Free Radical Aromatic Substitution. III. The Relative Reactivities of Benzene, Benzonitrile and Methyl Benzenesulfonate toward Phenyl Radical Attack[1,2]

BY RALPH L. DANNLEY AND EARL C. GREGG, JR.

Benzoyl peroxide has been thermally decomposed in three equimolecular binary mixtures of ring compounds. By comparing the yields of biaryls produced from the competitive mononuclear aromatic solvents, the following relative reactivities toward phenyl radical attack have been established: pyridine–benzene, 1.5:1.0; pyridine–benzonitrile, 1.0:2.4; methyl benzenesulfonate–chlorobenzene, 1.1:1.0. The individual biaryl fractions have been analyzed by means of their infrared absorption spectra to determine the percentages of *ortho*, *meta* and *para* isomers produced. The *ortho* isomer was predominant (roughly 60%) in all cases, with the *meta* and *para* isomers in approximately statistical ratio to one another except in the substitution of benzonitrile (*meta* 10%, *para* 30%). Determination of the solvent nuclei incorporated in the high molecular weight residues has given some indication of the composition of these tars.

The present paper is a continuation of an investigation of the relative reactivities of benzene derivatives toward phenyl radical attack. Pyridine has been used as a reference material in the previous work[3] for the solubility of its derivatives in aqueous acid facilitates their isolation and purification. In the present paper, the activity of pyridine is related to that of benzene which is obviously the most desirable primary reference standard in studies of aromatic compounds. Radioactive benzene has been used to permit measurement of benzene nuclei incorporated in unidentified high molecular weight residues.

In ionic aromatic substitution reactions, the dipole moment of benzene derivatives has been related to their orientation influences.[4] The possibility that the dipole moment might also be of consequence in free radical substitution prompted the investigation of benzonitrile and methyl benzenesulfonate in the present work, for these compounds have high dipole moments as well as being excellent representatives of the multiple bond type substituents which have characteristic influences in ionic reactions. The reactivity of methyl benzenesulfonate was related to chlorobenzene as a reference material in place of pyridine with which the sulfonate combines to form a quaternary salt.

Experimental

All infrared spectra were measured as films of *ca.* 0.001 in. thickness with a Perkins–Elmer model 12A spectrometer. The composition of isomeric mixtures was determined by comparison of the spectra of unknown mixtures to the spectra of known artificial mixtures of pure isomers until duplication was obtained. Comparison measurements were taken from samples contained in the same cell of fixed thickness. In the spectrum of each of the isomeric mixtures absorption peaks of measurable intensity characteristic of at least two of the three components were obtained.[5]

(1) Taken from a thesis submitted by Earl C. Gregg, Jr., to the Graduate School, Western Reserve University, in partial fulfillment of the requirements for the doctor's degree.

(2) Presented at the Buffalo meeting of the American Chemical Society, March, 1952.

(3) R. L. Dannley, E. C. Gregg, R. E. Phelps and C. B. Coleman, THIS JOURNAL, 76, 445 (1954).

(4) W. J. Svirbely and J. C. Warner, *ibid.*, 57, 655 (1935).

(5) The spectra of the biphenylcarbonitriles and methyl phenyl benzenesulfonates are reported for the first time and have been deposited as Document number 4195 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting in advance $1.25 for photoprints, or $1.25 for 35 mm. microfilm by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

The preparation of *o*-, *m*- and *p*-chlorobiphenyls, *o*-, *m*- and *p*-phenylpyridines, and methyl *o*-, *m*- and *p*-phenylbenzoates was described in a previous communication.[3]

o- and *p*-aminobiphenyls were obtained from the Monsanto Chemical Co.

m-Aminobiphenyl.—*m*-Nitroaniline (Eastman Kodak Co.) was converted to *m*-nitrobiphenyl by the Gomberg[6] reaction and the nitrobiphenyl was hydrogenated over Raney nickel at 120° in ethanol solution contained in a stainless steel bomb to yield *m*-aminobiphenyl, b.p. 125–130° (1 mm.).

