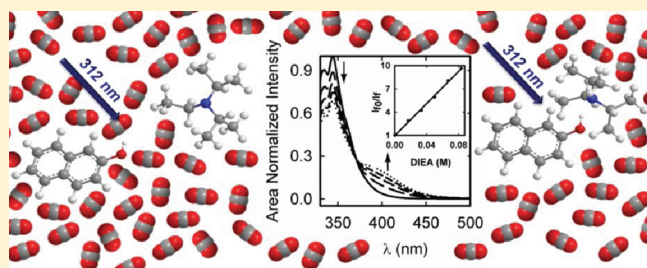


Proton Transfer from 2-Naphthol to Aliphatic Amines in Supercritical CO₂

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S Supporting Information

ABSTRACT: The proton transfer from 2-naphthol to aliphatic amines was studied in supercritical CO₂ (scCO₂) and in cyclohexane as reference solvent, by absorption and fluorescence spectroscopy and by time-resolved emission. Irradiation of 2-naphthol in scCO₂ in the presence of ethyldiisopropylamine shows dynamic fluorescence quenching of the acidic form of 2-naphthol and emission from the basic form. Fluorescence excitation spectra show that the emission of the basic form is originated upon excitation of the acidic form. The interaction between 2-naphthol and the amines is described by the formation of a complex with proton donor–acceptor character in the ground and excited states of 2-naphthol. The acidity increase of 2-naphthol upon electronic excitation to the first excited singlet in scCO₂ is as high as in water. Proton transfer quantum yields of 0.6 can be easily achieved in scCO₂. The results have implications for carrying out acid–base catalyzed reactions in scCO₂.



INTRODUCTION

Proton transfer reactions are ubiquitous elementary reaction steps in many fundamental processes in chemistry and biochemistry. Because the proton transfer is normally a very fast reaction, photochemistry was extensively used to study this process.¹ Photoacids, chemical species having an enhanced acidity in the excited state compared to the ground state, have been extremely helpful for this purpose.² Among the photoacids, 2-naphthol is a classic example of a simple substance with many favorable features. Its pK_a in water decreases from 9.5, in the ground state, to 2, in the singlet excited state.³ The transfer of a proton from the first excited singlet state of the acidic form to many different types of substrates is very fast, favorably competing with excited state deactivation in the nanosecond time range. Furthermore, the absorption and especially the emission spectra of the acid form and its conjugate base are easily distinguishable.

Reactions in supercritical fluids have attracted great attention because their medium density can be strongly and continuously changed at constant temperature by moderate pressure variations.⁴ This provides a unique opportunity for studying the effect of solvation on reaction mechanisms and dynamics, and in practice it offers the possibility of completely removing the solvent by pressure changes. Carbon dioxide has been used in this sense much more than any other solvent because of its favorable chemical and physical properties: it is non-toxic, non-flammable, inexpensive, easily available, inert to most reactive intermediates, and its critical point is located at 30.98 °C and 73.77 bar, conditions achievable with low effort.

Therefore, understanding the factors controlling elementary reactions in scCO₂ has an importance which parallels its use as a processing solvent. We recently investigated the cage effect in geminate radical production, escape, and recombination in scCO₂⁵ and we now undertake the study of proton transfer reactions because of their above appointed importance.

Previous attempts to observe excited state proton transfer (ESPT) in scCO₂ include the study of the emission of 2-naphthol and 5-cyano-2-naphthol in scCO₂ and its mixtures with water and with methanol as cosolvents. These experiments did not show any naphtholate-type emission.⁶ The failure was attributed to the relatively low acidity of the naphthol excited state and to the limited amount of water (proton acceptor) that CO₂ can dissolve. Nunes et al.⁷ reported a successful ESPT from 5,8-dicyano-2-naphthol in supercritical CO₂-methanol mixtures for alcohol concentrations over 3 M, its success stemming from the extremely high acidity of this super photoacid (pK_a^{*} = −4.5 in aqueous solution). Despite the strength of the photoacid, no proton transfer was observed in neat scCO₂.

