TABLE II

THE ANALYSIS OF THE *p*-TOLUIDIDES

No.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
I	$C_{12}H_{15}ON$	76.19	76.03 76.16	7.94	8.09 8.13
II	$C_{15}H_{23}ON$	77.19	76.86	9.94	9.98
III	$C_{17}H_{27}ON$	78.10	78.04	10.42	10.53
IV	$C_{19}H_{31}ON$	78.81	79.09	10.80	10.92
V	$C_{21}H_{35}ON$	79.42	79.10	11.12	11.19
VI	$C_{23}H_{39}ON$	79.93	79.45	11.38	11.36

nally, was saponified with alcoholic potassium hydroxide. The lead salt–ether method was then employed to separate any stearic acid from the liquid unsaturated acids. Only a small quantity of insoluble lead salt was obtained, from which 0.5 g. of free acid was isolated. This free acid was practically completely soluble in *cold* methanol; the higher saturated fatty acids are insoluble in methanol. It is unlikely, therefore, that any considerable quantity of stearic acid or higher homolog is combined in the original resin.

The Saponification Equivalents of the Methyl Esters.—The method of Chargaff[17] was used. Since no *n*-propyl alcohol was available, isobutyl alcohol was used instead; 25 to 50 mg. samples were used for each determination. The results are given in Table I.

Summary

1. The saponification of croton resin has been studied.
2. The petroleum ether–soluble fatty acids have been shown to comprise approximately 32% of the saponification products.
3. Tiglic, caprylic, capric, lauric, myristic, palmitic, oleic and linoleic acids have been shown to be present in the mixed acids obtained by saponification.

(17) Chargaff, *Z. physiol. Chem.*, **199**, 221 (1931).

COLLEGE PARK, MD. RECEIVED OCTOBER 26, 1934

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 115]

The Reactivity of Atoms and Groups in Organic Compounds. XV. The Relative Reactivities of the Hydrogen of the Hydroxyl Group in Benzoic Acid and Certain of its Derivatives[1]

BY JAMES F. NORRIS AND WILLIAM H. STRAIN

The determination of the influence of the structure of alcohols on the relative reactivities of the hydroxyl-hydrogen in these compounds[2] led to simple and definite conclusions in regard to the effect of the position of a substituent on the reactivity. The results were used in developing a new synthetic method for the preparation of ethers which contain two different alkyl radicals.[3]

As it seemed probable that a similar study of the acidic hydrogen atoms in acids would give information of value, the work was undertaken.

The results of such an investigation would show whether or not there exists a relationship between the relative ionization of acids in water and the relative reactivities of the acidic hydrogen atoms of these same acids when measured under conditions that apparently do not lead to ionization. If any such relationship were found to exist, the large number of ionization constants which have been determined would prove of great value to the organic chemist. A knowledge of the effect of the structure of the radical joined to the carboxyl group in an acid on the reactivity of the acidic hydrogen atom would be very helpful in elucidating the mechanism of esterification and other types of reactions.

The acids selected for study were benzoic acid and certain of its substitution products, because these acids have widely different ionization constants and form esters at rates that differ greatly. The reaction selected for study was that between the acids and di-*p*-tolyldiazomethane. The solvent used was toluene except with the acids which were so slightly soluble in the hydrocarbon that solutions of sufficient concentration could not be prepared with which to make accurate measurements. In the case of these acids ethyl acetate was the solvent. The particular diazo compound selected was used because it reacted with all the acids at such rates that they could be measured conveniently. Staudinger and Gaule[4] in their study of aliphatic diazo compounds made some semi-quantitative measurements of the rates at which these compounds reacted with several aliphatic acids.

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[1] From the thesis of William H. Strain submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1931.

[2] Norris and Cortese, THIS JOURNAL, **49**, 2640 (1927).

[3] Norris and Rigby, *ibid.*, **54**, 2088 (1932).

[4] Staudinger and Gaule, *Ber.*, **49**, 1897 (1916).

The reaction

$$RCOOH + N_2C(C_6H_4CH_3)_2 = N_2 + RCOOCH(C_6H_4CH_3)_2$$

involves the liberation of nitrogen and the addition of the hydrogen of the acid and the RCOO residue to the methane carbon atom. The rate at which the reaction took place was determined by noting from time to time the pressure produced by the nitrogen as it was evolved. The constant volume apparatus developed by Brönsted for the study of rates of reactions in which a gas is evolved was used with minor modifications.

