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REACTION OF CROWN-POTASSIUM WITH 1,3-DINITROBENZENE AND 4-NITROBENZYL FLUORIDE

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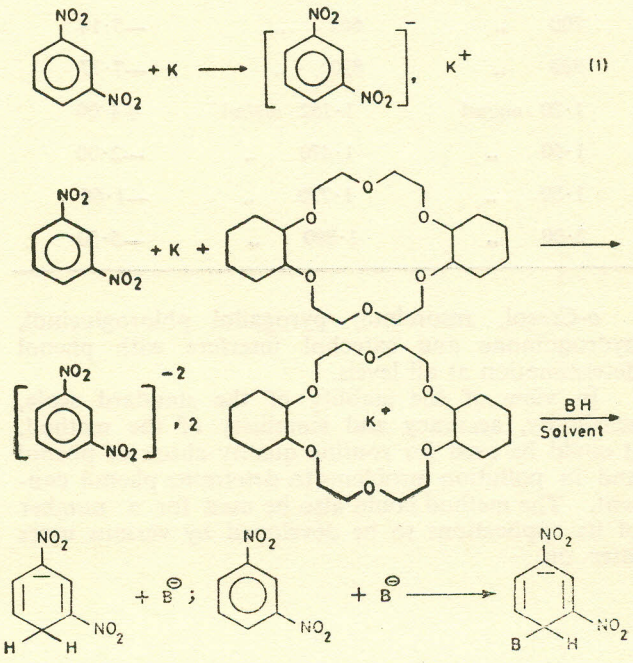
Abstract. Reaction of crown-potassium with 1,3-dinitrobenzene produces Meisenheimer complex while with 4-nitrobenzyl fluoride the anion radical of 4-nitrobenzyl fluoride is produced.

We report here different results obtained when crown potassium (cyclohexyl-18-crown-potassium)[1] is reacted with 1,3-dinitrobenzene (DNB) and 4-nitrobenzyl fluoride (NBF).

Treatment of crown-potassium[1] with 1,3-dinitrobenzene (DNB) led to a strongly absorbing species of modest stability (λ_{max} 520 nm, ε 8,000). The intense red colour was obtained in 2-methyltetrahydrofuran (MTHF) solution of crown potassium mixed at —80° (or lower) under high vaccum (10^{-4} mm or lower pressure). The contrast with results obtained with the reaction of DNB with alkali-metal (λ_{max} 495 nm, ε_{app} 100) [2a](eq 1) leads us to believe that the anion radical of DNB in not formed with crown-potassium. This red species, at low temperature (—100°), and in vaccum, is farily stable ($t_{\frac{1}{2}}$ about 3×10^4 sec). Also it is not very sensitive to air. This precludes it from being the dianion or trianion or dimer (of the monoanion radical). Thus the red species could be any of the following: the protonated product of the dianion or trianion or some decomposition product of Meisenheimer complex type. Since there is no proton donar except the solvent itself (as MTHF was very dry), the dianion or trianion formed immediately reacts with the solvent to form the Meisenheimer type complex.[2b] It cannot be said unequivocally, at this stage, which of the reactive species, the dianion or trianion, is responsible for the Meisenheimer type complex. Thus a tentative scheme for the production of red species (the Meisenheimer complex) is proposed which involves the formation of dianion of DNB (Eq 2).

Ttreatment of crown-potassium in 2-methyltetrahydrofuran with 4-nitrobenzyl fluoride (4NBF) under the same conditions led to absorption at 470 nm with ε 1600. The species absorbing at 470 nm was quite stable in vaccum but very sensitive to air. It is believed that this species is the anion radical of 4-nitrobenzyl fluoride, which studied electrochemically, has been found to be moderately stable (decomposition rate constant is about 0.014/sec) in the absence of air,[3] the anions radicals of nitrobenzene[4] and that of 4-nitrotoluene[5] also absorb in the same region 456–470 nm and the anion radical of nitrobenzene has molar extinction coefficient 1200 as compared to 1600 for 4NBF anion radical. Kosower and his coworker have reported λ_{max} and molar extinction ε of 4NBF anion radical (generated by pulse radiolysis) as 490 nm and 1600, respectivley.[6]

Yet another type of compound is formed when DNB is treated with the decomposed crown-potassium solutions (the deep blue colour of the solution is lost on standing for an hour or so at 25°).[1,2]



This sigma complex[2] has absorption at λ_{max} 540 nm and ε 5,500. In contrast to the air sensitivity exhibited by the solutions of radical anions described above, the σ-complexs olution were not rapidly changed upon exposure to air.

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