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Ozonolysis of 1-Phenylazo-2-naphthol

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SUMMARY

The ozonolysis of 1-phenylazo-2-naphthol was studied using ozone in an oxygen stream. 1-Phenylazo-2-naphthol reacts with ozone to give benzene, chlorobenzene, phenol, o-naphthoquinone, phthalide and phthalic anhydride. The mechanism of the reaction is explained as an electrophilic attack of ozone with the hydrazone tautomer of 1-phenylazo-2-naphthol.

1. INTRODUCTION

The ozonisation reaction of dyes has been studied in connection with wastewater treatment. Ozone treatment has been evaluated on the basis of decolorising and/or the reduction of total organic carbon (TOC). But it is also necessary to identify ozonisation products and to elucidate the reaction mechanisms involved. Identification of the reaction products in the ozonisation of dyes has been reported only in regard to pyrazolone dyes,[1] various azo dyes,[2] Orange I and II,[3] 4-phenylazo-1-naphthol,[4] *p*-aminoazobenzene,[5] and indigo.[6]

In this paper, the authors discuss the ozonolysis of 1-phenylazo-2-naphthol, a model compound for the most widely used *o*-hydroxyazo dyes.

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2. EXPERIMENTAL

2.1. General

Visible spectra were obtained with a Hitachi EPS-3T spectrometer. Gas chromatography was performed on a Shimadzu 4C-PF apparatus. Mass spectra were obtained with a Hitachi M-52 spectrometer. Liquid chromatography was performed on a Jasco Familic 100N liquid chromatograph. Melting points were measured with a Yanagimoto micro melting point apparatus and uncorrected. Ozone was generated by a Nihon Ozon 0-1-2 type ozoniser.

2.2. Materials

1-(Substituted phenylazo)-2-naphthols were synthesised by a diazo-coupling method and purity was confirmed by gas chromatography. The materials employed and their melting points are presented in Table 1.

2.3. Ozonolysis reaction

Ozonolysis was carried out in all cases with ozone–oxygen mixtures (ozone, 4·0 mg min^{-1}; oxygen, 200 ml min^{-1}) on 2 mmole of 1-phenylazo-2-naphthol in 20 ml of solvent at 0 °C. Products were immediately determined by gas and liquid chromatography, and mass

TABLE 1
1-(Substituted phenylazo)-2-naphthols

Substituent	*Melting point (°C)*	
	Exptl	*Lit.*
p-CH_3	132·0–132·5	134–135
m-CH_3	140·0–141·0	141
H	131·5–132·5	134
m-OCH_3	143·5–144·0	145
p-Cl	162·5–163·0	162·5
p-Br	169·0–170·0	172–173
m-Cl	157·5–158·0	158
p-$COCH_3$	186·0–187·0	180

spectra of the products were compared with those of authentic samples. Yields were determined by comparison with standard solutions of known compounds. The columns employed in the gas chromatography were (1) 2% FFAP on Gas Chrom Q, 3Ф × 1 m; and (2) Gaskuropak 54, 3Ф × 1 m. The column employed in the liquid chromatography was SS-10, the mobile phase was dichloromethane and detection was at 254 nm.

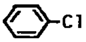
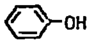
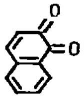
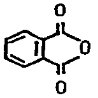
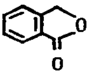
2.4. Rate constants of ozonolysis reactions

Ozonolysis was carried out with ozone–oxygen mixtures (ozone, 4·0 mg min^{-1}; oxygen, 200 ml min^{-1}) on 0·12 mmole of 1-(substituted phenylazo)-2-naphthols in 500 ml of solvent at 0 °C. The rate constants of the ozonolysis reactions were calculated on the basis of first-order kinetics.