When the solvent was toluene there was no evidence of the formation of an intermediate complex. Experiments in which different concentrations of the reactants were used gave the same velocity constant and furnished evidence that the reaction was one of the second order.

The results obtained with benzene as the solvent are summarized in Table I, which also contains, for comparison, the relative ionization constants and the rates of catalyzed esterification of the acids.

TABLE I

RELATIVE VISCOSITY CONSTANTS OF REACTIONS OF BENZOIC ACID AND CERTAIN SUBSTITUTION PRODUCTS

I. With di-*p*-tolyldiazomethane: solvent toluene, temperature 25°. II. Ionization constants in water at 25°.[5] III. With ethyl alcohol (first order) catalyzed by HCl at 25°.[6]

Substituent	I With diazo compound	II Ionization constants	III Catalyzed esterification
Benzoic acid	1	1	1
o-NO_2	83	104	0.065
o-Br	21.8	23	.47
o-Cl	16.5	21	..
m-Br	10.0	2.2	1.2
m-Cl	9.6	2.4	..
m-CH_3	0.6	0.82	1.1
o-CH_3	.4	1.9	0.28
o-CH_3O	.04	1.3	..

A comparison of the values given in Table I brings out the following facts. (1) The relative reactivities of the hydrogen atoms show a relationship to the relative values of the ionization constants. Acids with the higher constants have the more reactive hydrogen atoms. Factors other than the labilities of the hydrogen atoms as determined by the reaction studied are evidently involved but these are not effective enough to obscure the relationship in the case of the stronger acids. (2) The effect of the chemical nature of the substituent is marked in the two series. Chlorine, bromine and the nitro group in the ortho position greatly increase both reactivity and ionization. Methyl and methoxyl in the ortho position increase ionization and decrease reactivity. (3) There appears to be no effect of steric hindrance. (4) The relationship between the relative rates of catalyzed esterification and relative reactivities of the hydrogen atoms in the acids shows clearly that the former are not directly dependent on the latter. The significance of this fact will be treated in a later paper.

When the velocity constants of the reactions between certain of the acids and the diazo compound dissolved in ethyl acetate were determined, it was found that the reaction proceeded much more slowly than when toluene was used. For example, the relative rates in the two solvents were with *o*-bromobenzoic acid 1 to 15.4 and with *o*-nitrobenzoic acid 1 to 16. The relationship between the constants of the other acids was not the same in the two solvents. It is highly probable that ethyl acetate forms more or less stable addition products with some or all of the acids and that these influence the rates of the reactions with the diazo compounds. Kendall and Booge[7] have shown that acids form such compounds, the stabilities of which are related to the tendency of the acids to form hydrates. It appears that the results obtained when ethyl acetate was the solvent cannot be taken as a measure of the relative reactivities of the hydrogen atoms in the acids.

Preparation and Purification of Materials

Di-*p*-tolyldiazomethane.—The di-*p*-tolyldiazomethane was prepared according to the directions of Staudinger and Goldstein[8] from di-*p*-tolyl ketone hydrazone by oxidizing it with yellow mercuric oxide, the reaction being carried out in mixed pentanes. The product was recrystallized twice from pentane solutions by cooling to −20° and was then dried *in vacuo* over paraffin. The compound was prepared in small amounts and preserved in Dry-Ice until needed.

The diazo compound prepared in this way was never completely pure (*cf.* Staudinger and Goldstein). Microscopical comparison showed the presence of tetra-*p*-tolylethylene and, as described later, di-*p*-tolylketazine was present, also. Since further purification could not be effected by recrystallization, standard solutions were prepared by analyzing a prepared standard solution in the gas evolution apparatus and adding enough of the diazo compound to bring the strength up to 100%. Generally the crystalline material had a purity of about 96%. The standard solutions were prepared in amounts of 500 cc. and

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[5] "Int. Crit. Tables" (with correction of evident typographical errors).

[6] Goldschmidt, *Ber.*, **28**, 3218 (1895).

[7] Kendall and Booge, THIS JOURNAL, **38**, 1712 (1916).

