[Contribution from the Chemical Laboratory of Harvard University]

COMPARATIVE REACTIVITIES OF SOME CHLORO- AND BROMONITROBENZENES[1]

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The nitrophenyl halides react with alkali sulfites in alcoholic or aqueous alcoholic solution to give nitrophenyl sulfonates.[3]

In the expectation that this reaction would furnish another means for quantitative study of the nitrophenyl halides, and in the hope of obtaining some additional information relating to the mechanism of activation of groups in aromatic compounds, the velocity measurements reported in the preceding paper have been extended to some of these more reactive nuclear halogen compounds.

Practically all of the previous data concerning the reactivity of aromatic halogen have been obtained by using as reagents either amines[4] or alcoholates.[5] Rheinlander,[4d] using aniline and monomethylaniline as reagents, found that the ratio between the reactivity of a 2,4-dinitro-halogeno-benzene and the corresponding symmetrical trinitrophenyl halide was approximately 1:7. Brewin and Turner,[4e] using pyridine in boiling benzene, found a surprising difference in reactivity between an ortho and para mononitro halide; but they also found that the introduction of a second nitro group did not materially increase the reactivity. Thus the ratio of the reactivities of the nitrochloro compounds was para:ortho:2,4-dinitro = 1:36.3:56.9. For the corresponding bromo compounds the ratio was 2.38:43.5:56.4, while the iodo ratio was 2.24:17.9:34.4.

The Dutch school, led by Lobry de Bruyn, Lulofs, and Holleman, has

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[3] E. and H. Erdmann, German patent 65,240, *Friedländer*, **3**, 41 (1891); *Ann.*, **294**, 380 (1897); Willgerodt, *J. prakt. Chem.*, [2] **32**, 117 (1885); Willgerodt and Mohr, *ibid.*, [2] **34**, 118 (1886); Geigy and Company, German patent 94,504, *Friedlander*, **4**, 188 (1897); German patent, 88,952, *Friedländer*, **4**, 133 (1896); Purgotti and Lunini, *Gazz. chim. ital.*, **33**, II, 334 (1903).

[4] (a) De Mooy, *Rec. trav. chim.*, **35**, 5 (1915); (b) Ter Weel, *ibid.*, **35**, 44 (1915); (c) Franzen and Bockhacker, *Ber.*, **53**, 1174 (1920); (d) Rheinlander, *J. Chem. Soc.*, **123**, 3099 (1923); (e) Brewin and Turner, *ibid.*, 332, 334 (1928).

[5] Lobry de Bruyn, *Rec. trav. chim.*, **9**, 197 (1890); Löwenherz, *Z. physik. Chem.*, **29**, 401 (1899); **36**, 469 (1901); Lulofs, *Rec. trav. chim.*, **20**, 292 (1901); Brand, *J. prakt. Chem.*, [2] **67**, 145 (1903); Beekmann, *Rec. trav. chim.*, **23**, 254 (1904); De Mooy, *ibid.*, **35**, 5 (1915); Ter Weel, *ibid.*, **35**, 44 (1915); Holleman, *ibid.*, **37**, 195 (1917); **39**, 736 (1920); den Hollander, *ibid.*, **39**, 436 (1920); Holleman and van Haeften, *ibid.*, **40**, 67 (1921); Mattaar, *ibid.*, **41**, 103 (1922); Van de Vliet, *ibid.*, **43**, 620 (1924); Baudet, *ibid.*, **43**, 718 (1924); Van der Kam, *ibid.*, **45**, 564 (1926); Lorang, *ibid.*, **46**, 891 (1927); Talen, *ibid.*, **47**, 329 (1928).

been particularly interested in determining which group of a phenyl compound highly substituted by both nitro and chloro groups would be replaced, and from which position it would be replaced. Working mainly with sodium methylate or ethylate, they have amassed much valuable information of this kind. The conclusions in which we are most interested at present are these: a chlorine atom ortho or para to one or more nitro groups will usually be replaced; in some cases a nitro group ortho or para to one or more other nitro groups may be replaced; a para nitro group usually has considerably more mobilizing influence than an ortho nitro group; a halogen atom, especially when in the meta position, may to some degree activate a second halogen atom or a nitro group. Di and tri meta compounds were shown to be in all cases decidedly unreactive. In general, a trinitro-chloro compound was about thirty times more reactive than a dinitro-chloro compound. The 2,4,6-trinitro halides were stated to be "very reactive."

In both of the above series of researches (with amines and with alcoholates) there was no general agreement as to the relative replaceability of halogen atoms in analogous compounds. In many cases bromine atoms were replaced more readily than chlorine, but frequently just the reverse was true.