Methyl Ester of o-Phenylbenzenesulfonic Acid.—Benzidine was converted to *o*-phenylbenzenesulfonyl chloride according to the method of Courtot.[7] The sulfonyl chloride was converted to the methyl ester of *o*-phenylbenzenesulfonic acid by the action of an equivalent amount of sodium methoxide in methanol. The methyl ester was crystallized from petroleum ether; m.p. 83.5–85°. *Anal.* Calcd. for $C_{13}H_{12}O_3S$: C, 62.88; H, 4.83. Found: C, 63.26, 63.10; H, 4.70, 4.69.

Methyl Ester of m-Phenylbenzenesulfonic Acid.—*p*-Aminobiphenyl was converted to *p*-aminobiphenyl-*m*-sulfonic acid according to the method of Jones.[8] This acid was deaminated by diazotizing it in aqueous sulfuric acid with sodium nitrite solution and treating the diazonium salt with ethanol and copper powder. The ethanol solution was concentrated and added to an excess of concentrated solution of methanolic potassium hydroxide to precipitate the potassium salt which was filtered and dried. This salt was treated with excess phosphorus pentachloride and the reaction mixture was extracted with petroleum ether. The petroleum ether extract was washed with water and evaporated to yield the sulfonyl chloride, a pale yellow liquid which crystallized on standing; m.p. 37–40°, 18% yield, 13.4 g. (0.054 mole).

The sulfonyl chloride was dissolved in 50 ml. of methanol and treated with 1.2 g. (0.05 mole) of sodium. The reaction mixture was dissolved in water and the oil liberated was extracted with chloroform. The chloroform extract was dried and evaporated. The residue was distilled at reduced pressure; b.p. 150–160° (0.3 mm.), yield 5 g. (0.02 mole). *Anal.* Calcd. for $C_{13}H_{12}O_3S$: C, 62.88; H, 4.83. Found: C, 63.01, 62.88; H, 4.90, 5.07.

Methyl Ester of p-Phenylbenzenesulfonic Acid.—Xenylsulfonyl chloride was prepared according to the method of Gabriel.[9] Five grams (0.02 mole) of xenylsulfonyl chloride was dissolved in 50 ml. of methanol and treated with 0.46 g. (0.02 mole) of sodium in 25 ml. of methanol. The reaction mixture was poured into water and the precipitate which formed was filtered and dried; yield 3.6 g.; m.p. 76–77° after one crystallization from petroleum ether. *Anal.* Calcd. for $C_{13}H_{12}O_3S$: C, 62.88; H, 4.83. Found: C, 62.43, 62.41; H, 4.81, 4.91.

Biphenylcarbonitriles.—*o*-, *m*- and *p*-Biphenylcarbonitriles were prepared from the corresponding aminobiphenyls by the Sandmeyer reaction and isolated by distillation at reduced pressure, b.p. 170–175° (9 mm.); *o*-biphenylcarbo-

(6) M. Gomberg and W. E. Bachmann, THIS JOURNAL, 46, 2339 (1924).

(7) Ch. Courtot and R. Evain, *Bull. soc. chim.*, [4] 49, 527, 1555 (1931).

(8) J. E. Jones, *J. Org. Chem.*, 10, 537 (1945).

(9) S. Gabriel and A. Deutsch, *Ber.*, 13, 386 (1880).

nitrile, m.p. 30–32°, lit. m.p. 37°[10]; *m*-biphenylcarbonitrile, m.p. 43–45° after one crystallization from methanol, lit. m.p. 49°[6]; *p*-biphenylcarbonitrile, m.p. 85–86° after one crystallization from petroleum ether, lit. m.p. 86°.[11]

Reaction of Benzoyl Peroxide with Methyl Benzenesulfonate and Chlorobenzene.—A slurry of 124 g. (0.500 mole) of 97.8% pure benzoyl peroxide (Lucidol) in 300 ml. of a mixture of 450 g. (4.0 moles) of chlorobenzene and 688 g. (4.0 moles) of methyl benzenesulfonate was added to the balance of the solvent mixture maintained at 70 ± 1°. The addition required two hours, after which the reaction mixture was maintained at 70 ± 1° for 54 hours. The yield of carbon dioxide collected in an ascarite train was 16.50 g. (0.375 mole).