[8] Staudinger and Goldstein, *Ber.*, **49**, 1924 (1916).

were used over a period of two days, within which time, as shown by occasional analyses, the strength did not vary appreciably. Except during the time of sampling the standard solutions were kept in the dark at 0°.

Toluene.—The toluene used as solvent was "Commercial Pure Toluene" (Barrett) purified by a sulfuric acid treatment and dried over sodium. The dried product was distilled and the fraction boiling at 110.4–110.8° was collected. This was stored in a glass carboy and pumped out as needed by blowing in dry air. The toluene gave a negative Laubenheimer[9] test and had a density of d^{25}_{25} 0.8642 (Young and Fortey[10] find d^{25}_{25} 0.8649).

Ethyl Acetate.—The ethyl acetate was purified according to the method of Lewis and Burrows.[11] The final product had a boiling range of 0.2°, 77.05–77.25; d^{25}_{25} 0.8940.

Acids.—The acids used were obtained, for the most part, from the Eastman Kodak Company; a few were synthesized and one was obtained from Kahlbaum. The purification was carried out by recrystallization from water or 50% water–alcohol mixture. Each acid was recrystallized several times until the melting point remained constant. The melting points were determined in an electrically heated bath with forced circulation. Thermometers with Bureau of Standards certificate were employed. The data are given with the reaction constants in Table III.

The Apparatus

The velocity constants were determined by following the rate of evolution of nitrogen as shown by pressure increase in a constant volume system. The apparatus developed by Brönsted and Duus[12] was adapted to the investigation of reactions of the second order where zero time determinations are necessary. Their apparatus consists essentially of a stoppered distilling flask connected through a glass spring to a manometer. The reaction flask employed by Brönsted and his students was equipped with an electrical device for releasing a small platinum pail containing one of the reactants. This arrangement does not lend itself to the study of bimolecular reactions. The reaction flask was modified, therefore, as follows: to the bulb (designated by A in the following considerations) of a 300-cc. Pyrex distilling flask was sealed a reservoir (B) through a stopcock of 2-mm. bore. The reservoir was tubular in shape and had a capacity of about 93 cc. A pressure equalizing tube of 3-mm. bore was sealed from near the top of the reservoir to the neck of the distilling flask. Both the reservoir and the flask proper were closed by means of ground-glass stoppers of thimble-like shape ground to fit the outside. The side arm of the distilling flask was bent up and connected through the glass spring to the manometer in substantially the same way as employed by Brönsted. The construction of the manometer was similar, also; the leg of the manometer had an internal diameter of 4 mm. and that of the mercury bulb was 56 mm. Readings were made on a zylonite scale to which a slide rule indicator was fitted and by which readings to 0.1 mm. were easily made.

The flask and its connections were immersed in a thermostat operated at 25.00 ± 0.02°. During the course of a reaction the flask was shaken mechanically at the rate of 237 vibrations per minute through an amplitude of 19 mm. The rate and amplitude gave a maximum disturbance of the volume of liquid routinely employed. Pedersen[12] has shown that the velocity of the evolution of gas is a function of the rate and amplitude of shaking of such an apparatus. For comparative purposes it is only necessary to have constant conditions.

Since the evolved nitrogen is appreciably soluble in the two solvents employed, it was necessary to know the volume of the apparatus before corrections could be applied. This was determined by noting the change in pressure produced by a known volume of air when released into the evacuated system. To this end a bulb of measured volume was sealed temporarily onto the apparatus by means of capillary tubing and stopcock. The effect of releasing this volume of air into the evacuated system was determined and the bulb removed. After making suitable calculations and estimations of the error introduced in the process of calibration, the volume was taken to be 442 ± 1 cc. with the mercury at the same level in both arms of the manometer.

