tion, m.p. 52–53°; literature[16] m.p. 53–55°; neutral equivalent, calcd. 132, found 130.

Dimethyl-*t*-butylacetic acid was used without further purification, m.p. 200°; literature[17] m.p. 196–197°; neutral equivalent, calcd. 144, found 146.

Ethyl-*t*-butylacetic acid was used without further purification, m.p. 79.5–80.5°; literature[18] 76–77°; neutral equivalent, calcd. 144, found 146.

Triethylacetic acid was used without further purification, m.p. 39°; literature[19] m.p. 39°; neutral equivalent, calcd. 144, found 142.

Diisopropylacetic acid was used without further purification, b.p. 82–83° at 2 mm., $n^{24.4}\text{D}$ 1.4243; neutral equivalent calcd. 144.2, found 144.7.

Ionization Constants.—The apparent ionization constants were determined in 50 volume per cent. methanol-water solution at 40° by the method of one-quarter, one-half and three-quarter points in the titration curve.

A Beckman *p*H meter, model G, was used with calomel and glass electrodes and was standardized against buffer solutions at *p*H 4 and 7.

The measurements were obtained by dissolving approximately 0.75 meq. of the acid in 100 ml. of the aqueous methanol and titrating with 0.0957 *N* methanolic sodium hydroxide.

AMES, IOWA

---

[16] J. G. Aston, J. T. Clarke, K. A. Burgess and R. B. Greenburg, THIS JOURNAL, **64**, 300 (1942).

[17] F. C. Whitmore, *et al.*, *ibid.*, **63**, 1626 (1942).

[18] K. L. Loening, A. B. Garrett and M. S. Newman, *ibid.*, **74**, 3929 (1952).

[19] F. C. Whitmore, *et al.*, *ibid.*, **64**, 2964 (1942).

[A CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

The Displacement of Halogen from 1-X-2,4-Dinitrobenzenes

BY GEORGE S. HAMMOND AND LAWRENCE R. PARKS

RECEIVED JUNE 4, 1954

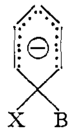
The rates of the reaction of N-methylaniline with the 1-X-2,4-dinitrobenzenes in which X is F, Cl and Br have been measured in nitrobenzene and in 99.8% ethanol as solvents. In both media the order of reactivity, at the temperatures studied, is Br > Cl > F. Preliminary estimates show that variations in the activation entropies make significant contributions to the relative reactivities. It is inferred that bond breaking must have progressed to a significant extent in the transition states.

Considerable attention has recently been directed toward the study of the nucleophilic displacement reactions of activated aryl halides.[1–9] The review of Bunnett and Zahler[1] established the frame of reference for the discussion of the mechanism of such reactions. Further discussions have been presented by Berliner and co-workers[2] and by Chapman and his co-workers.[4–7] The latter have stated the status of the problem succinctly.[6,7]

One of the striking features of the reaction is the regularity with which fluoride appears as a more reactive leaving ion than the other halide ions. This observation stands in sharp contrast to the behavior of the halides in displacements at saturated carbon atoms,[10] and the phenomenon has been the focal point of the work reported at this time.

Results and Discussion

The high reactivity of activated aryl fluorides as compared with other, similarly activated, aryl halides may be taken as an implication that bond-breaking has not made nearly as much progress in the transition states of the rate-controlling steps as is inevitably accomplished in the transition states involved in nucleophilic aliphatic displacements. This view is in substantial agreement with the conclusions concerning the nature of such transition states.[4–7] While there is much uncertainty as to exact timing of the reaction it is generally conceded that the transition states are usually near configuration I in which the carbon atom undergoing substitution is nearly tetrahedral. It is understandable that, if the free energy of formation of such a structure determines the rate of the reaction, the relative reactivity of the halogens might be largely determined by the C–X bond moments rather than by the other factors, such as atom polarizability,[11] which come into prominence in reactions in which the rate-controlling steps involve stretching the old bonds well beyond normal covalent distances. If this view is correct it should be possible to accomplish the inversion of the "normal" reactivity order by changing the reactions in such a way as to require more bond breaking in the rate limiting transition states.