The reaction mixture was divided into two portions and each was extracted with two 200-ml. portions of 10% aqueous sodium hydroxide followed by two 200-ml. portions of water. There was isolated 64.3 g. of benzoic acid which also contained some isomeric phenylbenzoic acids. During this operation there was formed by hydrolysis 18.1 g. (0.10 mole) of sodium benzenesulfonate which precipitated and which was identified as the benzenesulfonamide.

The organic raffinate was distilled at pressures ranging from 155 to 2 mm. to separate it into three fractions: a chlorobenzene fraction, a methyl benzenesulfonate fraction, and a distilland of higher boiling compounds. The chlorobenzene fraction was uncontaminated. The methyl benzenesulfonate fraction contained any chlorobiphenyls formed during the reaction and some benzoic acid. To isolate the chlorobiphenyls the methyl benzenesulfonate was hydrolyzed with 3.74 moles of potassium hydroxide in 3 l. of methanol. Crystals of potassium benzenesulfonate formed. These were separated by filtration, dissolved in a minimum of water and extracted with ether to remove chlorobiphenyls adhering to the crystals. The aqueous layer was acidified and extracted again to recover any benzoic acid. The ether extracts were combined with the methanolic filtrate which was then distilled at atmospheric pressure. Periodically the distillation was interrupted, the distilland was cooled, a crop of crystals removed and treated as just described. This procedure was continued until the distilland temperature rose to 100°. The distilland was dissolved in water and treated as described for the crystals mentioned above, except that the ether solutions of chlorobiphenyls were kept separate. There was isolated 8.9 g. of benzoic acid and 23.7 g. (0.126 mole) of chlorobiphenyls. Analysis by infrared methods showed the isomeric composition of the chlorobiphenyls to be 64% *o*-, 23% *m*- and 13% *p*-chlorobiphenyl.

The benzoic acid fractions were combined and a portion treated with diazomethane to permit isolation and analysis of any isomeric phenylbenzoic acids present as described in a previous communication.[3] From the reaction mixture there was isolated 68.8 g. (0.565 mole) of benzoic acid and 4.4 g. (0.022 mole) of isomeric phenylbenzoic acids. Analysis by infrared methods showed the isomeric composition of the phenylbenzoic acids to be 59% *o*-, 15% *m*- and 26% *p*-phenylbenzoic acid, determined as the methyl esters.

The distilland fraction of the original reaction mixture contained any methyl biphenylsulfonates formed. The distilland fraction was extracted with ether, the ether evaporated, and the residual material extracted with petroleum ether. The residues from the two extractions were combined; weight 17.8 g. The petroleum ether extract upon evaporation weighed 39.9 g. and an infrared spectrum of it showed the presence of the three isomeric methyl biphenylsulfonates along with other compounds not separated by the extraction. To determine the amount of methyl biphenylsulfonates present in the mixture, a portion of it was hydrolyzed with excess methanolic potassium hydroxide and then diluted with three volumes of water which liberated 11.2% of a water insoluble oil. The solution was then acidified which liberated 5.9% of an acid insoluble phenolic oil. Therefore, the petroleum ether extract contained 83% isomeric methyl biphenylsulfonates or 33.0 g. (0.133 mole).

Analysis of the petroleum ether extract was effected by infrared methods. The impurities, isolated as described above, were combined in the ratio determined by analysis

with known mixtures of methyl biphenylsulfonates until duplication of the methyl biphenylsulfonate fraction spectrum was obtained. The composition of the methyl biphenylsulfonates was found to be methyl 53% *o*-, 33% *m*-, 14% *p*-biphenylsulfonate.

The residues from the ether extractions of the distilland were combined in proper ratio with the impurities isolated from the hydrolysis of the methyl biphenylsulfonates and analyzed for chlorine and sulfur content: % S, 8.36, 8.34; % Cl, 3.10, 3.12.

