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Determination of Lewis Acidity using ³¹P NMR



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Objectives

The aim of this experiment is to use NMR to evaluate Lewis acidity of solvents using the Gutmann-Beckett Acceptor Number. Triethylphosphine oxide is used as a ^{31}P NMR probe. The acceptor number of classic Lewis acids such as boron trihalides may be determined by advanced chemistry students or as a demonstration.

Introduction

Many chemical reactions are determined by the interaction between substrates and solvent molecules. Solvent interaction with a polarised substrate can occur either nucleophilically at A or electrophilically at B, leading to the formation of a molecular complex in solution with increased A-B bond length.

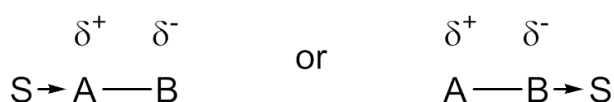


Figure 1: Nucleophilic and electrophilic interaction of the solvent, S, with a polar substrate.

$\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ are examples of important reactions introduced early in chemistry that have a strong solvent dependence. In these substitution reactions, both the polarity and H^+ -donating properties affect the rate of the reaction. It is therefore useful to have a measure of the electrophilic/nucleophilic nature of the solvent so that you can accurately predict which solvent would be best suited for your reaction.

The Donor number is a quantitative measure of the nucleophilic nature of solvents, defined as the negative ΔH -value of the adduct formation of the solvent and SbCl_5 in dilute solution of 1,2-dichloroethane. In 1975, Gutmann recognised that there was no analogous quantity for measuring the electrophilic nature of a solvent, thus Gutmann devised a method using ^{31}P NMR.

^{31}P NMR is attractive because the ^{31}P nucleus is 100% abundant and has good sensitivity, and it has a very large chemical shift range. Triethylphosphine oxide was chosen as a probe to measure the Lewis acidity (electrophilicity)

of solvents. This is because the oxygen atom is a very strong base, so interaction between the solvent and solute occurs at a well defined site. The interaction at the oxygen atom is sufficiently remote from the probe ^{31}P nucleus, eliminating ill-definable contact contributions. Due to the partial double bond nature of the P-O bond, a high sensitivity of the phosphorus resonance results from changes at the oxygen atom.

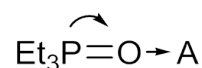


Figure 2: Interaction of triethylphosphine oxide with the electrophilic site(s) of the solvent molecule.

In solutions of protonic acids, HX, an equilibrium between the hydrogen-bonded complex and the fully protonated phosphine oxide exists.

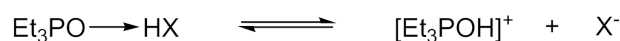


Figure 3: Interaction of triethylphosphine oxide with protic solvents.

Triethylphosphine oxide was chosen over other alkyl oxides because the ethyl groups provide efficient electronic shielding without steric hindrance and also ensure that the compound is soluble in almost all solvents. Fortunately, it is also incredibly stable.

The change in chemical shift of the ^{31}P resonance in different solvents was correlated with the 'Acceptor Number' which is a measure of the Lewis acidity or electrophilicity of the solvent. Hexanes was arbitrarily set to 0 and the $\text{Et}_3\text{PO}:\text{SbCl}_5$ adduct set to 100. Using H_3PO_4 as a

0 ppm reference, the Acceptor Number can be calculated using the following equation:

$$AN = 2.21 (\delta_{\text{sample}} - 41)$$

In this experiment, students measure the acceptor number of common laboratory solvents and use this to discuss the properties of the solvent. This discussion can then be used to determine the appropriate solvent for an S_N1 or S_N2 reaction.

Boron-containing Lewis acids are very useful in synthetic chemistry, however there are few methods to quantitatively measure the Lewis acidity. Beckett simplified Gutmann's method for measuring the electrophilicity of solvents and applied it to boron-containing Lewis acids. This method has become one of the most common and convenient methods for determining Lewis acidity, especially in main group Lewis acids. Therefore, the use of triethylphosphine oxide to determine Lewis acidity is often referred to the Gutmann-Beckett method.

