 4-amino-2,6-dimethylbenzoate was prepared by reaction of diazomethane with 4-amino-2,6-dimethylbenzoic acid which was obtained essentially as described.[6] Because of the instability of the amino ester the hydrochloride was prepared. This compound crystallized in colorless needles (from aqueous methanol) which sublimed on heating.

Anal. Calcd. for $C_{10}H_{14}O_2NCl$: C, 55.7; H, 6.5; N, 6.5. Found[7]: C, 55.1, 55.1; H, 6.5, 6.5; N, 6.7, 6.5.

Methyl 4-bromo-2,6-dimethylbenzoate was prepared by esterification of 4-amino-2,6-dimethylbenzoic acid with diazomethane and diazotization of the ester in hydrobromic acid solution. The complex mercuric diazonium salt precipitated by mercuric bromide was mixed with sodium bromide and decomposed at 90–100° in a dry flask.[8] Methyl 4-bromo-2,6-dimethylbenzoate distilled at 107° at 3 mm. and crystallized from aqueous methanol in colorless crystals, m.p. 54°. The yield based on original amino acid was 24%.

Anal. Calcd. for $C_{10}H_{11}O_2Br$: C, 49.4; H, 4.6. Found: C, 49.0, 49.1; H, 4.3, 4.5.

4-Bromo-2,6-dimethylbenzoic acid was recovered as a product of the hydrolysis of its methyl ester. On recrystallization from benzene, the acid melted at 196.5–197.0°.[9]

Methyl 2,6-dimethyl-4-nitrobenzoate was prepared in 25% yield from 4-amino-2,6-dimethylbenzoic acid by esterification with diazomethane, diazotization in hydrochloric acid solution and treatment with sodium cobaltinitrite.[10] The ester distilled at 126–130° at 1 mm. and crystallized from aqueous methanol in pale yellow needles, m.p. 91.0–91.2°.

Anal. Calcd. for $C_{10}H_{11}O_4N$: C, 57.4; H, 5.3; N, 6.7. Found: C, 57.7, 57.6; H, 5.2, 5.3; N, 7.2, 7.0.

Methyl 2,6-dimethylbenzoate was prepared from 2,6-dimethylbenzoic acid by esterification with diazomethane.

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[1] Taken from the Ph.D. thesis, O.S.U., 1950, of H. L. Goering.

[2] Standard Oil Company of Indiana Fellow, 1949–1950.

[3] V. Meyer, *Ber.*, **27**, 510 (1894); V. Meyer and J. J. Sudborough, *ibid.*, **27**, 3146 (1894).

[4] J. F. Bunnett, M. M. Robison and F. C. Pennington, THIS JOURNAL, **72**, 2378 (1950). The dissociation constant for mesitoic acid reported in this paper is that recorded in "Beilstein," Vol. IX, p. 553, which is in error. The correct value of 3.75×10^{-4} was reported by M. B. Breed, Bryn Mawr College Monograph, Vol. I, p. 1 (1901). The correlation between acid strength and cleavage by methoxide reported by B., R. and P. falls down if the correct value for the strength of mesitoic acid is used.

[5] See P. D. Bartlett and G. Small, Jr., THIS JOURNAL, **72**, 4867 (1950) and references therein.

[6] W. A. Noyes, *Am. Chem. J.*, **20**, 789 (1898). Improvements suggested by Dr. T. L. Jacobs, UCLA, were incorporated and these will be described by him.

[7] Analyses by Mrs. E. H. Klotz.

[8] von Swechten, *Ber.*, **65**, 1605 (1932); M. S. Newman and P. H. Wise, THIS JOURNAL, **63**, 2847 (1941).

[9] R. C. Fuson, S. L. Scott and R. V. Lindsey, Jr., *ibid.*, **63**, 1679 (1941), give m.p. 197–198°.

[10] H. H. Hodgson and E. Marsden, *J. Chem. Soc.*, 22 (1944).