Typical Determination

The determination of the constants was substantially the same as reported by Brönsted and Duus and Brönsted and King.[12] Reference to their work will aid in understanding the procedure in the case of a typical acid, *o*-chlorobenzoic acid. Into portion "A" of the reaction flask, 50.0 cc. of 0.05 *M* solution of the acid was pipetted. Reservoir "B" was shut off by turning the stopcock and 50.0 cc. of 0.05 *M* solution of di-*p*-tolyldiazomethane was transferred to it. The flask and the reservoir were stoppered and sufficient water at 25° was added to the thermostat to just cover the reaction flask and its stoppers. The thermostat, which was rapidly agitated, quickly came to the temperature of 25.00 ± 0.02°. At this point the manometer was evacuated to 0.01 mm. of mercury by means of a Cenco Hyvac pump. Then, with the shaker running, the reaction flask and its connections were pumped out for exactly five minutes. The solvent removed was caught in a trap cooled to −70°; in the case of toluene 4.0 ± 0.2 cc. was removed in this time. At the end of the five-minute pumping period the reaction flask and its system was connected to the manometer by suitable stopcock manipulation. When the manometer showed a constant reading, the shaking was interrupted and the stopcock connecting the reservoir "B" with the flask proper was opened three seconds before taking zero time. Experiment showed that five to six seconds were necessary for the discharge of 50 cc. of liquid through the stopcock. Readings of pressure were taken at suitable intervals of one, two or five minutes depending on the rate of increase of pressure. Partial data for *o*-chlorobenzoic acid are shown in Table II, where the read pressure values are given in the column labeled "Pressure."

Corrections to Readings.—The readings as obtained were in terms of centimeters of mercury.

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[9] Laubenheimer, *Ber.*, **8**, 224 (1875); *cf.* V. Meyer, *ibid.*, **16**, 1624 (1883).

[10] Young and Fortey, *J. Chem. Soc.*, **83**, 52 (1903).

[11] Lewis and Burrows, THIS JOURNAL, **34**, 1515 (1912).

[12] Brönsted and Duus, *Z. physik. Chem.*, **117**, 299 (1925); see also Brönsted and King, THIS JOURNAL, **47**, 2523 (1925); King, *ibid.*, **49**, 2689 (1927); **50**, 2089 (1928); Pedersen, *ibid.*, **49**, 2681 (1927); Brönsted and Bell, *ibid.*, **53**, 2476 (1931).

These pressure readings are in error due to (1) a change in the level of the mercury in the two arms of the manometer and (2) the absorption of the nitrogen in the solvent. The corrections were applied in each case to the ΔP values which were obtained by subtracting the pressure at zero time from that read at time, t.

The first of these corrections is readily obtained from the dimensions of the two arms of the manometer. As cited previously the mercury reservoir had an internal diameter of 56 mm. while the leg of the manometer had a diameter of 4 mm. A rise of 19.6 cm. in the leg of the manometer is accompanied by a fall of 0.1 cm. in the level of the reservoir. From these data a curve was drawn to show the correction that had to be added to the read pressure to give the true pressure. The correction is small and may be neglected without introducing too serious an error (maximum correction, 0.06 cm. Hg).

A larger error is that due to the absorption of the nitrogen by the solvent. Fortunately, data[13] on the solubility of nitrogen in various solvents are available. Where l = Concn. liq./Concn. gas, Just found that for toluene $l_{25} = 0.1235$, and for ethyl acetate $l_{25} = 0.1727$.

The correction due to gas absorption is obtained by considering what pressure the dissolved gas would have exerted had it been present in the gas space. Since the experiments are uniform in that 50 cc. of each reactant was used and of this amount a definite quantity of solvent was removed by pumping (4 cc. in the case of toluene), one calculation for each solvent is sufficient. The nitrogen evolved from 50 cc. of 0.05 M di-*p*-tolyldiazomethane would occupy 61.1 cc. at 25° and 760 mm. of mercury. From Just's data 2.02 cc. of this would be dissolved by 96 cc. of toluene, $p = 760$. Assuming adherence to Henry's law and the perfect gas law at the pressure employed, each read value of pressure is 3.3% too low.[14] The corrections were applied by means of a curve giving the value that must be added to any read pressure increase (ΔP) + manometer correction.

In Table II these corrections and the resulting corrected ΔP values are shown for *o*-chlorobenzoic acid. The reciprocals of these values and the reciprocals of the time are used in the calculation of the constants.

TABLE II

o-CHLOROBENZOIC ACID IN TOLUENE

Volume of 0.05 M diazo solution, 50.0 cc.; volume of toluene in trap, 3.8 cc.; volume of 0.05 M acid solution, 50.0 cc.; volume of solution in reaction flask, 96.2 cc.

