



Effect of primary and tertiary alcoholic solvents on the rate of solvolysis: A kinetic approach

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Abstract

Solvolysis reactions, in which the solvent itself acts as the nucleophile, remain one of the most informative mechanistic probes in physical organic chemistry. This article examines how the class of an alcoholic solvent — primary (e.g., methanol, ethanol) versus tertiary (e.g., tert-butanol) — governs the rate of solvolysis of alkyl halides and related electrophiles. Using the Grunwald–Winstein linear free-energy relationship (Grunwald and Winstein, 1948) and its later two-parameter extension incorporating solvent nucleophilicity, the kinetic consequences of solvent polarity, dielectric constant, hydrogen-bond-donating ability and steric bulk are analysed. Primary alcohols combine moderate-to-high ionizing power with appreciable nucleophilicity and low steric hindrance, providing significant nucleophilic solvent assistance and comparatively fast solvolysis. Tertiary alcohols, in contrast, are poor nucleophiles because of steric crowding around the oxygen atom and possess markedly lower dielectric constants, which together depress both the ionizing and nucleophilic components of the rate law. Representative kinetic trends, a Grunwald–Winstein correlation, and Arrhenius data are used to illustrate these effects, and the mechanistic implications for the SN1–SN2 continuum are discussed.

Keywords: Solvolysis, SN1 mechanism, Grunwald–Winstein equation, solvent ionizing power, nucleophilic solvent participation, alcoholic solvents, carbocation stability, reaction kinetics

Introduction

Solvolysis occupies a special place among nucleophilic substitution reactions because the solvent performs a dual role: it provides the reaction medium and, at the same time, acts as the nucleophile that attacks the substrate. In its simplest form, an alkyl halide RX dissolved in an alcohol ROH is converted to the corresponding ether (or, following loss of a proton and further reaction, an alcohol), with concurrent release of the hydrogen halide HX. Because the solvent is present in enormous excess relative to the substrate, its concentration remains effectively constant during the reaction, and the observed kinetics collapse to a pseudo-first-order rate law, $\text{rate} = k_{\text{obs}}[\text{RX}]$, irrespective of whether the underlying mechanism is unimolecular (SN1) or bimolecular (SN2) in character.

This apparent kinetic simplicity conceals a rich mechanistic story. Solvolysis reactions have historically served as the principal experimental battleground on which the SN1 and SN2 mechanisms were distinguished, and were later systematised into a quantitative framework by Grunwald and Winstein. Because the solvent is simultaneously medium and nucleophile, its physical and electronic properties — dielectric constant, hydrogen-bond-donating ability, polarizability, and the steric accessibility of the nucleophilic oxygen — directly control the rate. Alcoholic solvents are particularly instructive in this respect because a simple change in the substitution pattern of the hydroxyl-bearing carbon, from primary (methanol, ethanol, 1-propanol) to tertiary (tert-butanol), simultaneously alters the solvent's polarity, its hydrogen-bond-donor strength and, critically, the steric accessibility of the oxygen lone pair that must engage the developing electrophilic centre.

The present article develops a kinetic account of how this primary-versus-tertiary distinction among alcoholic solvents

governs the rate of solvolysis. Using the classical Grunwald–Winstein framework (Grunwald and Winstein, 1948^[4]; Winstein, Grunwald and Jones, 1951)^[11] and its later two-parameter extension (Kevill and co-workers, 2009)^[6], the ionizing power and nucleophilicity of primary and tertiary alcohols are compared, and representative kinetic and activation data are used to illustrate the resulting rate trends. Particular emphasis is placed on tert-butyl chloride solvolysis, historically the reference reaction for the Grunwald–Winstein Y-scale and one of the most extensively studied solvolytic systems in physical organic chemistry (Bentley, 2001^[2]; Abraham *et al.*, 2021).