The ester was obtained as a colorless liquid, b.p. 109° at 19 mm., n^{20}_D 1.5059.

2,6-Dimethylbenzoic acid was prepared by carbonation[11] of 2,6-dimethylphenylmagnesium iodide in 44% yield. The 2,6-dimethylphenylmagnesium iodide was prepared from 2-amino-1,3-dimethylbenzene (redistilled Eastman Kodak Co. white-label) by diazotization, decomposition of the diazonium salt in the presence of potassium iodide and reaction of the iodo compound with magnesium in dry ether.

Recrystallization of 2,6-dimethylbenzoic acid from water yielded colorless crystals, m.p. 113.0–113.8°.[12]

In an attempt to apply the von Schwechten[8] procedure to the preparation of 2-bromo-1,3-dimethylbenzene, the acetone-dried complex salt decomposed vigorously at room temperature. This unusual behavior may be due to steric effects and further work here is indicated.

Methyl 2,4,6-trimethylbenzoate was prepared from the acid with diazomethane, b.p. 113–113.5° at 11 mm., n^{20}_D 1.5085.[13]

2,4,6-Trimethylbenzoic acid[11,14] was recrystallized from methanol yielding colorless crystals, m.p. 153.0–153.6°, lit. value[11] m.p. 150–151° uncor.

Dioxane was purified by the method described by Fieser.[15] After the final distillation the dioxane was kept under nitrogen in a Pyrex glass container and the contents forced out of the flask with nitrogen as needed. Doubly distilled water was used in the preparation of all solutions required for kinetic runs. Water containing approximately 1.5 mole % of O^{18} was supplied by the Stuart Oxygen Co., San Francisco, California, through the Atomic Energy Commission. Hydrochloric acid solutions were titrated against standard sodium hydroxide solutions. Barium hydroxide solutions used in back-titrations were prepared by diluting a saturated solution of C.P. barium hydroxide. These solutions were protected from atmospheric carbon dioxide by Ascarite (soda lime) absorption tubes.

Kinetic Studies.—The hydrolysis experiments were made in stainless steel tubes since Pyrex and soft glass tubes reacted with the base at the temperatures required in this study. Stainless steel nuts and gold gaskets were used to seal the tubes.

Solutions for runs were prepared by weighing the desired amount of ester into a 100-ml. volumetric flask to which was added 40 ml. of carbonate-free sodium hydroxide solution of such a strength that the final concentration of hydroxide ion was approximately twice that of the ester. The volumetric flask was then filled to the mark with purified dioxane and the solution thoroughly mixed. Pipets and volumetric flasks were calibrated.

Approximately 6 ml. of solution was transferred to each stainless tube and the tubes were flushed with purified nitrogen and sealed. The tubes were placed in a copper screen holder, immersed in the constant temperature bath, removed at regular intervals and quenched in kerosene.

The extent of reaction was determined from the loss of base during the reaction. Five ml. of the quenched reaction solution was pipetted into a known excess of standard hydrochloric acid solution and the resulting solution was back-titrated with barium hydroxide. Five ml. of methanol was added before back titration to ensure the complete solubility of the unchanged ester and of the organic acid formed in the reaction. Titrations were made in a nitrogen atmosphere using a Beckman *p*H meter, model H-2, using a glass electrode.

The rate constants were determined by use of the integrated form of the second-order rate equation $k = {}^1/t(b - a) \ln (a/b)(b - x/a - x)$, where a is the initial concentration of ester, b is the initial concentration of base, x is the amount reacted at time t, and k is the specific rate constant in liters/mole sec. The rate constants were corrected for solvent expansion by multiplying the factor, density at 25°/density at T. Results of a typical run are shown in Table I and the results obtained for the series of compounds studied are given in Table II.

