Application of Molecular Modeling in the Optimization of Reactive Cotton Dyeing in Supercritical Carbon Dioxide

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Reactive dyeing of cotton in supercritical carbon dioxide is a green alternative to reduce water consumption and wastewater. Cotton could be successfully dyed and the reaction kinetics was determined; however, several issues need to be clarified for further optimization of the dyeing process. For instance, it was observed that the difluorotriazine dye reacted very fast with cotton but its kinetics showed a negative activation energy. Furthermore, it seemed that fixation was strongly related to the nature of cosolvents methanol and dimethyl sulfoxide. Finally, the dihalogenotriazine dye reacted selectively with cotton in the presence of methanol, commonly used as a model for cotton. A molecular modeling approach was applied to provide explanations for the above-mentioned experimental phenomena. In combination with experimental data, molecular modeling was shown to be a powerful tool for the understanding and optimization of the process of cotton dyeing in supercritical carbon dioxide.

Introduction

Supercritical carbon dioxide ($scCO_2$) has been extensively studied as an alternative solvent for different industrial process due to its green properties.[1] An important potential application of $scCO_2$ can be found in the textile industry, which is one of the largest water consumers. In this new textile dyeing process, water is replaced by $scCO_2$, so water can be eliminated from the process, as well as the costly wastewater treatment.[2,3] Cotton represents 35% of the fiber world market share;[4] therefore, several studies were done to develop a method to dye cotton with this new textile dyeing process.[5−7] Nonpolar reactive dyes are used for dyeing cotton in $scCO_2$. This type of dye can be dissolved in $scCO_2$, and they also react with the cotton, forming a strong covalent bond that determines the coloration of the cotton and dye fixation.

Cotton is built up from cellulose fibers and is believed to react with the dye via its primary alcohol function. Methanol, the most simple primary alcohol and soluble in $scCO_2$, is commonly used as a model for cotton[8] to explore the kinetics of the reaction experimentally.

Moreover, we developed a novel process for dyeing cotton based on physical interactions between the cotton and polar solvents.[9] With this process the dye transport and diffusion, as well as the cotton accessibility, were improved.

Although the reaction kinetics was determined[10,11] and cotton was successfully dyed,[12] several issues need to be clarified. As expected, the difluorotriazine dye reacted faster as the dichloro analogue; however, unexpectedly, it showed a negative activation barrier in methanol as solvent. Cotton could be even more successfully dyed in supercritical CO_2 when polar solvents (methanol or dimethyl sulfoxide, DMSO) were used either as pretreatment or as cosolvent. Dye fixation was good with methanol but not with DMSO. Furthermore, it was puzzling why cotton reacts predominantly with dyes in the presence of the cotton model methanol.

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Molecular modeling has been extensively used for elucidating reactions and reaction mechanisms.[13−16] Therefore; it can be a very useful tool for understanding and optimizing the dyeing process of cotton. In this study, molecular modeling was used to elucidate the most plausible reaction mechanism of the dihalogenotriazine dyes (Figure 1) with methanol and with cotton as well. The effects of the two solvents used, methanol and DMSO, were investigated as well.