Excited state intramolecular proton transfer (ESIPT) in scCO₂ was observed in 4'-dimethylamino-3-hydroxyflavone.⁸ Steady state emission spectra show the two emission bands due to the tautomers. The total emission intensity, and more notably the lower energy tautomer emission, rapidly decreases at pressures lower than 97 bar in CO₂ at 34 °C.

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Keeping in mind the importance of understanding proton transfer reactions in scCO_2 , we report in this work the successful quantification of the equilibrium and the dynamics of proton transfer from excited state 2-naphthol to aliphatic amines in scCO_2 at 35 °C and in the pressure range between 100 and 200 bar. Our results show that, depending on the amine used, static emission quenching of the acidic form, or dynamic quenching of the excited state of the acidic form and emission from the basic form can be observed.

EXPERIMENTAL SECTION

Materials. 2-Naphthol (Merck, 99%) was recrystallized from toluene. The following chemicals were used as received: 2-Methoxynaphthalene (Aldrich, 99%), *N*-ethyl-diisopropylamine, DIEA, (Fluka, $\geq 98\%$), morpholine, MP, (Merck, for synthesis, $\geq 99\%$), triethylamine, TEA, (Sigma-Aldrich, $\geq 99.5\%$), cyclohexane (Aldrich, spectrophotometric grade), and CO_2 (AGA, Coleman 99.99%). It is estimated that the oxygen content of the carbon dioxide used in all measurements is lower than 1 ppm.⁵

Absorption and Emission Spectra. For all spectroscopic measurements, a high-pressure optical cell made of stainless steel was used, as described in previous work.⁵ A Shimadzu UV3101PC spectrophotometer and a PTI-Quantmaster spectrofluorometer were used for the absorption and steady state fluorescence measurements, respectively. The absorption spectra were recorded between 200 and 350 nm with a bandwidth of 1 nm. For fluorescence emission spectra, excitation wavelengths and emission ranges were as follows: $\lambda_{\text{exc}} = 312$ nm, $\lambda_{\text{em}} = 330$ –500 nm and $\lambda_{\text{exc}} = 335$ nm, $\lambda_{\text{em}} = 350$ –500 nm. For fluorescence excitation spectra, emission wavelength, and excitation range were as follows: $\lambda_{\text{em}} = 347$ nm, $\lambda_{\text{exc}} = 290$ –331 nm and $\lambda_{\text{em}} = 410$ nm, $\lambda_{\text{exc}} = 290$ –393 nm. Emission spectra were corrected by the instrument response function.

Fluorescence Decay Lifetimes. Time-resolved fluorescence decays were collected using a PTI-Time Master instrument. For the excitation, a hydrogen pulsed lamp was used, operating at 19 kHz repetition rate with a 2.5 ns fwhm pulse. The instrument response function was measured using a colloidal suspension of Ludox, by recording the scattering of the incident light. Emission time traces were collected at 345 nm.

Sample Preparation. An adequate volume of a solution of 2-naphthol in cyclohexane was loaded into the high pressure cell, to obtain a final concentration of 2-naphthol in the whole cell of about 0.040 mM. Solvent was then completely evaporated and the cell was evacuated and purged with small amounts of CO_2 in order to remove oxygen. After thermostating, the cell was filled with CO_2 , using an automatic high-pressure syringe (ISCO DM-100). The equipment also included a six port valve with a calibrated capillary loop used for injecting known volumes of the pure liquid amines into the cell. Subsaturated conditions of 2-naphthol and amines in supercritical CO_2 were assured for all of the measurements. The density of CO_2 was calculated from measured temperature and pressure by an appropriate equation of state using REFPROP.⁹

Experiments in cyclohexane with 2-methoxynaphthalene instead of 2-naphthol were used as reference systems for the spectroscopic and quenching behaviors.

