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ARTICLE

Inverse solvent effects in the heterogeneous and homogeneous epoxidation of *cis*-2-heptene with [2-percarboxyethyl]-functionalized silica and *meta*-chloroperbenzoic acid

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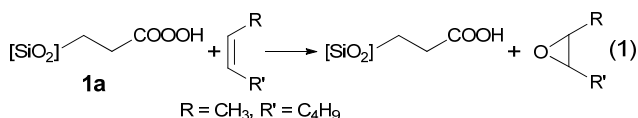
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The rate constants for the epoxidation of *cis*-2-heptene with [2-percarboxyethyl]-functionalized silica (**1a**) and *meta*-chloroperbenzoic acid (*m*CPBA) (**1b**) in different solvents have been determined at temperatures in the -10-40 °C range. The heterogeneous epoxidation exhibits a dependence of the reaction rate on solvent polarity opposite to its homogeneous counterpart and anomalous activation parameters in *n*-hexane, which are interpreted in terms of the surface-promoted solvent structure at the solid-liquid interface. The results show that highly polar solvents can strongly inhibit heterogeneous reactions performed with silica-supported reagents or catalysts.

Introduction

Heterogeneous reactions performed in liquid phases with solid reagents or catalysts take place at solid-liquid interfaces. In these regions, the solvent properties differ from the bulk due to the interactions of solvent molecules with the solid surface.¹ Nonlinear optical techniques² have indeed evidenced³ significant differences in solvent polarity, structure, and dynamics in relation to the bulk, as well as confinement and topological effects on solvent and adsorbates in the interfacial region. The changes in the reaction medium promoted by the solid surface are crucial for the selection of the solvent for heterogeneous reactions, as they can modify the reaction rate, regio- and stereoselectivity, or even mechanism in relation to their homogeneous counterparts.⁴ However, the impact of the solvent properties at solid-liquid interfaces on the course of heterogeneous reactions has not been studied⁵ as systematically as on the structure and conformation of adsorbates, notwithstanding its relevance for research areas dealing with reactions on solid surfaces, such as surface engineering, sensors, functional materials, heterogeneous catalysis, or environmental chemistry.



These considerations prompted us to explore the solvent properties at solid-liquid interfaces by using the epoxidation of *cis*-2-heptene with [2-percarboxyethyl]-functionalized silica (**1a**)^{6,7} as a model reaction (Equation 1). The epoxidation of simple olefins with solid peracid **1a** exhibits the usual reactivity patterns described for soluble peracids,^{7a,b} without significant

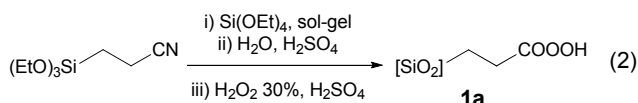
interferences of adsorption or surface diffusion phenomena on the reaction course.^{7b,c} Furthermore, the epoxidation of olefins with soluble organic peracids (Prilezhaev reaction)⁸ is a well-described reaction both experimentally⁹ and theoretically,¹⁰ and the kinetic solvent effects under homogeneous conditions are well-understood.¹¹

Herein we report on the rate constants and activation parameters for the epoxidation of *cis*-2-heptene with [2-percarboxyethyl]-functionalized silica (**1a**), and *meta*-chloroperbenzoic acid (*m*CPBA) (**1b**) as a control, in different solvents. The experimental data reveal an inverse dependence of the reaction rates on solvent polarity for each peracid and anomalous activation parameters for the heterogeneous reaction in *n*-hexane. These results are interpreted in terms of the organization of the solvent at the solid-liquid interface, which interfere with the specific adsorption of the substrate on the surface peroxydic ligands. The results indicate that polar basic solvents that are able to organize compact solvent layers onto the polar and protic silica surface can strongly inhibit heterogeneous reactions with silica-supported reagents or catalysts.