Molecular Modeling. The Spartan '02 package[17] was used for all calculations. All structures underwent complete geometrical optimization on the B3LYP level (6-31G**), starting from PM3 structures. Transition states have been checked by frequency analysis, showing one imaginary vibration. Close to the commonly accepted experimental simplification, methanol and glucose were used as models for cotton. Unsubstituted 6-H dihalogenotriazines were used as models for the actual dyes, 6-substituted dihalogenotriazines, because the reaction with cotton takes place with the triazine moiety of the dyes. The solvent model of Cramer and Truhlar and co-workers[18] (SM5.4) for aqueous solvation was used to get an impression of the effect of methanol on the activation energies.
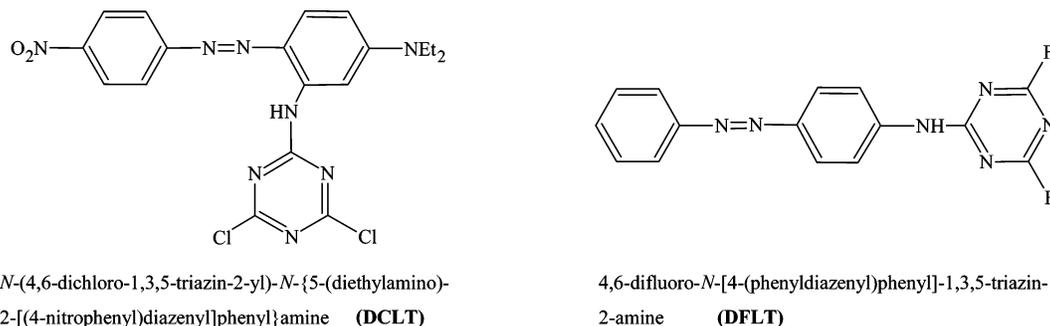
Results and Discussion

Summary of Experimental Results. Dihalogenotriazine dyes react with methanol via a two-step consecutive nucleophilic reaction (Scheme 1). Experimentally it was found that the reactions obeyed pseudo-first-order kinetics, which is to be expected given the huge excess of methanol. In $scCO_2$ the system is even 5 times more diluted.

In Table 1 the experimental activation energies are shown. From Table 1 is clear that 2,4-dichlorotriazine (DCLT) has almost identical activation energies ($\sim$ 60 kJ/mol) in methanol and $scCO_2$ for both steps. The experimental error in the second step seems to be higher due to the fact that no separate kinetic runs are available on the intermediate 2-methoxy-4-halogenotriazine. 2,4-Difluorotriazine (DFLT) showed very different behavior. It has apparent negative activation energy ($\sim$ −10 kJ/mol) for both steps in methanol and positive activation energy of $\sim$30 kJ/mol in $scCO_2$.

N-(4,6-dichloro-1,3,5-triazin-2-yl)-N-{5-(diethylamino)-
2-[(4-nitrophenyl)diazenyl]phenyl}amine **(DCLT)**

4,6-difluoro-N-[4-(phenyldiazenyl)phenyl]-1,3,5-triazin-
2-amine **(DFLT)**

Figure 1. Chemical structures of the nonpolar reactive dyes used in this study.

Scheme 1. Reaction Sequence for the Two-Step Consecutive Nucleophilic Substitution of Dialogenotriazine Dyes

X = Cl, F
chrom = 4-NO$_2$C$_6$H$_4$N$_2$C$_6$H$_3$N(C$_2$H$_5$)$_2$NH- or C$_6$H$_5$N$_2$C$_6$H$_4$NH-
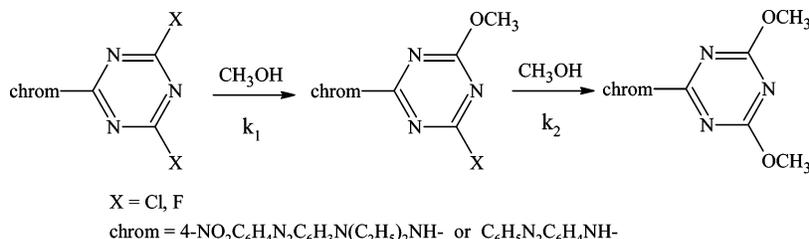
Table 1. Activation Energies Experimentally Obtained[10,12] for the Reactions of 2,4-Dichlorotriazine and 2,4-Difluorotriazine in Supercritical Carbon Dioxide and Methanol

	activation energy (kJ mol^{-1})			
	DCLT		DFLT	
	MeOH	scCO$_2$	MeOH	scCO$_2$
k_1 (TS1)	60	61	−9	30
k_2 (TS2)	74	50	−10^a	32