TABLE I

HYDROLYSIS OF METHYL 4-BROMO-2,6-DIMETHYLBENZOATE IN 60% DIOXANE–40% WATER (BY VOLUME) SOLUTION

$T = 111.24 \pm 0.02°$, $d = 0.954$, $d_{25} = 1.036$

t, sec.	(OH^-)	(ester)	$k \times 10^3$
0	0.0405	0.01819	..
1200	.03842	.01611	2.56
3600	.03560	.01329	2.30
5100	.03373	.01142	2.49
6600	.03222	.00991	2.57
8400	.03091	.00860	2.55
10800	.02944	.00713	2.56
13200	.02796	.00565	2.71
		Av.	2.53
		Cor. for solvent expansion	2.75 l./mole sec.

TABLE II

RATE CONSTANTS FOR THE HYDROLYSIS OF METHYL 4-X-2,6-DIMETHYLBENZOATES IN 60% DIOXANE–40% WATER (BY VOLUME) SOLUTIONS

Compound	Temp., °C.	$k \times 10^3$ l./mole sec.
Methyl 4-amino-2,6-dimethylbenzoate	174.24 ± 0.02	16.1 ± 0.47
	148.98 ± .04	4.01 ± .080
	134.47 ± .03	1.63 ± .063
	120.93 ± .02	0.669 ± .023
Methyl 2,4,6-trimethylbenzoate (with 0.07 *M* mesitoate ion)	139.98 ± .05	3.64 ± .16
	130.30 ± .05	1.88 ± .096
	126.00 ± .05	1.40 ± .054
	111.44 ± .05	0.534 ± .010
Methyl 2,6-dimethylbenzoate	149.46 ± .02	8.34 ± .32
	140.10 ± .05	5.17 ± .036
	124.50 ± .06	1.50 ± .057
	102.65 ± .05	0.349 ± .011
Methyl 4-bromo-2,6-dimethylbenzoate	129.71 ± .02	9.00 ± .17
	111.24 ± .02	2.75 ± .088
	99.51 ± .03	1.31 ± .026
Methyl 2,6-dimethyl-4-nitrobenzoate	114.05 ± .02	19.0 ± .36
	105.12 ± .02	10.6 ± .13
	94.80 ± .02	5.84 ± .11
	82.83 ± .06	2.62 ± .081

The temperatures were measured by the use of a platinum resistance thermometer which was calibrated by the U. S. Bureau of Standards. The resistance of the thermometer was obtained with a Leeds and Northrup Mueller bridge. The temperature was maintained constant to within ±0.06°.

Densities.—The densities of the dioxane–water solutions used were determined with a pycnometer over the temperature range 25 to 158°. For temperatures near 100° and higher, the pycnometer was filled at room temperature and placed in a stainless steel bomb which contained 50 ml. of the dioxane–water solution. The bomb was sealed and placed into the thermostat at the desired temperature. After two hours the bomb was removed and allowed to cool slowly to room temperature. When cool, the pycnometer was weighed and the density determined. The volume of the pycnometer was corrected for glass expansion at each temperature. The values found are listed in Table III.

TABLE III

DENSITY OF 60% DIOXANE–40% WATER (BY VOLUME) SOLUTIONS

Temp., °C.	Density	Temp., °C.	Density
24.78	1.037	103.6	0.962
24.94	1.036	129.5	.934
55.0	1.010	145.8	.914
78.2	0.998	157.55	.900

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(11) R. T. Arnold, H. Bank and R. W. Liggett, THIS JOURNAL, **63** 3444 (1941).

(12) H. A. Smith and R. B. Hurley, *ibid.*, **72**, 112 (1950), report m.p. 116°.

(13) M. S. Newman, *ibid.*, **63**, 2434 (1941), reported b.p. 114.8–115.2° at 7.0-7.5 mm., n^{20}_D 1.5083.

(14) L. I. Smith, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 95.

(15) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1941, p. 369.

