earlier work.[5,20] They were purified by previously described procedures.[5,20]

Solvents. Acetic acid was purified as in a previous paper.[21] Acetic acid–0.56 *M* water was made up by weighing out 10.09 g of water and diluting with purified acetic acid to 1-l. total volume. Stock solutions of acetic acid–0.56 *M* water–1.00 *M* H_2SO_4 and acetic acid–0.56 *M* water–2.00 *M* H_2SO_4 were made up as follows. A sample of reagent grade sulfuric acid (Baker and Adamson) was titrated with standard sodium hydroxide and found to be 96.25% sulfuric acid. The remaining 3.75% was assumed to be water. The stock solutions were prepared by weighing out the appropriate amount of sulfuric acid, adding enough water so that the final solution would be 0.56 *M* in water, and then diluting to volume with acetic acid. Acetic acid-*d* was prepared as described in another paper.[22] Stock solutions for the kinetic runs in deuterated solvent were prepared in the same manner as outlined above using acetic acid-*d*, deuterium oxide, and the undeuterated reagent grade sulfuric acid. (Since the final solutions for the runs in acetic acid-*d* were only 0.10 *M* in sulfuric acid, the use of undeuterated sulfuric acid instead of D_2SO_4 leads to no significant isotopic dilution of the solvent medium.)

Procedure for Kinetic Runs. The thiolsulfinate and the sulfinic acid were weighed out directly and dissolved in acetic acid–0.56 *M* water in a volumetric flask. Stock solutions of sulfuric acid and, when appropriate, of the sulfide being used as catalyst were then pipetted into the flask, and the entire solution was made up to volume with acetic acid–0.56 *M* water. (For those few runs with a stoichiometric water concentration other than 0.56 *M*, special stock solutions of acetic acid–water were prepared containing the proper amount of water.)

The final solution was transferred to a reaction vessel of the type previously used[21] to study the kinetics of the disproportionation of sulfinic acids, and the solution was then deaerated by passing prepurified nitrogen through the solution for 5 min. The reaction vessel was then placed in a constant temperature bath, and after allowing 5 min for temperature equilibration a zero-time sample was removed. This sample (1 ml) was immediately pipetted into a volumetric flask containing 95% ethanol and diluted with that solvent to a volume such that the optical density of the solution could be conveniently determined at a wavelength in the 295–310-mμ range. Either a Beckman Model DB or a Cary Model 15 spectrophotometer was used for the determination of the optical density. Other samples were removed from the reaction vessel at appropriate time intervals thereafter, and their absorbance was measured at the same wavelength after dilution with ethanol. After eight to ten half-lives an infinity point was taken in the same manner, and the experimental first-order rate constant for the run was determined from a plot of $\log(A_t - A_\infty)$ *vs.* time.

The molar extinction coefficient of Ib in 95% ethanol is 6000 at 295 mμ and 3250 at 310 mμ. In ethanol at these wavelengths the sulfinic acid has no significant absorbance at the concentrations used. The molar extinction coefficient of Ib is from six to ten times larger than the molar extinction coefficient of the thiolsulfonate formed as the major product of the thiolsulfinate–sulfinic acid reaction. It is from three to four times larger than the extinction coefficient of the disulfide formed as a minor product in the nonsulfide-catalyzed reaction. Consequently the occurrence of the thiolsulfinate–sulfinic acid reaction leads to a significant decrease in the optical density of the solution.

Product Studies of the Thiolsulfinate–Sulfinic Acid Reaction. Solutions for the various product studies were prepared in the same manner as for the kinetic studies. The reactions were then allowed to proceed for ten half-lives. At the end of this time an aliquot of the solution was removed and titrated for residual sulfinic acid content with standard sodium nitrite solution.[21] The remainder of the reaction solution was then poured into ten times its volume or water, and the resulting mixture was extracted twice with a total of 400–500 ml of ether. The ether extracts were washed several times with water and then with sodium bicarbonate solution until the washings remained slightly alkaline. After one final washing with water the ether extracts were dried over magnesium sulfate, and the ether was removed under reduced pressure. The residue was then chromatographed on acid-washed alumina to separate the products.

Any disulfide formed was eluted with hexane. Its identity was then determined by infrared and melting point comparisons with known samples of phenyl disulfide and *p*-tolyl disulfide.