3. RESULTS AND DISCUSSION

The results of the ozonolysis of 1-phenylazo-2-naphthol in the solvents are shown in Table 2. The initial products detected in identifiable yields from the ozonolysis in dichloromethane were benzene, chlorobenzene, phenol and *o*-naphthoquinone. *o*-Naphthoquinone reacts with excess

TABLE 2
Ozonolysis of 1-Phenylazo-2-naphthol[a]

Run	*Solvent*	*Conversion* (%)	*Yield*[b] (%)					
								
1	CH_2Cl_2	22	23	3	20	62	—	—
2	CH_2Cl_2	54	26	2	16	24	trace	5
3	CH_2Cl_2	84	23	2	15	11	7	8
4	$CHCl_3$	22	28	23	14	65	6	13
5	CCl_4	22	[c]	19	11	6	21	trace

[a] Ozonolysis was carried out with ozone–oxygen mixtures (ozone, 4·0 mg min^{-1}; oxygen, 200 ml min^{-1}) on 0·12 mmole of 1-phenylazo-2-naphthol in 20 ml of solvent at 0 °C.

[b] Yields are based on 1-phenylazo-2-naphthol reacting with ozone.

[c] Benzene could not be determined.

ozone to give phthalide and phthalic anhydride. Similar results were obtained with chloroform. When the ozonolysis was carried out in carbon tetrachloride, product yields decreased because of the formation of hygroscopic compounds. The reaction rate of 1-phenylazo-2-naphthol with ozone is considered to depend on the concentrations of the substrate and ozone. Since ozone was introduced continuously into the sample solution, the concentration of ozone was assumed to be constant. It was found that *ca.* 10–22 molar equivalents of ozone dissolved in the solution. The concentration of ozone was sufficient for discussion of the reaction in terms of pseudo first-order kinetics. The rate constants of the ozonolysis calculated in this way are shown in Table 3. Generally, *o*-hydroxyazo compounds exist in azo–hydrazone tautomeric equilibrium in solution. It has been reported that the absorption of 1-phenylazo-2-naphthol at 420 and 480 nm corresponds to the azo and hydrazone tautomers, respectively.[7] Although a quantitative analysis of the equilibrium is not possible, the values of the ratio A^{505}/A^{420} are considered to provide an approximate measure of the relative changes in equilibria resulting from

TABLE 3
Pseudo First-order Rate Constants for the Ozonolysis of 1-Phenylazo-2-naphthol, η Values of the Solvents Employed, Ratios of Absorbance at 505 to 420 nm of 1-Phenylazo-2-naphthol and Concentrations of Dissolved Ozone[a]

Run	*Solvent*	$k \times 10^3$ [b] (s^{-1})	η[c] (*cp*)	A^{505}/A^{420} [d]	*Dissolved ozone*[e] (*mmol litre*$^{-1}$)
1	n-C_6H_{14}	1·39	0·397	0·65	2·5
2	CH_2Cl_2	7·92	0·537	1·23	3·7
3	n-C_8H_{18}	0·764	0·703	0·67	2·2
4	$CHCl_3$	8·30	0·701	1·45	3·6
5	CCl_4	3·97	0·734	1·13	4·7
6	C_2H_5OH	0·238	1·78	1·07	6·5[f]
7	n-C_3H_7OH	0·183	3·85	1·13	4·8[f]

[a] Ozonolysis was carried out with ozone–oxygen mixtures (ozone, 4·0 mg min^{-1}; oxygen, 200 ml min^{-1}) on 0·12 mmole 1-phenylazo-2-naphthol in 500 ml of solvent at 0 °C.

[b] Rate constants relate to pseudo first-order kinetics.

[c] At 0 °C.

[d] Ratio of absorbance of 1-phenylazo-2-naphthol at 505 nm to that of 1-phenylazo-2-naphthol at 420 nm.

[e] Dissolved ozone was determined by iodometric titration.