RESULTS

The solubility of 2-naphthol in scCO_2 was determined as a function of fluid density along the 35 °C isotherm. In Figure 1,

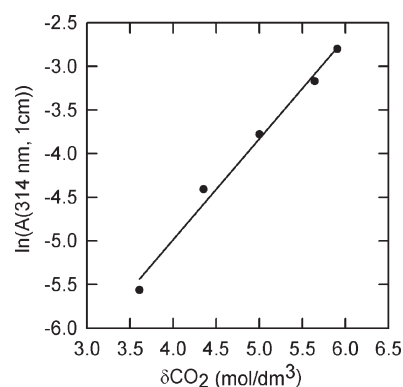


Figure 1. Solubility of 2-naphthol in scCO_2 (proportional to the absorbance A at 314 nm in 1.00 cm optical path) as a function of solvent bulk density at 35 °C.

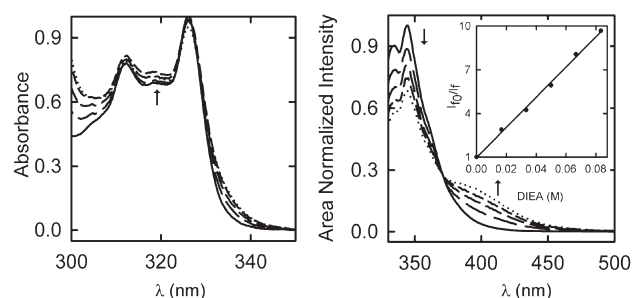


Figure 2. Left: Absorption spectra of 2-naphthol with increasing amounts of DIEA in scCO_2 ($\delta = 1.55 \pm 0.05$ δ_c ; $\delta_c = 10.6$ M) at 35 °C. Concentrations of amine are 0.00; 0.017; 0.033; 0.050; 0.067; and 0.083 M. Right: Area normalized corrected emission spectra ($\lambda_{\text{exc}} = 312$ nm) for the same sample. In both plots, the arrows indicate the direction of the spectral changes with increasing amine concentration. Inset: Stern–Volmer plot for the quenching of emission at 335 nm ($K_{\text{SV}} = 103 \text{ M}^{-1}$).

the linear relation between the natural logarithm of the absorbance at 314 nm and the molar density of the fluid can be observed. Considering that there is an excess of solid in equilibrium with the solution, the absorbance at 314 nm is proportional to the solubility.

All proton transfer experiments were performed at 35 °C, with values of $\ln(A(314 \text{ nm}, 1 \text{ cm}))$ below -4.2 and solvent bulk densities above $16.4 \text{ mol} \cdot \text{dm}^{-3}$; these working conditions are located well apart from the saturation curve shown in Figure 1, ensuring the complete dissolution of the loaded 2-naphthol.

Absorption spectra of 2-naphthol/amines solutions display characteristic changes previously observed for similar systems.¹⁰ In cyclohexane, as a result of proton transfer, the absorption band of the acidic form of 2-naphthol becomes progressively less prominent with the increase of the amine concentration while the band corresponding to 2-naphtholate in the ground state increases (see Figure S1, Supporting Information, SI).¹¹ None of these features is present upon addition of DIEA (up to 0.250 M) to 2-methoxynaphthalene, as previously observed,¹⁰ nor was the fluorescence lifetime of 2-methoxynaphthalene (7.5 ns) affected by the addition of DIEA.

This indicates that the interaction of DIEA with 2-naphthol involves the hydroxyl moiety, and therefore, the absorption increase in the 310–325 and in the 330–350 nm ranges is

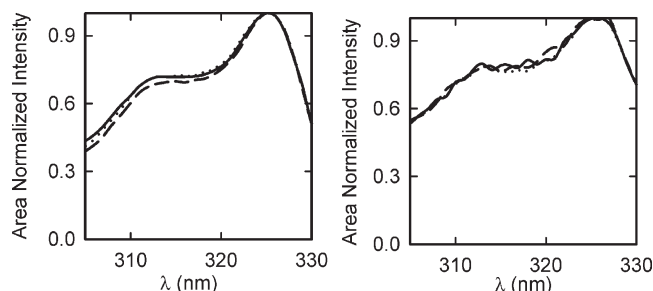


Figure 3. Area normalized corrected excitation spectra of 2-naphthol in scCO_2 at $\delta = 1.85 \pm 0.05 \delta_c$ and different concentrations of DIEA: 0.000 M (full line); 0.020 M (dashed line), and 0.030 M (dotted line) observed at $\lambda_{\text{em}} = 347$ nm (left) and $\lambda_{\text{em}} = 410$ nm (right).