Theoretical Background

1. The SN1 pathway and carbocation stability

In the limiting SN1 pathway, the rate-determining step is the unassisted ionization of the substrate to give a planar, sp²-hybridised carbocation and a departing leaving group. Because this step involves charge separation without covalent participation by the nucleophile, its rate depends almost entirely on the stability of the incipient carbocation and on the solvent's ability to stabilise the developing charges in the transition state. Alkyl substitution stabilises carbocations through hyperconjugative donation from adjacent C–H bonds and through the inductive electron-donating effect of alkyl groups, so tertiary carbocations are markedly more stable than secondary, and secondary more stable than primary (LibreTexts, 2020a). This order explains why tertiary alkyl halides undergo solvolysis far more readily than primary ones for a fixed solvent — but the present article addresses the complementary question of how the solvent's own degree of substitution (primary versus tertiary alcohol) affects the rate for a given substrate.

2. The Grunwald–Winstein equation

Grunwald and Winstein (1948) ^[4] formalised the empirical observation that, for a fixed substrate, the rate of solvolysis correlates linearly with a solvent-dependent parameter *Y*, the “ionizing power” of the medium:

$$\log_{10}(k/k_0) = mY + c \quad (1)$$

Here *k* and *k*₀ are the specific rates of solvolysis in the solvent under study and in the reference solvent (80% v/v aqueous ethanol), respectively; *c* is a small residual constant; and *m* is a substrate-specific sensitivity parameter, fixed at unity for the reference substrate tert-butyl chloride. Because tert-butyl chloride solvolysis was originally taken to be a “limiting” S_N1 reaction with negligible nucleophilic assistance from the solvent, *Y* values derived from its rates were interpreted as a measure of the solvent’s electrophilic (ionizing) character — closely related to, but not identical with, its dielectric constant and hydrogen-bond-donor strength.

Subsequent work showed that even tert-butyl chloride solvolysis is not entirely free of nucleophilic solvent participation in strongly nucleophilic media, prompting an extension of Equation 1 to a two-term expression (Winstein, Grunwald and Jones, 1951; Kevill and co-workers, 2009) ^[6, 11]:

$$\log_{10}(k/k_0) = lN + mY + c \quad (2)$$

in which *N* is a solvent nucleophilicity parameter and *l* the corresponding substrate sensitivity. Reactions dominated by ionization (large *m*, small *l*) are classified as S_N1-like, while those with substantial nucleophilic solvent assistance (appreciable *l*) sit closer to the S_N2 end of the mechanistic continuum. Values of *l* as high as 1.6–1.7 have been reported for solvolyses proceeding through an addition–elimination pathway at an acyl centre, compared with *l* values close to zero for substrates solvolysing through a limiting ionization pathway (Kevill and co-workers, 2009; Kyong *et al.*, 2012) ^[6, 7].

3. Why primary and tertiary alcohols differ

Both *Y* and *N* are sensitive to the substitution class of the alcohol. Primary alcohols such as methanol and ethanol possess a relatively unhindered oxygen atom, moderate-to-high dielectric constants (methanol $\epsilon \approx 33$, ethanol $\epsilon \approx 24$), and strong hydrogen-bond-donating ability, all of which raise both their ionizing power and their nucleophilicity. Tertiary alcohols such as tert-butanol, by contrast, have a markedly lower dielectric constant ($\epsilon \approx 12$) and, more importantly for the nucleophilic component, an oxygen atom that is sterically shielded by three methyl groups, hindering its approach to an electrophilic carbon (Bentley, 2001) ^[12].

A detailed quantitative treatment of this substitution dependence is provided by the hydrogen-bond-donation-density parameter, DHBD, which explicitly incorporates whether the alcoholic hydroxyl group is primary, secondary or tertiary through a structural weighting factor, *f*, and which correlates strongly with the log *k*₁ rate constants for the solvolysis of tert-butyl chloride (2-chloro-2-

methylpropane) across a wide range of alcohol–water mixtures (Spange, Weiß and Mayerhöfer, 2022) ^[10]. In short, moving from a primary to a tertiary alcohol simultaneously lowers *Y* (poorer ionizing power) and *N* (poorer nucleophilicity), and both effects act in the same direction: they slow the solvolysis.

