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Short Communication

Stability of Disodium 2-Arylazo-1-Naphthol-3,6-Disulfonates to Ozone

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ABSTRACT

The stability of the title compounds to ozone has been investigated. Electron-withdrawing and bulky nitro and nonafluorobutyl groups substituted at the 2-position of the aryl moiety improved the stability.

INTRODUCTION

Photocopiers which generate a small amount (approximately 0·025 ppm) of ozone are widely used in offices. As ozone is a strong oxidizing agent, dyes used for ink-jet and thermal printings need to have a good stability to ozone. In our continuing study on the reaction of dyes with ozone,[1] the reactivity of water-soluble monoazo dyes with ozone is examined in this paper.

RESULTS AND DISCUSSION

Dyes **1** used in this study are shown in Table 1. All dyes were synthesized by a diazotization–coupling reaction. To estimate the reactivity of dyes with ozone, the reaction was studied by first-order kinetics. An example is shown

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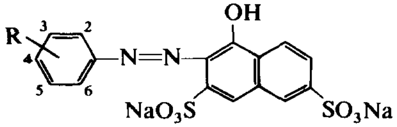
TABLE 1
Reactivity of Dyes with Ozone



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Run	*R*	*k* × *10*^{3} (*s*$^{-1}$)
1	H	5·3 ± 0·4
2	2-CF_3	4·3 ± 0·1
3	3-CF_3	5·7 ± 0·5
4	4-CF_3	3·6 ± 0·1
5	3,5-diCF_3	4·5 ± 0·5
6	2-C_4F_9	2·9 ± 0·3
7	2-CH_3	5·4 ± 0·6
8	2-NO_2	2·7 ± 0·3
9	2-Br	4·6 ± 0·1

in Fig. 1, where A_0 and A_t are the absorbance at times 0 and t (in seconds) at the maximum absorption, respectively. In the initial stage of the reaction, the plots were linear and the rate constant (k) was calculated to be $5{\cdot}6 \times 10^{-3}\ s^{-1}$. Table 1 shows also the reaction rate constants of **1** with ozone. Introduction of electron-withdrawing trifluoromethyl groups into the molecule inhibited the reaction (runs 1–6). The reactivity was in the following order of substituents: 2-NO_2, 2-C_4F_9 < 2-Br, 2-CF_3 < H, 2-CH_3 (runs 1, 2 and 6–9).

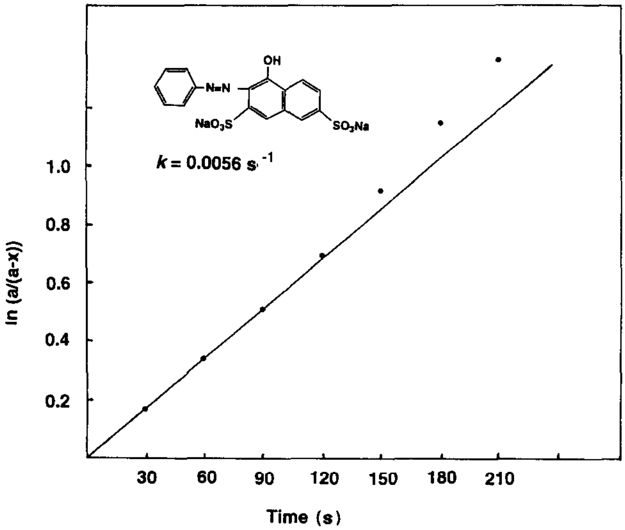

Fig. 1. Reaction rate of dye with ozone.

The electron-withdrawing property of the nonafluorobutyl group is similar to that of the trifluoromethyl group.[2] Ozone readily reacts with *o*-hydroxyazo dyes, as a result of the formation of the hydrazone tautomer in the solution.[3] The electron-withdrawing and bulky substituent at the 2-position of the aryl moiety inhibited ozone attack on the hydrazone form of **1**.

EXPERIMENTAL

Instruments

Ozone was generated with a Nihon Ozon 0-1-2 ozone generator; UV spectra were measured with a Shimadzu A-160 spectrometer; and nuclear magnetic resonance (NMR) and mass spectra were obtained with Jeol 270 and Shimadzu QP-1000 spectrometers, respectively.

Synthesis of 2-nonafluorobutylaniline

To a dimethylsulfoxide solution (40 ml) of 2-iodoaniline (2·2 g, 10 mmol) were added copper powder (1·5 g) and nonafluorobutyl iodide (3·5 g, 10 mmol). The mixture was heated at 110°C for 19 h using an autoclave. After the reaction, 250 ml of water was added to the mixture. The product was extracted with ether (250 ml), dried with sodium sulfate and distilled under reduced pressure. 2-nonafluorobutylaniline was obtained in 48% yield (1·5 g). bp: 99·5–100·5°C/19 mm Hg; ^{1}H NMR ($CDCl_3$) δ 4·21 (s, 2H), 6·71 (d, $J = 7{\cdot}7$ Hz, 1H), 6·79 (*t*, $J = 7{\cdot}7$ Hz, 1H), 7·29–7·32 (m, 2H); EIMS (70 eV) m/z (rel. intensity) 311 (M^+, 74), 142 (100), 102 (13), 69 (13).

Synthesis of dyes (1)

Dyes (**1**) were prepared by a diazotization–coupling reaction. The general procedure was as follows. To an aqueous solution (5 ml) of an aniline (5 mmol) and concentrated hydrochloric acid (15 mmol) was added 20% aqueous sodium nitrite solution (5 mmol) at 0°C, and the mixture was stirred for 30 min. To an aqueous solution (15 ml) of disodium 1-naphthol-3,6-disulfonate (5 mmol) was added the diazonium salt at 0°C. The pH of the solution was adjusted to 10 with 10% aqueous sodium hydroxide, and the mixture was then stirred overnight. After reaction, the product was obtained by salting-out. The crude product was extracted with ethanol and dried.

Reaction of dyes with ozone

To an aqueous phosphate buffer solution (pH 7·0, 500 ml) of dye (0·05 mmol) was introduced an ozone–oxygen mixture (ozone 0·17 mmol min^{-1}, oxygen

100 ml min^{-1}) at 25°C. The reaction rate (k) was calculated on the basis of the changes of absorbance at the absorption maximum (λ_{max}).

REFERENCES

1. Matsui, M., *Shikizai Kyokai Shi*, **64** (1991) 29.
2. Matsui, M., Kawamura, S., Shibata, K., Muramatsu, H., Mitani, M., Sawada, H. & Nakayama, N., *J. Fluorine Chem.*, **57** (1992) 209.
3. Matsui, M., Konda, A., Shibata, K. & Takase, Y., *Bull. Chem. Soc. Jpn*, **58** (1985) 2829.