[f] These values are total amounts of dissolved ozone and peroxides.

the solvents and substituents. The values of the ratio A^{505}/A^{420} were obtained in a manner similar to the method described in the literature.[7]

It can be seen from Table 3 that the rate constants of the ozonolysis reaction depend on both the viscosity of the solvents and the values of the ratio A^{505}/A^{420}. For example, although the values of the ratio A^{505}/A^{420} of 1-phenylazo-2-naphthol in *n*-hexane and *n*-octane and the amount of dissolved ozone are approximately equal, the rate constant of the reaction in *n*-hexane is greater than that in *n*-octane because the η value of *n*-octane is greater than that of *n*-hexane. A similar tendency was noted when using carbon tetrachloride and *n*-propanol. When the η values are approximately equal, the rate constants increase in order of the solvents *n*-octane < carbon tetrachloride < chloroform; this agrees with the order of the values of the ratio A^{505}/A^{420} rather than with the amounts of dissolved ozone. If the amount of dissolved ozone were the dominant factor in the experimental conditions, the rate constant in chloroform would be smaller than that in carbon tetrachloride. Thus, it appears reasonable to suggest that the faster the diffusion of ozone and the greater the ratio of hydrazone to azo tautomer of 1-phenylazo-2-naphthol in solution, the faster the ozonolysis reaction.

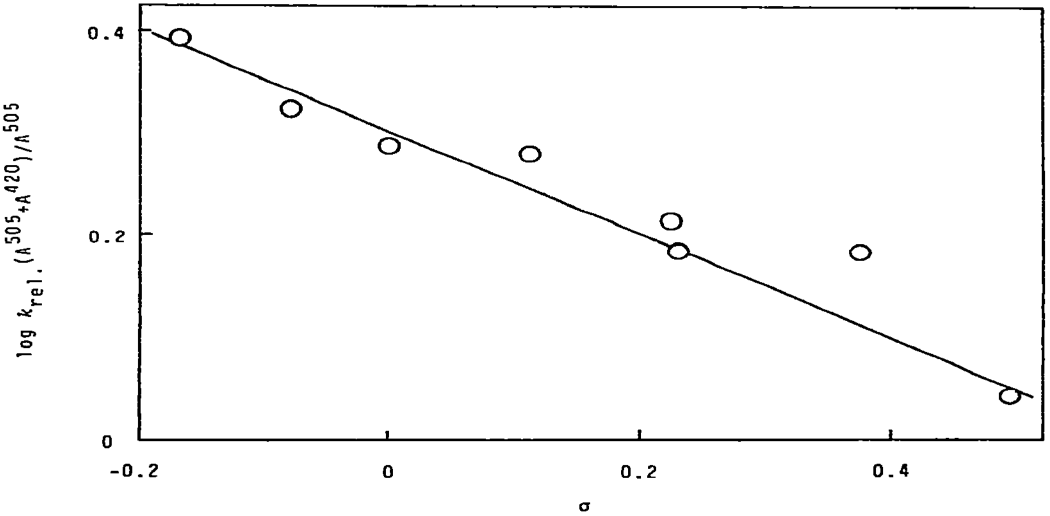
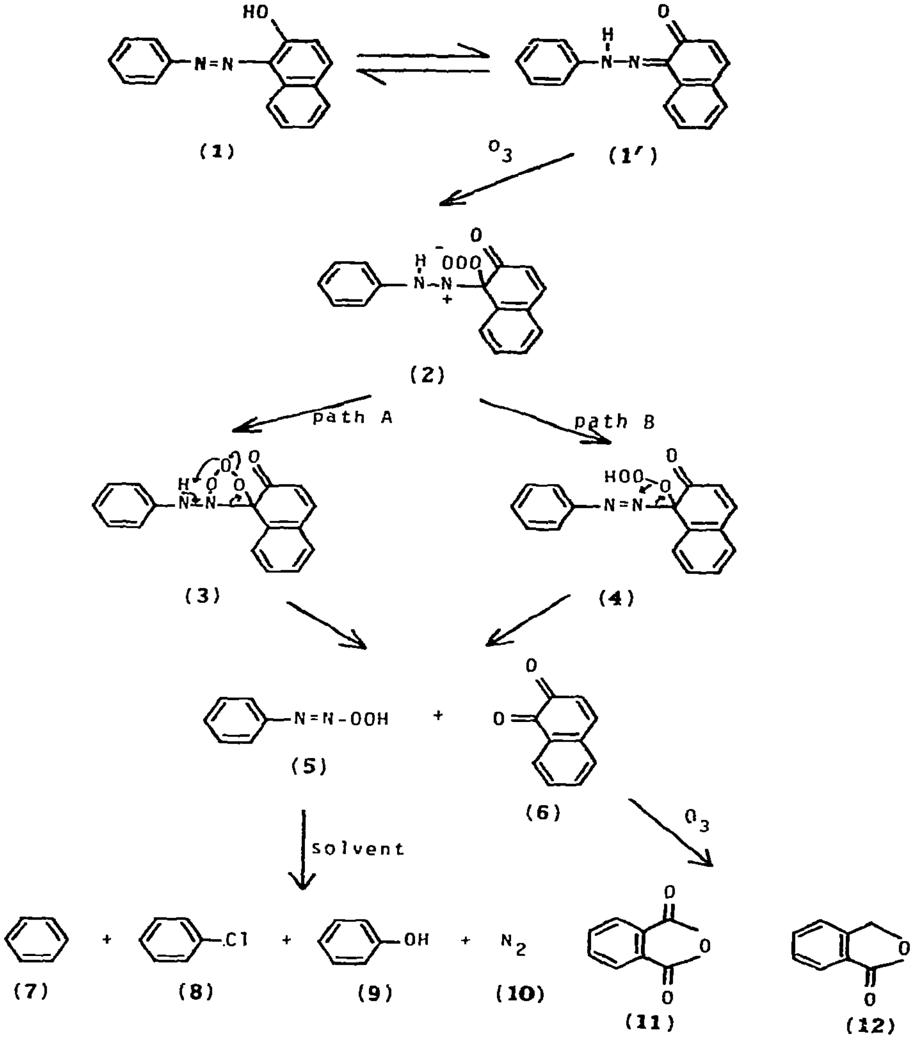