Time, min.	Press., cm.	ΔP	Manom. corr.	Absorp. corr.	Corr. ΔP	$1/\Delta P$	$1/t$
0	3.82						
1	10.55	6.73	0.03	0.23	6.99	0.1431	
3	13.67	9.85	.04	.33	10.22	.0978	0.3333
4	14.27	10.45	.05	.35	10.85	.0922	.2500
6	14.95	11.13	.05	.38	11.56	.0865	.1667
8	15.32	11.50	.05	.39	11.94	.0837	.1250
10	15.57	11.75	.06	.40	12.21	.0819	.1000
12	15.72	11.90	.06	.40	12.36	.0809	.0833
18	16.02	12.20	.06	.42	12.68	.0789	.0556
24	16.19	12.37	.06	.42	12.85	.0778	.0417
32	16.30	12.48	.06	.42	12.96	.0772	.0333
50	16.43	12.61	.06	.43	13.10	.0763	.0200
Final	16.72	12.90	.06	.44	13.40	.0740	

The values of $1/\Delta P$ and $1/t$ are plotted in Curve I.

Calculation of the Constant.—The constants were calculated by modifying the second order equation where equal molecular concentrations are involved

$KC_0t = X/(1 - X)$ (where X is the fraction transformed at time, t)

If P_f = final pressure, ΔP_t = pressure at time t, then $X = \Delta P_t/P_f$. Substitution in the second order equation gives

$$KC_0t = \Delta P_t/(P_f - \Delta P_t)$$

The reciprocal of this expression, $1/KC_0t = (P_f - \Delta P_t)/\Delta P_t$, has the derivative, $(1/KC_0)\,\mathrm{d}\,1/t = P_f\,\mathrm{d}\,1/\Delta P_t$, or

$$KC_0 = 1/P_f \frac{\mathrm{d}\,1/t}{\mathrm{d}\,1/\Delta P_t}$$

This equation shows that the constant of the reaction may be obtained by dividing the slope of the line $(1/t)/(1/\Delta P_t)$ by P_f, the intercept of the line with the axis, $1/t = 0$. The method has the advantage that final pressures are not necessary for the determination of the constant.

In the diagram the data for six acids in toluene have been plotted. Taking the values for *o*-chlorobenzoic acid from this curve

$1/P_f = 0.0748$; $1/t = 0.2$ when $1/P_t = (0.0877 - 0.0748)$

$$KC_0 = 0.0748 \times 0.2/(0.0877 - 0.0748) = 1.079$$

Values for the several acids in the two solvents, toluene and ethyl acetate, are given in Table III.

The Mechanism of the Reaction

The mechanism of the reaction was tested by allowing unequal quantities of an acid—*m*-

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(13) Just, *Z. physik. Chem.*, **37**, 361 (1901).

(14) The gas space in the apparatus when 96 cc. of toluene is present is 442 − 96 = 346. 61.1 cc. of nitrogen confined in this space in the presence of the above amount of toluene would distribute itself as calculated.

TABLE III

VELOCITY CONSTANTS OF THE REACTIONS BETWEEN ACIDS LISTED AND DI-*p*-TOLYLDIAZOMETHANE

Solvent, toluene; $C_0 = 0.026\ M;^c$ temp., 25°; time in min.

Acid	M. p., °C.	KC_0 I	KC_0 II	KC_0 Av.	Rel. values benzoic = 1
Benzoic	121.5	0.0648	0.0622	0.0635	1
o-Methylbenzoic	104.8	.0240	.0266	.0253	0.4
m-Methylbenzoic	110.5	.0377	.0381	.0379	.6
o-Chlorobenzoic	140.6	1.079	1.012	1.045	16.5
m-Chlorobenzoic	154.7–0.8	0.612	0.610	0.611	9.6
o-Bromobenzoic	148	1.376	1.383	1.380	21.8
m-Bromobenzoic	150.6	0.646	0.654	0.650	10.2
o-Nitrobenzoic	145.2	5.27	5.27	5.27	83
o-Methoxybenzoic	97.8	0.0028			0.044[a]
o-Hydroxybenzoic	158.8	15.4–23.2			300[b]

