



Substituent effects in acid-catalyzed hydration of alkenes, measured under consistent reaction conditions

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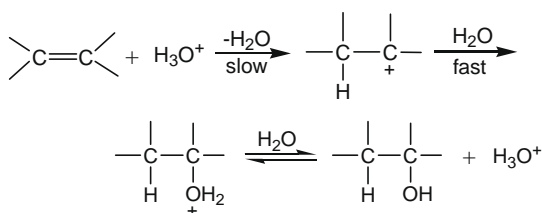
ABSTRACT

A set of convenient conditions for the title reaction is used to determine directly relative reactivities of alkenes with widely-varying steric requirements. Previous determinations did not use one set of conditions for all alkenes, but developed parameters in order to compare alkene reaction rates run in different solvents and in different concentrations; such an indirect reactivity comparison can introduce errors. Relative rates established under this common set of reaction conditions are compared to those previously calculated by using correction parameters. Comparison reveals that the approximate method overestimated effects of some groups attached to C=C, such as methyl and chloro.

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1. Introduction

Acid-catalyzed hydration of alkenes is a fundamental and intensively studied^{1–5} organic reaction, which converts an alkene into an alcohol by a mechanism that follows Markovnikov's rule.



The first step, protonation of C=C to give a carbocation intermediate, is reported to be rate-determining.¹ Kinetic studies indicate that the first step is irreversible^{1a,2a,b} under hydration conditions and that the reaction is of first order^{3a,4a,e,5a,e} in both alkene and hydronium ion, which support protonation of C=C as the rate-determining step.

Electron-donating groups on C=C accelerate this electrophilic addition⁴ reaction, while electron-withdrawing groups decelerate it. Surprisingly, one general set of experiment conditions, applicable to sterically different alkenes (mono-, di-, tri-, and tetrasubstituted), seems not to have been established. Approximations to account for differences in solvent and concentration create some

uncertainty in using these data to analyze steric effects upon alkene reactivity toward hydration. Therefore, it was desirable to study sterically different alkenes under one set of reaction conditions and to compare substituent effects, as was done previously for other alkene additions.⁶

2. Results and discussion

Relative reaction rates of acid-catalyzed hydration of alkenes are listed in Table 1, with the proton being attached to the carbon on the left side of the double bond, as drawn. Cyclic and aryl alkenes are not included, in order to avoid complications due to ring strain or aryl group conjugation.

A previous study of substituent effects upon alkene reactivities in acid-catalyzed hydration^{4d} collected data from different sources. In that study, rate data were extrapolated to $H_0 = 0$ from different acidities for comparison.⁴ Reaction rates in other solvents were converted to rates for water solvent, by applying a correction factor.⁴










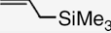









There are some significant differences between the effects of substituents in the previous series versus the series herein. For example, the rate increase caused by adding a methyl to the geminal position of a monosubstituted alkene is much larger in the earlier study (Fig. 1a) than that found herein (Fig. 1b).

Similarly, the rate decrease caused by adding a vinyl –Cl to a 1,1-disubstituted alkene is larger in the former study (Fig. 2a) than the current one (Fig. 2b).

Also, the previous study reported that the rate (1) increases in going from monosubstituted to vicinal disubstituted alkene (Fig. 3a), and (2) remains constant in going from geminal disubstituted alkene to a tetrasubstituted one. Conversely, in the current study, the rate decreases in both (Fig. 3b).

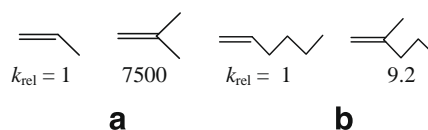
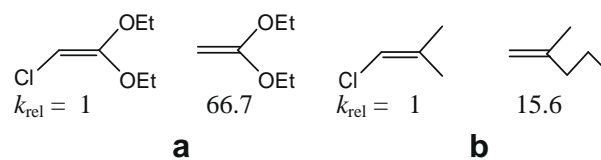
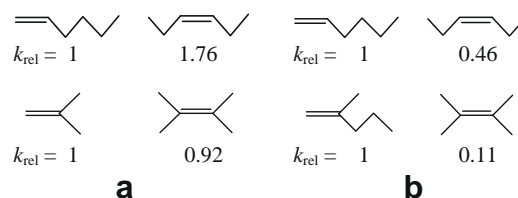
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Table 1Rates of acid-catalyzed hydration of alkenes in aqueous H₂SO₄ (60%) at 50 °C, relative to 1-hexene

No	Alkene	k_{rel}
1		103
2		253
3		129
4		86
5		70
6		46
7		40
8		45
9		17
10		449
11		920
12		138
13		100
14		59
15		17
16		109
17		23
18		29
19		21

3. Conclusion

A set of reaction conditions applicable to alkenes with different steric requirements determines directly the relative reactivities of alkenes in acid-catalyzed hydration of alkenes. Competitive acid-catalyzed hydrations of 19 alkenes with different steric requirements (mono-, di-, tri-, and tetrasubstituted) were run under the same conditions.

**Figure 1.****Figure 2.****Figure 3.**

The current study compares alkenes directly under one set of reaction conditions, while the former data were collected from different sources, under different reaction conditions, and converted by extrapolation. Comparison between the two reveals that the former overestimates the effects of chloro and methyl, in some cases. The differences are most likely due to different rate data collection methods. The use of parameters, corrections, and factors in the previous study could cause some inaccuracies.

4. Experimental section

4.1. Materials

Alkenes were purchased from Wiley Organics and Aldrich Chemical Company. Alkanes were purchased from Humphrey Chemical Company.

4.2. Instruments

GC analyses were done on a Hewlett–Packard 5890A gas chromatograph, with a 3.66 m 10% SE-30 on 100/120-mesh Chromosorb W column, programmed from 35 °C (5 min) to 200 °C (5 min) at 5 °C/min, and connected to a Hewlett–Packard 3390A integrator.

4.3. General experimental procedure

An alkene/standard solution, 2 alkenes (5 mmol each) and nonane (2.5 mmol, as internal standard), was mixed with 3 mL of H₂SO₄ (60%) in a 50 mL round bottom (RB) flask equipped with a side arm and condenser. Using a 25 mL RB flask caused no change in relative rates, demonstrating the absence of mass transport effects. This was stirred vigorously for a time, depending upon the alkene reactivity, in a water bath at 50 °C. The reaction mixture was added to 3.1 g of solid KOH and 5 mL of ethanol, submerged in an ice-water bath, and vigorously shaken in an ice-water bath until all KOH disappeared. The white precipitate (K₂SO₄) was separated by centrifugation, and a liquid phase sample was analyzed by GC for residual alkenes. Relative reactivity of the two alkenes was calculated by using the Ingold–Shaw equation.⁷

Acknowledgments

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