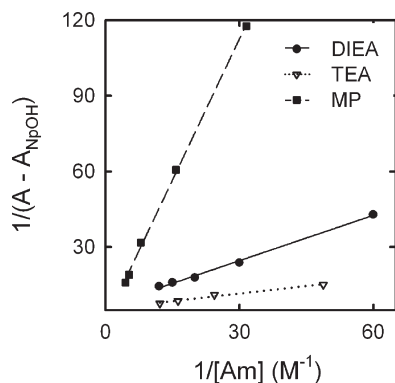


Figure 4. Proton transfer complex formation equilibrium constants of 2-naphthol to amines in scCO_2 sample with $\delta = 1.55 \pm 0.05 \delta_c$ DIEA (circle, full line), TEA (triangle, dotted line), and MP (square, dashed line). The ordinate values for MP have been divided by ten to fit in the graph.

originated in the absorption of increasing amounts of the naphtholate moiety in its ground state. The increase in absorption below 310 nm observed with the increase in the amount of amine is due to the absorption of the amine.

The changes in the emission spectra parallel those in absorption, but they are evident at lower concentrations of amine. Fluorescence emission spectra, $\lambda_{\text{exc}} = 312$ nm, show an isoemissive point, which is a characteristic of the presence of two emitting species (Figure S1, SI). The decrease in emission in the 330–375 nm range and the increase above that wavelength with amine concentration are attributed to the deprotonation of the naphthol. This latter emission is seen as a shoulder with hypsochromic emission in scCO_2 with respect to cyclohexane solution. Figure 2 displays the changes in absorption and in emission upon addition of DIEA to 2-naphthol dissolved in scCO_2 . The behavior is very similar to that in cyclohexane.

Fluorescence excitation spectra, monitored at $\lambda_{\text{em}} = 347$ nm and $\lambda_{\text{em}} = 410$ nm, which are wavelengths suitable to monitor the emission of protonated and deprotonated chromophores, respectively, are shown in Figure 3 for three concentrations of added DIEA. They are, within experimental uncertainty, identical.

Thus, when 2-naphthol is excited, 2-naphthol and 2-naphtholate-type emission are observed but both display the same excitation spectrum, which in turn matches the absorption of the predominant ground state protonated species. Therefore,

Table 1. pK_a Values for the Proton Transfer Reaction from 2-NpOH (ground state) to Amines (eq 1) in Cyclohexane and scCO_2 at Three Different Densities at 35 °C

amine	pK_a	cyclohexane	$\delta\text{CO}_2 / \delta_c^a$		
			1.55 ± 0.05	1.75 ± 0.05	1.85 ± 0.05
DIEA	11.26 ^b	−1.0	−1.0	−0.7	−0.6
TEA	10.75 ^c	−1.5	−1.4		
MP	8.36 ^d	−2.0	0.9		

^a $\delta_c = 10.6$ M is the critical density. pK_a refers to proton transfer to water.

^b Information supplied by the manufacturer (<http://www.arkema-inc.com/literature/pdf/355.pdf>). ^c Lange, N. A. *Handbook of Chemistry*; McGraw-Hill Book Co., Inc.: New York, N. Y., 1961, pp 1203–1204.

^d Hall Jr., H. K. *J. Am. Chem. Soc.* **1957**, *79*, 5441–5444.

we can conclude that the deprotonated form builds up in the excited state, and further emits. The evidence from the spectra in Figure 3 and their independence on the amine concentration indicate that the ground state complex between the amine and 2-naphthol does not emit.