Ionization Constants.—The apparent ionization constants of the 2,6-dimethyl-4-x-benzoic acids were determined in 21.1 dioxane–78.9% water by weight (20% dioxane by volume at 26°) by the method of one-half end-point in the titration curve. Titrations were carried out in a nitrogen atmosphere at 26°. The *p*H value at the half-point was taken as the approximate pK_A value. The *p*H meter was standardized against standard buffers at *p*H 4 and *p*H 7. The pK_A values listed in Table IV are those obtained in this investigation and, for comparison, those obtained in 50% (vol.) alcohol for these and other acids by other investigators.[16] Also included in Table IV are pK_A values in 21.1 dioxane which have been obtained by extrapolation of pK values actually found in 26.5 and 43.5 wt. % dioxane.[17]

The values were obtained in this investigation by dissolving 0.02 to 0.03 g. of the acid in 20 ml. of the dioxane–water solution and titrating with 0.025 *N* 20% (vol.) dioxane barium hydroxide solution. An average of three values was taken as the pK_A value.

TABLE IV

APPARENT IONIZATION CONSTANTS OF VARIOUS SUBSTITUTED BENZOIC ACIDS

	In 20% dioxane		In 50% (vol.) alcohol	
Acid	pK_A	$K \times 10^5$	pK_A	$K \times 10^5$
Benzoic	4.60^a $(4.69)^b$	2.51 (2.04)	5.75^c	0.178
4-CH_3-	4.80^a	1.58	5.94^c	.115
4-Br	4.33^a	4.68	5.35^c	.447
4-NO_2	3.70^a	20.0	4.53^c	2.95
2-CH_3-	...	...	5.76^c	0.174
2,4-Di-CH_3-	...	...	6.09^c	.0812
2-CH_3-4-Br-	...	...	5.38^c	.416
2-CH_3-4-NO_2-	...	...	4.42^c	3.80
2,4,6-Tri-CH_3-	4.18^b	6.61	5.38^d	0.417
2,6-Di-CH_3-	3.98^b	10.5	5.18^d	0.661
2,6-Di-CH_3-, 4-Br-	3.68^b	20.9	4.78^d	1.66
2,6-Di-CH_3, -4-NO_2-	3.12^b	75.9	...	...

[a] Extrapolated values obtained from pK values in 26.5 and 43.5 wt. % dioxane solutions[17] containing LiCl in total ionic strength of 0.05. [b] Values obtained in this investigation in 20% (vol.) dioxane at 26°. pK_A values are readings on *p*H scale of Beckman *p*H meter, calibrated for aqueous buffer solutions, at half end-point using glass and saturated calomel electrodes without correction for liquid junction potentials. [c] Values in 50% (vol.) ethanol, ref. 16. [d] Data from J. D. Roberts and C. M. Regan, THIS JOURNAL, **76**, in press (1954).

Discussion

A plot of the second-order specific rate constant *versus* $1/T$ (°K.) is shown in Fig. 1. From the slopes of the best straight lines in this plot, the energy of activation for the hydrolysis of each of the esters was obtained. Table V is a tabulation of the rate constant at 125°, the energy of activation and the $\log_{10} PZ$ term for each reaction.

TABLE V

THE SECOND-ORDER RATE CONSTANTS, ACTIVATION ENERGIES AND LOG *PZ* FACTORS OBTAINED IN THE BASIC HYDROLYSIS OF METHYL 4-SUBSTITUTED-2,6-DIMETHYLBENZOATES AT 125° IN 60% DIOXANE–40% WATER (BY VOLUME)

Ester, benzoates	$k_{125} \times 10^3$, l./g. mole/sec.	E_{act}, kcal./mole	$\log_{10} PZ$
Methyl 4-amino-2,6-dimethyl	0.884	20.9	8.41
Methyl 2,4,6-trimethyl	1.35	21.2	8.66
Methyl 2,6-dimethyl	1.73	21.8	9.22
Methyl 4-bromo-2,6-dimethyl	6.82	19.1	8.32
Methyl 2,6-dimethyl-4-nitro	35.2	17.3	8.04

