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Novel Substituent Effect Controlling the Stability of α-Azohydroperoxides

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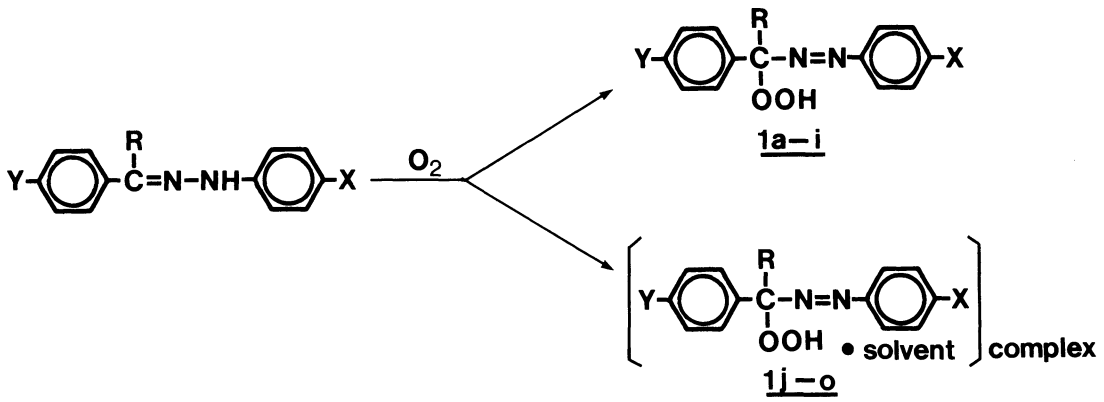
Several substituted α-azohydroperoxides were prepared, and their stabilities were found to be strongly controlled by novel substituent effects. The general trend of the effects was deduced.

α-Azohydroperoxides have been frequently reported to be unstable and explosive.[1-8] However, the precise nature of the explosiveness or instability of these compounds has not been adequately described. In the present study we have investigated the substituent effects for the destabilization of α-azohydroperoxide (1), finding that the stability of the compound is strongly controlled by the novel electronic effects of the substituents. To our knowledge these effects have not yet been reported. The general trend of the effects was deduced on the basis of the usual organic electronic theorem. This study also provides some insight into the so-called explosive α-azohydroperoxides.

Several substituted α-azohydroperoxides (1a-o) were prepared by autoxidation of hydrazones in high yields (Scheme 1).[1,9] Some of these compounds have been known for many years without any recognition of their peculiar properties of stability or instability. In the present study we have found that the α-azohydroperoxides 1a-o are classified into two types, A and B (Table 1). Type A is a relatively stable nonexplosive compound existing as a solvent free form (1a-i), while type B is an unstable explosive compound which is isolable only as a molecular complex with solvent at room temperature (1j-o).[10,11] The molecular complex decomposed suddenly or explosively when all the solvent molecule in the complex was taken away.[12] Diazonium ions were formed by the decomposition.[6,7]

Therefore, it is evident that the instability of α-azohydroperoxide is greatly influenced by the substituents. From the data in the table, the general trend of the substituent effects for the stability or instability of α-azohydroperoxides is deduced.

First, we discuss the substituent effects of the monosubstituted compounds. A comparison of the data for the stability of the compounds with Y = H leads us to deduce the following general trend for the substituent effects of X in the arylazo group. The Br, Cl, and MeO substituents located at the para position of the arylazo group stabilize the compound (1a-c, 1f, and 1g), while the Me and H substituents at the same position destabilize it (1j, 1k, and 1m). The α-methyl deriva-



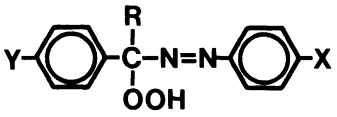
Scheme 1.

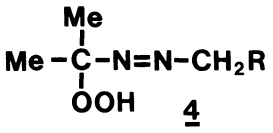
tives (1f and 1g) showed the same trend of the substituent effects as observed in the parent compounds (1a and 1b).

These observations suggest that either the inductive effect (electron-withdrawing) or the strong electron donating resonance effect of the MeO, Cl, and Br substituents (σ_R^p = -0.50 ∿ -0.22) in the arylazo group stabilizes the compound. However, the fact that the nitro derivatives 2 and 3 are unstable,[4,13] suggests that the latter plays a role in the stabilization of the monosubstituted compounds with Y = H.

On the other hand, the general trend of the substituent effect for Y is deduced by a comparison of the data of the compounds with X = H. The MeO and Me substituents located at the para position in the benzyl group stabilize the compound (1d and 1e), while the Cl and H substituents at the same position destabilize it (1j, 1l, and 1m). These observations suggest that the substituent effect of Y in the monosubstituted compound with X = H is correlated with the parameter such as the Hammett σ constants. It seems that the substituent (Y) having a negative or positive σ value stabilizes or destabilizes the compound respectively.