The thiolsulfonate formed was eluted with hexane–benzene or benzene. The thiolsulfonate fraction was then recrystallized and the identity of the thiolsulfonate was established by melting point, mixture melting point, and infrared comparisons with samples of either *p*-tolyl *p*-toluenethiolsulfonate[21] or phenyl *p*-toluenethiolsulfonate.[23]

No other reaction products besides disulfide and thiolsulfonate were detected in any of the chromatographic fractions. In the phenyl sulfide catalyzed reaction of Ib with *p*-toluenesulfinic acid the large amount of phenyl sulfide which had to be used as catalyst, and which was recovered in the hexane eluent on chromatography, prevented any determination of the amount of phenyl disulfide formed.

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[21] J. L. Kice and K. W. Bowers, *ibid.*, **84,** 605 (1962).

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Relative Reactivities of Solid Benzoic Acids[1a]

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Abstract: Reactions of solid *meta*- or *para*-substituted benzoic acids ($RC_6H_4CO_2H$) with solid *meta*- or *para*-substituted potassium benzoates ($R'C_6H_4CO_2K$) have been carried out at 70° in sealed thin-walled glass capillary tubes or in sealed weighing bottles. For all reactions tried: (1) where R and R′ are identical, the product is always the acid salt, $(RC_6H_4CO_2)_2HK$ and (2) where R and R′ are different and Hammett's σ for R is more positive than σ for R′, the reaction, $RC_6H_4CO_2H + R'C_6H_4CO_2K \rightarrow RC_6H_4CO_2K + R'C_6H_4CO_2H$, goes to completion.

Substituent effects on equilibria and rates of reactions in solution involving *meta*- and *para*-substituted benzene derivatives have been extensively investigated and frequently correlated successfully with Hammett[2] substituent constants. The purpose of the present study was to determine if Hammett's σ obtained from studies in solution could be used successfully to predict

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[1] (a) Abstracted in part from the M.S. Thesis of E. J. W., Texas A&M University, Jan 1967. (b) To whom inquiries should be sent.

[2] D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23,** 420 (1958).

Table I. Results of the Reactions between Solid Benzoic Acids ($R'C_6H_4CO_2H$) and Solid Potassium Benzoates ($R'C_6H_4CO_2K$)

	R′										
R	*p*-NH_2	*p*-OH	*p*-*t*-Bu	*p*-CH_3	*m*-CH_3	H	*m*-OH	*p*-Cl	*m*-NO_2	*p*-NO_2	σ
p-NH_2	0[a]	−[b]									−0.66
p-OH	+[c]	0									−0.37
p-*t*-Bu		+	0	−		−					−0.197
p-CH_3			+	0		−					−0.170
m-CH_3				+	0						−0.069
H				+	+	0					0.000
m-OH						+	0				0.121
p-Cl						+	+	0			0.227
m-NO_2						+		+	0	−	0.710
p-NO_2						+		+	+	0	0.778

[a] Zeros denote reactions in which $(RC_6H_4CO_2)_2HK$ is produced. [b] Minus signs denote reactions which did not occur. [c] Plus signs denote reactions which did occur.

the products of reactions between solids. A series of reactions between solid *meta-* or *para*-substituted benzoic acids and solid *meta-* or *para*-substituted potassium benzoate salts was chosen for study because this series is directly related to the Hammett substituent constants.

Results and Discussion

The results obtained for the reactions attempted between the solid benzoic acids and solid potassium benzoates are shown in Table I. The following notation is used in Table I: plus signs for reactions between an acid and a salt to form a new acid and a new salt, zeros for reactions in which the acid salt, $(RC_6H_4CO_2)_2HK$, was the product, and minus signs for reactions which did not occur.

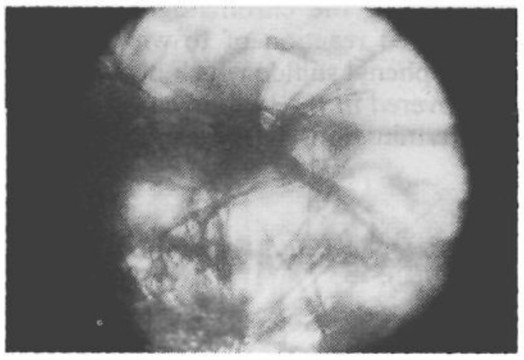

Figure 1. Photomicrograph (175×) of the reaction between *p*-*t*-butylbenzoic acid and potassium *p*-*t*-butylbenzoate after 16-hr reaction time.