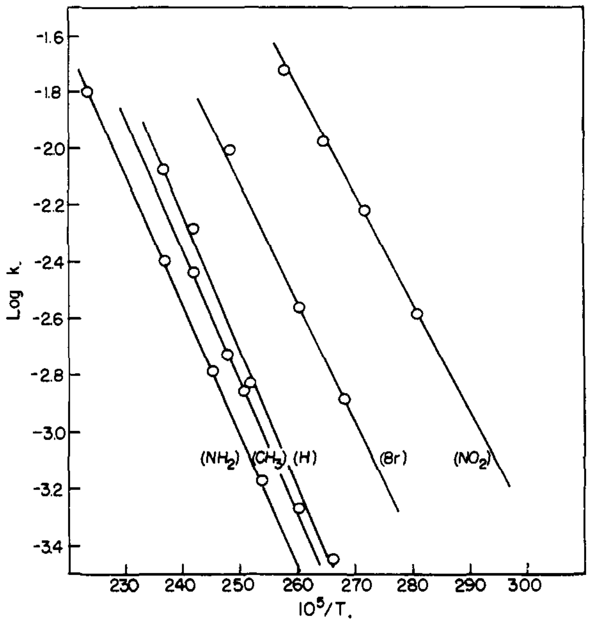

Fig. 1.—Plot of log *k vs.* the reciprocal of the absolute temperature in the basic hydrolysis of methyl 4-substituted-2,6-dimethylbenzoates.

The slow rate of hydrolysis of methyl 2,6-dimethylbenzoates is seen to be due to a high energy of activation. The log *PZ* terms are found to be entirely comparable to those found in the basic hydrolysis of meta and para mono-substituted aromatic esters.[18] The log *PZ* factors for hydrolysis of mono-ortho substituted aromatic esters, with some exceptions such as orthofluoro esters, are about tenfold smaller than their meta and para isomerides. Log *PZ* terms for hydrolysis of diortho substituted esters might thus be expected to be still smaller and since this is not observed, a change in mechanism of hydrolysis is indicated. The alkaline hydrolysis of carboxylic esters proceeds by an attack at the carbonyl carbon by the nucleophilic reagent and is accompanied by acyl–oxygen fission.[19] The other possible second-order bimolecular reaction mechanism involves an S_N2 type displacement on the alkyl carbon of the ester grouping accompanied by alkyl–oxygen fission.

Evidence in support of the second suggested mechanism in the hydrolysis of methyl 2,6-dimethylbenzoate is the value of rho[20] found for this reaction in this work. Figure 2 is a plot of log $k_{125°}$, for this reaction *versus* Hammett's sigma constants. The sigma values are used as though the 2- and 6-methyl groups were absent and 2,6-dimethylbenzoic acid is given the sigma value of 0.00. The rho value is thus found to be +1.26 with a median

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(16) J. D. Roberts, E. A. McElhill and R. Armstrong, THIS JOURNAL, **71**, 2923 (1949); J. D. Roberts and J. A. Yancey, *ibid.*, **73**, 1011 (1951); J. D. Roberts and C. M. Regan, *ibid.*, **76**, in press (1954).

(17) J. H. Elliott and M. Kilpatrick, *J. Phys. Chem.*, **45**, 485 (1941).

(18) K. Kindler, *Ann.*, **450**, 1 (1926); C. K. Ingold and W. S. Nathan, *J. Chem. Soc.*, 222 (1936); W. B. S. Newling and C. N. Hinshelwood, *ibid.*, 1357 (1936); E. Tommila and C. N. Hinshelwood, *ibid.*, 1801 (1938). E. Tommila, *Ann. Acad. Sci. Fennicae, Ser. A57*, No. 13, 3 (1941).

(19) See C. K. Ingold, "Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 754 ff, and references therein.

(20) Hammett, L. P. "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York and London, 1940, Chapter VII.