The generalization deduced above is applicable to the compounds 4 and 5. They are unstable and explosive.[2,3] This is because in 4 the alkyl group located at the azo moiety exerts no stabilization effect (see 1k), and in 5 the Br and F substituents for Y destabilize the compound as observed in 1l.





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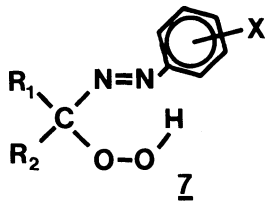
2: X=NO_2; Y=H; R=H
3: X=NO_2; Y=H; R=Me
5: X=H; Y=Br (or F); R=H
6: X=NO_2; Y=Cl; R=Me



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Second, the substituent effects for the disubstituted compounds are the followings. The dimethoxy derivative (1h) is stable, while the methyl-chloro deriva-

Table 1. Solvent free and solvated α-azohydroperoxides (molecular complex)

	1	substituent R	X	Y	dec. (°C)	^{1}H-NMR (ppm)[c),14)] -OOH[d)]	-CH[d)]
	solvent free compound[a)]						
A	1a	H	Br	H	114	8.58	6.26
	1b	H	Cl	H	106	8.71	6.28
	1c	H	OMe	H	49	8.97	6.43
	1d	H	H	OMe	91	8.75	6.42
	1e	H	H	Me	65	8.72	6.42
	1f	Me	Br	H	54	9.14	-[e)]
	1g	Me	Cl	H	51	9.29	-[e)]
	1h	H	OMe	OMe	57	8.79	6.46
	1i	H	Br	Cl	55	11.76[f)]	6.03[f)]
	molecular complex[b)]						
B	1j	H	H	H	58	9.14	6.39
	1k	H	Me	H	38	9.20	6.42
	1l	H	H	Cl	41	9.03	6.19
	1m	Me	H	H	(oils)	9.90	-[e)]
	1n	H	Cl	Cl	66	(7.80)[g)]	6.14
	1o	H	Me	Cl	56	9.30[h)]	6.15

a) Yellow needles from benzene. b) A 1:1 or 1:0.5 molecular complex with benzene. All complexes are yellow needles from benzene. The number of the solvent molecule in the complex was determined NMR spectroscopically in acetone-d_6. c) Values in benzene-d_6 d) Singlet. e) Not corresponding. f) In acetone-d_6. g) Obscure. h) Broad singlet.

tive (1o) is unstable. These properties are explainable on the basis of the general trend deduced above. However, the same generalization dose not explain the difference in the stabilities of 1i[15)] and 1n. The former is stable, while the latter is unstable. In addition, the chloro-nitro derivative (6) is stable.[4,16)] These imply that the substituent effect of the disubstituted compound is complicated more than that of the monosubstituted one.

All our observations, therefore, indicate that the accumulation of data and physico chemical studies are necessary before drawing the conclusion of the substituent effects for the stability of α-azohydroperoxides including mono and disubstituted derivatives. Meanwhile, Bozzini et al. from the X-ray studies indicated

an intramolecular hydrogen bonding structure (7).[17] This suggest that intramolecular hydrogen bonding plays a role in the stabilization of α-azohydroperoxides.

The molecular complex of α-azohydroperoxide is stable as far as the solvent molecule is included in the complex. But, it decomposes suddenly or sometimes explosively when all the solvent molecule is eliminated. In contrast, the solvent free compound does not decompose in the manner observed in the molecular complex. We suspect that the so-called explosive α-azohydroperoxides belong to type B, and are a molecular complex with solvent.

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9) Satisfactory elemental analyses were obtained for 1a-i. However, due to the instability, the elemental analyses of 1j-o were difficult to achieve.
10) The number of the solvent molecule in the complex depends on dryness (Ref. 6).
11) We have reported previously that 1j forms a molecular complex with petroleum ether (Ref. 6). However, we correct it as a benzene complex with the contamination of petroleum ether.
12) At ca. -20 °C the decomposition occurred when the solvent in the complex was removed in vacuo. As to the decomposition at room temperature, see Ref. 6.
13) Preparation of the compounds 2 and 3 was attempted using the method reported by Nishinaga et al. (Ref. 4). But, due to the instability, the isolation of these compounds has not been successful.
14) The chemical shifts of the methine and hydroperoxy protons are in accordance with those reported in the literature (Ref. 8).
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16) We have prepared this compound by the method reported by the previous authors (Ref. 4), confirming that 6 exists as a solvent free form.
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