I

That such an inversion has been accomplished is borne out by the data in Table I. With N-methylaniline as the nucleophile, the relative rates of halide displacement from 1-X-2,4-dinitrobenzenes are Br > Cl > F in both nitrobenzene and ethanol

---

[1] J. F. Bunnett and R. E. Zahler, *Chem. Revs.*, **49**, 273 (1951).

[2] E. Berliner, M. J. Quinn and P. J. Edgerton, THIS JOURNAL, **72**, 5305 (1950); E. Berliner and L. C. Monack, *ibid.*, **74**, 1574 (1952).

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

[4] N. B. Chapman, R. E. Parker and Soanes, *Chem. and Ind.*, 148 (1951).

[5] N. B. Chapman and R. E. Parker, *J. Chem. Soc.*, 3301 (1951).

[6] R. R. Bishop, E. A. S. Cavell and N. B. Chapman, *ibid.*, 437 (1952).

[7] E. A. S. Cavell and N. B. Chapman, *ibid.*, 3392 (1953).

[8] J. Miller, *ibid.*, 3550 (1952); A. L. Beckwith, J. Miller, and G. D. Leahy, *ibid.*, 3552 (1950); J. Miller, THIS JOURNAL, **76**, 448 (1954).

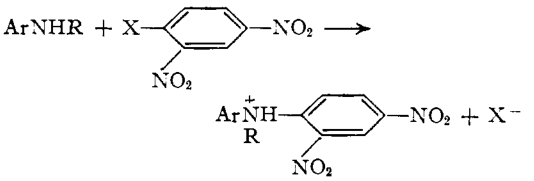
[9] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapt. 15.

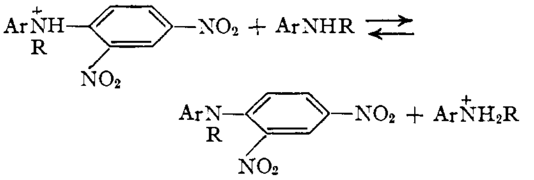
[10] C. K. Ingold, ref. 9, p. 338.

[11] J. O. Edwards, THIS JOURNAL, **76**, 1540 (1954), mentions the fact that the second term in his double basicity scale is apparently of much greater importance in determining relative nucleophilic reactivity in displacements at unsaturated carbon atoms than in saturated displacements. This leads to conclusions similar to those developed herein except that the application is to the extent to which the new bond has developed covalent character in the transition state.

as solvents at temperatures which give reaction rates suitable for easy measurement. The rates are, however, more closely grouped in ethanol solution. For purposes of comparison we show, in Table II, the published data for the rates of the more rapid reactions of aniline with the same substrates in ethanol solution.[5] On the basis of the reasoning presented above we may infer that two factors can accomplish an increase in the importance of bond breaking in the rate-determining steps. The first is the decrease in the reactivity of the nucleophile as represented by the change from aniline to N-methylaniline and the second is a change to a "slower" solvent as in the change from ethanol to nitrobenzene.

Displacements on activated aryl halides by neutral nucleophiles can be described by the equations


(1)


(2)

The process represented by equation 1 is rate determining since the reactions are first-order with respect to the nucleophiles. However, reaction 1 may consist of either one discrete step or of two steps with the intermediate formation of a high energy adduct which would be represented approximately by structure I. Two transition states would then be located on either side of the unstable intermediate with configurations which are modified only slightly by stretching of either the old or the new bond of I. Since bond breaking appears to make a notable contribution in the rate-determining steps of the reactions of N-methylaniline it can probably be assumed that, if there are two steps, the second is rate determining *in these cases*. There is no way in which this situation can be distinguished from a one step mechanism on the basis of existing data.[12] The latter picture will be adopted for the sake of simplicity as has been done previously.[6]

Reaction 1 is probably actually endothermic so a decrease in the stability of the products of this step should shift the transition state configuration toward that of the reaction products. In the present work this has been done both by increasing the steric requirements of the nucleophile and by decreasing the solvation energy of the halide ions when they are produced in a solvent, nitrobenzene, which has little ability to provide electrophilic solvation for the anions.