Reaction of Benzoyl Peroxide with Benzonitrile and Pyridine.—This reaction was conducted in a manner identical with the methyl benzenesulfonate reaction. From 124 g. (0.500 mole) of 97.7% benzoyl peroxide acting on a mixture of 412 g. (4.0 moles) of aniline-free benzonitrile and 316 g. (4.0 mole) of pyridine was obtained 13.54 g. (0.308 mole) of carbon dioxide.

The unreacted solvents were removed by distillation at reduced pressure and the distilland was dissolved in dry benzene. Benzoic acid was removed by passing anhydrous ammonia into the benzene solution and the resulting ammonium benzoate was removed by filtration in an amount equivalent to 69.9 g. of benzoic acid. Also 2.6 g. of benzamide and 3.05 g. of benzoic acid were recovered from the reaction mixture during subsequent operations. Hence a total of 74.0 g. (0.607 mole) of benzoic acid was isolated. The benzene filtrate was concentrated and extracted quickly with three 100-ml. portions of chilled 6 *N* hydrochloric acid which removed 10.1 g. (0.065 mole) of isomeric phenylpyridines and 2.5 g. of residue. Infrared analysis of the phenylpyridines showed them to be 58% *o*-, 28% *m*- and 14% *p*-phenylpyridine.

The benzene raffinate from the above extraction was fractionated at reduced pressure. The fraction of b.p. 105–155° (1 mm.) was collected as biphenylcarbonitriles. An infrared spectrum showed carbonyl containing compounds in this fraction which was therefore dissolved in ether, extracted with dilute aqueous sodium hydroxide, subsequently dried and treated with 0.20 g. of LiAlH₄. This treatment successfully removed the impurities, and infrared analysis showed the composition of the isomeric biphenylcarbonitriles to be 60% *o*-, 10% *m*- and 30% *p*-biphenylcarbonitrile. The yield of biphenylcarbonitriles was 27.8 g. (0.155 mole).

The residues obtained were combined and analyzed for nitrogen content: % N, 6.04.

Reaction I of Benzoyl Peroxide with Benzene and Pyridine.—This reaction was conducted like the methyl benzenesulfonate reaction except that the reaction time was 26 hours. From 124 g. (0.500 mole) of benzoyl peroxide (97.8% pure) acting on a mixture of 312 g. (4.0 moles) of thiophene-free benzene and 316 g. (4.0 moles) of pyridine there was obtained 18.41 g. (0.418 mole) of carbon dioxide.

The unreacted solvents were removed by distillation and benzoic acids were removed by extraction of a benzene solution of the distilland with aqueous sodium hydroxide. A total of 0.481 mole of benzoic acid and 0.090 mole of isomeric phenylbenzoic acids was isolated and represented 0.571 mole of benzoic acids.

The benzene raffinate was extracted with aqueous sulfuric acid and 17.2 g. (0.111 mole) of isomeric phenylpyridines along with 2.9 g. of residue were isolated. The isomeric composition of the phenylpyridines was determined by infrared methods and found to be 58% *o*-, 28% *m*- and 14% *p*-phenylpyridines.

The benzene raffinate from the acid extraction was fractionated at reduced pressure. The fraction of b.p. 83–90° (1 mm.) was collected as impure biphenyl. This fraction was washed with aqueous potassium hydroxide and there remained 11.2 g. (0.073 mole) of biphenyl, m.p. 68–69°. A mixed melting point with an authentic sample showed no depression.

The residues from the biphenyl and phenylpyridines distillation were combined and analyzed for nitrogen content; % N, 3.03.

Reaction II of Benzoyl Peroxide with Benzene and Pyridine.—A duplicate reaction was run on the benzene–pyridine solvent mixture using the same amounts of components. There was obtained 18.03 g. (0.410 mole) of carbon dioxide, 0.570 mole of benzoic acids, 16.0 g. (0.103 mole) of isomeric phenylpyridines and 10.2 g. (0.065 mole) of biphenyl.

The isomer analysis of the phenylpyridine fraction re-

(10) S. H. Zaheer and S. A. Fahseeh, *J. Indian Chem. Soc.*, **21**, 27 (1944).