Solvent, ethyl acetate; $C_0 = 0.029\ M;^c$ temp., 25°

					m-Bromobenzoic = 10.2
p-Chlorobenzoic	241.2	0.0352	0.0354	0.0353	4.8
o-Bromobenzoic	148	.0865	.0893	.0879	11.9
m-Bromobenzoic	150.6	.0747	.0765	.0753	10.2
p-Bromobenzoic	250.4	.0388	.0395	.0392	5.3
o-Nitrobenzoic	145.2	.328	.330	.329	44.5
m-Nitrobenzoic	141.1	.334	.339	.337	45.7
p-Nitrobenzoic	242.2	.280	.293	.287	38.8

[a] Too slow for accurate determination in an apparatus of the type used. [b] Too fast. Reaction completed in three minutes. Of qualitative interest. [c] Molarity calculated by considering amount of solvent pumped off from 0.025 *M* solution—4 cc. for toluene, 14 cc. for ethyl acetate.

bromobenzoic—to react with the diazo compound in toluene. In one case the ratio acid: di-*p*-tolyldiazomethane was 2:1, in the other 1:2.

The constants follow from the usual equation for second order reactions in which the reactants are present in unequal concentrations

$$Kt = \frac{2.303}{(C_A - C_D)} \log \frac{C_D(C_A - C_E)}{C_A(C_D - C_E)}$$

where C_A represents the concentration of the acid, C_D the diazo compound, and C_E the ester. As the measurements were made in terms of pressure, this equation must be rewritten[15]

$$Kt = \frac{2.303}{k(2P_f - P_f)} \log \frac{P_f(2P_f - P_t)}{2P_f(P_f - P_t)}$$

which becomes

$$Kt = \frac{2.303}{kP_f} \log \frac{2P_f - P_t}{2(P_f - P_t)}$$

Because of the different volume of the solution new values had to be calculated for the absorption effect. This was done as outlined above.

The average constant, *K*, when all readings are taken into account, is $Kk = 0.070$. When the acid: diazo compound ratio was reversed, practically identical results were obtained. Average of all readings, $Kk = 0.071$.

Sources of Error

The method of calculating the constants minimizes the effect of errors. Possible leaks in the apparatus would be shown up during the plotting. There remain only errors due to side reactions to be discussed. At the end of each run there was always present small amounts of di-*p*-tolylketazine in the reaction mixture. Colorimetric comparison with the standard solutions of the ketazine showed that (1) the amount present was not proportional to the time of the reaction and that (2) the total amount present could not account for more than 2–5% of the consumed diazo compound. When it was found, in addition, that the amount of free acid in the end reaction mixture was negligible, it was concluded that the ketazine present was not formed during the reaction but was an impurity in the standard solutions of the diazo compound.

The di-*p*-tolylketazine used in the colorimetric comparison was synthesized by a new procedure[16] which is presumably general for all ketazines. The Grignard compound prepared from *p*-bromotoluene was brought into reaction with *p*-tolunitrile. The resulting addition compound on treatment with iodine yielded the ketazine.

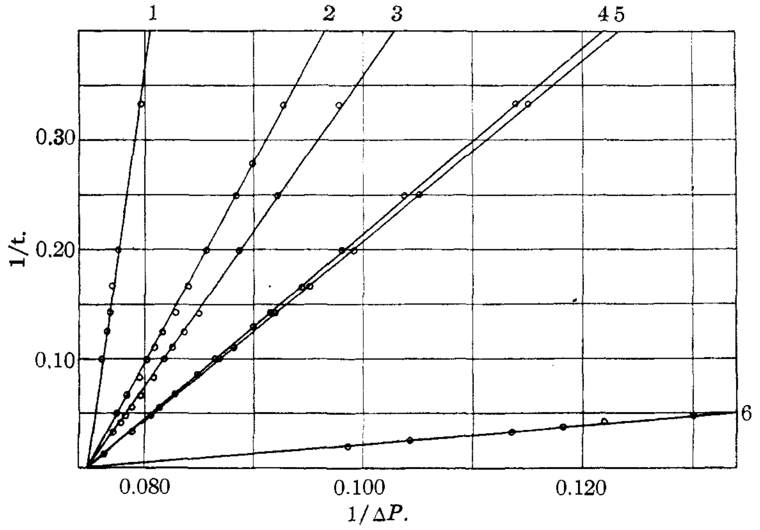

Fig. 1.—1, *o*-Nitrobenzoic acid, 2, *o*-bromo, 3, *o*-chloro, 4, *m*-bromo, 5, *m*-chloro, 6. benzoic acid.