Boron trihalides are classic examples of Lewis acids and the Gutmann-Beckett method accurately describes the increase in Lewis acidity from BF_3 to BBr_3 ($\text{BF}_3 < \text{BCl}_3 < \text{BBr}_3$). This part of the experiment may be carried out with advanced chemistry students or as a demonstration, as these compounds are strong Lewis acids and can therefore be difficult to handle. Nevertheless, students may be asked to explain the trend which is in contrast to what is expected based on the electronegativity and sterics of the halides.

Experiment

Triethylphosphine oxide may be purchased or synthesised by oxidising the product of ethylmagnesium bromide and phosphorus trichloride. Note that it is very hygroscopic so care must be taken to avoid exposure to air and dry solvents must be used.

Make a stock solution of triethylphosphine oxide by dissolving in dichloromethane so that the solution is $\sim 0.75 \text{ mol L}^{-1}$. Transfer 0.25 mL of the triethylphosphine oxide solution into a dry vial.

Remove the dichloromethane using a vacuum and transfer 1 mL of dry solvent to be analysed to the vial (the trihalides were used as neat liquids, except BF_3 was used as the ether adduct). Ensure that the triethylphosphine oxide is dissolved and transfer the solution to an NMR tube. Measure the ^{31}P NMR spectrum using 64 scans and 10 seconds repetition time (10 minutes).

Safety

Triethylphosphine oxide and dichloromethane are harmful if swallowed and may cause skin, eye and respiratory irritation. Hexanes, acetone, methanol and acetic acid are highly flammable. Use in a fume hood and keep away from sources of ignition. Methanol is toxic if swallowed. Glacial acetic acid, trifluoroacetic acid and methanesulfonic acid are corrosive acids that can cause skin burns and eye damage, avoid contact with skin and use with eye protection. Methanesulfonic acid may be fatal in contact with skin.

Boron trifluoride, boron trichloride and boron tribromide are corrosive acids that cause skin burns and eye damage, and may be fatal if inhaled. Use in the fume hood with gloves and eye protection.

Tasks & Questions

1. Tabulate the chemical shift of Et_3PO in each solvent and determine the Acceptor Number. Compare the values to those in the literature.
2. Discuss the trend, considering bonding interaction and the polarization of the P-O bond. Is there a correlation between pKa and AN?
3. Acetic acid, trifluoroacetic acid and methanesulfonic acid are all acids but have different line shapes in the NMR spectrum. Explain the different lineshapes considering the equilibrium between the hydrogen-bonding complex and protonated species.