^{a} Reinspection of the experimental values showed one maverick.
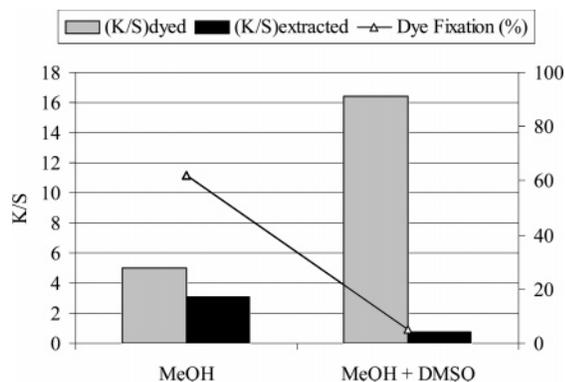
Figure 2. Effect of cosolvents on the dyeing of cotton pretreated in methanol.[9] Dyeing conditions: 300 bar and 393 K for 2 h.

Dye fixation is good with methanol but not with DMSO (Figure 2), despite both solvents increasing the accessibility of the fiber for the dye. Furthermore, it was puzzling why cotton reacts predominantly with dyes in the presence of the cotton model methanol.

Reaction Mechanism with Methanol as a Model for Cotton Fiber. Several reaction mechanisms for nucleophilic substitution in conjugated rings have been proposed in the literature.[19,20] Sawunyama et al.[15] suggested a concerted mechanism in the acid-catalyzed hydrolysis of 2-chloro-s-triazines, which is shown in Scheme 2. As a result of protonation, attack of water, and deprotonation, net addition of water to a C=N of the triazine ring occurs, immediately followed by elimination of HCl to produce 2-hydroxy-s-triazine. This addition-elimina-

**Scheme 2. Addition−Elimination Mechanism for Nucleophilic Substitution**
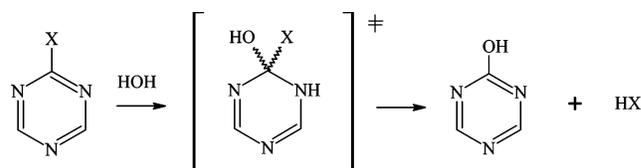
Table 2. Activation Energies Derived from B3LYP for Addition of MeOH to the Dihalogenotriazines^a

|	Ha-1 (kJ/mol)		Ha-2 (kJ/mol)	
reaction mechanism	gas phase	aqueous solvent	gas phase	aqueous solvent
DCLT addition−elimination	23.3	50.2	19.7	51.3
DFLT addition−elimination	−1.8	27.8	−5.8	29.6

^{a} Activation energies for the elimination of HX are <20 kJ/mol related to the corresponding adduct·HX complex.

tion mechanism shows some similarities with our case, wherein methanol acts both as nucleophile and solvent and HX is eliminated.