Kinetic Methodology

1. Monitoring the reaction

Solvolysis reactions are conveniently followed by one of two classical methods. In the conductometric method, the reaction is monitored via the increase in electrical conductivity of the medium as the covalent substrate is converted into ionic products; this method is well suited to tert-butyl-chloride-type substrates and has long been used to follow the hydrolysis or alcoholysis of tertiary alkyl halides in aqueous-alcohol mixtures at controlled temperature (Cropper and Olson, 1954) ^[3]. In the titrimetric method, aliquots of the reaction mixture are withdrawn at fixed intervals, quenched, and the liberated acid is titrated against a standard base, often with a pH-sensitive indicator to mark the endpoint.

2. Extracting the rate constant

Because the alcoholic solvent is present in large excess, the reaction follows pseudo-first-order kinetics:

$$-d[RX]/dt = k_{obs} [RX] \quad (3)$$

Integration gives $\ln[RX]_t = \ln[RX]_0 - k_{obs} t$, so a plot of $\ln[RX]_t$ (or an equivalent conductivity- or titre-based surrogate) against time yields *k*_{obs} as the negative of the slope. Repeating the measurement across a systematic solvent series — pure methanol, pure ethanol, pure tert-butanol, and mixed aqueous compositions of each — allows *k*_{obs} to be converted into the relative rate ratios (*k* / *k*₀) required for the Grunwald–Winstein analysis (Equations 1 and 2).

3. Activation parameters

Carrying out the kinetic runs at several temperatures (typically spanning roughly 15–55 °C) allows the Arrhenius equation to be applied:

$$\ln k = \ln A - E_a / RT \quad (4)$$

A plot of $\ln k$ against $1/T$ is linear with slope $-E_a/R$, giving the activation energy for solvolysis in each solvent; enthalpy and entropy of activation follow from the Eyring equation. Comparative activation parameters for related solvolyses have been reported for ethanol and for strongly ionizing, weakly nucleophilic fluoroalcohols (Kyong *et al.*, 2012) ^[7], and the solvent deuterium kinetic isotope effect (*k*_H/*k*_D, from rates measured in ROH versus ROD) has been used as an additional diagnostic of nucleophilic solvent participation: values close to unity indicate little nucleophilic assistance, whereas larger values (~1.3–2.5, as reported for several methanolyses) point to a kinetically significant role for the solvent O–H bond in the transition state (Kyong *et al.*, 2012) ^[7].

Results and Discussion

1. Rate trend across primary and tertiary alcohols

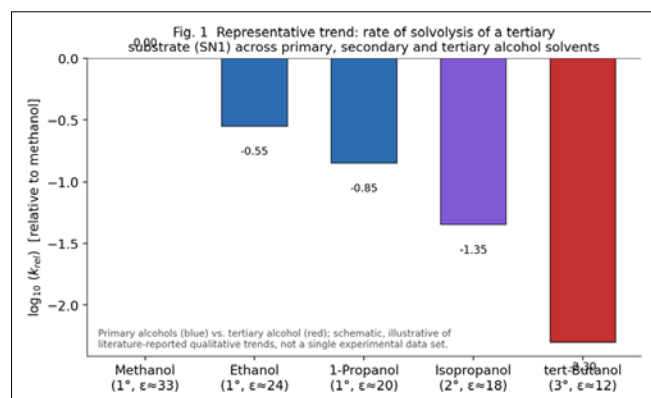


Fig 1: Representative trend in the rate of solvolysis of a tertiary substrate (e.g., tert-butyl chloride) across alcoholic solvents of increasing steric bulk and decreasing dielectric constant. Values are schematic, illustrating the qualitative order reported in the literature rather than a single experimental data set.