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(15) If the case where the ratio of C_A to C_D is 2:1 is considered, it is vident that $C_A = k(2P_f)$, and $C_D = kP_f$ while $C_E = kP_t$, the *k* obviously dropping out in the logarithmic term.

(16) Suggested by Professor A. A. Morton and later described by him, THIS JOURNAL, 53, 2769 (1931).

Preparation of Di-*p*-tolylketazine.—In a 500-cc. three-necked distilling flask, fitted with mercury-seal stirrer and reflux condenser, 3.2 g. (0.125 mole) of magnesium was treated with a solution of 21.7 g. (0.118 mole) of *p*-bromotoluene in 50 cc. of dry ether. When about half of the solution had been added the mixture was warmed to start the reaction. After all had been added the mixture was refluxed with stirring for one-half hour. At the end of this time nearly all of the magnesium had gone into solution. To the Grignard compound was added, with stirring and cooling, 13 g. (0.11 mole) of *p*-tolunitrile in 20 cc. of ether. A reaction took place with the evolution of heat and after a few moments the mixture became pasty; to aid the stirring 50 cc. of ether was added at this point. After about two hours of refluxing with stirring, a solution of 16.1 g. (0.127 mole) of iodine in 50 cc. of ether was run into the mixture. No heat was evolved but the mixture became brown with the separation of a brown solid. Refluxing with stirring was continued for about six hours, after which the reaction product was poured into 400 cc. of water containing 10 g. of concd. sulfuric acid (*d* 1.84). The ketazine which separated was extracted with ether, in which it is sparingly soluble, the ether washed with a dilute solution of sodium hydroxide to remove iodine, and the solution dried over sodium sulfate. On evaporating the ether 9 g. of material was obtained. Recrystallization from absolute alcohol gave 7.5 g. (0.018 mole) of a product melting at 189–190°; yield 33%. The melting point of the ketazine was unchanged when mixed with a sample prepared by the decomposition of di-*p*-tolyldiazomethane according to the method of Staudinger and Goldstein.[8]

Anal. Calcd. for $C_{30}H_{28}N_2$: C, 86.49; H, 6.78. Found: C, 86.37; H, 6.97.

Discussion

The data obtained by carrying out the reactions in the two solvents, toluene and ethyl acetate, are not immediately compatible with the ionization constants of the acids determined in water. Wynne-Jones[17] has recently pointed out that ionization constants may vary considerably from solvent to solvent. Perhaps with further information as to the change with solvent an exact relationship can be established but at present none is apparent even if the determinations made in ethyl acetate are ruled out on the basis of intermediate compound formation of variable nature. The interesting suggestion of Sykes and Robertson[18] that activity coefficients may be of greater value than ionization constants as a measure of reactivity, if shown to be true, will have to take into account the effect of the solvent. Their determination of the activity coefficients of the mononitrobenzoic acids gives the order, *m o p*, which is the same as that reported here; the relative magnitudes are similar, too.

Sufficient data for the comparison of the effect of substitution on the reactivity in any given solvent are available only for the ortho acids in toluene. When the substituting groups are arranged in the order of increased effect on the lability of the hydroxyl-hydrogen of the carboxyl group the following series is obtained: CH_3O–, CH_3–, H–, Cl–, Br–, O_2N–.

The authors wish to acknowledge valuable suggestions from Professor George Scatchard and Dr. V. F. Harrington.

Summary

1. The rates have been determined at which benzoic acid and certain of its substitution products react with di-*p*-tolyldiazomethane in solution in toluene and in ethyl acetate.

2. The reaction in toluene was shown to be one of the second order.

3. The rates in toluene serve as a measure of the relative reactivities of the acidic hydrogen atoms in these compounds.

4. The relative reactivities bear a relationship to the relative ionization constants of the acids.

5. Due to the probable formation of complexes the relative rates in ethyl acetate were not the same as those in toluene.

6. A simplified method of calculating velocity constants has been developed for bimolecular reactions which are followed by measuring, from time to time, the pressure of a gas evolved in the reaction.

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