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Protic vs aprotic solvents examples

Solvents used in organic chemistry are characterized by their physical characteristics. Among the most important are whether the solvents are polar or non-polar, and whether they are protic or aprotic. Because non-polar solvents tend to be aprotic, the focus is upon polar solvents and their structures. Solvents are generally classified by the polarity, and considered either polar or non-polar, as indicated by the dielectric constant. However, as with many properties, the polarity is a continuous scale, and the correct question is not "is it polar or non-polar" but "how polar is it." Nonetheless, guidelines have been created to make it easier. Generally, solvents with dielectric constants greater than about 5 are considered "polar" and those with dielectric constants less than 5 are considered "non-polar." Table 1: Examples of a few common solvents used in organic chemistry Solvent Boiling Point, Celsius Dielectric Constant NON-POLAR SOLVENTS Pentane, C5H12 36 1.8 Hexane, C6H14 69 1.9 Benzene, C6H6 80 2.3 Chloroform, CHCl3 61 4.8 Diethyl ether, (CH3CH2)2O 35 4.3 1,4-Dioxane, cyc-(CH2CH2OCH2CH2O) 101 2.3 POLAR PROTIC SOLVENTS Water, H2O 100 78.5 methanol, CH3OH 65 32.6 ethanol, CH3CH2OH 78.5 24.3 isopropyl alcohol, CH3CH(OH)CH3 82 18 acetic acid, CH3COOH 118 6 POLAR APROTIC SOLVENTS dichloromethane, CH2Cl2 40 9.1 tetrahydrofuran (THF), cyc-(CH2)4O 66 7.5 ethyl acetate, CH3C(O)OCH2CH3 77 6 acetonitrile, CH3CN 81.6 37.5 dimethylformamide (DMF), HCON(CH3)2 153 38 dimethyl sulfoxide (DMSO), CH3SOCH3 189 47 acetone, CH3COCH3 56.5 21 hexamethylphosphoric triamide (HMPT), [(CH3)2N]3PO 232 30 The table above distinguishes between protic and aprotic solvents. For the solvents included in the table, the distinguishing feature is the presence of an -OH group, and that is the most common characteristic of a protic solvent. However, there are exceptions, such as nitromethane, CH3NO2, which is also considered a protic solvent. That might suggest that Bronsted acidity is the most important feature, because nitromethane is very acidic, with a pKa of about 10. However, acetone is still considered a polar aprotic solvent, despite the fact that it is relatively acidic, and not significantly less acidic than alcohols. Then again, acetone (and other carbonyl containing solvents) are, indeed, poor solvents when using strong bases due to their relatively high acidity. Solvent properties are in important consideration in many chemical reactions, including nucleophilic substitution reactions. As strong hydrogen-bond donors, protic solvents are very effective at stabilizing ions. Therefore, they favor reactions in which ions are formed, such as the SN1 reaction, and disfavor reactions where ions are reactants, such as the SN2 reaction. Chapter 8: Nucleophilic Substitution Solvent Effects In general terms, the choice of solvent can have a significant effect on the performance of a reaction. Factors when choosing a solvent are: solubility : need to get reagents in the same phase, the molecules need to collide to react ! usually, the solvent needs to unreactive towards the reagents (except in reactions where the solvent is the Nu : "solvolyis") how will the solvent affect the rate of reaction ? For an SN1 reaction, the polarity and ability of the solvent to stabilise the intermediate carbocation is of paramount importance, as shown by the relative rate data for the solvolysis of tBuCl. Solvent Dipole moment, μ Dielectric constant, ϵ Relative Rate CH3CO2H 1.68 6 1 CH3OH 2.87 33 4 H2O 1.84 78 150,000 Dipole moment, μ in debye For an SN2 reaction, the effect of solvent polarity is usually much less, but the ability (or really lack thereof) of the solvent to solvate the nucleophile is the important criteria, as shown by the relative rate data for the SN2 reaction of nBuBr with N3-. Solvent Dipole moment, μ Dielectric constant, ϵ Relative Rate Type CH3OH 2.87 33 1 protic H2O 1.84 78 7 protic DMSO 3.96 49 1,300 aprotic DMF 3.82 37 2,800 aprotic CH3CN 3.92 38 5,000 aprotic POLAR PROTIC SOLVENTS (polar and ability to be H-bond donor) have dipoles due to polar bonds can H atoms that can be donated into a H-bond examples are the more common solvents like H2O and ROH remember basicity is also usually measured in water anions will be solvated due to H-bonding, inhibiting their ability to function as Nu POLAR APROTIC SOLVENTS (polar but no ability to be H-bond donor) have dipoles due to polar bonds don't have H atoms that can be donated into a H-bond examples are acetone, acetonitrile, DMSO, DMF anions are not solvated and are "naked" and reaction is not inhibited Overall All nucleophiles will be more