Materials

The following compounds were obtained from Eastman and purified as given: picryl chloride was recrystallized twice from ethyl alcohol–benzene mixture, m. p. 81.5–82.5°; 2,4-dinitrochlorobenzene was recrystallized three times from alcohol, m. p. 50.5–50.6°; *o*-nitrochlorobenzene was recrystallized three times from alcohol, m. p. 32.0–32.6°; *m*-nitrochlorobenzene was recrystallized from alcohol, m. p. 44–45°; *p*-nitrochlorobenzene was recrystallized three times from alcohol, m. p. 82.5–83.5°; *o*-nitrobromobenzene (m. p. 42.5–43°), *m*-nitrobromobenzene (m. p. 55–55.5°), *p*-nitrobromobenzene (m. p. 126.5–127°) and 2,4-dinitrobromobenzene (m. p. 72–72.5°) were available in a pure state.

Method

The present experiments were carried out using the method described in the preceding paper. Because of the slow solubility of the nitro halides in 50% alcohol, the reactions were not started by adding the sulfite solution to the pure halide. Instead, a solution of the halide in 50% alcohol was made up to a definite volume just prior to use, and an equal volume of the sulfite solution was rapidly added to this. In the case of the mononitro compounds the progress of the reaction was followed by running portions into cold water and titrating the unused sulfite directly with iodine. In the case of the more reactive di- and trinitro compounds, the reactions were stopped by running the solutions into excess iodine and titrating the excess with standard thiosulfate.

Discussion of the Results

Two typical runs are shown in Table I, and the complete results are assembled in Table II. The accuracy of the results in respect to the dinitro compounds is considered to be about 5%, which is the general accuracy of the results obtained with the benzyl bromides. The average velocity constants found for the mononitro halides are of the order of 0.010, and are considered to be subject to an error of ±0.002. The value for picryl chloride (160) is probably correct to within 20%.

TABLE I

TYPICAL DATA CONCERNING THE REACTION BETWEEN SOME NITROPHENYL HALIDES AND SODIUM SULFITE IN 50% AQUEOUS ALCOHOL

o-Nitrochlorobenzene at 40.00° *o*-Nitrochlorobenzene, 0.02176 *M;* sodium sulfite, 0.02176 *M;* titration (50 cc.) with 0.02686 *M* iodine

Time, minutes	Iodine, cc.	K_{mean} (bimol.)
0	40.4	....
15	40.3	0.0084
45	40.1	.0075
105	39.7	.0077
225	39.05	.0071
475	38.2	.0070
465	37.5	.0076
		Av. .0075

2,4-Dinitrobromobenzene at 40.00° 2,4-Dinitrobromobenzene, 0.02390 *M;* sodium sulfite, 0.02390 *M;* titration (50 cc.) with 0.02686 *M* iodine and 0.03888 *M* $Na_2S_2O_3$

Time, minutes	Iodine (net), cc.	K_{mean} (bimol.)
0	42.5	....
2	21.7	18.5
5	11.8	18.7
9	6.8	18.8
14	4.1	18.6
21	2.3	18.7
30	1.2	18.5
		Av. 18.6

TABLE II

RELATIVE REACTIVITIES OF NITROCHLORO- AND NITROBROMOBENZENES TOWARD SODIUM SULFITE

Compound	Temp., 30.00° K_{mean} (bimol.)	Temp., 40.00° K_{mean} (bimol.)	Temp. coeff.
p-Nitrochlorobenzene[a]	0.003	0.006	Approx. 2
o-Nitrochlorobenzene[a]	.004	.008	Approx. 2
m-Nitrochlorobenzene[a]	.005	.011	Approx. 2
p-Nitrobromobenzene[a]	....	.016	....
o-Nitrobromobenzene[a]	....	.006	....
m-Nitrobromobenzene[a]	....	.008	....
2,4-Dinitrochlorobenzene[b]	6.14	10.25	1.67
2,4-Dinitrobromobenzene[c]	....	18.6	....
2,4,6-Trinitrochlorobenzene[d]	160	Immeasurably fast	

[a] At the end of each reaction (or, in the cases of the very slow ones, after the reaction had proceeded for several hours) the solutions were tested qualitatively for chloride, nitrite, and for the presence of reduced nitrogen compounds. The latter test was carried out as follows: a portion of the solution was boiled with strong sulfuric acid, then cooled, and made alkaline with sodium hydroxide. A few cc. of chloroform was added and the solution boiled. No carbylamine odor was detectable in any case, showing that no amines or sulfamic acids or similar reduced nitrogen compounds which could be hydrolyzed to amines were formed. Nitrite ion could be detected in none of the reaction mixtures. A positive test for chloride ion was obtained in each case.

[b] When the reactants were mixed, a pink color developed. The color faded as the reaction proceeded and had turned to a pale yellow when the reaction was approximately 60% complete. This change is due, in all probability, to the indicator action of 2,4-dinitrophenylsulfonic acid, the reaction product (see footnote *d*).

[c] A similar pink color was produced here. It had turned to a pale yellow when the reaction was approximately 60% complete.