The activation heats and entropies listed in Table I are not highly accurate because the accurately measured rate constants span only relatively small temperature intervals. The very slow rates of reaction at low temperatures in nitrobenzene were not measured with high accuracy but give reasonably accurate values for the thermodynamic parameters when compared with the high temperature rates. The heats of activation may be in error by 1-2 kcal. which leads to an uncertainty of as much as 6 entropy units in the tabulated values for ΔS^+.

TABLE I

RATES OF DISPLACEMENT OF HALOGEN FROM 1-X-2,4-DINITROBENZENES BY N-METHYLANILINE

Halogen displaced	Solvent	Temp., °C.	$k \times 10^7$, l. mole^{-1} sec.$^{-1}$	ΔH^+, kcal./mole[a]	ΔS^+, e.u.
F	Nitrobz.[b]	131.5	267 ± 10		
F	Nitrobz.	120	182 ± 20	10	−56
Cl	Nitrobz.	131.5	4400 ± 40		
Cl	Nitrobz.	120	2750 ± 50	12	−48
Cl	Nitrobz.	25	15 ± 4	12	
Cl	Nitrobz.	0	7 ± 3	10	
Br	Nitrobz.	131.5	13000 ± 50		
Br	Nitrobz.	120	8450 ± 350	11	−44
Br	Nitrobz.	25	54.7 ± 1.6	12	
F	Ethanol	50	4.53 ± 0.7		−68
F	Ethanol	77	12.4 ± 0.7	7	
Cl	Ethanol	50	6.22 ± 2		−62
Cl	Ethanol	76	16.6 ± 2	8	
Br	Ethanol	50	13.7 ± 2		−50
Br	Ethanol	76	51.0 ± 1	12	

[a] The values listed were calculated using the values for the rates at the particular temperature and at the highest temperature. This procedure was adopted because the low precision of the low temperature rate constants was compensated by the very large temperature intervals. [b] Nitrobenzene.

TABLE II

RATES OF DISPLACEMENT ON 1-X-2,4-DINITROBENZENES BY ANILINE IN 99.8% ETHANOL[a]

Halogen displaced	$k_{50} \times 10^4$, l. mole^{-1} sec.$^{-1}$	ΔH^+, kcal./mole[b]	ΔS^+, e.u.
F	168	5.8	−49
Cl	2.69	10.6	−43
Br	4.05	10.6	−42

[a] From the summary by Chapman and Parker.[4] [b] The value of RT has been subtracted from the values of E listed by Chapman and Parker to effect the conversion to heats of activation.

The very large negative values for the entropy of activation are not unusual for a reaction of the charge type of 1.[13] It has been pointed out previously[4] that the superiority of fluoride in most displacements of this type is due to low heats of activation which are compensated partially by large negative activation entropies. If, as was suggested by Chapman and Parker, this is correlated with the large heat and negative entropy of solvation of the fluoride ion, the fact that the entropies are increased when N-methylaniline is substituted for aniline in ethanol solution is consistent with our hypothesis that bond breaking has become more important to the activation process. It is not really profitable to undertake a more detailed analysis of the heat and entropy data at the present time. However, it seems reasonable that the mechanistic arguments

---

[12] For a discussion of concepts relevant to this line of reasoning see, G. S. Hammond, THIS JOURNAL, **77**, 334 (1955).

[13] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, Chapt. 7.

presented above are still valid despite the redistribution of the free energy of activation for an idealized vapor phase process by solvation.

In view of the interpretation which we have placed upon the relative reactivities of aryl halides some comment should be made concerning the monohalobenzenes. The order of reactivity Br > Cl > F is reported for a number of reactions with powerful nucleophiles.[14-16] This pattern of behavior is inconsistent with our views unless these reactions proceed by some mechanism other than direct displacement. In our opinion it is likely that these reactions involve the elimination–addition mechanism which has been shown to occur in the reactions of aryl halides with amide ion in liquid ammonia.[17]

Experimental

1-Fluoro-2,4-dinitrobenzene (Eastman Kodak Co.) was recrystallized from absolute ethanol, m.p. 25–26°.