reactive in aprotic than protic solvents Those species that were most strongly solvated in polar protic solvents will "gain" the most reactivity in polar aprotic (e.g. F-). Polar aprotic solvents are typically only used when a polar protic solvent gives poor results due to having a weak Nu, (esp. F-, -CN, RCO2-) © Dr. Ian Hunt, Department of Chemistry The key difference between protic and aprotic solvents is that protic solvents have dissociable hydrogen atoms whereas aprotic solvents have no dissociable hydrogen atom. A solvent is a liquid compound that can dissolve other substances. There are different forms of solvents that can be categorized basically into two groups as polar and nonpolar solvents. The polar solvents can be divided into two groups as protic and aprotic solvents. Protic solvents can form hydrogen bond because they have chemical bonds required for the hydrogen bonding, i.e. O-H bond and N-H bond. In contrast, aprotic solvents lack those chemical bonds required for hydrogen bonding. CONTENTS 1. Overview and Key Difference 2. What are Protic Solvents 3. What are Aprotic Solvents 4. Similarities Between Protic and Aprotic Solvents 5. Side by Side Comparison – Protic vs Aprotic Solvents in Tabular Form 6. Summary What are Protic Solvents? Protic solvents are polar liquid compounds that have dissociable hydrogen atoms. These solvents have many O-H bonds and N-H bonds. The dissociable hydrogen atoms are those that are bonded to oxygen atoms and nitrogen atoms in these O-H and N-H bonds. Therefore, hydroxyl groups (-OH) and amine groups (-NH2) are essential components in protic solvents. Protic solvents share ion dissolving power with aprotic solvents and are acidic (because they can release protons). The dielectric constant of these protic solvents is very high (dielectric constant is a property of electrical insulating materials and is a quantity measuring the ability of a substance to store electrical energy in an electric field). Examples of protic solvents include water, alcohols such as methanol and ethanol, hydrogen fluoride (HF), and ammonia (NH3). These solvents are often used to dissolve salts. Polar protic solvents prefer to undergo SN1 reactions. What are Aprotic Solvents? Aprotic solvents are polar liquid compounds that have no dissociable hydrogen atoms. These solvents lack chemical bonds such as O-H bonds and N-H bonds. Hence, aprotic solvents lack hydroxyl groups (-OH) and amine groups (-NH2) and are unable to form hydrogen bonds. Aprotic solvents share ion dissolving power with protic solvents. These aprotic solvents lack acidic hydrogen, thus no considerable release of hydrogen ions. Polar aprotic solvents have low or intermediate dielectric constant values. These solvents show a moderate polarity. Figure 01: Comparison Between Protic and Aprotic Solvents Examples of aprotic solvents include dichloromethane (DCM), tetrahydrofuran (THF), ethyl acetate, and acetone. Aprotic solvents can be used to dissolve salts. These solvents prefer to undergo SN2 reactions. What are the Similarities Between Protic and Aprotic Solvents? Both Protic and Aprotic Solvents are polar solvents. Both Protic and Aprotic Solvents solvents can dissolve salts. What is the Difference Between Protic and Aprotic Solvents? Protic solvents are polar liquid compounds that have dissociable hydrogen atoms. Aprotic solvents are polar liquid compounds that have no dissociable hydrogen atoms. Hydrogen Bond Formation Protic solvents are capable of hydrogen bond formation. Aprotic solvents are unable to form hydrogen bonds. Acidity Protic solvents are acidic. Aprotic solvents are not acidic. Chemical Bonds Present Protic solvents are rich with O-H bonds and N-H bonds. Aprotic solvents lack O-H bonds and N-H bonds. Dielectric Constant Protic solvents have a high dielectric constant. Aprotic solvents have a low dielectric constant. Preferred Reaction Type Protic solvents prefer to undergo SN1 reactions. Aprotic solvents prefer to undergo SN2 reactions. Solvents are liquids that are capable of dissolving substances. Solvents can be found in two major forms as polar solvents and nonpolar solvents. Polar solvents can be again divided into two groups as protic solvents and aprotic solvents. The difference between protic and aprotic solvents is that protic solvents have dissociable hydrogen atoms whereas aprotic solvents have no dissociable hydrogen atom. Reference: 1."Polar Protic? Polar Aprotic? Nonpolar? All About Solvents." Master Organic Chemistry RSS. Available here 2."Protic Solvent." Wikipedia, Wikimedia Foundation, 17 Dec. 2017. Available here 3."Aprotic and Protic Solvents." Scribd, Scribd. Available here

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