Ozonolysis of 3-Methyl-1-phenyl-4-phenylazo-5-pyrazolone

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In chlorinated solvents, 3-methyl-1-phenyl-4-phenylazo-5-pyrazolone (**1**) easily reacts with ozone to give benzene (**2**), phenol (**3**), chlorobenzene (**4**), *o*-chlorophenol (**5**), biphenyl (**6**), and 3-methyl-1-phenyl-2-pyrazoline-4,5-dione (**7**). The formation of these products is explained by an electrophilic ozone attack on the hydrazone tautomer **1′**.

It is of interest to study the reaction of coloring matter with ozone in view of an ozone treatment of dye wastewater and the ozone fading of dyes.

The authors have reported a series of ozonization reactions of dyes and their model compounds.[1)]

We discuss here the ozonolysis of 3-methyl-1-phenyl-4-phenylazo-5-pyrazolone, a model compound of azo-pyrazolone dyes.

Experimental

Instruments. Ozone was generated by a Nihon Ozon 0-1-2 type ozonizer. Melting points were measured with a Yanagimoto micro melting-point apparatus. Gas chromatography was performed on Shimadzu 4CPF and Ohkura 802 gas chromatographs. IR, UV, NMR, and MS spectra were obtained with Hitachi EPI-S2, Hitachi EPS-3T, JEOL JUM-GX 270, and Hitachi M-52 spectrometers, respectively.

Materials. 3-Methyl-1-phenyl-4-phenylazo-5-pyrazolone (**1**) was synthesized by a diazotization-coupling method and recrystallized from ethanol; mp 157°C (lit,[2)] 155°C). 4-Arylazo-3-methyl-1-phenyl-5-pyrazolones were also synthesized by the same procedure. Benzene (**2**), phenol (**3**), chlorobenzene (**4**), *o*-chlorophenol (**5**), and biphenyl (**6**) were pure grades which were available commercially. 3-Methyl-1-phenyl-2-pyrazoline-4,5-dione (**7**) was isolated from the reaction mixture by glc using a Silicone OV-1 column; mp 118°C (lit,[3)] 119°C). The purity of materials was confirmed by gas chromatography.

Ozonolysis Reaction. Ozonolysis was carried out with an ozone-nitrogen mixture (ozone: 0.39—1.10 mmol, nitrogen: 200 ml min^{-1}) on 1 mmol of substrate in 50 ml of solvent at 0°C. The reaction mixture was allowed to stand for 40 min and was treated with dimethyl sulfide. The disappearence of peroxide activity was confirmed by a KI test. The products were analyzed by gas chromatography using 2% OV-1, 2% FFAP, and Gaskuropak 54 columns. Product identification was made by comparing the mass spectra with those of authentic samples. Product determination was also made by gas chromatography.

Calculation of Rate Constant. Ozonolysis was carried out with an ozone–oxygen mixture (ozone: 0.15 mmol min^{-1}, oxygen 200 ml min^{-1}) on 0.5 mmol of substrate in 200 ml of chloroform at 0°C. The reaction was followed by measuring the absorption maximum (395 nm) every 1 min. The reaction was then applied to pseudo first-order kinetics, shown in Eq. 1.

$$\ln S_0/S_t = k_x(\text{obsd}) \times t, \quad (1)$$

where S_0 is an initial concentration of substrate, S_t is the concentration after ozonolysis reaction for t min, and k_x (obsd) is a pseudo first-order rate constant. The treatment gave a good relation and the rate constant was calculated. The obtained rate constant was then corrected for the existence ratio of the hydrazone tautomer, as shown in Eq. 2.

$$k_x(\text{corr}) = \frac{k_x(\text{obsd})}{R_{\text{Hydrazone}}} \times 100, \quad (2)$$

where k_x (corr) is a pseudo first-order rate constant corrected, and $R_{\text{Hydrazone}}$ is an existence ratio (%) of the hydrazone tautomer in chloroform. The result is shown in Table 1.

Table 1. Pseudo first-order rate constants on the ozonization of 4-(substituted phenylazo)-3-methyl-1-phenyl-5-pyrazolones[a)]

Substituent	k_X(obsd) / min^{-1}	Existence ratio of hydrazone tautomer[b)] / %	k_X(corr) / min^{-1}	log k_X(corr)/k_H(corr)
4-OCH_3	1.75	97	1.80	0.269
4-CH_3	1.45	96	1.51	0.192
3-CH_3	0.95	96	0.99	0.009
H	0.92	95	0.97	0
3-OCH_3	0.78	91	0.86	−0.052
4-Cl	0.71	87	0.82	−0.073
4-$COCH_3$	0.36	86	0.42	−0.363
4-NO_2	0.30	85	0.35	−0.442

a) Ozonization was carried out with an ozone–oxygen mixture (ozone: 0.15 mmol min^{-1}, oxygen: 200 ml min^{-1}) on 0.5 mmol of substrate in 200 ml of chloroform at 0°C. b) The existence ratio was determined by the ^{1}H NMR analysis.