(11) M. Pestemer and E. Mayer-Pitsch, *Monatsh.*, **70**, 104 (1937).

mained unchanged from the previous reaction, *i.e.*, 58% *o*-, 28% *m*- and 14% *p*-phenylpyridine.

Reaction III of Benzoyl Peroxide with Pyridine and Radioactive Benzene.—From 62.0 g. (0.250 mole) of 97.8% benzoyl peroxide acting on a mixture of 158 g. (2.00 moles) of pyridine and 156 g. (2.00 moles) of thiophene-free benzene which contained 0.51 millicurie of radioactive benzene (Tracerlabs, Inc.) there was obtained 9.28 g. (0.211 mole) of carbon dioxide. Since only the tarry residue of this reaction was of interest, it was the only fraction isolated. There was obtained 10.1 g. of residue which was analyzed for nitrogen content; % N, 3.18, 3.23. A count was made of the radioactivity of the residue which, compared to a count of the original solvent, permitted an estimation of the amount of solvent benzene in the residue. There was found 18.7% solvent benzene in the tarry residue. Samples of the residue and the original solvent were burned to CO_2 and precipitated as $BaCO_3$ to permit an accurate count of the radioactivity.

Results and Discussion.—The products of the reactions are listed in Table I. By comparison of the ratios of biaryls produced in the present work together with those reported in a previous paper[3] it is possible to establish Table II of relative reactivities of the parent nuclei toward attack by phenyl free radicals. Benzene has been taken as the reference material of unit reactivity. It is interesting that among the compounds studied, the one most reactive toward phenylation (benzonitrile) is also the one possessing a relatively high dipole moment.

TABLE I

Moles of products per mole of $(C_6H_5COO)_2$

Product	A C_5H_5N + C_6H_5CN	B	A C_6H_5Cl + $C_6H_5SO_3CH_3$	B	A C_5H_5N + C_6H_6	B
CO_2	0.62		0.75		0.84(0.84)[a]	
C_6H_5COOH	1.21[b]		1.13		0.96	
$C_6H_5C_6H_4COOH$	Not detd.		0.04		0.18	
Carbonyl compounds identified[c]	1.83[b]		1.92		1.98	
Carbonyl units added in $(C_6H_5COO)_2$[d]	2.04		2.04		2.04	
Biaryl from A	0.13		0.25		0.22	
Biaryl from B	0.31		0.27		0.15	
C_6H_5 radical products isolated[e]	0.44[f]		0.56		0.55	
C_6H_5 radicals from $(C_6H_5COO)_2$ in tar[g]	0.18[b]		0.19		0.29	
A in residue	0.14 max.[h]		0.04		0.11(0.09)[a]	
B in residue	0.14 max.[h]		0.12		(0.10)[a]	
Grams tar formed	31.6		44.6		20.2	

[a] Obtained in a duplicate determination using radioactive benzene. [b] Since phenylbenzoic acids were not isolated, this value is slightly high. [c] A sum of CO_2, C_6H_5COOH, and phenylbenzoic acids obtained. [d] The impurity in the $(C_6H_5COO)_2$ was assumed to be C_6H_5COOH. [e] A sum of biaryls from A and B and phenylbenzoic acids. [f] Slightly low as phenylbenzoic acids were not isolated. [g] Obtained by subtracting the moles of phenyl radical products isolated, from the phenyl radicals liberated (measured by CO_2 evolved). [h] Calculated on the basis that all of the nitrogen in the residue was present as nuclei of this type.

TABLE II

RELATIVE REACTIVITIES TOWARD PHENYL RADICAL SUBSTITUTION

Solvent	Reactivity	Solvent	Reactivity
Benzonitrile	3.7	Bromobenzene	1.4
Iodobenzene	1.7	Chlorobenzene	1.4
Pyridine	1.5	Benzene	1.0
Methyl benzenesulfonate	1.5		

The differences in quantities of phenylbenzoic acids obtained both in the present work and in the preceding paper of the series[3] are easily explained. In comparing the yields of phenylbenzoic acids produced in competitive reactions involving pyridine which may form a salt with the parent benzoic acid, it is seen that when the competitive solvents (*e.g.*, iodobenzene–pyridine) are of relatively higher reactivity toward phenylation, the benzoic acid initially formed from the peroxide does not suffer substitution. If the mixture of solvents (*e.g.*, benzene–pyridine) is of lower reactivity, the benzoic acid despite its low concentration, becomes competitive in reaction with the phenyl radical and appreciable yields of phenylbenzoic acids are obtained.

