Summary

The methoxyl group of 2,4-dinitroanisole is convertible to another alkoxyl group, by boiling dinitroanisole in the presence of caustic alkali with polyhydric alcohols or alcohols of the C_2–C_4 range. Aniline leads to 2,4-dinitrodiphenylamine.

Similar reactions are possible with some other 2,4-dinitrophenyl alkyl or aryl ethers.

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[CONTRIBUTION FROM THE DEPARTMENT OF INDUSTRIAL CHEMISTRY, THE FACULTY OF ENGINEERING, KYOTO UNIVERSITY]

Nucleophilic Substitution in Aromatic Ethers. II. Kinetics of the Methanolysis of 2,4-Dinitrodiphenyl Ethers

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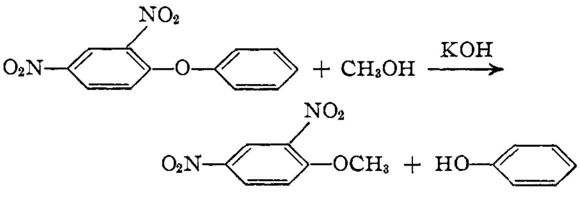
In the preceding paper[1] it was shown that 2,4-dinitroanisole is formed irreversibly, when a solution of 2,4-dinitrodiphenyl ether is boiled in alkaline methanol



In the present paper, the rate of reaction and the effect of structure on the rate were studied. The rate was determined by taking out aliquots of the reaction mixture after suitable time intervals, and estimating the phenol produced iodometrically.

Experimental

Materials.—Methanol (b. p. 64.5–65°) was purified by repeated rectifications from calcium oxide and silver nitrate. The 2,4-dinitrodiphenyl ethers were prepared by the condensation of 2,4-dinitrochlorobenzene with the corresponding sodium phenolates. They were recrystallized (twice) slowly from acetone or, with the α- or β-naphthyl derivatives, from a mixture of acetone and methanol. Among them, the 4′-chlorophenyl, 4′-nitrophenyl, α-naphthyl and β-naphthyl ethers were prepared in methanol (many hours boiling was necessary in the case of the nitro or naphthyl derivatives). The melting points agreed with those in the literature[2] as follows. 2,4-Dinitrodiphenyl ether, 70–71°; 2′-methyl, 89–90°; 3′-methyl, 72–73.5°; 4′-methyl, 91–92.5°; 4′-chloro, 122–123.5°; 4′-nitro, 115–116°; α-naphthyl 127–128°; β-naphthyl, 93–94.5°.

Apparatus and Procedure.—About 0.0025 mole of one of the ethers was weighed out and dissolved in 200 cc. of methanol. The solution was poured into a four-necked flask and placed in a thermostat (20 ± 0.1°) until temperature equilibrium was established. The flask was fitted with a stirrer[3] in its central neck, and in the other three were placed a thermometer, a tube suitable for withdrawing samples, and a tube into which air could be blown for pushing out the sample. The proper amount of potassium hydroxide was then dissolved in boiling methanol and its concentration was determined by titration with 0.05 N oxalic acid. An accurately measured amount of this solution (50 cc.) was taken out and kept in the thermostat until temperature equilibrium was reached and was then poured into the flask with gentle agitation (250–300 r. p. m.). This time was taken as the beginning of the reaction. A 25-cc. sample was taken out at regular intervals and run into a glass-stoppered flask containing 3 cc. of concentrated hydrochloric acid and 50 cc. of water. Twenty cc. of 0.1 N bromine water (a solution prepared from potassium bromate and bromide), were then added, the flask was stoppered tightly, and it was allowed to stand for fifteen seconds or thirty minutes before analysis.[4] The mixture was then treated with 5 cc. of 20% potassium iodide solution, and the freed iodine was titrated with 0.05 N sodium thiosulfate. The difference between the needed volume of thiosulfate solution and the blank test corresponded to the amount of phenol formed.

Results and Calculations

The bimolecular rate constants shown in Tables I and II were calculated by means of the following equation

$$k = \frac{2.303}{60t(b-a)} \log \frac{a(b-x)}{b(a-x)} \text{ (l./moles} \times \text{sec.)}$$

Here, a is the initial concentration of ether (moles/l.), b that of alkali (moles/l.), x the concentration of phenol after t minutes (mole/l.).[5] In Table I is shown the effect of changes in concentration on the second order rate constant of the methanolysis of 2,4-dinitrodiphenyl ether. It is evident that the rate of formation of phenol is proportional to the product of the concentration of the original ether and methylate ion.

In Table II are shown the rate constants for a number of runs in which various changes were made in the 2,4-dinitrodiphenyl ether molecule. It will be observed that the substitution of an electron attracting group (*e. g.*, NO_2) in the 4′ posi-

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[1] Ogata and Okano, THIS JOURNAL, **71**, 3211 (1949).

[2] (a) Raiford and Colbert, *ibid.*, **48**, 2652 (1926); (b) Bost and Nicholson, *ibid.*, **57**, 2368 (1935).

[3] Agitation was necessary, for the methanol solution tended to become heterogeneous when it was allowed to stand for a long time.