The reaction between the acid and salt involved the transport of the acid through the vapor phase to the surface of the salt crystal. This was shown by the decrease in the size of the acid crystal and the increase in the size of the "salt" crystal. For example, a typical photomicrograph, Figure 1, of the reaction between *p*-*t*-butylbenzoic acid and potassium *p*-*t*-butylbenzoate shows the growth of whisker-like protuberances of the reaction product on the surface of the salt crystal. After the whiskers virtually covered the salt surface, an X-ray powder pattern of the product was made. This powder pattern matched identically that of synthetically prepared potassium hydrogen di-*p*-*t*-butylbenzoate. No evidence of reaction on the surface of the acid was ever observed.

For $RC_6H_4CO_2H + R'C_6H_4CO_2K$ (denoted by plus or minus signs in Table I), the reactions followed the same order as that which would be expected from the relative acid strengths in aqueous solution. In turn, these acidities in aqueous solution define the values of the Hammett substituent constants.

In the case of $RC_6H_4CO_2H + RC_6H_4CO_2K$ (denoted by zeros in Table I), the product was always $(RC_6H_4CO_2)_2HK$. For one case, when *p*-nitrobenzoic acid was treated with potassium hydrogen dibenzoate, the products were potassium *p*-nitrobenzoate and benzoic acid. This indicates the following relative order of free energies: (p-$O_2NC_6H_4CO_2H + C_6H_5CO_2K + C_6H_5CO_2H$) > [$p$-$O_2NC_6H_4CO_2H + (C_6H_5CO_2)_2HK$] > ($p$-$O_2NC_6H_4CO_2K + 2C_6H_5CO_2H$).

Thus, it has been shown that the relative reactivities of solid *meta-* or *para*-substituted benzoic acids in these reactions can be predicted from Hammett's σ constants. Also, it has been shown in all cases studied that a solid acid reacts with its solid potassium salt to form the potassium acid salt.

Because only the sign and not the magnitude of the change in Gibbs free energy, ΔG, was obtained for these reactions, a numerical correlation of the type obtained for reactions occurring in solution was not possible here.

It would be desirable to extend this study to include other solids and other reactions in order to determine whether the effect of substituents upon solid-state reactions would be that predicted from Hammett σ constants or whether other effects including crystal lattice energies would overshadow the substituent effects.

One very favorable aspect of reactions that involve only solids is that they should be complete if they occur at all, barring such complications as the formation of solid solutions or of mixed salts.[3] One can immediately see the utility of these reactions as a preparative method since there are many reactions which in solution go only partially to completion because of the establishment of an equilibrium with appreciable amounts of reactants and products present. It is apparent that if the course of reactions between pure solids can be predicted, a means of deliberate preparation of organic materials in 100% yield may become available by their use. One instance of such a use of this method in preparative work was reported by Gluzman[4] who investigated the acylation of solid amines with solid acylating agents. A marked increase in yields was reported when no solvent was present. His work was not sufficiently

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(3) E. A. Guggenheim, "Thermodynamics," 3rd ed, North-Holland Publishing Co., Amsterdam, 1957, p 316.

(4) M. Kh. Gluzman and D. E. Plotkina, *Vch. Zap. Khar'kovsk. Gos. Univ. Tr. Khim. Fak. i Nauchn. Isseld. Inst. Khim.*, [14] **71,** 187 (1956); *Chem. Abstr.*, **54,** 4347*e* (1960).

complete to allow the assessment of the effect of substituents upon the course of these solid-state reactions.

Experimental Section

Materials. Spectroquality methanol, absolute ethanol, benzene, and N,N-dimethylformamide were purchased from commercial sources.

Benzene was purified by distillation through a 60 × 1.3 cm column packed with 5-mm glass helices. Only the middle fraction boiling at 80.1° was collected. N,N-Dimethylformamide was purified in a similar manner with the fraction boiling at 153° being collected. The refractive indices of all the solvents agreed satisfactorily with previously reported values.

The substituted benzoic acids were also purchased from commercial sources and were recrystallized from the first three solvents mentioned above and dried under vacuum over $CaCl_2$. Melting points of the purified acids agreed satisfactorily with those previously reported in the literature.