1-Chloro-2,4-dinitrobenzene was prepared by dinitration of chlorobenzene and purified by recrystallization from 80% ethanol, m.p. 51–52°.

1-Bromo-2,4-dinitrobenzene (Eastman Kodak Co.) was recrystallized from 80% ethanol; m.p. 71–72°.

N-Methylaniline (Eastman Kodak Co.) was purified by acetylation followed by recrystallization of the acetyl derivative from water to a constant melting point, 101–102°. Hydrolysis by aqueous hydrochloric acid followed by fractional distillation gave a pure, colorless product, b.p. 81–82° (14 mm.)

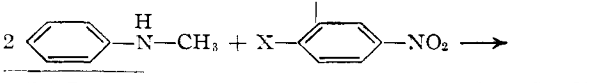
Ethanol was purified by drying commercial absolute ethanol by the method of Lund and Bjerrum.[18] The product obtained gave a negative test with aluminum ethoxide in benzene indicating that the material contained less than 0.05% water.[19]

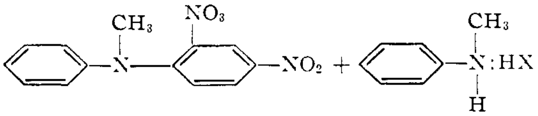
Kinetics of the Displacement of Halogen from 1-X-2,4-Dinitrobenzenes in Nitrobenzene Solvent.—The rate of displacement of halogen was followed by potentiometric titration of excess N-methylaniline with perchloric acid in glacial acetic acid. A Beckman *p*H meter, model G, was used as a potentiometer with glass and silver–silver chloride electrodes.

When N-methylaniline is added to nitrobenzene a deep red color forms due to complex formation. This is an often observed phenomenon with polynitro compounds and the complexes are stabilized by amino groups in the second molecule.[20] Since second-order kinetics were observed throughout the run in every case studied in nitrobenzene, the amount of material complexed *with the substrate* must have been very small.

Samples prepared from 4 ml. of 0.5 *M* N-methylaniline and 2 ml. of 0.5 *M* 1-X-2,4-dinitrobenzene dissolved in nitrobenzene were sealed in ampules and placed in a well-insulated thermostat. Samples were removed at regular intervals and frozen to quench the reaction. After rapid filtration of the sample, the unreacted amine in the samples was titrated potentiometrically with 0.1 *N* perchloric acid in glacial acetic acid. N-Methylaniline hydrochloride and hydrobromide did not interfere with this analysis and the hydrofluoride was insoluble in cold nitrobenzene and was removed quantitatively by the filtration procedure.

The reactions of all three halo compounds with N-methylaniline have the same stoichiometry in nitrobenzene solvent.





The rate law

$$dx/dt = k(a - 2x)(b - x)$$

where a = amine concentration and b = 1-X-2,4-dinitrobenzene concentration, simplifies to

$$k = \frac{1}{2t}\frac{x}{b(b - x)}$$

if $a = 2b$, gave good second-order rate constants in all three cases. Typical runs are summarized in Table III.

TABLE III

RATE CONSTANTS FOR THE REACTION OF N-METHYLANILINE WITH 1-X-2,4-DINITROBENZENE IN NITROBENZENE SOLVENT AT 120°

Time increment, hours	X = F, $k \times 10^5$ l. mole^{-1} sec.$^{-1}$	X = Cl, $k \times 10^4$ l. mole^{-1} sec.$^{-1}$	X = Br, $k \times 10^4$ l. mole^{-1} sec.$^{-1}$
1		2.70	9.02
2		2.78	
3		2.80	8.55
4		2.80	8.11
5	2.00	2.70	8.62
6		2.79	7.75
7		2.78	8.71
10	1.72		
25	1.97		
50	1.73		
75	1.54		
100	2.00		
Average	1.82	2.75	8.45

Some difficulty was encountered when the reaction of N-methylaniline with 1-fluoro-2,4-dinitrobenzene was carried out in glass tubes at low temperatures which necessitated long time intervals. The rate constant dropped consistently. The trouble was found to be due to the action of hydrogen fluoride on glass and the consequent release of N-methylaniline. This could be corrected by using copper tubes which were carefully cleaned with hydrofluoric acid before use. The tubes were sealed before being placed in the thermostat.