The information in the absorption spectra of 2-naphthol as a function of amine concentration can be used to evaluate the equilibrium constant of reaction 1 for proton transfer in the ground state, between the proton donor (2-naphthol) and the proton acceptor (amine) in cyclohexane and in scCO_2 . We postulate that the interaction between 2-naphthol and the amines does not lead to ion separation neither in cyclohexane, nor in scCO_2 . Instead, the interaction builds up a complex with a proton donor–acceptor character, which preserves the absorption and emission identity of the 2-naphtholate moiety. The equilibrium constant analysis renders a good fit of the data to eq 2 (see Figure 4), while the analysis considering ion separated products does not give a suitable description, thereby supporting the conclusion. Furthermore, the value of the equilibrium constant for TEA-2-naphthol in cyclohexane is practically equal to literature values.¹² To perform the calculations of the equilibrium constant, the equations of section 1 in the SI were used. Table 1 shows the pK_a values for each amine in cyclohexane and at three different densities of scCO_2 at 35 °C. The analysis leading to the results of Table 1 was performed with single wavelength absorption data at 335 nm. The results are identical within experimental uncertainty of ± 0.3 pK units with bilinear regression (see Table S1 in SI) performed using the whole absorption range (300–345 nm).¹³



$$K = \frac{[2 - \text{NpO}^- \cdots \text{AmH}^+]}{[2 - \text{NpOH}] \cdot [\text{Am}]} \quad (2)$$

For DIEA and TEA, the pK_a values in scCO_2 are the same compared to those in cyclohexane, which means that the proton transfer complex formation is as effective in scCO_2 as it is in cyclohexane. For DIEA, the data show a small increase in pK_a (decrease in the proton transfer constant) with the CO_2 density. This shift toward reactants in reaction 1 is due to the poor solvation capability of scCO_2 toward the charge separated species and to the increasing importance of CO_2 – DIEA interactions, reducing the availability of amine for proton transfer from 2-NpOH.

TEA leads to the highest equilibrium constant for the proton transfer interaction in scCO_2 , while surprisingly in cyclohexane,

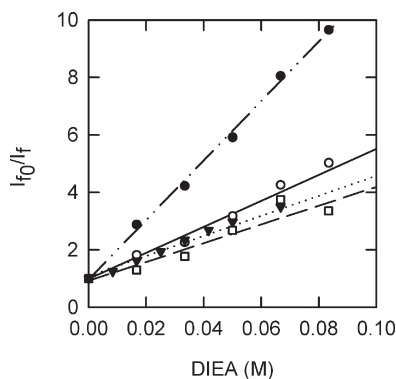


Figure 5. Stern–Volmer plots for the fluorescence quenching of 2-naphthol emission (recorded at $\lambda_{\text{em}} = 335$ nm) by DIEA in cyclohexane (triangle, dotted line) and for different molar densities of scCO_2 : $1.55 \pm 0.05 \delta_c$ (full circle, dashed-dotted line), $1.75 \pm 0.05 \delta_c$ (circle, full line) and $1.85 \pm 0.05 \delta_c$ (square, dashed line).

this parameter is highest for MP. The values of $\text{p}K$ do not parallel the $\text{p}K_a$ values of the amines in water. This observation points to other factors contributing to the stabilization of the proton transfer complex. For example, binding constants of different amines with a naphthol in acetonitrile did not correlate with the basicity measured by the $\text{p}K_a$ in the same solvent.¹⁴ In this line, the ability of the solvent to interact with the different neutral amines (which can affect their basicity) becomes relevant, considering that none of these low-dielectric constant solvents (CO_2 and cyclohexane) can probably change the energy of the ion-pair complex by solvation.