[4] From the results obtained with pure materials under these conditions, it was found that standing for thirty minutes is too long for *o*-, *m*-, *p*-cresol, and α- or β-naphthol. Even when the potassium iodide solution was added after fifteen seconds, the estimations of *o*- and *p*-cresol showed that the values were about 103 and 104% of the theoretical values. These estimations were, therefore, carried out rapidly and corrected by dividing the results by 1.04 and 1.03, respectively. See Day and Taggert, *Ind. Eng. Chem.*, **20**, 545 (1928).

[5] It should be noted that phenol and *m*-cresol consume 3 moles of bromine per mole. *p*-Substituted phenols and β-naphthol consume 2 moles, but α-naphthol reacts with 1 mole. Moreover, with *o*- and *p*-cresol, *x* should be divided by 1.03 and 1.04, respectively; see ref. 4.

TABLE I

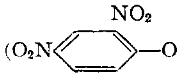
THE EFFECT OF ALKALI CONCENTRATION

2,4-Dinitrodiphenyl ether, 20 ± 0.1°

a	*b*	10^3k
0.01012	0.00454	4.78 ± 0.04
.01011	.00780	4.71 ± .03
.01008	.01030	4.76 ± .03
.00999	.01950	4.72 ± .01

TABLE II

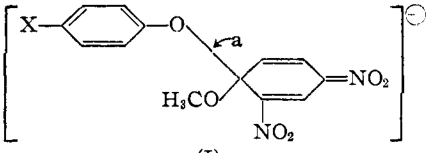
THE EFFECT OF SUBSTITUENTS



$(O_2N-C_6H_3(NO_2)-OR$, 20 ± 0.1°)

R	*a*	*b*	10^3k
C_6H_5	0.01016	0.01561	4.81 ± 0.03
C_6H_5	.00999	.01647	4.64 ± .01
4'-$C_6H_4NO_2$	.01008	.01561	64.4 ± .5
4'-$C_6H_4NO_2$	.00999	.01647	64.8 ± .3
4'-C_6H_4Cl	.01002	.01561	10.7 ± .1
4'-C_6H_4Cl	.01003	.01647	10.7 ± .1
β-$C_{10}H_7$	.01000	.01496	8.16 ± .03
β-$C_{10}H_7$	.01001	.01639	8.07 ± .04
α-$C_{10}H_7$	.01003	.01496	6.27 ± .03
α-$C_{10}H_7$	.00999	.01639	6.26 ± .03
3'-$C_6H_4CH_3$	.01004	.01496	3.66 ± .04
3'-$C_6H_4CH_3$	.00999	.01639	3.72 ± .03
4'-$C_6H_4CH_3$	.01002	.01561	2.77 ± .05
4'-$C_6H_4CH_3$	.01002	.01647	2.91 ± .04
2'-$C_6H_4CH_3$	.01001	.01561	1.40 ± .03
2'-$C_6H_4CH_3$	.01003	.01647	1.46 ± .03

tion of 2,4-dinitrodiphenyl ether increases the rate of reaction and the introduction of an electron releasing group (*e. g.*, CH_3) in the 2'- or 4'-position decreases the rate of reaction. This behavior resembles the effect of a substituent upon the reactivity of 4-substituted 2,6-dinitroanisoles with *p*-methoxydimethylaniline.[6] It is probaby due to the fact that the electron attracting group not only makes the formation of the activated complex I easier,[7] but also it facilitates fission of the carbon–oxygen bond a. By inserting into Hammett's equation, log $k/k_0 = \rho\cdot\sigma$,[8] the average values of k and k_0 shown in Table II, the values for ρ shown in Table III were calculated using Hammett's σ values. From the average value of ρ (1.46 ± 0.04), the σ value of the α-naphthyl group in α-naphthyl 2,4-dinitrophenyl ether was calculated to be 0.084.



(I)

TABLE III

Substituent	log (k/k_0)	ρ
4'-NO_2	1.1354	1.46
4'-Cl	0.3665	1.61
β-C_4H_4	.2347	1.38
3'-CH_3	− .1078	1.56
4'-CH_3	− .2215	1.30
	Av.	1.46 ± 0.04[9]

From this average value of ρ, the σ value of α-naphthyl was calculated to be +0.084.

Summary

The rates of exchange of the substituted phenoxy group of substituted 2,4-dinitrodiphenyl ethers for a methoxy group were measured. It was found that the rate is proportional to the product of the concentration of the original ether and methylate ion. Electron-attracting groups in the 4'-position of the ether increase the rate. Electron-releasing groups in the 2'- or 4'-position decrease it. The effect of the substituent on the rate constant of this reaction satisfied Hammett's equation, giving a σ value of + 1.46 ± 0.04.

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[6] Hertel and Lührmann, *Z. Elektrochem.*, **45**, 405 (1939).

[7] Meisenheimer, *Ann.*, **323**, 241 (1902).

[8] Hammett, "Physical Organic Chemistry," McGraw-Hill Book Company, Inc., New York, N. Y., 1940, pp. 186–188.

[9] Probable error.