Results

The reaction rates for the epoxidation of *cis*-2-heptene with [2-percarboxyethyl]-functionalized silica (**1a**) and *m*CPBA (**1b**) were determined in *n*-hexane at 20.0/30.0/39.6 °C, dichloromethane at -10.0/5.0/20.0 °C, chloroform at 5.0/20.0/35.0 °C, and carbon tetrachloride and acetonitrile at 20.0 °C, under pseudo first-order conditions (initial molar *cis*-2-heptene:1 ratio of 1:10) and under stirring (400 rpm). The reaction conditions for each peracid were optimized prior to the kinetic measurements by considering the solid character of **1a**,

the solubility of **1b** in the different solvents and the solvent's boiling point. Silica-supported peracid **1a** (2.5-3.5 mmol of organic ligands and 1.1-1.7 mmol of peroxidic ligands per gram of hybrid material) was prepared^{6,7} and characterized¹² following reported procedures (Equation 2). *m*CPBA (**1b**) w/w 99.9 % was obtained from commercial samples (60-70 %) by standard purification methods. Detailed experimental procedures are described in the Experimental Part.



The heterogeneous reactions were carried out by adding solid-supported peracid **1a** to a thermostatted solution of *cis*-2-heptene and adamantane as an internal standard in the corresponding solvent. Aliquots were withdrawn at regular periods, quenched with a solution of thioanisole in dichloromethane, filtered and analyzed by gas chromatography. Homogeneous reactions were performed by adding a solution of *m*CPBA (**1b**) to a solution of *cis*-2-heptene and adamantane as an internal standard, both in the selected solvent and thermostatted at the desired temperature. Aliquots were withdrawn at regular intervals, quenched with a solution of thioanisole in dichloromethane, and analyzed by gas chromatography. Substrate conversions were determined from the peak areas corresponding to *cis*-2-heptene and adamantane found for the starting solution and the successive aliquots. Plots of $\ln [cis\text{-}2\text{-heptene}]_t/[cis\text{-}2\text{-heptene}]_0$ vs. time, and $\ln k_2$ vs. $1/T$ (Arrhenius plot) showed satisfactory linear correlations for both peracids in the different solvents studied (see Experimental Part and Supplementary Material for details).

Second-order rate constants and activation parameters for *n*-hexane, chloroform and dichloromethane, obtained from the kinetic data, are shown in Table 1.¹³ The results are the average of at least three independent runs. The linear-free energy relationships for the epoxidation of *cis*-2-heptene with silica-supported peracid **1a** and *m*CPBA (**1b**) in different solvents and Dimroth-Reichardt solvent polarity parameter (E_T^N),⁴ which measures the dipolarity, polarizability, cohesion forces and specific Lewis acidity of the solvent, are shown in Fig. 1a and 1b.

Control experiments addressed to determine the adsorption of *cis*-2-heptene onto the silica surface were carried out by adding [2-carboxyethyl]-functionalized silica to a 0.01M solution of *cis*-2-heptene and adamantane as an internal standard in different solvents, at 20.0 °C under stirring. Aliquots were withdrawn at regular periods, filtered and analyzed by gas chromatography. The results showed that the *cis*-2-heptene:adamantane ratio did not change upon addition of the hybrid silica to the starting solution and remained steady for 2 h, indicating that adsorption of *cis*-2-heptene on the active surface of **1a** is negligible in all the solvents used. Therefore, the experimental results cannot be attributed to solvent-dependent surface concentrations of the substrate on **1a**.

Discussion

The reaction rates and activation parameters found for the homogeneous epoxidation of *cis*-2-heptene with *m*CPBA (**1b**) in *n*-hexane, carbon tetrachloride, chloroform, dichloromethane and acetonitrile (Table 1, Fig. 1b) are in agreement with the

Table 1. Kinetic parameters for the epoxidation of *cis*-2-heptene with peracids **1a** and **1b**.

1	Solvent	E_T^N	k_2^a	$E_a^{b,c}$	$\Delta H^\ddagger^{b,c}$	$\Delta S^\ddagger^{b,d}$
1a	<i>n</i> -Hexane	0.009	0.0361	1.26	0.67	-58
1a	CCl ₄	0.052	0.0304			
1a	CHCl ₃	0.259	0.0086	11.23	10.65	-31
1a	CH ₂ Cl ₂	0.309	0.0190	11.57	10.99	-29
1a	CH ₃ CN	0.460	0.0026			
1b	<i>n</i> -Hexane	0.009	0.0062	12.58	11.99	-27
1b	CCl ₄	0.052	0.0172			
1b	CHCl ₃	0.259	0.0515	13.52	12.94	-20
1b	CH ₂ Cl ₂	0.309	0.0456	10.47	9.89	-31
1b	CH ₃ CN	0.460	0.0011			

^a Rate constants (M⁻¹ s⁻¹) at 20.0°C. Values are the average of at least three independent experiments with a maximum standard deviation of ± 0.0044 . ^b Reaction temperatures were 20.0/30.0/39.6°C for *n*-hexane, -10.0/5.0/20.0°C for dichloromethane and 5.0/20.0/35.0°C for chloroform. ^c Kcal mol⁻¹. ^d Cal K⁻¹ mol⁻¹.