Figure 1 summarises the qualitative rate trend reported in the physical-organic literature for the solvolysis of a tertiary alkyl halide such as tert-butyl chloride across a series of alcoholic solvents of increasing steric bulk. Rates fall steadily in the order methanol > ethanol > 1-propanol > isopropanol > tert-butanol, tracking closely with the decrease in dielectric constant and hydrogen-bond-donor strength and with the increase in steric hindrance about the hydroxyl oxygen. This ordering is consistent with the specific-rate data reported for tert-butyl chloride solvolysis in aqueous methanol and related media (Cropper and Olson, 1954) [3], and with the ionizing-power trends compiled in more recent Grunwald–Winstein analyses (Kevill and co-workers, 2009; Abraham *et al.*, 2020) [1, 6].

2. Ionizing power and nucleophilicity: two reinforcing effects

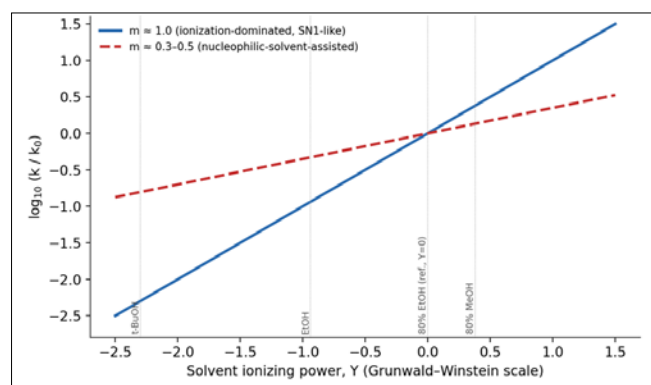


Fig 2: Schematic Grunwald–Winstein correlation, $\log_{10}(k/k_0)$ versus solvent ionizing power Y , for a limiting ionization-controlled substrate ($m \approx 1$) and a substrate that receives nucleophilic solvent assistance ($m \approx 0.3–0.5$). Dotted lines mark the approximate Y positions of representative alcohol/water solvents (after Grunwald and Winstein, 1948; Kevill and co-workers, 2009) [4, 6].

The Grunwald–Winstein plot in Figure 2 illustrates why the primary/tertiary distinction matters mechanistically as well as kinetically. For a substrate reacting through a limiting, ionization-controlled pathway ($m \approx 1$), the solvolysis rate is

highly sensitive to the ionizing power Y of the medium, and the low Y value characteristic of tertiary alcohols — arising from their lower dielectric constant and weaker hydrogen-bond donation — translates into a substantial rate depression. For a substrate that receives appreciable nucleophilic assistance from the solvent (moderate l), the rate is additionally depressed in tertiary alcohols because their sterically hindered oxygen is a poor nucleophile, an effect quantitatively documented for chloroformate and chlorothioformate ester solvolyses, where l values of roughly 0.1–1.7 have been reported depending on the degree of addition–elimination character at the reaction centre (Kevill and co-workers, 2009; Kyong *et al.*, 2012) [6, 7]. Because both the ionizing-power term (mY) and the nucleophilicity term (lN) move in the same direction on passing from a primary to a tertiary alcohol, the overall rate depression on going from methanol to tert-butanol is considerably larger than either effect would produce alone. This dual origin also explains a subtlety highlighted in re-examinations of tert-butyl chloride solvolysis: although tert-butyl chloride was chosen as the “limiting” SN1 reference substrate precisely because its solvolysis rate was assumed to be insensitive to solvent nucleophilicity, comparative mechanistic treatments applied to methanol and to primary, secondary and tertiary alcohols confirm that the alcohol’s degree of substitution still measurably affects the solvolysis pathway — partly through hydrogen-bond donation to the departing leaving group rather than through classical nucleophilic attack at carbon (Bentley, 2001) [2]. In other words, even reactions close to the SN1 limit are not wholly indifferent to whether the alcoholic solvent is primary or tertiary; both nucleophilic and electrophilic (hydrogen-bond-donating) character of the solvent contribute to accelerating solvolysis (Abraham *et al.*, 2020) [1].