TABLE 2. OZONOLYSIS OF 3-METHYL-1-PHENYL-4-PHENYLAZO-5-PYRAZOLONE[a)]

Run	Sol	Ozone introduced	Conv	Yield[b)]/%				Reactivity[c)]	Dissolved[d)] ozone	Hydrazone[e)] form	Viscosity[f)]
		mmol	%	2	3	4	7		mmol dm^{-1}	%	cp
1	$CHCl_3$	0.39	25	70	16	7	77	0.64	3.6	95	0.701
2	$CHCl_3$	0.71	45	54	7	5	30	0.63	3.6	95	0.701
3	CH_2Cl_2	0.74	54	54	6	10	14	0.73	3.7	98	0.537
4	CCl_4	1.10	50	—	5	22	26	0.45	4.7	87	0.734

a) The reaction was carried out with an ozone–nitrogen mixture (nitrogen: 200 ml min^{-1}) on 1.0 mmol of 3-methyl-4-phenylazo-5-pyrazolone in 50 ml of solvent at 0°C. Trace amounts of *o*-chlorophenol (**5**) and biphenyl (**6**) were also detected in each case. b) Yield was based on the substrate reacted with ozone. c) Reactivity was based on **1** (reacted)/ozone(introduced). d) Dissolved ozone was determined by iodometric titration. e) The ratio was based on the ^{1}H NMR analysis. f) η Value at 0°C.

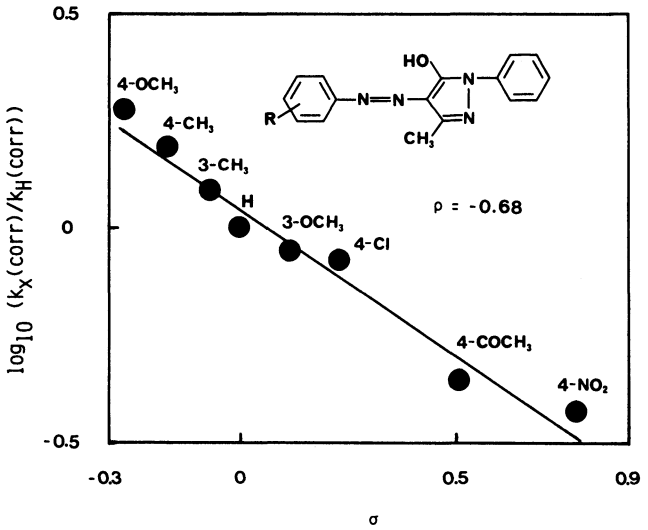
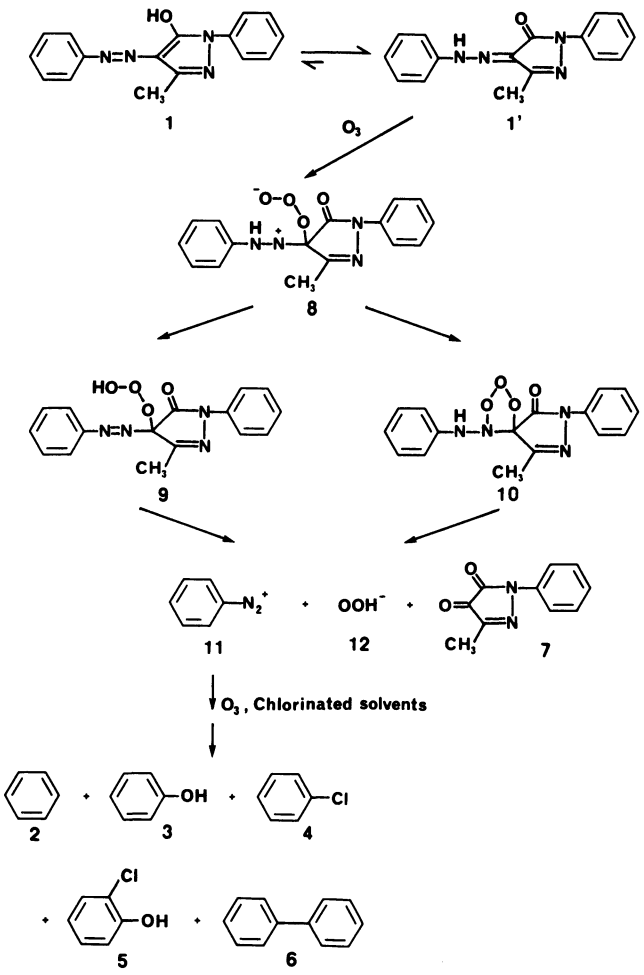


Fig. 1. Hammett's plot for the ozonolysis of 4-arylazo-3-methyl-1-phenyl-5-pyrazolones.
The reaction was carried out with an ozone-oxygen mixture on 0.5 mmol of substrate in 200 ml of chloroform at 0°C.