The equilibrium constant for the proton transfer reaction of 2-NpOH/Amine in its lowest singlet excited electronic state, denoted as K^* , can be estimated by the Förster equation,¹⁵

$$\text{p}K^* = \text{p}K - \frac{N_A \cdot h \cdot c}{2.303 \cdot R \cdot T} [\bar{\nu}_{2\text{-NpOH}} - \bar{\nu}_{2\text{-NpO}^-}] \quad (3)$$

where $\bar{\nu}_{2\text{-NpOH}} = 2.86 \times 10^4 \text{ cm}^{-1}$ and $\bar{\nu}_{2\text{-NpO}^-} = 2.50 \times 10^4 \text{ cm}^{-1}$ are the 0–0 transition frequencies for 2-NpOH and for the proton transferred complex, respectively. The difference in $\text{p}K$ values between the ground and excited states, $\Delta\text{p}K = \text{p}K^* - \text{p}K$, is -7.5 considering that the transition frequencies do not change much with pressure, amine nature, or amine concentration. This high increase in the value of the equilibrium constant upon excitation of 2-naphthol parallels the increase in $\text{p}K_a^*$ of this compound in water and is certainly a consequence of the known increased acidity of the first excited singlet state of 2-naphthol compared to the ground state. This evidence indicates that the change in acidity of 2-naphthol upon excitation in scCO_2 is as large as in water and that the absence of separated ions is a consequence of the poor ability of scCO_2 to solvate charged species.

Linear Stern–Volmer relations were observed in scCO_2 at all pressures as well as in cyclohexane (Figure 5) for the quenching of the acid form emission by amines. For the calculation of the emission ratios that are appropriate to plot in the Stern Volmer relation, the measured fluorescence intensities were corrected by the simultaneous absorption of 2-naphthol and the ground state complex, as described in section 2 of the SI, by using the equilibrium constants previously calculated. The Stern–Volmer constants, K_{SV} , are listed in Table 2.

For the system 2-naphthol/TEA in scCO_2 , the absorption of 2-naphthol and naphtholate anion in the complex are overlapped

Table 2. Stern–Volmer (K_{SV}), Bimolecular Quenching Rate Constants (k_q) for Deactivation of the Fluorescence of 2-Naphthol by DIEA in scCO_2 at 35 °C and in Cyclohexane at Room Temperature, and Diffusion Limited Constants (k_d) in the Stokes–Einstein Model^a

solvent	K_{SV} (M^{-1})	k_q^{DIEA} ($\text{M}^{-1}\text{s}^{-1}$)	k_d^{SE} ($\text{M}^{-1}\text{s}^{-1}$)	k_d^{SE}/k_q
$\delta\text{CO}_2 = 1.55 \pm 0.05 \delta_c$	103	7.0×10^9	1.0×10^{11}	16
$\delta\text{CO}_2 = 1.75 \pm 0.05 \delta_c$	45	3.0×10^9	9.0×10^{10}	30
$\delta\text{CO}_2 = 1.85 \pm 0.05 \delta_c$	32	2.0×10^9	8.0×10^{10}	40
Cyclohexane	36	5.0×10^9	7.0×10^9	1.4

^aThe last column displays the ratio between the prediction of this model and the corresponding experimental value of k_q .

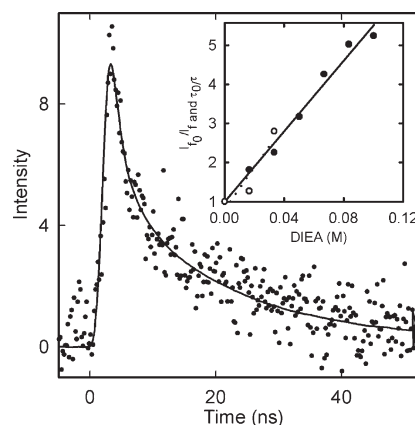


Figure 6. Fluorescence emission decay ($\lambda_{\text{em}} = 345$ nm) of 2-naphthol in scCO_2 $\delta = 1.75 \pm 0.05 \delta_c$. Inset: Total (I_0/I emission intensity, full circles) and dynamic (τ_0/τ , fluorescence lifetime ratio, empty circles) components of the fluorescence quenching of 2-naphthol upon addition of DIEA.

with the absorption of TEA (see Figure S2, SI). Therefore, it is not possible to correct the fluorescence emission spectra for the fraction of light absorbed by 2-NpOH in a trustful manner, and thus the quenching constant can not be obtained.

For 2-naphthol/MP in scCO_2 , increasing morpholine concentration did not lead to anion emission (see Figure S3, SI); only quenching of 2-NpOH emission is observed without spectral changes.