The isomeric biaryls isolated in the present work are listed in Table III. The composition of the biphenylcarbonitrile and methyl phenylbenzoate fractions correspond to invariable *ortho–para* substitution. The other three biaryl fractions, however, would be more properly described as predominately *ortho* with the *meta* and *para* isomers in statistical ratio to each other. Therefore, the so-called rule of invariable *ortho–para* substitution is of doubtful validity.

TABLE III

COMPOSITION OF ISOMERIC BIARYL FRACTIONS

	ortho, %	meta, %	para, %
Phenylpyridines	58	28	14
Chlorobiphenyls	64	23	13
Biphenylcarbonitriles	60	10	30
Methyl phenylbenzenesulfonates	53	33	14
Methyl phenylbenzoates	59	15	26

In a previous paper[3] it was observed that in competitive phenylation reactions involving pyridine, the phenylbenzoic acid fractions always were of the percentage composition: *ortho* 49, *meta* 20 and *para* 31. As the phenylbenzoic acids are probably formed by phenylation of benzoic acid originating from the peroxide, the isomer ratios of these acids obtained in pyridine solution should be affected by salt formation of the parent benzoic acid with the basic solvent. The isomer ratio reported in the chlorobenzene–methyl benzenesulfonate competitive reaction, on the other hand, should be representative of phenylation of free benzoic acid.

Some information has been obtained regarding the composition of the residues. (a) The elemental analyses show that no simple relationship exists between the quantities of parent solvents converted to biaryls and to high molecular weight compounds. This indicates that the tars are not formed by a simple polysubstitution mechanism. (b) In Table I it is seen that, with the exception of the benzonitrile experiment, a reasonably complete isolation of carbonyl compounds was obtained. Only benzonitrile, the most reactive of the compounds studied, apparently suffered considerable substitution by benzoyloxy radicals to form esters which were incorporated in unidentified tar. Such ester formation has been observed in the reaction of naphthalene derivatives with benzoyl peroxide.[12] (c) Phenyl radicals were incorporated on the residues in significant quantities in all of the reactions.

(12) R. L. Dannley and M. Gippin, THIS JOURNAL, 74, 332 (1952).

All of the conclusions presented in this paper are consistent not only with the present data but with that available in the preceding paper of this series.[3]

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CLEVELAND, OHIO

Molecular Compounds. III. The Effect of Molecular Compound Formation on the Rates of Reaction of Aniline with 2,4-Dinitrochlorobenzene

BY SIDNEY D. ROSS AND IRVING KUNTZ

The rate of reaction of aniline with 2,4-dinitrochlorobenzene has been measured in ethanol, 50% ethanol–50% ethyl acetate and ethyl acetate. In both ethanol and 50% ethanol–50% ethyl acetate at constant 2,4-dinitrochlorobenzene concentration the bimolecular rate constant decreases with increasing aniline concentration. It is shown by both kinetic analysis and spectroscopic measurements that the observed decreases in rate are attributable to molecular compound formation between aniline and 2,4-dinitrochlorobenzene. In ethyl acetate the rate constant is unchanged by increasing the aniline concentration, and in this solvent complex formation occurs, at most, to only a minor extent.