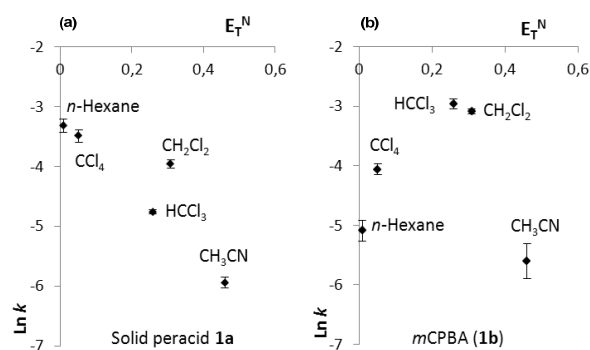
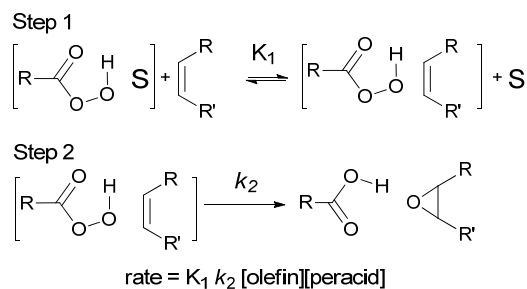


Fig. 1. Linear-free energy relationship $\ln k_2$ versus E_T^N of the solvent for the oxidation of *cis*-2-heptene with peracids **1a** (a) and **1b** (b).

kinetic data reported¹¹ for the epoxidation of olefins with different soluble organic peracids. Thus, the reactions follow second-order kinetics, first-order for each reagent, with negative activation entropies ranging from -20 to -40 cal mol⁻¹ K⁻¹, and show a direct dependence of the reaction rate on solvent polarity in non-basic solvents such as *n*-hexane and chlorinated hydrocarbons,¹¹ which is in agreement with the increase of dipole moment of the reacting system on going from the starting materials to the transition state.^{10,11}

The strong rate inhibition observed for the homogeneous epoxidation in acetonitrile (Table 1, Fig. 1b) can be rationalized in terms of the fast olefin-peracid complex equilibrium prior to the rate determining oxygen-transfer step, in which olefin and solvent molecules compete to coordinate with the hydroperoxydic group (Scheme 1).¹⁴⁻¹⁷ Basic solvents that are able to establish strong hydrogen bonding interactions with the peracid¹⁶ displace the equilibrium to the left side and diminish the reaction rate. Conversely, this pre-equilibrium remains largely unnoticed in weakly coordinating solvents and the kinetic solvent effect observed in these cases corresponds to the different solvation of reagents and transition state.^{10,11} Minor solvent effects on this pre-equilibrium may be responsible for the lack of linearity in the free energy relationship with E_T^N observed for homogeneous reactions with different soluble organic peracids in non-basic solvents (Fig. 1b).^{11,15,16}



Scheme 1. Reaction mechanism for the epoxidation of olefins with organic peracids (S represents a solvent molecule).^{10,11,16}

The heterogeneous oxidation of *cis*-2-heptene with [2-percarboxyethyl]-functionalized silica (**1a**) was expected to follow the same trend, and be consistently slower than its homogeneous counterpart due to the inability of the peroxydic groups bonded to silica nanoparticles to freely diffuse into the substrate solution. However, the experimental data reveal that: i) the reaction rate exhibits a negative dependence on solvent polarity, with acetonitrile, the most polar and basic solvent of the series, fitting the correlation (Fig. 1a), ii) the reactions in *n*-hexane and carbon tetrachloride are actually faster than for soluble peracid **1b** (Table 1), and iii) the reaction in *n*-hexane shows anomalous activation parameters¹⁷ ($\Delta H^\ddagger = 0.67 \text{ kcal mol}^{-1}$, $\Delta S^\ddagger = -58 \text{ cal K}^{-1} \text{ mol}^{-1}$, Table 1) which prove the existence of an initial olefin-peracid complex equilibrium^{15,17} in this apolar non-basic solvent (Scheme 1).

