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THE REACTION OF 1-ETHOXYCARBONYL-3-METHYLBENZIMIDAZOLIUM SALTS WITH ELECTROGENERATED AND POTASSIUM SUPEROXIDE

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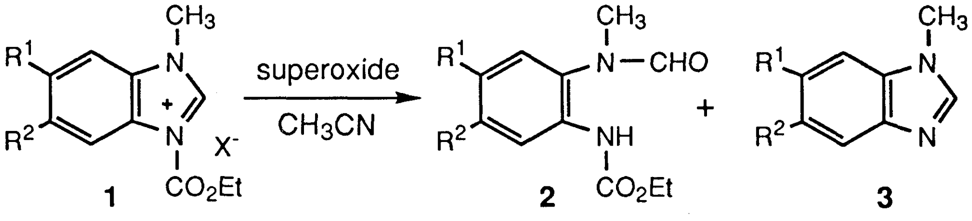
1-Ethoxycarbonyl-3-methylbenzimidazolium salts, which have two possible reactive sites toward superoxide, were allowed to react with KO_2 and electrogenerated superoxide to give the ring-opened products and 1-methylbenzimidazoles. The former compounds were specific products for superoxide, and the product distributions were revealed to depend on the counter cation of superoxide.

KEYWORDS 1-ethoxycarbonyl-3-methylbenzimidazolium salt; counter cation; potassium superoxide; electrogenerated superoxide; *o*-(*N'*-formyl-*N'*-methyl)amino-*N*-ethoxycarbonylaniline; 1-methylbenzimidaole

Superoxide is one of the most noteworthy active oxygen species, and has been attracting much attention from both the chemical and biological viewpoints.[1)] Superoxide has both radical and anionic characters; therefore it exhibits many chemical reactivities[2)] including nucleophilic reaction, one electron reduction, hydrogen abstraction, and proton abstraction. The study of superoxide has been progressing since potassium superoxide with 18-crown-6 was shown to be useful in polar organic solvents.[3)] However, there remain some disadvantages in the research on chemical reactivity. First, no superoxide salts were readily available other than KO_2; thus the influences of counter cation remain unclear. Secondly, the contamination of KOH is non-negligible; KOH is contained originally in the commercial reagent, or is formed by the absorption of moisture in the reaction process. Thus, in the reactions which are proceeded by both KO_2 and KOH, true reactive species cannot be identified, and there are many examples that belong to this category.



$X = ClO_4$, $MeSO_4$, or BF_4

Chart 1

In recent years, we have been investigating the reaction of azaheteroaromatics with superoxide, and have revealed the specific reactivity of superoxide with electron-deficient heterocycles.[4)] In the course of these studies, it was suggested that the compounds with multi-reaction sites to superoxide were apt to yield superoxide-specific products. In this paper, we describe the reaction of superoxide with 1-ethoxycarbonyl-3-methylbenzimidazolium salts **1**, which have an electron-deficient ring system and an ester group. The former is regarded as a one-electron acceptor, and the latter as an electrophilic site.

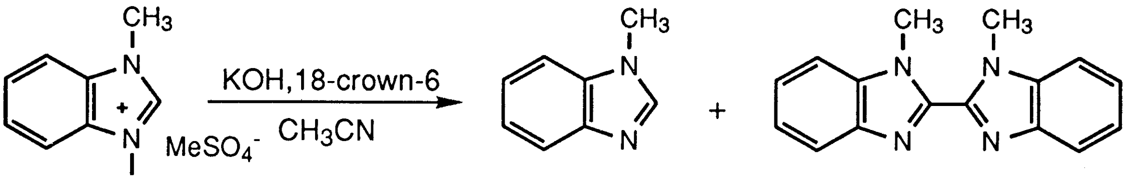
In the experiments, two general methods were used for the donation of superoxide. Method A involves the electroreduction of molecular oxygen. In the cathode chamber of H cell containing 0.1M tetraethylammonium perchlorate solution of acetonitrile (40 ml), a stream of oxygen was bubbled through a gas dispersion tube, and the potential was set and maintained at -0.90V vs. SCE until 40Q of electric current was consumed.[5] Then compound **1** (0.2 mmol) was added and the mixture was allowed to stand at room temperature for 2 h. Method B involves the use of KO_2 (0.4 mmol)[6] with 18-crown-6 (0.05 mmol). They were added to the solution of **1** (0.2 mmol) in acetonitrile (6 ml), and the mixture was allowed to react under the same conditions as method A. The results are summarized in Chart 1 and Table I.

Table I. The Reaction of 1-Ethoxycarbonyl-3-methylbenzimidazolium Salts with Superoxide

Entry	Substrate	Substituent	E1/2 (V vs.SCE)	Method	Yield of 2(%)	Yield of 3(%)
1	**1a**	$R^1=R^2=H$	-1.33	A	41	45
2	**1a**			B	6	52
3	**1b**	$R^1, R^2= -(CH=CH)_2-$	-1.10	A	47	-[7]
4	**1b**			B	33	trace
5	**1c**	$R^1=R^2=Me$	-1.36	A	29	23
6	**1c**			B	0	41
7	**1d**	$R^1=NO_2, R^2=H$	-0.47	A	61	33
8	**1d**			B	13	79
9	**1e**	$R^1=R^2=Cl$	-1.15	A	56	17
10	**1e**			B	38	14[8]

Method A: electrogenerated superoxide. Method B: potassium superoxide with 18-crown-6.

Next, control experiments were carried out using **1a** as a substrate. The use of hydrogen peroxide instead of $O_2^{\cdot-}$ resulted in the recovery of the starting material. When powdered KOH was allowed to react with **1a** under the same conditions, a dimer **4**[9] was obtained other than **3a** (Chart 2). Dimer **4** was never formed by superoxide; hence compounds **2** and **4** were revealed to be specific for superoxide and hydroxide ion, respectively.



1a **3a** 21% **4** 36%

Chart 2

The data in Table I show that methods A and B afforded different distribution of the products. Electrogenerated superoxide was suggested to favor the formation of **2**, whereas the use of KO_2 increased the yield of **3**, which is a common product for both KOH and KO_2. This phenomenon is clearly revealed in the cases of **1a**, **1c** and **1d**. To certify the results, the following experiment was performed. In the solution of electrogenerated superoxide (40 ml of CH_3CN) mentioned above, 1 eq of $KClO_4$ was added and then **1d** was dissolved into the solution. The mixture was allowed to stand for 3h to give **2d** and **3d** in 17% and 72% yields, respectively. That is, the addition of $KClO_4$ to the system of method (A) was revealed to change the product distribution to that of method (B) (Table II). The addition of the excess amount of Et_4NClO_4 to KO_2 solution (method B) gave rise to a moderate increase in the yield of **2d**. These facts suggest that a change of counter cations influenced the reactivity of superoxide, and there is a stronger interaction between potassium ion and superoxide in solution than that between tetraethylammonium ion and superoxide.

To the best of our knowledge, this is the first example that clearly reveals the effect of counter cation on the reaction of superoxide. We think the research using electron deficient azaaromatics will be useful for detailed study of superoxide chemistry. The reaction mechanism and application to the other imidazolium salts will appear in succeeding papers.

Table II. The Effect of the Counter Cation on the Distribution of **2d** and **3d**

Substrate	Conditions	Yield of 2d (%)	Yield of 3d (%)
1d	(A) electroreduction of O_2 in TEAP/CH_3CN	61	33
	(B) KO_2 - 18-crown-6 in CH_3CN	13	79
	(A) + 1.0eq. of $KClO_4$	17	72
	(B) + 20eq. of Et_4NClO_4	31	32

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