

SHORT
COMMUNICATIONS

Effect of Solvents on a Catalyzed Reaction between Aniline and Benzoic Acid

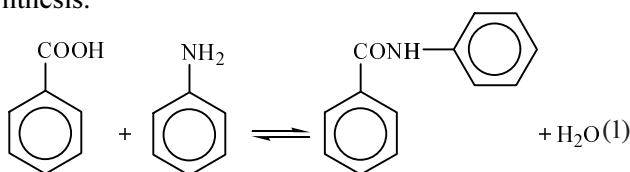
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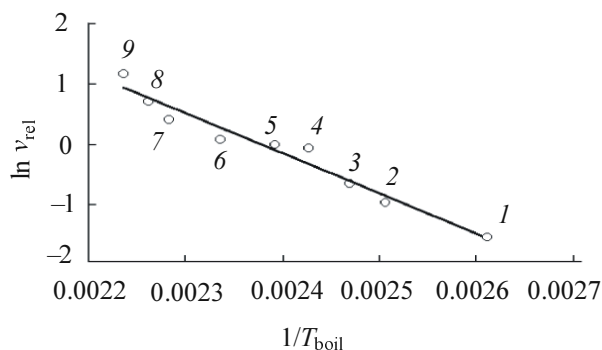
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We formerly studied [1–6] synthetic approaches, the effect of substituents and catalysts on reactions of direct acylation, namely on formation of anilides in reactions of aromatic amines with aromatic carboxylic acids.

Here we report on investigation of the solvent effect on the model reaction (1) in the presence of activated [5] titanium(IV) butoxide (0.02 mol per 1 mol of benzoic acid) aimed at finding optimum conditions for anilides synthesis.



The study of variations in the initial formation rate of benzanilide while carrying out reaction (1) in solvents differing in boiling points, polarity, and ability to coordinate with titanium(IV) ions revealed the following general relations.



Log relative initial rate ($\ln v_{\text{rel}}$) of reaction (1) as a function of reciprocal boiling point ($1/T_{\text{boil}}$) of nonpolar solvent. (1) toluene; (2) octane; (3) chlorobenzene; (4) *p*-xylene; (5) *o*-xylene; (6) *o*-chlorotolylene; (7) mesitylene; (8) pseudocumene; (9) decene.

Reaction (1) can proceed only at vigorous boiling and distilling off the forming water obviously in order to shift the equilibrium (1) to the right side. For instance, at boiling in *o*-xylene (145°C) reaction (1) within 1 h gave rise to 58% of benzanilide, whereas the acylation at 144°C in 1,3,5-trichlorobenzene, benzyl alcohol, or *o*-xylene without boiling and water distillation in 1–2 h yielded only 1–8% of benzanilide, and the results were irreproducible.

Reaction (1) proceeded best of all in aprotic media of low polarity (toluene, xylenes, decene, *o*-chlorotoluene, chlorobenzene etc.). The initial rate grows with increasing boiling point, and the log relative initial rate depends linearly on the reciprocal boiling point (see the figure). (The relative initial rates were calculated with respect to the initial reaction rate in *o*-xylene at equal reagents and catalyst concentrations). This dependence demonstrates that the rate of reaction (1) is governed mainly by the boiling point of the nonpolar solvent.

With growing polarity of the solvent the rate of reaction (1) considerably decreased. For instance, the yield of benzanilide after 4 h of boiling in nitrobenzene (32%, at 211°C) was nearly the same as after 30 min of boiling in mesitylene (38%, at 155°C). In reaction (1) carried out in boiling toluene and 1-butanol having close boiling points the yield in the former solvent was twice as high as in the latter one (30 and 15% in 2 h respectively).

In solvents of high polarity capable of coordination (DMF, HMPA, DMSO, and sulfolane) reaction (1) did not occur. Moreover, the small portions of these solvents added to the reaction mixture (10 mol% to the amount of benzoic acid) completely inhibited reaction (1) in *o*-xylene. This fact is apparently due to the competing complexing of these compounds with Ti(IV) preventing the entrance of reagents into the coordination sphere of titanium and thus inhibiting the catalytic process.

It is presumable that the linear relation of log relative initial rate to the reciprocal boiling point (see the figure) described by regression equation (2) (with the correlation factor 0.95) would be also valid for the substituted carboxylic acids and amines.

$$\ln v_{\text{rel}} = 15.80 - 6647/T_{\text{boil}} \quad (2)$$

Here T_{boil} is the boiling point of the solvent

In combination with the existing data on the effect of substituents in reaction (1) [2, 3] these results provide a possibility to forecast the reaction rates in various nonpolar solvent. These predictions can be applied to optimizing the preparation procedures for anilides of aromatic carboxylic acids, among which quite a number of compounds is of practical importance.

Benzoic acid, aniline, *o*-xylene, toluene, decene, and titanium(IV) butoxide were purified and handled as described in [2]. DMF, HMPA, DMSO, *p*-xylene, nitrobenzene, chlorobenzene, mesitylene, and octane of "pure" grade were purified as in [7–10]. The butanol and benzyl alcohol were boiled over CaO and distilled in a vacuum under nitrogen flow, *o*-chlorotoluene was dried over alkali and distilled.

The aniline acylation with benzoic acid was performed by procedure described in [2] with the use of various

solvents. The reaction progress was monitored either by isolation of benzanilide or by measuring the concentration of unreacted benzoic acid by means of nonaqueous potentiometric titration.

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