Mechanism of Oxidation of *trans*-Azobenzenes with Peroxybenzoic Acid

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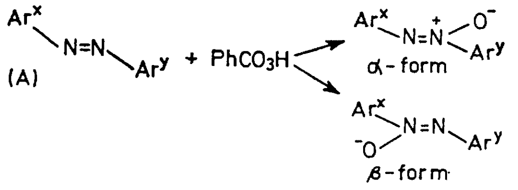
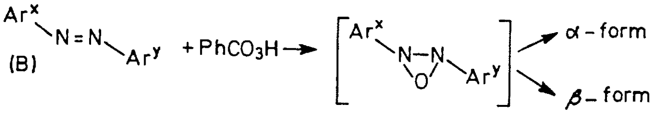
Summary Analysis of substituent effects on the rate and the product isomer ratio in the oxidation of *trans*-azobenzenes with peroxybenzoic acid to give *trans*-azoxybenzenes suggests a simple one-step mechanism which does not involve an oxadiaziridine intermediate.

ALTHOUGH the oxidation of *trans*-azobenzenes with peroxyacids has been investigated extensively,[1] no consideration has yet been given to the mechanism. Two possible modes of attack by the peroxy-acid on the azo-group may be considered; one is competitive attack at either of the lone pairs of azo-nitrogens (mechanism A) and the other an attack at the azo double bond, in which the transition state is symmetrical with respect to each benzene nucleus, leading to the rate-determining formation of an oxadiaziridine-type intermediate,[2] which is immediately converted into isomeric azoxy-compounds (mechanism B).





The quantitative correlation between the reaction rate and the product isomer ratio which has previously been derived for a similar reaction system on the assumption that the effects of substituents on the activation free energy are additive[3] seems useful as a criterion for distinguishing between the alternative mechanisms; thus the following relations hold for mechanism A,

$$k_{xy}/(k_{xx}\cdot k_{yy})^{1/2} = (r^{1/2} + r^{-1/2})/2 \qquad (1)$$

and for mechanism B,

$$k_{xy}/(k_{xx}\cdot k_{yy})^{1/2} = 1 \qquad (2)$$

where k_{xx}, k_{xy}, and k_{yy} are observed rate constants for compounds unsymmetrically and symmetrically disubstituted by group X and/or Y, respectively, and r is the product isomer ratio.

TABLE 1

Rate constants

Substituents (Ar^x and Ar^y)	10^4k (l. mole^{-1} sec.$^{-1}$)
(p-MeOC$_6$H$_4$)$_2$	31·6
(p-MeC$_6$H$_4$)$_2$	7·75
Ph$_2$	1·82
(o-MeC$_6$H$_4$)$_2$	0·566
(α-Naphthyl)$_2$	0·353
Ph, p-MeC$_6$H$_4$	4·05
Ph, p-MeOC$_6$H$_4$	9·77
o-MeC$_6$H$_4$, p-MeOC$_6$H$_4$	7·84
p-MeC$_6$H$_4$, α-Naphthyl	4·29

To test the applicability of this criterion and to elucidate the mechanism, we have determined the rates as well as the isomer ratios in the oxidation of a series of substituted *trans*-azobenzenes and *trans*-azonaphthalenes with peroxybenzoic acid in benzene at 25°. Second-order rate constants calculated from the rate of consumption of peroxybenzoic acid are summarized in Table 1.

Isomer ratios were determined on the products from *p*-methyl- and *p*-methoxy-substituted compounds by comparing the intensities of n.m.r. signals due to *p*-methyl or *p*-methoxy protons. The results summarized in Table 2 clearly show that the experimental data fit equation (1) fairly well, but not equation (2), thus indicating that the oxidation of azobenzenes with peroxybenzoic acid proceeds by way of mechanism A, contrary to the case of diaryltriazenes, which are oxidized by a mechanism similar to mechanism B.[3]

TABLE 2

Correlation between rates and isomer ratios

Substituents		Chemical shifts of *p*-methyl or *p*-methoxy protons in benzene (δ p.p.m.)		Isomer ratios		
Ar^x	Ar^y	α	β	r (α/β)	$(r^{1/2} + r^{-1/2})/2$	$k_{xy}/(k_{xx} \cdot k_{yy})^{1/2}$
p-MeC_6H_4	Ph	2·06	1·96	1·22	1·01	1·08
p-$MeOC_6H_4$	Ph	3·26	3·19	1·78	1·04	1·29
o-MeC_6H_4	*p*-$MeOC_6H_4$	3·25	3·30	9·2	1·68	1·85
α-Naphthyl,	*p*-MeC_6H_4	1·99	2·09	19	2·29	2·59

It is apparent from Table 2 that *o*-methyl or α-naphthyl (Ar^X) group enhances the formation of the α-form enormously in preference to the β-form, to an extent which probably surpasses what would be expected from the electronic effect; such an effect is certainly attributable to the steric effect exerted by the substitution at the *ortho*-position. In the derivation of the correlation between the reaction rate and the isomer ratio mentioned above, nothing is included which excludes any steric effects by substituents as far as these effects can be regarded as additive.[3] The present results demonstrate the validity of the additivity rule also for the effect of *ortho*-substituents.

(*Received, July* 22*nd*, 1970; *Com.* 1205.)

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[3] T. Mitsuhashi and O. Simamura, *J. Chem. Soc.* (*B*), 1970, 705.