A New Method for Converting Thiourea and Monosubstituted Thioureas into Cyanamides: Desulphurisation by Superoxide Ion

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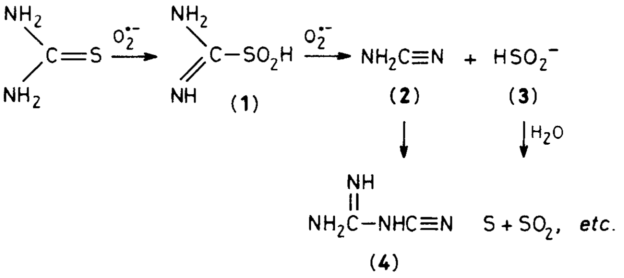
Superoxide ion, in aprotic media, converts thiourea and monosubstituted thioureas into cyanamides.

Investigations of the reactivity of superoxide ion ($O_2^{\cdot-}$) with organic compounds contribute to an understanding of its intriguing role in biological chemistry.[1] Organosulphur compounds are important in this respect and various types have been shown to be oxidised by $O_2^{\cdot-}$,[2,3] however, until recently none of the reported examples contained a C=S bond.

When thiourea, dissolved in pyridine under an N_2 atmosphere, was stirred with KO_2 (4 mol per mol of thiourea) at room temperature, no reaction took place, but after the mixture was heated to 60 °C for 2 h no thiourea remained. The reaction mixture was quenched with H_2O and the volatile components removed by evaporation. The residue was suspended in water and the pH adjusted to 7 by addition of HCl. The products were identified as elemental sulphur (0.5 mol per mol of thiourea), separated by filtration, and dicyandiamide (73% yield), obtained by concentration of the aqueous solution. An odour of SO_2 was noted.

The reaction was repeated under the same conditions using the monosubstituted compounds phenylthiourea and benzylthiourea and the products obtained were phenylcyanamide (82%) and benzylcyanamide (80%) respectively. In both cases, sulphur was also obtained and SO_2 detected during work up.

It is proposed that $O_2^{\cdot-}$ attacks the thiourea to form the *S,S*-dioxides (amidinesulphinic acids). The product in the case of thiourea will be formamidinesulphinic acid (**1**), which has previously been prepared from thiourea by the action of H_2O_2.[4] Sulphinic acids are good leaving groups[5] and readily undergo β-elimination reactions promoted by base. Compound (**1**) has been reported to eliminate HSO_2^- (**3**) when treated with base,[6] but its organic decomposition products were not identified. The isolation of dicyandiamide (**4**) in the present work indicates that the initial elimination product was cyanamide (**2**), which is known to dimerise in hot alkaline solution. The S and SO_2 are formed by breakdown of (**3**) during aqueous work up. In the case of the substituted thioureas the substituted cyanamides formed do not dimerise under the reaction conditions.



Thioamides can be desulphurised to nitriles by mercuric chloride–methylamine[7] or more moderately by diethyl azodicarboxylate–triphenyl phosphine.[8] The latter combination also converts thioureas into carbodi-imides.[9] In the present work the reactions described may be of some synthetic utility and may also contribute to a knowledge of the possible biological reactions of $O_2^{\bullet -}$.

After the completion of this work a publication covering the reactions of $O_2^{\bullet -}$ with diarylthioureas appeared.[10] These authors also obtained desulphurisation of the thioureas but their products were substituted guanidines and sulphate ion.

Received, 8th August 1983; Com. 1069

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