Scheme 1.

Results and Discussion

When 3-methyl-1-phenyl-4-phenylazo-5-pyrazolone (**1**) was ozonized in chloroform, benzene (**2**), phenol (**3**), chlorobenzene (**4**), *o*-chlorophenol (**5**), biphenyl (**6**), and 3-methyl-1-phenyl-2-pyrazoline-4,5-dione (**7**), were detected in the reaction mixture. The formation of trace amounts of hygroscopic compounds were also observed. The result is shown in Table 2. The reactivity of **1** with ozone in carbon tetrachloride was smaller than in the other solvents. The possible factors controlling the rate are the viscosity of the solvent, the amount of dissolved ozone, and the ratio of the hydrazone tautomer. The amount of dissolved ozone in each solvent was then measured by iodometric titration. Generally, *o*-hydroxy azo compounds exist as equiribrium mixture of azo-hydrazone tautomers. In 1963, Jones *et al.* determined the structure of the hydrazone tautomer of **1** as the quinone hydrazone form **1'**.[4] The IR and ^{1}H NMR spectra showed a presence of the NH and C=O groups (IR: 3400 (weak, ν_{NH}) and 1655 ($\nu_{C=O}$) cm^{-1} and ^{1}H NMR δ=13.70 (br. s)), suggesting that the hydrazone tautomer is predominant. The ratio of **1'** in each solvent was then calculated from an ^{1}H NMR analysis. Under the reaction conditions, the reactivity of **1** with ozone seems to depend on both the ratio of the hydrazone tautomer and the viscosity of the solvent. The reactivity increased with an increasing ratio of the hydrazone tautomer **1'** and a decreasing viscosity of the solvent.

The effect of a substituent on the ozonolysis reaction

of **1** was investigated. Since treatment by pseudo first-order kinetics gave a good relation, the rate constant was calculated in the same way. On the other hand, the effect of a substituent on the azo-hydrazone tautomeric equiribrium of *o*-hydroxy azo compounds has been reported.[5] As shown in Table 1, an existence ratio of 4-(substituted phenylazo)-3-methyl-1-phenyl-5-pyrazolones was in the following order of substituent, 4-OCH_3>3-CH_3,4-CH_3>H>3-OCH_3>4-Cl>4-$COCH_3$>4-NO_2. This is consistent with that of the electron-donative ability of the substituent. Then, the rates of the ozonolysis reactions of 4-(substituted phenylazo)-3-methyl-1-phenyl-5-pyrazolones were corrected for the existence ratio of the hydrazone tautomer. The results are shown in Table 1. The plots of the logarithms of the relative rates k(corr) thus obtained against Hammett's σ constants gave a straight line whose slope was found to be $\rho=-0.68$ ($r=-0.98$). The result is shown in Fig. 1. The negative value of ρ appears consistent with the electrophilicity of ozone.

The probable ozonolysis mechanism is shown in Scheme 1. Ozone electrophilically attacks the hydrazone tautomer **1'** to give a primary ozonide **9** and/or the hydrotrioxide **10** *via* **8**. These unstable intermediates could not be isolated. They cleave to benzenediazonium ion (**11**), hydroperoxide ion (**12**), and 3-methyl-1-phenyl-2-pyrazoline-4,5-dione (**7**). When the ozonolysis reaction was carried out in the presence of 2-naphthol, 1-phenylazo-2-naphthol was detected, suggesting the formation of **11** during the reaction. The diazonium ion **11** is converted into benzene (**2**), phenol (**3**), chlorobenzene (**4**), *o*-chlorophenol (**5**), biphenyl (**6**), and nitrogen gas in the chlorinated solvent. From the results that when 2-naphthol was added to the hygroscopic compound formed during the ozonolysis reaction of **1**, 1-phenylazo-2-naphthol was detected, and that the hygroscopic compound showed the presence of chlorine ions by a Beilstein test, it was concluded that benzenediazonium chloride is at least one of the components of the hygroscopic material.

References

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