The rate of reaction of aniline with 2,4-dinitrochlorobenzene in ethanol has been measured by Rheinlander[1] and Singh and Peacock.[2] In both instances it was observed that, although individual runs gave satisfactorily linear second-order plots, the derived rate constants were not independent of the initial concentrations of aniline and 2,4-dinitrochlorobenzene. In every experiment where one reactant was kept constant and the concentration of the second reactant was increased, a lower velocity constant resulted. Singh and Peacock pointed out this anomalous effect but did not comment on it. Rheinlander noticed further that when aniline and 2,4-dinitrochlorobenzene were mixed in ethanol the solution became colored, but argued that the concentration of colored complex was not sufficient to have any observable effect on the reaction rate. In contrast to these results, Brady and Cropper,[3] who measured the rates of reaction of 2,4-dinitrochlorobenzene with a series of aliphatic amines, found that the bimolecular rate constant was independent of the initial concentrations within the accuracy of their measurements.

On the basis of current theories of molecular compound formation,[4] one would expect appreciable complex formation between 2,4-dinitrochlorobenzene and aniline but not between the former and aliphatic amines. Moreover, although color formation is an indication of molecular compound formation of the charge-transfer type, other non-colored complexes or associations, capable of affecting a reaction rate, can exist in solution.[5] Because of these considerations, we have investigated the rate of reaction of 2,4-dinitrochlorobenzene and aniline in ethanol, ethyl acetate and 50% ethanol–50% ethyl acetate at 24.4 ± 0.1° and focused our attention on the previously observed anomalies.

(1) A. H. Rheinlander, J. Chem. Soc., 3099 (1923).

(2) A. Singh and D. H. Peacock, ibid., 1410, 1411 (1935); J. Phys. Chem., 40, 669 (1936).

(3) O. L. Brady and F. R. Cropper, J. Chem. Soc., 507 (1950).

(4) (a) J. Weiss, ibid., 245 (1942); (b) R. B. Woodward, THIS JOURNAL, 64, 3058 (1942); (c) W. Brackmann, Rec. trav. chim., 68, 147 (1949); (d) R. S. Mulliken, THIS JOURNAL, 72, 600 (1950); 74, 811 (1952); J. Phys. Chem., 56, 801 (1952).

(5) S. D. Ross, M. Bassin, M. Finkelstein and W. A. Leach, THIS JOURNAL, 76, 69 (1954).

Reaction Rate Studies.—Aniline reacts with 2,4-dinitrochlorobenzene to form 2,4-dinitrodiphenylamine and hydrochloric acid. The latter product reacts rapidly with another mole of aniline to give aniline hydrochloride.
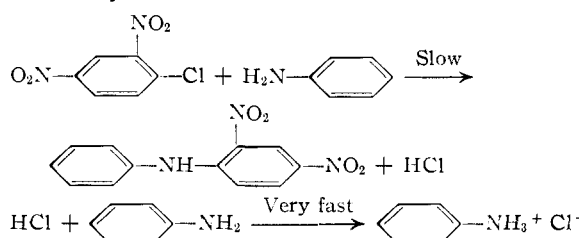
The differential equation for the above reaction sequence is given by

$$dx/dt = k^*(a - 2x)(b - x) \qquad (1)$$

where a is the initial concentration of aniline, b the initial concentration of 2,4-dinitrochlorobenzene and x is the concentration of 2,4-dinitrodiphenylamine at any time, t. For the case where a is greater than $2b$, the integrated form of this equation is

$$k^*t = \frac{2.303}{a - 2b} \cdot \log \frac{b(a - 2x)}{a(b - x)} \qquad (2)$$

We have measured the rate of this reaction in absolute ethanol at 24.4 ± 0.1°, maintaining the dinitrochlorobenzene concentration at 0.050–0.052 M and varying the aniline concentration from 0.2 to 1.0 M. As is apparent from Fig. 1, the individual runs give satisfactory second-order plots. The results, summarized in Table I, however, clearly demonstrate that the differential expression (1) does not represent an adequate mechanism for the

TABLE I

RATES OF REACTION OF 2,4-DINITROCHLOROBENZENE AND ANILINE IN ETHANOL

2,4-Dinitrochlorobenzene, mole/l.	Aniline, moles/l.	k^*, l. × mole^{-1} × hr.$^{-1}$
0.04993	0.2004	0.262
.05210	.5009	.232
.05230	.6737	.221
.04980	1.0106	.192