Potassium methoxide was prepared by the reaction of metallic potassium with methanol. The basicity of the resulting solution was determined by titration against potassium hydrogen phthalate using phenolphthalein as indicator. The solution was blanketed with nitrogen and stored in a 500-ml polyethylene flask. Periodic checks were made on the normality of the standard solution.

Potassium salts of the acids were prepared by dissolving 0.1 mole of the acid in methanol and adding the calculated volume of potassium methoxide. The solvent was partially evaporated and the product recrystallized from methanol. The salts were oven dried at 105° and stored in a vacuum desiccator over $CaCl_2$.

Potassium acid salts were prepared by a procedure similar to that described above for the normal salts; however, only one-half the equivalent amount of potassium methoxide was added to the acid. After recrystallization, the acid salts were dried and stored under vacuum over $CaCl_2$.

Single crystals of the benzoic acids were grown from the various solvents used in the recrystallizations. Salt and acid salt crystals obtained from methanol were found to be almost amorphous after drying. N,N-Dimethylformamide was a suitable solvent for growing more stable crystals of most of these materials but even these crystals deteriorated after 2- or 3- weeks storage under vacuum over $CaCl_2$. No crystals were obtained for the salts of *p*-amino, *p*-hydroxy, *m*-methyl, or *m*-hydroxy benzoic acids.

Procedure for the Reactions. The reactions involving the various acid and salt crystals were carried out in 0.5-mm, thin-walled (0.01 mm) glass capillary tubes.[5] A single crystal of a salt was placed in end-to-end contact with a single crystal of an acid in the capillary tube which was then sealed. This was placed in a test tube and heated at 70° for 72 hr in an oven. The sample was removed from the oven and examined under a Bausch and Lomb petrographic polarizing microscope at 8-hr intervals to visually observe the progress of the reaction. Photomicrographs of some of the reactions were taken with a Bausch and Lomb 35-mm Model N eyepiece camera.

For those salts for which no single crystals were available, a different technique was used. The salt and acid were powdered, and stoichiometric amounts were mixed and heated in a closed weighing bottle at 70° for 72 hr.

X-Ray powder patterns were obtained by means of a Philips 57.3-mm diameter powder camera with Zr-filtered Mo radiation for all of the individual acids and salts, the mixtures of reactants, and expected products.

These patterns were used for the identification of the product in the case of the reaction, $RC_6H_4CO_2H + RC_6H_4CO_2K \rightarrow (RC_6H_4CO_2)_2HK$, and for verification of the reaction, $RC_6H_4CO_2H + R'C_6H_4CO_2K \rightarrow RC_6H_4CO_2K + R'C_6H_4CO_2H$. Patterns made of the reaction product, $(RC_6H_4CO_2)_2HK$, and of synthetically prepared $(RC_6H_4CO_2)_2HK$ were compared visually and found to be identical in all cases. In the other reactions, stoichiometric amounts of the expected products were mixed, powdered, and examined with X-rays. Visual comparison of the patterns of the reaction products and the prepared mixtures were then carried out.

Where single crystals of both reactants were available, the capillary in which the reaction had been carried out was mounted directly in the powder camera. Otherwise, the product obtained in the closed weighing bottle was powdered and a sample placed in a 0.5-mm, thin-walled glass capillary for mounting in the X-ray camera.

Determination of Densities. The densities of the salts and acids not previously reported were determined at 30° by the volume displacement method.[6] For the salts, *n*-heptane was found to be the most suitable liquid for the determinations. *n*-Undecane was found to be a suitable liquid for the acid density determinations. Densities found for $RC_6H_4CO_2K$ (R first and density in g/cc second): H, 1.537; 4-$(CH_3)_3C$, 1.235; 4-CH_3, 1.453; 3-CH_3, 1.338; 4-NO_2, 1.574; 3-NO_2, 1.626; 4-OH, 1.578; 4-NH_2, 1.566; 3-OH, 1.614; 4-Cl, 1.698. Densities found for $RC_6H_4CO_2H$ (R first and density in g/cc second): 4-$(CH_3)_3C$, 1.045; 4-CH_3, 1.255; 3-CH_3, 1.245.

Acknowledgment. This study was supported in part by a research grant from the Robert A. Welch Foundation.

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(5) Caine Sales Co., Chicago, Ill.

(6) N. Bauer, "Physical Methods of Organic Chemistry," Vol. I, Part 1, 2nd ed, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., p 288.