Results

Acceptor Number of Solvents

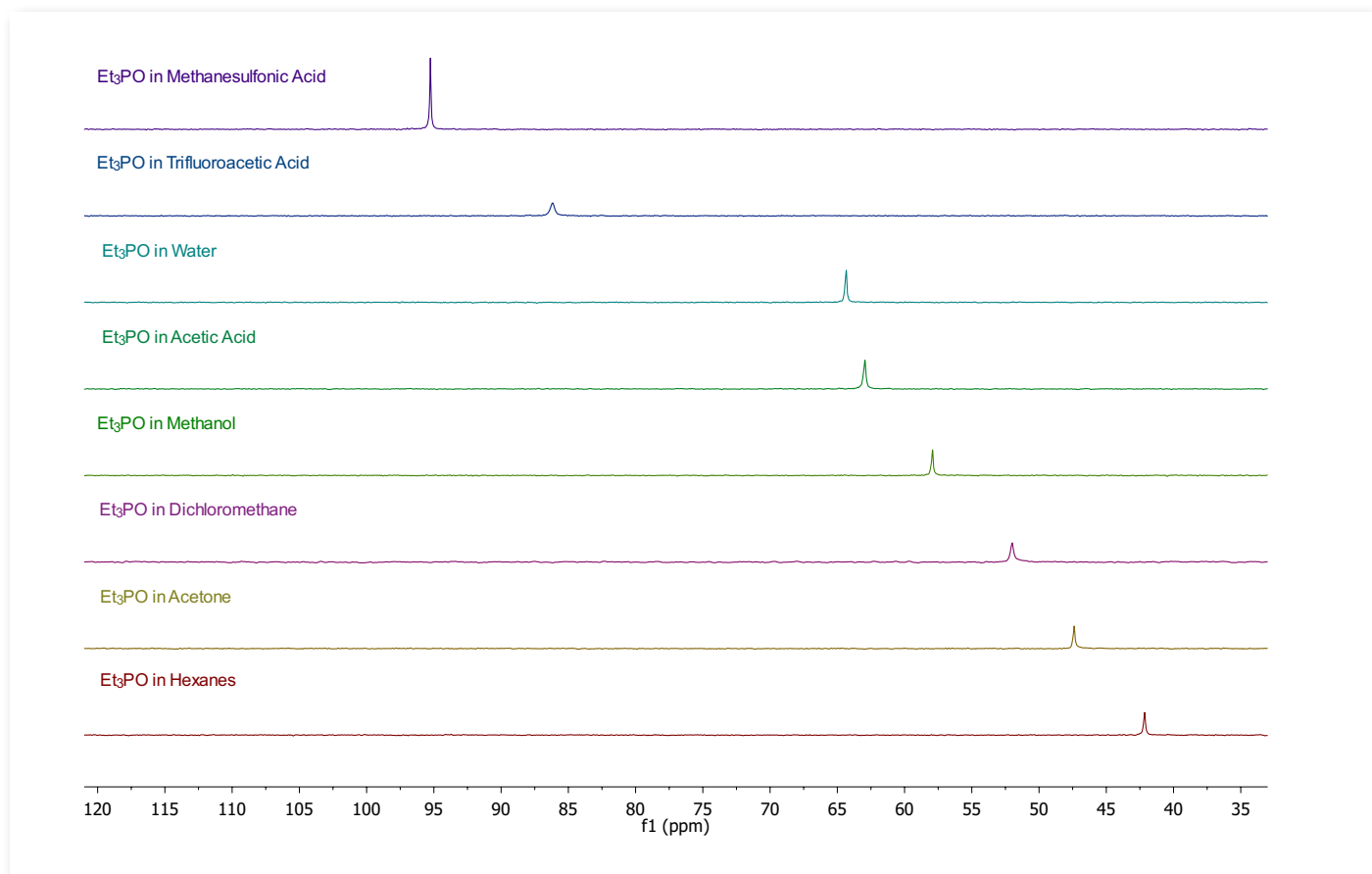


Figure 4: NMR spectra of triethylphosphine oxide in a range of laboratory solvents.

Using the equation $AN = 2.21 (\delta_{\text{sample}} - 41)$ the Acceptor Number of each solvent is determined and summarised in the table below.

Solvent	δ Et ₃ PO (ppm)	AN	Gutmann AN
Hexanes	42.2	2.6	0
Acetone	47.4	14.1	12.5
Dichloromethane	52.1	24.5	20.4
Methanol	58.0	37.6	41.3
Acetic Acid	63.0	48.6	52.9
Water	64.4	51.7	54.8
Trifluoroacetic Acid	86.3	100.1	105.3
Methanesulfonic Acid	95.3	120.0	126.3

There is a slight variation between the AN values determined using Spinsolve and Gutmann's values, however the variation is similar to that experienced by Beckett when he evaluated the method (e.g. H_2O , our AN=51.7, Beckett AN=51.4, Gutmann AN=54.8) and the values follow the same trend.