An important feature of this mechanism is the explicit participation of solvent molecules at several stages of the reaction. Gas-phase S$_N$2 reactions generally proceed with little or no barrier.[21−23] Experimental activation barriers in S$_N$2 reactions are predominantly due to the participation of a solvent.[24] In the present cases, where net proton transfer from methanol to the leaving halide is necessary, explicit participation of (solvent) molecules (MeOH, HX) seems to be quite obvious. Four cases of solvent participation were studied: two cases involving direct participation of MeOH or HX in the transition state of the nucleophilic substitution, and two cases involving participation of MeOH or HX in an addition−elimination mechanism. Surprisingly, it turned out that an addition− elimination mechanism, with HX in both the addition and the elimination step, provided the best description of the reaction. Nevertheless, it should be taken into consideration that HX might have limited availability at the beginning of the reaction. Table 2 shows the activation energies calculated for the two addition steps for DCLT and DFLT. Detailed structural infor- mation on the different transition states for the two substrates
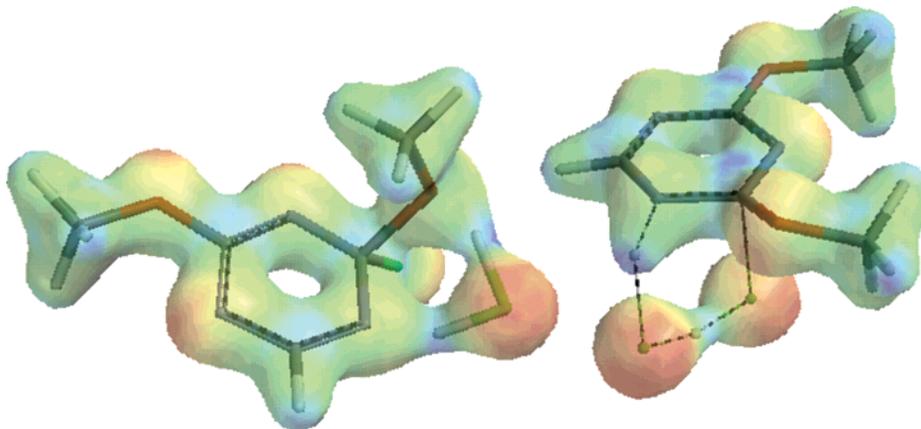
Figure 3. Transition states to which HF assisted in addition of MeOH, and elimination of HF from 2-fluoro-4-methoxytriazine. (B3LYP/6-31G**). Surface, density (bond) 0.08; property, electrostatic potential.
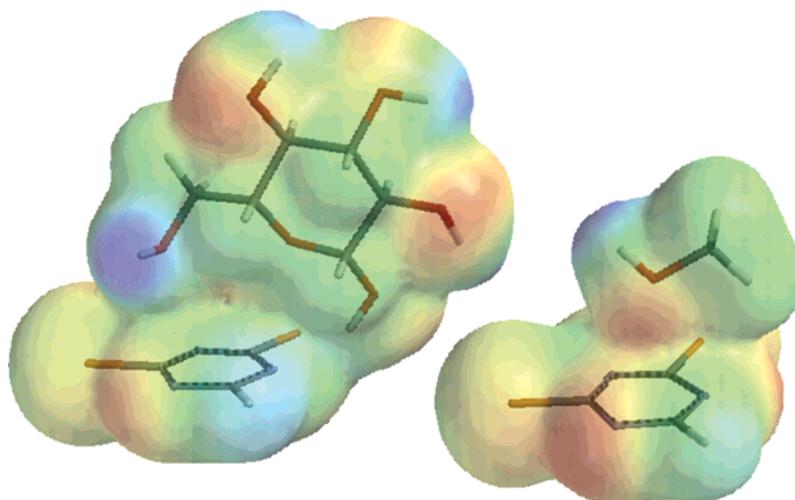
Figure 4. Precomplexation of glucose and methanol with 2,4-dichlorotriazine. Surface, electron density (0.002 e/au^3); property, electrostatic potential.

and the various reaction pathways is available on request. According to the calculations, the activation energies for the two steps with DCLT are $\sim$20 kJ/mol in the gas phase and $\sim$50 kJ/mol if corrected for aqueous solvation. The activation energies of HX elimination turned out to be negative in the gas phase and <20 kJ/mol if corrected for aqueous solvation in all cases. Thus the addition process, and not the subsequent elimination, is rate-determining. This is in agreement with the experimental observation that no (reactive) intermediate is observed except the one-time methoxy-substituted product. Furthermore, when it is taken into account that methanol and water are quite different from each other with respect to the stabilization of a proton transfer, the agreement with experiment is quite satisfactory.

From the calculations it becomes clear that DFLT indeed should have a lower activation barrier. In the gas phase they are negative with respect to their starting materials, but when aqueous solvation is taken into account, activation energies of $\sim$30 kJ/mol can be calculated, very close to those experimentally observed iin scCO$_2$. Figure 3 shows the transition States for the HF-assisted addition of MeOH to, and the elimination of HF from, 2-fluoro-4-methoxytriazine.

