

Reaction of 2,4-Dinitrochlorobenzene with Aromatic Amines in Toluene: Effect of Nucleophile Structure

C.E.S. Alvaro¹, M.C. Savini¹, V. Nicotra¹, J. S. Yankelevich¹ and N. S. Nudelman²

¹Dpto. de Química, Facultad de Ingeniería, Universidad Nacional del Comahue. Buenos Aires 1400. (8300) Neuquén, Argentina

E-mail: salvaro @uncoma.edu.ar

²Dpto. de Química Orgánica. Facultad de Ciencias Exactas y Naturales. Pabellón II, 3°p, Ciudad Universitaria. U.B.A., Argentina

E-mail: nudelman@qo.fcen.uba.ar

Abstract: The kinetics of the reaction of 2,4-dinitrochlorobenzene (DNCIB) with aniline and substituted anilines such as p-anisidine, p-toluidine and N-methylaniline have been studied in toluene. Except for N-methylaniline the reactions have shown a third order in amine rate dependence which is consistent with aggregates of the amine acting as the nucleophile. On the other hand, the reaction of DNCIB with N-methylaniline under the same conditions shows a linear dependence of the second order rate coefficient, k_A , vs [amine], which is consistent with the previous mechanism.

Introduction

Previous research carried out in our laboratory on aromatic nucleophile substitutions (S_NAr) of 2,4-dinitrochlorobenzene in aprotic solvent [1,2] have shown formation of aniline dimers acting as nucleophile, formation of molecular complexes substrate-nucleophile and substrate-product reaction, formation of mixed aggregates aniline-HBA additive and specific effects solvent on S_NAr mechanism.

In order to investigate the relevance of nucleophile structure in defining the mechanism of S_NAr with amines in aprotic solvent, kinetic studies of the reaction of DNCIB with aniline, p-anisidine, p-toluidine, 2,4-dimethylaniline and N-methylaniline in toluene at 40°C have been carried out.

Experimental

Aniline, p-toluidine, 2,4-dimethylaniline and N-methylaniline were distilled over zinc powder and then over sodium under nitrogen at reduced pressure; p-anisidine was purified to constant melting point by recrystallization with toluene; DNCIB was crystallized twice from absolute ethanol. Toluene was kept over sodium wire for several days and distilled twice over sodium. The reaction products

were prepared and purified following the procedure previously reported [3].

Results and discussion

The second order rate coefficients, k_A , were found to increase rapidly with amine concentration, $[B]$, the plots of k_A vs $[B]$ show a quadratic dependence for the reaction of the primary anilines. The present results can be interpreted in terms of “dimer nucleophile” mechanism in which a dimeric aggregate of the amine (B:B) is considered to attack the substrate in the first step [1].

In order to evaluate the magnitude of the curvature obtained, the experimental values were fitted to a second-degree polynomial function. The quadratic coefficients, except for N-methylaniline, are significantly different from zero.

When 2,4-dimethylaniline is used, the second order rate coefficients are considerably smaller than for aniline at any concentration and the quadratic coefficient is also much less relevant than for the other anilines. These results are consistent with the “dimer nucleophile” mechanism and can be easily explained by decreasing dimerization due to the steric hindrance produced by the methyl group at the ortho position.

For the reaction of DNCIB with N-methylaniline in toluene, the plot of k_A vs $[B]$ shows a clear linear dependence with a zero intercept; where the spontaneous decomposition of the zwitterionic intermediate is negligible. This kinetic behaviour is consistent with what could be expected for the N-alkylanilines, considering that they undergo less-association than aniline. For this reason the attack by the “dimer nucleophile” is not relevant.

References and Notes

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