

the reaction of Li_2O and Cu_2O etc. In the last step after the reaction of LiX and Cu and so on, its ocv occurs up to 3.07 V. So, in order to prepare the cell which ocv has to obtain a higher value under a pressure condition, make sure to connect all electrode/electrolyte interfaces (Table 1) well.

And also it's reasonable to believe that in increase of conductivity is caused by a remarkable decrease of the internal resistance by high pressure and heterogeneity by the presence of heterogeneous mixture at CuCl/LiCl (Li_2O_2) interface.

In consequence of our studies, the high voltage and the conductivity of solid ionic electrolytes, consisting of LiX ($\text{X}^- = \text{Cl}^-$, BF_4^- and AsF_6^-) and lithium peroxide which will probably be similar to the Al_2O_3 structure under 6877.6 atm, can be substantially improved up to 2.7 to 3.45 V and about 10^{-6} to 10^{-5} (ohm cm) $^{-1}$ at room temperature.

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Novel Reaction of N-Bromoamides with Superoxide Anion Radical: Formation of N,N'-Diacylhydrazines

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Recently, intensive studies have been focused on the reaction of superoxide anion with heteroatom compounds such as nitrogen¹ and sulfur compounds². N-Bromoamide was first reacted with potassium superoxide in acetonitrile expecting to obtain isocyanate by Hofmann rearrangement³. In this reaction, however, any formation of isocyanate could not be observed, but N,N'-diacylhydrazine was obtained as the main product. Now, we report this new reaction and a possible reaction mechanism.

In a typical run, a solution of N-bromobenzamide⁴ (200 mg, 1 mmol; dry acetonitrile: 2 ml) was added to the suspension of potassium superoxide (86 mg, 1.2 mmol; dry acetonitrile: 3 ml) at -35°C under argon atmosphere. The reaction mixture was stirred for 10 h at -20°C in a refrigerator. Ethyl ether (*ca.* 3 ml) was added to the reaction mixture to precipitate, and the resulting mixture was filtered and washed with water to afford white crystals (96.8 mg, 80%). The crystals were identified to be N,N'-dibenzoylhydrazine by ¹H NMR, mass spectrum ($m/e = 240$ (M^+)), and mp ($238 \sim 239^\circ\text{C}$, lit⁵ $239.5 \sim 240.5^\circ\text{C}$). The results obtained were summarized in Table 1.

The superoxide anion has been known to act not only as a base but also as a good oxidant by transferring one electron⁶. If the superoxide anion attacks N-bromoamide as a base, the N-bromoamide will be converted to the corresponding isocyanate by Hofmann rearrangement. The resulting products in Table 1, however, showed that no rearrangement occur-

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Table 1. Products from the Reaction of N-Bromoamide with Potassium Superoxide

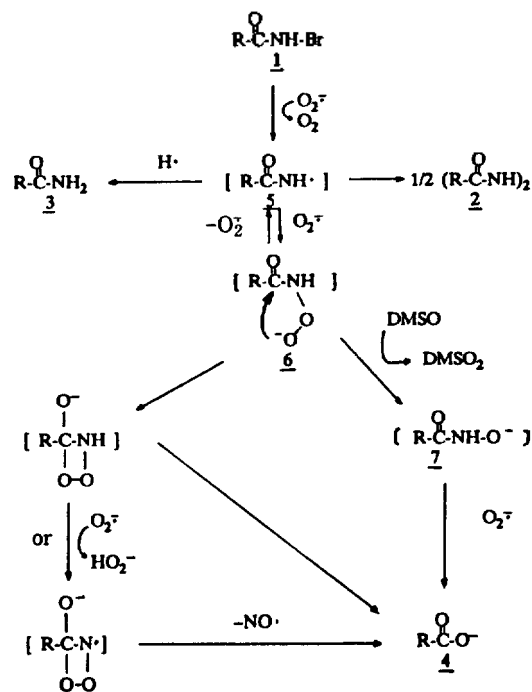
$$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}-\text{Br} + \text{KO}_2 \xrightarrow{\text{CH}_3\text{CN}} (\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH})_2 + \text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}_2 + \text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}^-$$

Entry	R	KO ₂ /1	2 (%)*	3 (%)*	4 (%)*
1	C ₆ H ₅	0.6	35	—	—
2	"	1.2	80	—	—
3	"	1.5	79	—	traceable
4	"	2.0	60	—	23
5	"	4.0	traceable	—	85
6	4-CH ₃ -C ₆ H ₄	1.2	83	—	—
7	CH ₃	1.2	56	32	—

*: Isolated Yields.

red. Since the superoxide anion is known to transfer one electron easily, it may attack N-bromoamide 1 to afford amide radical 5 and molecular oxygen⁷. The unstable amide radical 5 may be coupled to N,N'-diacylhydrazine 2 or converted to the amide 3 by abstraction of hydrogen atom.

When the excess amount of superoxide anion existed, the amide radical 5 might be converted into N-peroxyamide anion intermediate 6 by the coupling with superoxide anion,



Scheme 1

Table 2. Conversion of Dimethylsulfoxide to Dimethylsulfone During the Reaction

Entry	N-Bromoamide, 1	KO ₂ /1	DMSO ^a /1	Yield ^b of DMSO ₂ (%)
1	CH ₃ -C(=O)-NH-Br	1.2	0.5	traceable
2	"	2.2	0.5	15.5
3	"	3.0	0.5	18.6
4	"	4.0	0.5	15.6
5	CH ₃ -C(=O)-NH-Br	3.0	0.5	10.3

^aDMSO + KO₂ $\xrightarrow{\text{CH}_3\text{CN}}$ no reaction. ^bYields were determined by GC (Carbowax 20M).

and then finally converted to the carboxylic acid 4 (Entry 5 in Table 1).

Though such an N-peroxyamide anion intermediate 6 has

neither been isolated nor confirmed, it should have oxidizing ability. Dimethyl sulfoxide, which is easily oxidized with a nucleophilic oxidant⁸, was added to the reaction mixture in order to trap the N-peroxyamide anion intermediate 6 and the dimethyl sulfoxide was actually oxidized to the dimethyl sulfone as shown in Table 2. Dimethyl sulfoxide was not oxidized in the course of the reaction, when an equivalent amount of the superoxide was used (Entry 1 in Table 2). This result suggests that N-peroxyamide anion intermediate 6 may not be formed by the direct attack of superoxide to 1⁹. When more than two equivalent amount of superoxide was used, the major product was potassium benzoate 4. Benzohydroxamate, 7 was actually converted to benzoate by potassium superoxide under the same condition¹⁰. Further study on the scope and mechanism is under investigation.

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- A direct nucleophilic attack of superoxide anion to 1 can be considered to form 6, but it is not likely by the fact that DMSO was not oxidized to DMSO₂ when an equivalent or less amount of superoxide was used.
- Potassium benzohydroxamate (176 mg, 1 mmol) was readily reacted with KO₂ (172 mg, 2.2 mmol) in dry acetonitrile (ca. 5 ml) for 2 h at -35 °C under argon to afford potassium benzoate quantitatively.