Compared to hexane, the chemical shift of Et_3PO in other solvents is shifted downfield, corresponding to a reduction of electron density at the phosphorus atom. Protonic acids have the largest chemical shift (methanesulfonic acid, trifluoroacetic acid), followed by solvents containing hydroxyls (methanol) and acidic C-H protons (dichloromethane). Polar aprotic solvents have a slight shift and non-polar aprotic solvents are not shifted at all. The interaction of the electrophilic solvent, A, with the oxygen atom results in a reduction of the π -character of the P-O bond, accompanied by a polarisation of the σ -bond, leading to a decrease in electron density at the phosphorus atom related to the strength of the interaction.

Hexane, as an inert, non-polar hydrocarbon, is a very poor electrophile. Acetone, while being aprotic, has a carbonyl and thus a slightly positive carbon centre to coordinate with the nucleophilic oxygen atom of triethylphosphine oxide. This is a weak electrostatic attraction, so acetone has a low Acceptor Number.

Dichloromethane, methanol and water have protons attached to electronegative centres and are therefore capable of hydrogen bonding. Hydrogen bonding is a much stronger electrostatic attraction than simple dipoles, with some covalent bond character. The strength of the hydrogen bonding is reflected in the acceptor number, with water being the strongest and dichloromethane the weakest.

There is a correlation between pKa and Acceptor Number, with the exception of acetic acid. This is because, as a neat liquid, acetic acid has a strong association through hydrogen bonding to other acetic acid molecules, thus effectively reducing the acceptor strength of the solvent (Figure 5).

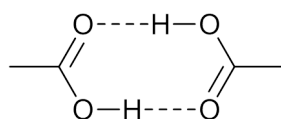


Figure 5: Acetic acid dimer formed in solution.

For protonic acids there is equilibrium between the hydrogen-bonded complex and the fully protonated phosphorus oxide which has a positive charge on the phosphorus atom. Only one resonance is observed due to the rapid exchange of the two species, with the observed chemical shift being a weighted average of the two. The resonance for trifluoroacetic acid, which has an intermediate acid strength between methanesulfonic acid and acetic acid, is broadened. Both the hydrogen bonded and protonated phosphine oxide appear to be in considerable quantities. The exchange is rapid enough that only one signal is observed but slow enough to broaden the peaks. The equilibrium in acetic acid lies more toward the hydrogen bonded complex whereas in methane sulfonic acid, which has an extremely sharp resonance, the Et_3PO appears to be almost exclusively present as the fully protonated form. This is reflected in the downfield chemical shift of the positively charged phosphorus centre.