[d] A deep red color formed upon mixing the reactants and faded gradually as the reaction proceeded, finally attaining a yellow-green shade. This color change is due, undoubtedly, to the fact that *sym.*-trinitrophenylsulfonic acid is an indicator of the same type as *sym.*-trinitrobenzene. The color reactions of trinitrobenzene which lead to its use as an acidimetric indicator are usually attributed to the ability of this compound to take on addenda of various sorts. The addition products are stable in alkaline solution, but usually break down into their constituents in solutions of a lower *P*H. (Trinitrobenzene changes color at a *P*H of about 12.) The addition products have been formulated as quinonoid complexes [Hantzsch, *Ber.*, **42,** 2120 (1909)] and as secondary valency complexes. [See, for example, Sudborough and Beard, *J. Chem. Soc.*, **97,** 780 (1910); Sudborough, *ibid.*, **109,** 1339 (1916); Pfeiffer, *Z. anorg. Chem.*, **137,** 287 (1924).] The change from the "alkaline" to the "acid" color during the course of the present reaction is probably due to the fact that as the reaction proceeds sodium sulfite is used up and sodium trinitrophenyl sulfonate is formed. Since trinitrophenyl sulfonic acid is undoubtedly a stronger acid than sulfurous acid, the *P*H of the solution decreases, eventually reaching the "neutrality" point, that is, the point where the red complex is completely dissociated into its components, the yellow "acid" color being due to the trinitrophenyl sulfonate ion.

From one of these experiments the sodium trinitrophenyl sulfonate was isolated (2.55 g. from 2.55 g. of the trinitrophenyl chloride) and its indicator action noted. It is a fairly good acidimetric indicator, having quite an abrupt change from red to yellow. It may be used in the titration of either strong or weak acids.

It is interesting to note that the reactivities of analogous bromine and chlorine derivatives are very close together, and that there is evidently no general rule as to which is more reactive. This is in accord with general experience with nuclear halogen. About as many pairs of compounds have been investigated in which the bromine compound has shown a greater reactivity than the chlorine compound as of those in which the reverse relationship has been found to hold.

The mononitrochlorobenzenes reacted, at 30°, at a rate which was just measurable by means of the present experimental technique. The velocity constants for the ortho, meta and para isomers differ by less than the experimental error. However, all three compounds were run at the same time and under exactly parallel conditions, so that it is certain that the relative reactivities are in the order given, that is, meta $>$ ortho $>$ para. The same relative order holds also at 40°. In the mononitrobromo series, the order at 40° is para $>$ meta $>$ ortho, the para isomer reacting over twice as fast as either of the other two. Here again one may be sure of the relative order by virtue of the fact that the three compounds were run under as nearly as possible identical conditions. From the fact that the meta compounds show the same order of reactivity as their ortho and para isomerides, it seems that in the reaction of the mononitrophenyl halides with sulfite the activation of the halogen atom by the nitro group must be due to its specific polar influence, and not to its ability to induce any sort of alternating effect within the benzene ring.

In this reaction the 2,4-dinitrophenyl halides were found to be approximately two thousand times as reactive as the mononitrophenyl halides, a result which is in marked contrast to those obtained by Brewin and Turner,[4e] who found that the introduction of a second nitro group did not materially alter the reactivity of a mononitrophenyl halide toward pyridine. Picryl chloride, the only trinitrophenyl halide studied during the present investigation, was about 25 times more reactive than either of the dinitrophenyl halides, a result which is approximately in agreement with those of Rheinlander,[4d] and also with those of the Dutch chemists.[5] None of these latter investigators compared the reactivities of the mono and dinitro halides. However, some of the qualitative results of the Dutch school[4a] indicate that the ratio of reactivities of tri- and dinitro halides toward alcoholates would be of the order of magnitude of 10^3, and therefore in agreement with the present results.

It is significant that the large increase in activating power occurs upon the introduction of the second nitro group, while the third nitro group has comparatively small influence. The fact that the mononitro compounds show the same order of reactivity irrespective of the position of the nitro group should also be emphasized, for it is well known, in regard to dinitrophenyl compounds, that two nitro groups in the meta positions with respect to a third group affect the reactivity of this group remarkably less than two nitro groups in the ortho and para positions with respect to the third group. A similar feeble activating influence of a single meta nitro group, relative to that of an ortho or para nitro group, might be expected, but is certainly not found in the present reaction.

Summary

1. The reaction between some nitrophenyl halides and sodium sulfite has been studied kinetically.

2. Toward this reagent, analogous chloro- and bromonitrophenyl halides show the same order of reactivity.

3. *m*-Nitrobromobenzene and *m*-nitrochlorobenzene react with approximately the same speeds as their ortho and para isomerides.

4. A 2,4-dinitrophenyl halide is about 2000 times more reactive than a mononitrophenyl halide. Picryl chloride is only about 25 times more reactive than 2,4-dinitrochlorobenzene.

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