The decrease in the rate of reaction for DFLT in methanol, leading to the apparent negative activation energy, should be due to a shift in the stability of solvation complexes of HF with the corresponding triazines and methanol. Indeed, it was calculated that a triazine·HF complex is $\sim$12 kJ/mol more stable than a MeOH·HF complex; however, at higher temperature,

entropy (excess of MeOH) will favor the latter, and therefore the reaction will slow down slightly. In the much more diluted DFLT/MeOH/scCO$_2$ system this is not visible yet. Since the difference in stability of a triazine·HCl complex and a MeOH·HCl complex is even larger, this behavior is not observed within the DCLT/MeOH system.

Glucose versus Methanol as a Model for Cotton Fiber. Cotton consists of an assembly of cellulose chains connected via interchain hydrogen bridges. Cellulose can be described as a condensation polymer of β-D-glucopyranose with 1,4-glycosidic bonds. It is generally believed that the primary alcohol functions, present in cellulose, react via nucleophilic substitution with the dye. Methanol is commonly used as an experimental model for cotton fibers to investigate the reaction; however, we observed that cotton fiber reacts predominantly with the dye even in the presence of methanol as solvent. In an attempt to get a plausible explanation for this rather unexpected behavior, we considered glucose as a slightly less simple model for cotton fiber also. It was found that, prior to reaction, precomplexation of glucose and methanol with DCLT can take place. The main difference between the two complexes is an extra stabilization of $\sim$8 kJ/mol by the ether function in the glucose ring with the triazine ring, as can be seen in Figure 4. This positive interaction is present in the transition state as well, leaving the activation barrier virtually unaffected.

Methanol and DMSO as Cosolvents. The solvents methanol and DMSO both have been tried to improve the dyeability of cotton fibers.[9] Both solvents are capable of breaking up the

hydrogen bridges between the cellulose chains, but their effect on dyeability is opposite. In the presence of methanol, increased dyeability is observed, and in the case of DMSO, there is decreased dyeability.

A series of interactions was considered: DMSO with a primary alcohol, DMSO with DCLT, methanol with another primary alcohol, and methanol with DCLT. The interaction of DMSO with a primary alcohol is much stronger ($\sim$20 kJ/mol) than the interaction of two primary alcohols with each other, thus confirming the idea of breaking up the hydrogen bridges between the cellulose chains. The interaction of DMSO with DCLT is also stronger ($\sim$8 kJ/mol) than the interaction of methanol with DCLT but equally as strong as the interaction of glucose with DCLT (see above). However in the transition state of the nucleophilic substition of DCLT with glucose, it is not possible to maintain both interactions with DMSO, thus leading to an increased activation barrier of at least 17 kJ/mol. This will lead to a much lower reaction rate and decreased dyeability.

Conclusions

Molecular modeling offers attractive explanations for differences in reactivity of DCLT and DFLT toward nucleophilic substitution with methanol in such different solvent environments as methanol, DMSO, and scCO$_2$. Difluorotriazine and dichlorotriazine react with methanol most likely via an HX-assisted addition−elimination pathway. When the severe limitations of the conceptual experimental and computational approach are taken into account, the quantitative agreement is rather good. The experimental differences observed for DFLT between methanol and scCO$_2$ were satisfactorily explained by the difference in stability of the triazine·HF and MeOH·HF complexes as a function of temperature and methanol concentration.

The observed experimental difference in reactivity between cotton fiber and methanol was explained by precomplexation of the dye with the fiber; glucose was used as a slightly less simple model than methanol itself for the cotton fiber.

The observed opposite behavior of DMSO and methanol in dyeing cotton fibers could be rationalized by the strong complexation of DMSO to the primary alcohol functions in the cotton fiber, disabling the reaction between the fiber and the dye, while in the case of methanol beneficial participation of HX in the reaction can still take place.

Molecular modeling serves as a powerful visualizing and quantifying tool to elucidate reaction pathways and unravel solvent effects. The results obtained are very useful for further optimization of the dyeing process of cotton in scCO$_2$.

Acknowledgment

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