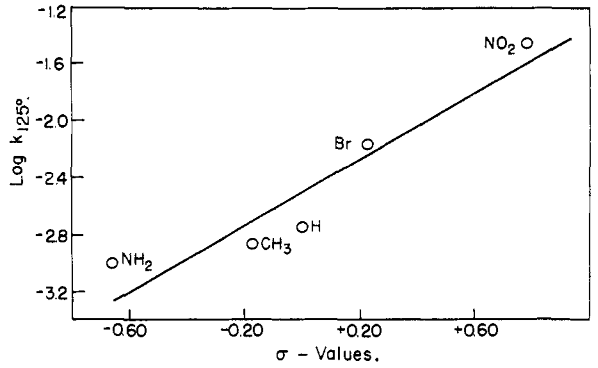

Fig. 2.—Plot of log k_{125} *vs.* Hammett's sigma values in the basic hydrolysis of methyl 4-substituted-2,6-dimethylbenzoates.

deviation, *r*, for the log *k* values of 0.15. This rho value is much lower than is the rho value, +2.498 found in the case of the basic hydrolysis of unhindered ethyl benzoates for reaction in 87.83% ethanol at 30° and +2.373 for reaction in 56% acetone at 25°. A more favorable comparison of our rho value of +1.26 is the rho value of +1.19 found for the hydrolysis of benzenesulfonic ethyl esters[20] in 30% ethanol at 25°.

Since benzenesulfonic ester hydrolysis proceeds with alkyl–oxygen fission, is not inhibited by ortho substituents, and is characterized by a rho value of +1.19, we conclude that the hydrolysis of methyl 4-x-2,6-dimethylbenzoates herein reported proceeds with alkyl–oxygen fission.[21]

Ionization Constants.—The ionization constants for a number of *p*-substituted benzoic acids have been determined in 26.5 and 43.5% (weight per cent., containing sufficient added lithium chloride to make the ionic strength 0.05)[17] dioxane–water solutions. By plotting pK_A for these acids against the sigma values listed in Hammett[21] rho values of 1.23 and 1.35 are obtained, respectively. By plotting these rho values and the value of 1.00 (standard rho for pure water) against weight per cent. of dioxane a straight line is obtained (see Fig. 3). By interpolation, a rho value of 1.17 is found for the ionization of *p*-substituted benzoic acids in the 20% dioxane–water solution used in this work. This value is quite close to the rho value of 1.12 we have found (see Fig. 4) for the 4-x-2,6-dimethylbenzoic acids in 20% dioxane–water, by assigning sigma values to these acids the same as those for the corresponding *p*-substituted acids. Thus, the sigma value for 2,6-dimethylbenzoic acid is 0.00. No pK_A values are available for the 2-methyl-4-x-benzoic acids[16] in 20% dioxane.

All three series of acids[16] have been measured in 50% alcohol and values for each have been calculated. The results are summarized in Table VI.

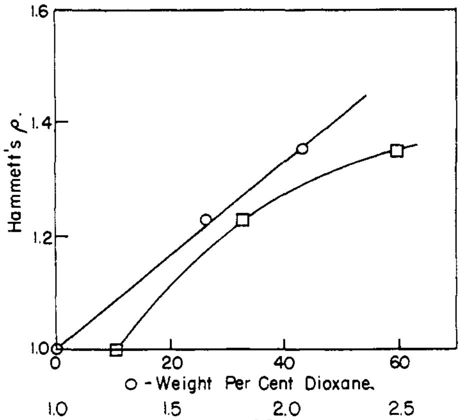

Fig. 3.—Weight per cent. dioxane and 1/*D* *vs.* Hammett's rho values for ionization of *p*-substituted benzoic acids.