The reversal of the dependence of the reaction rate on solvent polarity observed on changing from homogeneous to heterogeneous reaction conditions can be attributed to the structure of the solvent at the solid-liquid interface. The silanol, carboxylic acid and peracid groups on the active surface of **1a** are acidic adsorption sites for any polar and polarizable molecule in solution. As these functional groups remain immobile on the silica surface, their interactions with the solvent dipoles bring about a structured solvent layer on the solid surface.³ The exchange of the solvent molecules integrated into this organized layer is slower than for solvation shells in liquid phases since aggregation hinders the rotation and reorientation of the adsorbed solvent molecules (Fig. 2).³

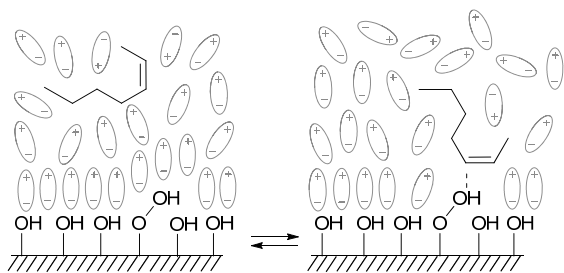


Fig. 2. Illustration of the olefin-peracid complex pre-equilibrium in the organized solvent layer at the solid-liquid interface of **1a**.

Stronger solid-solvent interactions determine larger and more structured solid-liquid interfaces,³ and this trend justifies the dependence of the reaction rates on solvent polarity observed for the epoxidation of *cis*-2-heptene with [2-percarboxyethyl] functionalized silica (**1a**). At this instance, the olefin-peracid complex pre-equilibrium represents the specific

adsorption of *cis*-2-heptene on the surface peroxydic ligands. Thus, *n*-hexane, unable to establish significant interactions with the polar and protic active surface of **1a**, allows for *cis*-2-heptene to freely interact with surface peracids.¹⁸ The olefin-peracid complex equilibrium displaces to the right-hand side in this case, and the activation barrier determined experimentally is lower than expected (Table 1).¹⁵⁻¹⁷

As solvent polarity increases, the solvent structure at the interface becomes progressively more efficient to hinder the approach of the olefin to the surface peracids, the initial complex equilibrium progressively displaces to the left-hand side, and the reaction rate diminishes. Conversely, the highly dynamic solvation shells⁴ in the homogeneous reactions allow for *cis*-2-heptene to efficiently displace weakly coordinating non-basic solvents from the hydroperoxydic group of *m*CPBA (**1b**) and the olefin-peracid complex pre-equilibrium (Scheme 1) remains unnoticed. In these cases the solvent effects observed correspond mainly to the different solvation of reagents and transition state of the rate determining oxygen-transfer step (Fig. 1b).^{10,11}

The shape of the solvent molecules and solvent's viscosity are probably significant parameters for the formation of the organized solvent layer onto the silica surface³ of solid peracid **1a**. These factors, which are not measured by the E_T^N parameter,⁴ may justify the deviations in the free-energy relationships observed for the heterogeneous reaction in dichloromethane and chloroform (Fig. 1a).

The faster reaction rates observed in *n*-hexane and carbon tetrachloride for solid peracid **1a** in comparison to *m*CPBA (**1b**) (Table 1) cannot be attributed to a higher reactivity of the former, as this does not agree well with the reactivity pattern known for aliphatic and aromatic peracids^{10,11} and the data reported^{6,7} on oxidations with solid oxidant **1a**. These results rather suggest that the effective concentration of *cis*-2-heptene in the solid-liquid interface is higher than in the solution bulk due to the better adsorption of the alkene on the highly polar silica surface compared to *n*-hexane and carbon tetrachloride.¹⁸ Moreover, given that the solvation of the reacting system in the solid-liquid interface is not as effective as in solution due to the steric hindrance posed by the silica surface to the formation of the solvation shell, the resistance opposed by the apolar solvent to the increase in dipole moment in the oxygen-transfer step^{10,11} is expected to be lower in the interfacial region than in solution.

