

Notes

Effect of Dielectric & Thermodynamic Properties of Solvents on Hydrogenation of Nitrobenzene in Slurry Phase over Platinum-Alumina Catalyst

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The effect of dielectric and thermodynamic properties of solvents on the yield of aniline during the hydrogenation of nitrobenzene at room temperature and atmospheric pressure in slurry phase over platinum-alumina catalyst has been investigated. The yield of aniline increases linearly with increase in dielectric constant, but decreases with increase in standard entropy and standard specific heat at constant pressure. The observed data are explained in terms of separation and orientation of charges in the transition state.

Though attempts have been made to correlate the rate of chemical reactions with physical properties of the solvents¹, no systematic investigation seems to have been undertaken with respect to the dielectric and thermodynamic properties of the solvents. In the present investigation hydrogenation of nitrobenzene has been investigated in several solvents over platinum-alumina catalyst to establish a relationship between the yield of aniline from nitrobenzene and dielectric constants, standard entropies and standard specific heats of solvents at constant pressure.

The solvents (GR or AR) used were: methyl, ethyl, 1-propyl, 2-propyl, 1-butyl and 2-butyl alcohols; acetone, methyl ethyl and methyl isobutyl ketones, cyclohexanone; and methyl, ethyl, 1-propyl and 1-butyl acetates.

Alumina was prepared from aluminium isopropoxide according to the literature method². Platinum-alumina catalyst was obtained by adding calculated volumes of chloroplatinic acid (Johnson-Mathey, UK) solution in water to a weighed amount of alumina to give 0.8% by weight of platinum. The slurry was stirred for 2 hr at room temperature and dried in a furnace at 120°C for 24 hr. The temperature of the furnace was raised slowly to 500°C while passing purified and dried hydrogen and kept at this temperature for 8 hr. The activated material was crushed and ground into powder and sieved to 180-200 mesh particle size.

Nitrobenzene (AR) was purified by distillation and its purity checked by gas chromatography.

The reactions were carried out at room temperature and atmospheric pressure. The experimental set-up consisted of a three-necked round bottomed flask fitted with a water condenser, a thermowell and a manometer tube arranged for controlling the flow of hydrogen gas.

For each experiment, catalyst (1g) and the solvent (100ml) were transferred to the reaction flask. Hydrogen gas was bubbled through the contents at the rate of 250ml/min for 20 min to prehydrogenate the catalyst. Thereafter, nitrobenzene (0.8 mol, 80ml) was added to the flask and hydrogenation continued with effective stirring for 3 hr under the same conditions.

The catalyst after filtration was washed with acetone and the liquid analysed quantitatively by gas chromatography (Packard - 427 with SE-30 dual glass column). The optimum conditions for good resolution were found to be: carrier gas (hydrogen) flow, 20 ml/min; and temperatures of the injection port, column and detector, 170°, 160° and 180°C respectively.

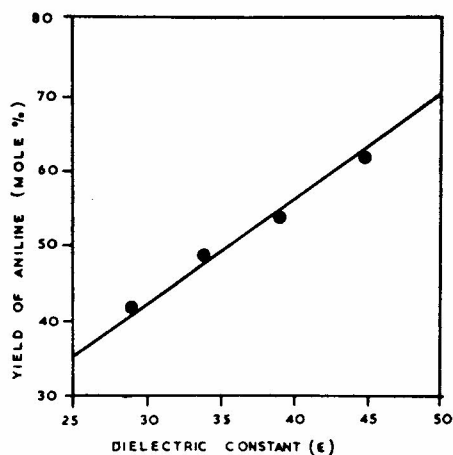
Using methanol as standard, the activity of the catalyst was checked after completing the runs with each solvent. It was observed that the activity of the catalyst remained almost constant.

Figure 1 illustrates the variation in the yield of aniline as a function of dielectric constant for ethanol-water system. The amount of aniline formed in the absence of a solvent is only 6%. However, in the presence of a solvent the yield varies and the actual yield depends on the nature of the solvent used. The results of studies on the effect of alcohols, ketones and esters as solvents on the formation of aniline are given in Table 1 along with the values³ of dielectric constant (ϵ), standard entropy (S°) and standard heat capacity at constant pressure (C_p°) of solvents. The variation in the yield of aniline with ϵ , S° and C_p° is linear and the existence of linear relationship has been established by the analysis of the data using a microprocessor; the values of coefficient of linearity, intercept and slope for solvents are given in Table 2.

It is observed that in a given homologous series of solvents, the higher the dielectric constant, higher is the yield of aniline. On the other hand, the yield decreases with increasing values of C_p° and S° .

It is reported⁴⁻⁶ that reactions involving charge separation in the transition state will be accelerated by solvents of high dielectric constants. The variation in the formation of aniline with dielectric constant clearly indicates that the reduction of nitrobenzene to aniline

ETHANOL - WATER SYSTEM

Fig. 1—Yield of aniline versus ϵ of alcohol-water mixtureTable I—Values of ϵ , S° and C_p° of Solvents and the Yield of Aniline

Solvent (Alcohol)	Yield of aniline (mol %)	ϵ	C_p°	S°
Methanol	45.33	32.70	10.49	30.41
Ethanol	35.41	24.55	15.64	38.49
1-Propanol	27.50	20.33	20.82	46.50
1-Butanol	22.90	17.50	26.29	54.10
2-Propanol	4.00	18.30	36.06	—
2-Butanol	2.00	15.80	47.50	—
Acetone	32.58	20.70	19.48	47.90
Methyl ethyl ketone	29.74	18.51	24.59	—
Methyl isobutyl ketone	18.55	13.11	46.00	—
Cyclohexanone	21.49	18.30	—	—
Methyl acetate	13.50	6.68	37.19	—
Ethyl acetate	12.06	6.02	40.40	—
1-Propyl acetate	11.50	5.69	46.90	—
1-Butyl acetate	9.90	5.01	57.84	—

Table 2—Correlation Parameters of Solvents

Physical properties	Correlation parameter	Alcohols	Ketones	Esters	Ethanol-water mixture
ϵ	Coefficient of linearity	0.9896	0.9287	0.9978	0.9770
	Intercept	-2.3248	-5.6595	-0.7723	-5.4100
	Slope	1.4771	1.8266	2.1389	1.2610
S°	Coefficient of linearity	0.9794	—	—	—
	Intercept	73.1622	—	—	—
	Slope	-0.9529	—	—	—
C_p°	Coefficient of linearity	0.9707	0.9999	0.9326	—
	Intercept	58.9079	42.7838	18.9263	—
	Slope	-1.4267	-0.5272	-0.1577	—

passes through a transition state with charge separation. Further, in the case of reactions in 2-propanol and 2-butanol, the yield of aniline is 4 and 2 per cent respectively though their ϵ values are not significantly different from those of the corresponding primary alcohols. The low yield of aniline in 2-propanol and 2-butanol can be attributed to the dispersion of the positive charges on either side of the hydroxyl group which may not be able to bring about the necessary separation and orientation of the charges of the nitro group in the transition state. This lends further support to the fact that the charge separation and proper orientation in the transition state are essential. This observation agrees well with the postulates of Isaac⁴ that if the charges, instead of separation and orientation, are merely dispersed, the reaction will be retarded.

A solvent of high entropy may increase dispersion (decrease in orientation) of charges in the transition state and this will lead to a decrease in the yield of aniline. The observed decrease in the formation of

aniline for solvents of higher entropies, is thus quite in order. Standard heat capacity at constant pressure also behaves like standard entropy as these parameters are related to each other.

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