Acceptor Number of Boron Trihalides

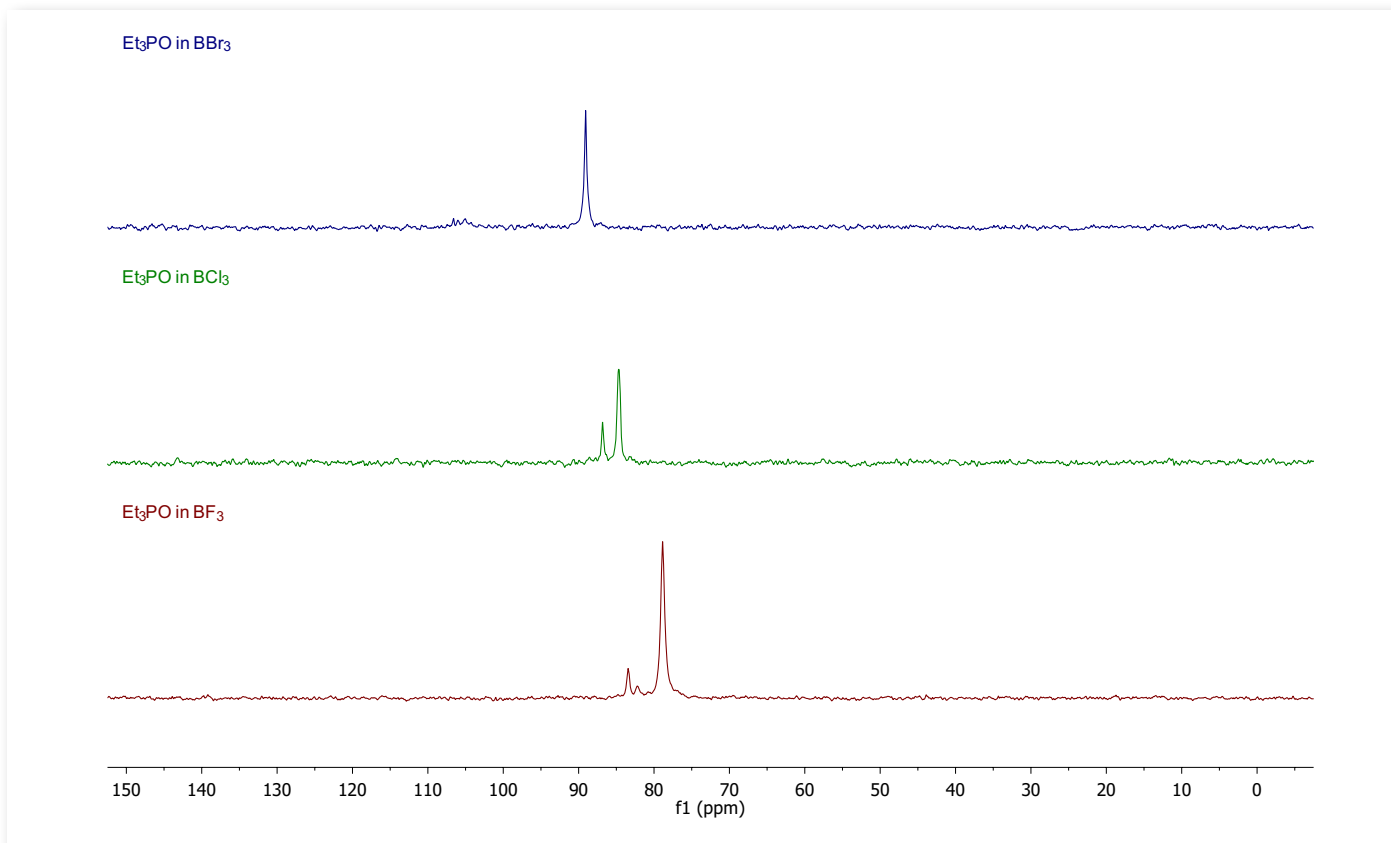


Figure 6: NMR spectra of triethylphosphine oxide in boron trihalides.

Compound	δ Et ₃ PO (ppm)	AN	Beckett AN
BF ₃ · Et ₂ O	79.0	84	88.5
BCl ₃	84.7	96.6	105.7
BBr ₃	89.1	106.3	109.3

Using the Spinsolve Phosphorus system, the correct trend for Lewis acidity of the boron trihalides is observed (BF₃ < BCl₃ < BBr₃).

Based on the electronegativity of the halides, this result is counter intuitive. BF₃ has the most electronegative halogen and therefore it would be sensible to assume that it draws more electron density from the boron centre than the other halogens and therefore able to better stabilise the negative charge of boron in [BX₄]⁻. However, it is the degree of π -bonding that determines the relative Lewis acidity. The boron trihalides are trigonal planar with sp² hybridisation. To form [BX₄]⁻, which is tetrahedral, the hybridisation at the boron centre must change to sp³ resulting in the loss of the partial π -bonding involving the p_z orbital of boron and the halide. Because B and F are in the same period, the p_z orbitals are a similar size so they have the best overlap, forming the strongest bond. This means it requires more energy to break and form [BX₄]⁻, making it the weakest Lewis acid. The heavier halogens, Cl and Br, have larger p_z orbitals so there is less overlap so the π -bond is much weaker and the formation of [BX₄]⁻ is more energetically favourable.



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