Kinetics of the Displacement of Halogen from 2,4-Dinitrobenzene in 99.8% Ethanol Solvent.—The reaction of N-methylaniline with 1-bromo- and 1-chloro-2,4-dinitrobenzene was followed by determining the amount of halogen displaced by the Volhard method. Ten ml. of 0.2 *M* N-methylaniline was mixed with 10 ml. of 0.1 *M* halo compound in individual stoppered tubes which were immersed in a thermostat. At regular intervals samples were removed and poured into a separatory funnel containing 30 ml. of benzene and 20 ml. of silver nitrate and the mixture was shaken thoroughly. The aqueous layer containing the excess silver nitrate was drawn off and the benzene layer was washed twice with distilled water. The unreacted starting materials and the tertiary amine product remained in the benzene layer. The silver bromide or silver chloride remained at the boundary between the two layers causing no difficulty in the analysis. The excess silver nitrate was titrated with standard potassium thiocyanate using ferric ammonium sulfate as the indicator. Good second-order rate constants were obtained using the same rate law that was used for the bromo and chloro compounds in nitrobenzene solvent.

The reaction of N-methylaniline with 1-fluoro-2,4-dinitrobenzene was followed by bromination of excess N-methylaniline as described by Siggia.[21] Ten ml. of 0.2 *M* N-methylaniline and 10 ml. of 0.2 *M* 1-fluoro-2,4-dinitrobenzene were mixed thoroughly and immersed in the thermostat in tightly stoppered tubes. The samples were removed at regular intervals and poured into a separatory funnel

---

(14) B. V. Tronov and F. A. Kruger, *J. Russ. Phys. Chem. Soc.*, **58**, 1270 (1926).

(15) F. W. Bergstrom, R. E. Wright, C. Chandler and W. A. Gilkey, *J. Org. Chem.*, **1**, 170 (1936).

(16) F. W. Bergstrom and C. H. Horning, *ibid.*, **11**, 34 (1946).

(17) J. D. Roberts, H. E. Simmons, L. A. Carlsmith and C. W. Vaughan, THIS JOURNAL, **75**, 3290 (1953).

(18) H. Lund and J. Bjerrum, *Ber.*, **64**, 210 (1931).

(19) F. Henle, *ibid.*, **53**, 719 (1920).

(20) G. W. Wheland, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 62.

(21) S. Siggia, "Quantitative Organic Analysis *via* Functional Groups," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 111.

containing 30 ml. of benzene and 25 ml. of concentrated hydrochloric acid which stopped the reaction by converting all the free amine to the anilinium ion. The separatory funnel was shaken, allowed to stand and the aqueous layer was removed. The benzene layer was washed twice with water. Excess 0.1 *N* bromate–bromide solution was added to the aqueous layer and after the solution had been allowed to stand for 12 minutes an excess of potassium iodide was added. The iodine liberated was titrated with standard sodium thiosulfate. The excess bromate–bromide solution was never allowed to exceed 3 ml. of 0.1 *N* solution. Under these conditions it was shown by Chapman[5] that none of the other substances present, particularly ethanol, was oxidized or brominated.

Acknowledgment.—The authors are grateful to Dr. M. F. Hawthorne for helpful discussions.