Conclusions

In summary, the dependence of the reaction rate on the polarity of the solvent found for the heterogeneous epoxidation of *cis*-2-heptene with [2-percarboxyethyl]-functionalized silica (**1a**) and its homogeneous counterpart with *m*CPBA (**1b**) are opposite. The results are interpreted in terms of the surface-promoted solvent structure in the solid-liquid interface, which inhibits solvent dynamics and hinders the interaction of the olefin with the surface peroxydic ligands. In this way, the olefin-peracid complex pre-equilibrium in the heterogeneous reaction becomes more solvent-sensitive than the rate-determining oxygen-transfer step. These results indicate that heterogeneous reactions with silica-supported reagents or catalysts may be strongly inhibited by highly polar solvents like acetonitrile, dimethylformamide or dimethylsulfoxide.

Experimental Section

General

Solvents and reagents were purified before use by following standard procedures.¹⁹ Glassware was successively washed with an aqueous EDTA solution (0.125 g mL⁻¹), ultrapure water and acetone purified by distillation from KMnO₄. The GC analyses were performed with a capillary column Agilent HP1 (30 m length, internal diameter 0.32 mm and film thickness 0.25 μm), with an injector temperature of 250°C and FID temperature 280°C.

[2-Pericarboxyethyl]-functionalized silica (**1a**) was prepared by the sol-gel method following reported procedures.^{6,7} Prior to each kinetic experiment, solid peracid **1a** was dried under vacuum (0.01 mm Hg) at room temperature until it reached a constant weight, and its peroxydic content was determined by standard iodometric titration. *meta*-Chloroperbenzoic acid (*m*CPBA) (**1b**) 96-99% w/w was obtained by treating commercial samples (60-70%) with a K₂HPO₄/NaH₂PO₄ buffer solution at pH 7.5 and at room temperature for 6 h, followed by recrystallization at -20°C from *n*-hexane/diethyl ether 3:1. Peracids **1** were stored at 3°C in the dark. The *m*CPBA solutions (**1b**) (0.05 M) in the different solvents were prepared at the same temperature of the experiments using a thermostatted bath. The peroxydic content of the solution was determined prior to each kinetic experiment.

Solutions of *cis*-2-heptene (0.01 M) and adamantane, as an internal standard (0.005 M), in the different solvents (Table 1) were prepared at the kinetic experiment temperature with a thermostatted bath. The reaction conditions for each kinetic experiment were previously optimized for each peracid and solvent, and depended mainly on the boiling point of the solvent and the solubility of *m*CPBA (**1b**) in each case. The kinetic experiments were performed at least three times for each solvent and temperature.

Kinetic experiments for 1a. General procedure. To a solution (4 mL) of *cis*-2-heptene (0.01 M) and adamantane (0.005 M), as an internal standard in dichloromethane, placed in a jacketed flask thermostatted at 20.0 ± 0.1°C by a recirculating bath, solid peracid **1a** (0.4 mmol) was added at once under stirring (400 rpm). The aliquots (0.2 mL) withdrawn from the reaction mixture were quenched with 0.4 mL of a 0.25 M solution of thioanisol in dichloromethane, filtered through a Teflon syringe filter (0.2 μm) and analyzed by gas chromatography. Substrate conversions were determined from the ratio of peak areas *cis*-2-heptene/adamantane found for the starting solution and the corresponding aliquot.

Kinetic experiments for 1b. General procedure. To a solution (2.5 mL) of *cis*-2-heptene (0.01 M) and adamantane (0.005 M), as an internal standard in dichloromethane, placed in a jacketed flask thermostatted at 20.0 ± 0.1°C by a recirculating bath, a 0.05 M solution of *m*CPBA (**1b**) (5 mL, 0.25 mmol) in the same solvent, thermostatted at the same temperature, was added under stirring (400 rpm). The aliquots (0.4 mL) withdrawn from the reaction mixture were quenched with 0.1 mL of a 1 M solution of thioanisol in dichloromethane, and were analyzed by gas chromatography. Substrate conversions were determined from the ratio of peak areas *cis*-2-heptene/adamantane found for the starting solution and the corresponding aliquot.

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Notes and references

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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