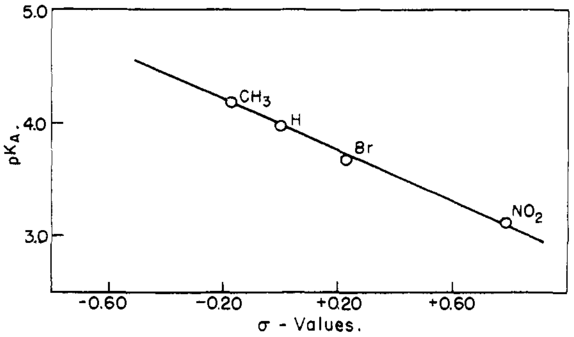

Fig. 4.—Plot of pK_A *vs.* Hammett's sigma values, in the ionization of 4-substituted-2,6-dimethylbenzoic acids.

It is possible to rationalize these results by assuming that there are two opposing effects, each of which is affected by steric factors: a polar effect and a solvation effect.

TABLE VI

RHO VALUES FOR THE IONIZATION OF SEVERAL SERIES OF BENZOIC ACIDS

Acid series	Rho in dioxane–water[a] 21.1%	26.5%	43.5%	Rho in alcohol-water 50%[b]
4-x-C_6H_5COOH	1.17[c]	1.23[d]	1.35[d]	1.46[e]
4-x-2-$CH_3C_6H_3COOH$	...	...	...	1.67[e]
4-x-2,6-$(CH_3)_2C_6H_2COOH$	1.12[f]			1.40[e]

[a] % is wt. %, total ionic strength of 0.05 attained by adding LiCl.[17] [b] By volume.[16] [c] Value obtained by interpolation on curve of Fig. 3. [d] Calculated from literature data.[17] [e] From data by Roberts, *et al.*[16] [f] Obtained in this work.

It seems likely that the polar effect of groups in the para position would be transmitted with maximum effectiveness if there were no steric factor which might prevent coplanarity of the carboxyl or carboxylate function with the ring. However, with the increasing hindrance to coplanarity offered by one and two ortho methyl groups, the transmission of polar effects should be increasingly damped and accordingly the rho values should *decrease*.[22]

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[21] It is realized, however, that the small value of rho may be due to the fact that the two ortho methyl groups prevent the ester function from coplanarity with the ring thus reducing the influence of the para substituent by interfering with resonance effects. The proof of the alkyl–oxygen fission must await further O^{18} work. However, from the work already done we can conclude that considerable reaction, at least, takes place by means of alkyl-oxygen fission.

[22] It should be emphasized that when we are discussing changes in rho values we are dealing with the sensitivity of a rate or equilibrium to changes in structure and not with changes in relative magnitudes.

We propose that the rho values for the ionization of substituted benzoic acids *increase* as the solvation of the carboxylate ion decreases.[23] With regard to the solvation of the ion, two variables may be considered: the water content of the solvent and the effect of ortho methyl groups. It seems evident that the solvation will decrease with decreased water content and with increased ortho methyl substitution. In line with the first of these hypotheses it may be noted that as the weight per cent. of dioxane varies from 0 to 21.1 to 26.5 to 43.5 the rho values vary from 1 to 1.17 to 1.23 to 1.35 for the *p*-substituted benzoic acids. Also, the rho value increases from 1 to 1.46 in going from water to 50% alcohol.

In assessing the effect of ortho methyl groups on solvation it is seen that the rho value rises from 1.46 to 1.67 in going from non-ortho substituted acids to mono-ortho methyl substituted acids. This result may be explained by assuming that the change produced by one ortho methyl group is exerted more on the solvation effect than on the polar transmission effect and would lead one to believe that in the diortho methyl substituted series an even greater rho value would be obtained. However, for the latter series the rho value falls to 1.40. This must mean that although both polar transmission and solvation are affected by the increased steric factor, the former is affected to a much greater extent. In other words, the coplanarity of the carboxylate function is not greatly affected by one ortho methyl group but is greatly affected by two ortho methyl groups.

The above explanations are obviously only working hypotheses and must be tested by further experimental approaches.

