The Inherent Instability of Dimethylformamide–Water Systems containing Hydroxide Ion: Further Observations

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Summary The reaction of OH^- with dimethylformamide (DMF) in DMF–water mixtures has been re-examined using $Me_4N^+OH^-$ and $PhCH_2\overset{+}{N}Me_3OH^-$ in homogeneous systems, giving results in qualitative agreement with previous work.

DIMETHYLFORMAMIDE, as a dipolar aprotic solvent,[1] has been used with advantage as a medium for conducting reactions involving basic reagents with a variety of substrates.[2] Recently we drew attention to the reactivity under mild conditions of OH^- with dimethylformamide (DMF) to form HCO_2^- and Me_2NH and commented on the observed maximum in rate at the solvent composition of *ca.* 30 mole % DMF.[3] The basic system employed in that study was aqueous NaOH (0·02M) and both the OH^- consumed and the Me_2NH liberated were determined as a function of the composition of the medium.

In a continuation of that work with tetramethylammonium hydroxide as base, with the intention of reaching media of very high DMF content, partial insolubility of the base was observed at *ca.* 80 mole % DMF by the presence of a precipitate. A re-examination of the NaOH–DMF system also showed partial insolubility at this composition as small colourless globules visible on careful inspection. The apparently consistent results that had been obtained in the previous work resulted from the particular method employed (see footnote to Figure in ref. 3). Essentially, after allowing the reaction to proceed for a given time, the *total* reaction mixture was quenched and titrated for OH^- consumed and Me_2NH produced; the analysis hence included both soluble and insoluble OH^- and showed a good material balance for total base (OH^- plus Me_2NH). On repetition of the work, the reaction mixture was centrifuged before a sample was removed, and then analysed as previously. A deviation resulted between the initial stoicheiometry of the NaOH and that of the titrated Me_2NH plus soluble NaOH, in media of concentration greater than *ca.* 55 mole % DMF. Hence the results reported previously are quantitatively valid only to *ca.* 45 mole % DMF. This suggests that the large decrease in rate previously obtained in solutions of high concentrations of DMF was in large measure due to the insolubility of OH^-.

Additional experiments have been performed to evaluate the basic hydrolysis of DMF by $Me_4\overset{+}{N}OH^-$ and $PhCH_2\overset{+}{N}Me_3OH^-$ by the aliquot method under homogeneous conditions. One-point determinations[3] (15 min reactions at room temperature, base concentration 0·02M) were taken up to *ca.* 70 mole % DMF for $Me_4\overset{+}{N}OH^-$ and *ca.* 90 mole % DMF for $PhCH_2\overset{+}{N}Me_3OH^-$. In the latter case a few sample kinetic runs were also performed (in 10·2, 41·3, and 77·6 mole % DMF, at 25°). The results are in qualitative agreement with the previous report,[3] *i.e.* there is an initial increase in rate, followed by a levelling off at *ca.* 30 mole % DMF, and then a decrease in rate. However, as expected, the decrease in rate is not as sharp as previously indicated for the partly insoluble NaOH–DMF system. Thus the present work qualitatively confirms the essential finding of our previous report concerning the reactivity of OH^- in DMF–H_2O mixtures and the inherent instability of such systems.

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