Fig. 1. Hammett's plots for the ozonolysis of 1-(substituted phenylazo)-2-naphthols. Ozonolysis was carried out with ozone–oxygen mixtures (ozone, 4·0 mg min^{-1}; oxygen, 200 ml min^{-1}) on $8 \cdot 1 \times 10^{-2}$ mmole 1-(substituted phenylazo)-2-naphthols in 500 ml of ethanol at 0°C.

The effect of the substituents on the ozonolysis reaction of 1-phenylazo-2-naphthol was investigated. A plot of the logarithm of the relative rates of ozonolysis of 1-(substituted phenyazo)-2-naphthols, corrected for the hydrazone tautomer, against Hammett's σ constants gave a straight line whose slope was found to be $\rho = -0{\cdot}50$. The negative value of ρ appears consistent with the electrophilicity of ozone. The effect



Scheme 1.

of substituents was similar to that known for the photooxidation of arylazonaphthols.[8,9] The attack of electrophilic ozone on 1-phenylazo-2-naphthol in its hydrazone tautomeric form (**1'**) is reflected by the effects of the solvents and substituents. Several mechanisms have been proposed for the ozonisation of the hydrazones.[10–12] In the ozonolysis of 1-phenylazo-2-naphthol, the following two paths account for the products:

(A) Formation of the corresponding primary ozonide (**3**) via (**2**) as proposed by Erickson *et al.* in the ozonisation of 2,4-dinitrophenylhydrazone.[11]

(B) Formation of the hydrotrioxide (**4**) via (**2**) as proposed by Bailey *et al.* in the ozonisation of a series of nucleophiles.[13] The NH proton is sufficiently positive to combine with the negative terminal oxygen.

Unfortunately, paths A and B could not be differentiated in our study. It is reasonable that the peroxide (**5**) and *o*-naphthoquinone (**6**) come from the primary ozonide (**3**) and/or the hydrotrioxide (**4**). The peroxide (**5**) is converted into benzene (**7**), chlorobenzene (**8**), phenol (**9**) and nitrogen gas (**10**) in solution. *o*-Naphthoquinone is further ozonated to phthalic anhydride (**11**) and phthalide (**12**). The probable mechanism is shown in Scheme 1.

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