NOTES

The Rates of Condensation of Piperidine with 1-Chloro-2,4-dinitrobenzene in Various Solvents

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We record some miscellaneous measurements made in conjunction with other work. Our results are summarized in Table I.

Table I

The Reaction of Piperidine with 1-Chloro-2,4-dinitrobenzene in Various Solvents

Solvent	Rate coefficient at 30.06°, l. mole^{-1} min.$^{-1}$	ΔE, kcal./mole	$\Delta S^{\ddagger}$, cal./deg./mole
50% Dioxane	6.38^a	11.2	−28.0
60% Dioxane	5.94^a	10.5	−30.5
75% Dioxane	5.61^a	10.2	−31.6
93% Ethanol	1.54	..	....
Methanol	0.935	11.6^b	−30.2^b
50% Methanol–50% benzene	0.932	..	....

[a] Extrapolated from measurements at lower temperatures. [b] These values arise from an independent study by J. F. Bunnett and E. W. Garbisch, Jr.

In view of the probability that in this reaction a zwitterionic transition state is formed from uncharged reactants, it is noteworthy that the rate, energy of activation and entropy of activation are relatively insensitive to changes in the solvent. Reactions of this charge type usually are accelerated greatly by changing to a more polar solvent,[1] owing to a lesser decrease in entropy during formation of the transition state. In the transition state of the present reaction, we believe, there is partial positive charge on the piperidine nitrogen atom and corresponding negative charge distributed between the two nitro groups. The geometry is such that the positive pole can engage in direct electrostatic interaction with a partially negatively charged oxygen of the 2-nitro group. This mutually satisfying electrostatic interaction decreases the need for solvation of these poles by external solvent molecules, and consequently the reaction rate is less sensitive to changes in the solvent. We have described this effect as "built-in solvation" and discussed it at greater length elsewhere.[2]

A plot of ΔE *vs.* $\Delta S^{\ddagger}$ for the three aqueous dioxane solvents is linear with slope 280°K. This slope is, as Leffler[3] has observed, the "isokinetic temperature" at which all reactions whose energies and entropies of activation are linearly related should proceed at the same rate. Our determinations at 0° were carried out just below the isokinetic temperature, and indeed our measured rates at 0° in two solvents are identical within experimental error. The rate in 50% dioxane, the "fastest" solvent, is actually somewhat lower. We thus have partially realized the inversion in relative reactivity that one should observe as the isokinetic temperature is passed. The point for methanol solvent does not fall on the above linear plot.

It is surprising that the rate, at 30.06°, is identical within experimental error in methanol and in 50% methanol—50% benzene solvents. The full significance of this observation is not apparent.

Experimental

Piperidine, 1-chloro-2,4-dinitrochlorobenzene and the pure solvents were prepared as previously described.[2,4] Reagent grade benzene was redistilled. Commercial "95%" ethanol was redistilled and found by density determination to contain 93% ethanol by weight. The other mixed solvents were prepared on a volume basis.

In all runs the initial concentration of 1-chloro-2,4-dinitrobenzene was approximately 0.015 *M* and of piperidine approximately 0.030 *M*. Rate coefficients were calculated from the expression: $2kt = 1/(a - x) + C$. Runs in aqueous dioxane solvents were followed by titration of chloride ion,[4] and runs in other solvents by spectrophotometric measurements[2] (at 460 mμ), as previously described. Runs in 50% dioxane at *ca.* 25.25° were followed by both techniques, and the resulting rate coefficients were identical within experimental error.

Following are the experimental rate coefficients not already listed in Table I. Each is a mean value from two or more supposedly identical runs. In all cases the average deviation was less than 1%. Units are l. mole^{-1} min.$^{-1}$. In 50% dioxane: at 25.23, 4.72; at 0.0°, 0.821. In 60% dioxane[4]: at 25.22°, 4.48; at 0.0°, 0.874. In 75% dioxane: at 25.22°, 4.26; at 0.0°, 0.870.

Arrhenius activation energies and entropies of activation were calculated from standard expressions. ΔE values are uncertain by about ±0.1 kcal., and $\Delta S^{\ddagger}$ by about ±0.2 cal./deg.

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(1) R. G. Pearson, *J. Chem. Phys.*, **20**, 1478 (1952).

(2) J. F. Bunnett and R. J. Morath, This Journal, **77**, 5051 (1955).

(3) J. E. Leffler, Florida State Univ., private communication.

(4) J. F. Bunnett and G. T. Davis, This Journal, **76**, 3011 (1954).

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Decalin-2,7-diol and Decalin-2,7-dione[1]

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In the course of a search for possible new routes to derivatives of bicyclo[5.5.0]dodecane having functional groups on both rings decalin-2,7-diol and decalin-2,7-dione were prepared. However, the synthesis *via* these intermediates was not pursued further. No previous report of either compound was found.

High pressure hydrogenation of 2,7-dihydroxynaphthalene with W-4 Raney nickel catalyst gave a 63% yield of the decalindiol. Chromic acid oxidation of the diol produced the corresponding dione (43%). The configuration at the ring juncture of the reduced compounds was not determined.

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(1) From the Ph.D. Thesis of David O. Barlow.