

Complex Formation between Pentafluorobenzene and Hexamethylphosphoramide

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In a previous paper¹ concerned with solvent effects on the ¹H and ¹⁹F NMR chemical shifts of fluorinated phenols and thiols, evidence was given for interaction between electron donor centers in solvent molecules and the aromatic proton in compounds like 2,3,5,6-tetrafluorophenol and 2,3,5,6-tetrafluorobenzenethiol. Due to participation of the OH- and SH proton in equilibria with solvent molecules, a quantitative measure of the interaction involving the aromatic proton could not easily be made. A compound, suitable for studying the aromatic proton effect, is pentafluorobenzene. In this molecule, solvent interaction centers, besides the aromatic proton, can to a good approximation be neglected, the pentafluorophenyl residue being known to behave as a relatively inert group.²

To test the degree to which pentafluorobenzene participates in complex formation with an electron donor, the well known NMR method for studying hydrogen bond complexes³ was applied. From the information obtained by measuring the ¹H chemical shift of the proton donor (present in fixed concentration) as a function of the electron donor concentration, values of equilibrium constants and complex frequencies at the actual temperature can be calculated. The experimental results obtained for pentafluorobenzene when using hexamethylphosphoramide as electron donor in carbon tetrachloride at three different temperatures, are illustrated in Fig. 1.

Although the concentration of proton donor used in this experiment is somewhat larger than what usually is the case (due to the complexity of the signal involved), the effect of possible self-association can be neglected. The validity of this conclusion becomes evident when measuring the ¹H chemical shift of a 2.0 M pentafluorobenzene solution. At 35°C, this shift is, within experimental error, identical to the one obtained for the 0.2 M solution.

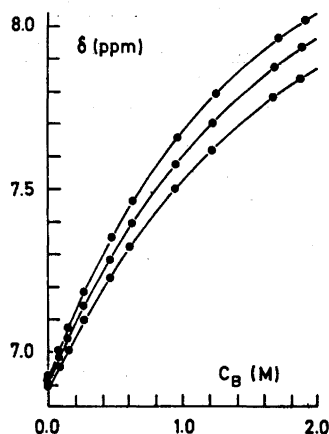


Fig. 1. ¹H chemical shift, measured at the center of the symmetrical multiplet (ppm relative internal TMS) of pentafluorobenzene (0.2000 M at 20°C) as a function of hexamethylphosphoramide concentration (C_B) in carbon tetrachloride solution at 20, 35, and 50°C.

Qualitatively, the dilution curves are analogous to those observed in the case of ordinary 1-1 hydrogen bond complex formation. A curve fitting procedure, executed by means of an iterative computer program, leads to excellent agreement between theoretical and experimental dilution curves if 1-1 interaction is postulated, indicating the validity of the assumed model. Values of parameters calculated are listed in Table 1.

Table 1. NMR chemical shifts (ppm relative internal TMS) for free (δ_1) and complexed (δ_x) proton donor, equilibrium constants for 1-1 association and ΔH -values (kcal/mol) for the association of proton donor to hexamethylphosphoramide in CCl_4 .

H-donor	°C	δ_1	δ_x	$\delta_x - \delta_1$	K	$-\Delta H$
C_6F_5H	20	6.905	9.027	2.122	0.61	
	35	6.892	9.019	2.127	0.53	1.7
	50	6.877	8.980	2.103	0.47	
$CHCl_3$	20	7.246	9.036	1.790	3.02	
	35	7.235	9.036	1.801	2.36	2.7
	50	7.231	9.046	1.815	1.98	

For comparison, the results obtained when using chloroform as proton donor, are also included.⁴ It is seen that pentafluorobenzene forms a weaker association complex than does chloroform, as expressed by the respective values of K and ΔH . Nevertheless, there is no doubt that pentafluorobenzene exhibits considerable proton donor properties, a result which should be born in mind when dealing with ethylenic protons in a medium having electron donor properties.

1. Dale, A. J. *Acta Chem. Scand.* **24** (1970) 1486.
2. Dale, A. J. *Spectrochim. Acta* (1970). *In press.*
3. See, e.g., Nakamo, M., Nakamo, N. I. and Higuchi, T. *J. Phys. Chem.* **71** (1967) 3954.
4. Gramstad, T. and Mundheim, Ø. *Unpublished results.*

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Diacetyl and Formic Acid as Decomposition Products of 2-Acetolactic Acid

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In fermentation solutions, 2-acetolactic acid appears as an intermediate in valine synthesis; it is unstable, and decarboxylates readily to acetoin, both enzymatically¹⁻³ and under the influence of strong mineral acids.³⁻⁴ Acetolactic acid also tends towards spontaneous decomposition, with or without the contribution of certain metal cations,^{5,6} and also in fermentation solutions;⁷ one of the products of spontaneous decomposition is diacetyl.⁵⁻⁷ Quite recently, the formation of diacetyl from 2-acetolactic acid, and the reaction mechanism, have been studied more thoroughly by us,^{8,9}

and by Japanese researchers.¹⁰⁻¹³ Inoue *et al.*¹⁰⁻¹³ have interpreted the reaction of diacetyl formation from 2-acetolactic acid as a "spontaneous oxidative decarboxylation". According to Lewis,¹⁴ the redox potential for the oxidative decarboxylation in a commercial brew is likely to be suitable for 2-acetolactate conversion only at the beginning of fermentation; at the time when diacetyl is produced, strong reducing conditions should exist, and consequently 2-acetolactate should be stable. Our experiments made by application of the head-space technique have shown that 2-acetolactic acid decomposes in solutions at a definite velocity under aerobic⁹ and anaerobic⁸ conditions, as well as in fermentation solutions;^{8,9} moreover, the rate of decomposition increases when the pH is lowered, or the temperature raised. The concentration of diacetyl in the fermentation solutions is near zero during fermentation, as diacetyl is consumed by the yeast to the extent that it is split off from the 2-acetolactic acid.^{8,15} After the yeast has been removed, the level of diacetyl in the solution increases, but again diminishes rapidly when the yeast has been added to the solution.⁸

We have continued studies of the spontaneous decomposition of 2-acetolactic acid, and our attention has further been directed towards the carboxylic acids formed in addition to diacetyl.

The ethyl ester of 2-aceto-2-acetoxypropionic acid (b.p. 96°/7 mmHg) was prepared from 2-methyl-substituted ethyl acetoacetate (*cf.* Ref. 9) (*pract.*, Fluka AG, Buchs, Switzerland). The synthesised ester was hydrolysed by means of 0.1 N NaOH solution at a temperature of 4°C. Both the carboxyl and the α -hydroxyl are released from the ester-form by alkaline hydrolysis, and consequently a base solution of 2-acetolactate can be prepared in this way. For this purpose, 53.0 mg (0.262 mmol) of the ethyl ester of 2-aceto-2-acetoxypropionic acid was weighed, and dissolved in 7.5 ml of cold (4°C) 0.1 N NaOH solution; the total volume was regulated to 50 ml with cold (4°C) distilled water. This base solution was allowed to stand overnight at 4°C. Samples of 1 ml (containing 5.24×10^{-3} mmol of acetolactate) and 2 ml (containing 10.5×10^{-3} mmol) were taken from this solution, and acidified to pH 5-6 with a buffer (phosphate or citrate) or 0.001 N HCl solution, and diluted with water to 25 ml. These solutions were kept in a constant-temperature bath at 40°C for