3. Activation parameters

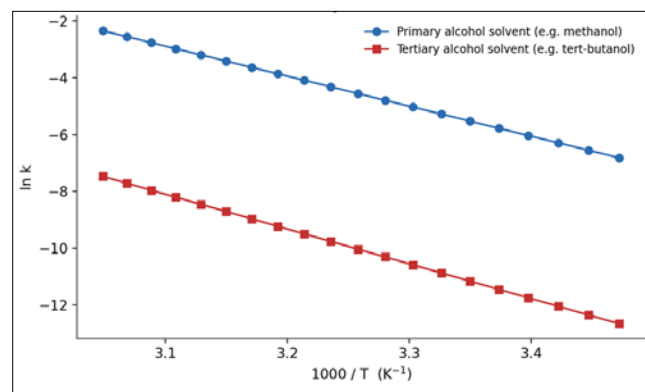


Fig 3: Schematic Arrhenius plots contrasting solvolysis in a primary alcohol (methanol) with solvolysis in a tertiary alcohol (tert-butanol); illustrative activation energies, not measured values.

Figure 3 presents schematic Arrhenius plots contrasting solvolysis in a primary alcohol (methanol) with solvolysis in a tertiary alcohol (tert-butanol). The lower ionizing power and nucleophilicity of the tertiary alcohol raise the free energy of the transition state relative to the ground state, which is reflected kinetically as a higher apparent activation energy and a lower rate at any common temperature. Reported activation parameters for structurally related solvolyses — for example, enthalpies and entropies of activation for chlorothioformate-ester solvolysis in ethanol

compared with the strongly ionizing but weakly nucleophilic fluoroalcohol 2,2,2-trifluoroethanol (Kyong *et al.*, 2012) ^[7] — show a broadly similar qualitative pattern: solvents of low nucleophilicity tend to require a larger enthalpic contribution to reach the transition state, an effect that can be partly compensated by a more favourable (less negative) entropy of activation, since less organisation of solvent molecules around the developing charge is needed when nucleophilic solvent participation is weak.

4. Mechanistic implications

Taken together, these observations place primary and tertiary alcohols at different points along the SN1–SN2 mechanistic continuum for a given substrate. Primary alcohols, with their combination of reasonable ionizing power, strong nucleophilicity, and minimal steric hindrance, tend to promote faster solvolysis and can supply significant nucleophilic solvent assistance, shifting the mechanism toward greater SN2 character for substrates that are not fully “limiting.” Tertiary alcohols, by contrast, slow the reaction substantially through both suppressed ionizing power and suppressed nucleophilicity; but by curtailing the nucleophilic-assistance pathway, they can produce comparatively “cleaner” ionization-controlled kinetics — a property exploited when highly ionizing, weakly nucleophilic solvents (including bulky and fluorinated alcohols) are used to isolate the ionization step for mechanistic study (Abraham *et al.*, 2020; Kyong *et al.*, 2012) ^[1, 7].

Conclusion

The rate of solvolysis in alcoholic media is governed jointly by the solvent’s ionizing power and its nucleophilicity, both of which are systematically modulated by whether the alcohol is primary or tertiary. Primary alcohols such as methanol and ethanol combine a comparatively high dielectric constant, strong hydrogen-bond-donor character, and an accessible oxygen lone pair to give both good ionizing power and good nucleophilicity, and consequently support comparatively fast solvolysis with the possibility of significant nucleophilic solvent assistance. Tertiary alcohols such as tert-butanol possess a markedly lower dielectric constant and a sterically shielded oxygen atom; both properties depress the rate, and they do so by reinforcing rather than opposing mechanisms, so the rate difference between primary and tertiary alcoholic solvents is considerably larger than either the polarity argument or the steric argument alone would predict. The Grunwald–Winstein framework, and its extension to include an explicit solvent-nucleophilicity term, provides a quantitative and mechanistically transparent way to rationalise these trends, and continues to underpin the choice of solvent systems used to dissect SN1 and SN2 character in modern physical organic chemistry.

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