In conclusion we would like to thank Professor J. D. Roberts for valuable discussions about this work and for his data on ionization in 50% alcohol prior to publication.

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[23] In connection with solvation we assume that the solvation is effected mainly by the water and that the solvation is more pronounced in the carboxylate ion than in the acid molecule.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE RICE INSTITUTE]

Isotope Effects in Carbonium Ion Reactions. I. Determination of Solvent and Leaving Group Participations

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The solvolysis of 2-pentyl bromide and toluenesulfonate is retarded by substitution of deuterium for hydrogen in the 1- and 3-positions. The retardation is attributed to a difference in the loss of zero point energy of vibration of the bonds to these hydrogens on going to the transition state for this ionization process. The loss of zero point energy arises from a reduction in the vibrational force constants, which is believed to arise from the withdrawal of the bonding electrons to satisfy the electron deficiency on carbon by a hyperconjugation process. It is proposed that the extent of rate retardation is a measure of the importance of the hyperconjugation, and therefore a measure of electron deficiency on carbon. The solvents and the leaving group are believed to modify the electron deficiency, and the nucleophilic characters of the solvent and of the leaving group are in complete agreement with those determined by other methods. The magnitudes of the retardation by extensive deuterations vary between factors of 1.3 and 1.7.

Introduction

The extensive study of solvolytic reactions has used a great variety of methods to get information about the nature of the intermediate. Recently, emphasis has been placed on the role of the solvent. The approach to this has been based on determining the order with respect to nucleophilic "solvents,"[2] the effect of solvent changes on the rate,[3] and also by the effect of solvents on the extent of racemization of optically active esters.[4] In all cases the solvent was shown to be a very important part of the carbonium ion and the transition state leading to it. The recently observed retardation in rate of ionization of 2-pentyl chlorosulfite with deuterium substitution[5,6] suggested that the same tool would be useful in studying solvolytic reactions, and the presence of the effect in solvolytic reactions would also confirm the ionic nature of the chlorosulfite decomposition. In this paper the effect has been found in the solvolytic reactions, the magnitude of the effect is related to solvent participation and leaving group nature, and the source of the effect is examined in some detail. In a recent paper by Shiner[7] a similar retardation in the rate of solvolysis of *t*-amyl chloride has been observed.

Experimental

Materials.—The anhydrous formic acid, m.p. 4.80°, was prepared by distillation and fractional crystallization of J. T. Baker 99–100% formic acid. The acetic acid, Baker best grade glacial acid, was used without further purification. The "80%" ethanol was prepared by mixing 100 g. of U.S.P. 100% ethanol and 31.75 g. of distilled water as described by Grunwald and Winstein.[8] The method described by Cason and Mills[9] was used to prepare 2-bromopentane, b.p. 117.0–117.8° (uncor.), and 1,1,1,3,3-pentadeutero-2-bromopentane, b.p. 116.5–117.0° (uncor.), in 80% yield from phosphorus tribromide and the corresponding alcohols. The alcohols were the same ones used in the ex-

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[1] From the 1953 Ph.D. Thesis of C. E. Boozer, Ethyl Corporation Fellow 1952–1953.

[2] C. G. Swain, THIS JOURNAL, **72**, 4578 (1950).

[3] S. Winstein, E. Grunwald and H. W. Jones, *ibid.*, **73**, 2700 (1951).

[4] W. v. E. Doering and A. Streitwieser, Jr., Abstracts, 119th Meeting of the American Chemical Society, 45 M (1951).

[5] E. S. Lewis and C. E. Boozer, THIS JOURNAL, **74**, 6306 (1952).

[6] C. E. Boozer and E. S. Lewis, *ibid.*, **76**, 794 (1954).

[7] V. J. Shiner, Jr., *ibid.*, **75**, 2925 (1953).

[8] E. Grunwald and S. Winstein, *ibid.*, **70**, 846 (1948).

[9] J. Cason and R. H. Mills, *ibid.*, **73**, 354 (1951).