AMES, IOWA

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT LABORATORIES OF THE UNIVERSAL OIL PRODUCTS COMPANY]

Oxidative Condensation of *p*-Cymene, Isopropylbenzene and Chloroisopropylbenzene[1]

BY HERMAN PINES,[2] BRUNO KVETINSKAS AND V. N. IPATIEFF[3]

RECEIVED MAY 22, 1954

Oxidative condensation took place when air was passed through *p*-cymene at its reflux temperature. The principal identified products were 2,3-dimethyl-2,3-di-*p*-tolylbutane (di-*p*-cymene), *p*-acetyltoluene and dimethyl-*p*-tolylcarbinol. A 32% yield of di-*p*-cymene was obtained when aluminum turnings were used as a contacting material and the reaction was carried out in the presence of potassium carbonate. Oxidative condensation occurred also when isopropylbenzene was treated with air; 2,3-dimethyl-2,3-diphenylbutane was one of the principal products of reaction. A mixture of *o*-, *m*- and *p*-chloroisopropylbenzene yielded on oxidation a solid corresponding to di-chloroisopropylbenzene.

A crystalline substance, later identified as 2,3-dimethyl-2,3-di-*p*-tolylbutane ("di-*p*-cymene") was observed in the residue after distilling a large amount of *p*-cymene at atmospheric pressure. The distillation required several shutdowns before completion, allowing air each time to come in contact with the hot liquid. It was assumed that the formation of di-*p*-cymene resulted from oxidative condensation owing to the contact between the hot *p*-cymene and the air. This assumption was proved to be correct since it was found possible to prepare a large amount of the di-*p*-cymene by passing air through *p*-cymene at its reflux temperature. The study of oxidative condensation was extended to include isopropylbenzene and chloroisopropylbenzene.

To obtain comparative data the experiments were run for 18 hours during which not more than 20% of the alkylbenzene used underwent reaction.

***p*-Cymene. Effect of Potassium Carbonate and Contacting Materials.**—It was found that when air was passed through *p*-cymene at near reflux temperature oxidation occurred. The principal identified products were di-*p*-cymene, *p*-acetyltoluene and dimethyl-*p*-tolylcarbinol. Smaller amounts of 2-methyl-2,4-di-*p*-tolylpentane (VIII), *p*-isopropylbenzoic acid, *p*-isopropenyltoluene, methanol, water, methane, ethane and carbon dioxide were formed.

When glass rings were placed in the reaction flask to give a more intimate contact between the air and the *p*-cymene, the extent of reaction was increased.

The addition of potassium carbonate decreased the amount of higher boiling material and increased the amount of carbinol in the product without materially affecting the amount of the other compounds formed. It seems that the potassium carbonate reacted with the acids produced thus preventing the dehydration of the carbinol to isopropenyltoluene, which under these conditions condenses to higher boiling compounds. This conclusion was further supported by an experiment in which a small amount of benzoic acid was added to the *p*-cymene; the product contained less carbinol and more high boiling material than when potassium carbonate was added.

The addition of a small amount of 2,3-dimethyl-6-*t*-butylphenol to the *p*-cymene decreased the extent of reaction.

It was found that by substituting aluminum turnings for glass rings as the contact material, the yield of dimeric material was increased. The addition of potassium carbonate further enhanced the yield of dimeric compounds and at the same time increased the yield of carbinol and reduced the amount of high boiling material formed. The experimental results are summarized in Table I.

Other contacting materials such as turnings made from magnesium, iron, copper, zinc, nickel, silver and aluminum bronze were also evaluated. Di-*p*-cymene was formed in the presence of all of these to an extent equal to or higher than when glass rings were used, but to a lower extent than when aluminum turnings was the contacting material. There was a marked increase in the production of compounds boiling above the dimer when contacting materials other than aluminum turnings were used; this was especially true in the case of cadmium and silver.

Effect of Temperature.—The temperature at which the oxidation was carried out greatly affected the composition of the reaction product. At 140°, in the presence of glass rings, 79% of the reacted product was ketone–carbinol fraction and only 3.2% was dimeric compound. At 171°, however, the oxygenated compounds amounted only to 48% while the amount of the dimeric compound increased to 22.9%. The peroxide number of the product was higher at the lower temperature, but the extent of reaction was about the same at the two temperatures. A similar effect of temperature was noticed when aluminum turnings were used as a contact material.

---

(1) U. S. Patent 2,614,130 (October 14, 1952).

(2) The Ipatieff High Pressure and Catalytic Laboratory, Department of Chemistry, Northwestern University.

(3) Deceased November 29, 1952.