Further insight about the dynamics of the excited state of 2-NpOH in the presence of DIEA and of MP in scCO_2 is provided by fluorescence lifetime measurements. The fluorescence decay lifetime for 2-NpOH in scCO_2 was found to be $\tau_0 = 14.0$ ns (Figure 6), higher than reported lifetimes in cyclohexane of 3.9 ns^{10a} or 8.1 ns¹² or than our measured value in cyclohexane of 7.6 ns. At 410 nm, traces could not be adequately fitted, due to the low fluorescence intensity.

In the case of DIEA, as the inset in Figure 6 shows, the quenching is entirely dynamic. However, the decay lifetime of 2-naphthol does not vary when MP is added in scCO_2 . This fact points to a static quenching of the acidic form by MP. In this case, the value of $K_{\text{SV}} = 1.7 \text{ M}^{-1}$ for this system in scCO_2 $\delta = 1.55 \pm 0.05 \delta_c$ at 35 °C is interpreted as the equilibrium constant for the formation of the non-emissive complex in the ground state. This is in good agreement with the equilibrium constant value of 0.1 M^{-1} measured for this system by absorption spectroscopy.

The fact that no emission from the deprotonated form is seen in this system can be explained assuming a fast in-cage backward proton transfer yielding the ground state species. In cyclohexane, all three amines quench the emission of 2-naphthol in a dynamic way with rate constants near the diffusion limited value (see Table S2 in SI).

DISCUSSION

Proton transfer takes place in scCO_2 from 2-naphthol to TEA, DIEA, and MP through the formation of a proton donor–acceptor complex. This is not surprising taking into account the poor solvation ability of CO_2 molecules toward charged species. As apparently surprising it might be at first sight, the acidity enhancement of 2-naphthol in the first excited state, compared to the ground state, is almost equal in scCO_2 and in water. This evidence can be well understood considering the Förster eq 3. In fact ΔpK , the difference in pK of the excited and ground states, can be changed only if there is a great difference in solvatochromism between protonated and deprotonated forms, which is actually not the case. A change in ΔpK of one unit would imply a change in free energy of $5.9 \text{ kJ}\cdot\text{mol}^{-1}$ at 35°C . Taking an average emission wavelength of 360 nm ($330 \text{ kJ}\cdot\text{mol}^{-1}$), this would mean a 2% change, or 7 nm shift in emission.

In the system 2-naphthol/DIEA, the quenching is dynamic. We can compare the quenching constant with the diffusion limited rate constant (k_d^{SE}) as predicted by the Stokes–Einstein equation,

$$k_d^{\text{SE}} = \frac{8RT}{3\eta} \quad (4)$$

where, η is the viscosity of the solvent. The comparison (Table 2) indicates that only a fraction of collisions between 2-NpOH and amine molecules are effective in CO_2 .

A K_{SV} value of 49 M^{-1} is informed in the literature for the quenching of 2-naphthol fluorescence by TEA¹² in cyclohexane, very similar to our measurement of 36 M^{-1} for DIEA in the same solvent. The quenching rate constants in scCO_2 decrease with the increase of solvent density. This is an expected result for diffusion controlled processes, but the rate constants in scCO_2 deviate from this dynamic limit more appreciably than in cyclohexane. Evidence in the literature points to a preformed hydrogen bond complex as requirement for proton transfer in 2-NpOH.^{2a,12} In scCO_2 the quenching observed is dynamic. The decrease, not only in the absolute value of the rate constant for quenching but also in its value relative to the Stokes–Einstein limit, can be attributed to the diminishing probability of encounters with the adequate orientation for proton transfer, due to the competitive interaction of acidic and electrophilic CO_2 with the amine: for entropic reasons, the higher the bulk density of CO_2 the larger its local density around both solutes, and this reduces the probability of proton transfer.

There is a further point that supports that the quenching of naphthol by DIEA in scCO_2 is only dynamic: Figure 3 shows that excitation spectra are identical when monitored at 347 or 410 nm, which are wavelengths suitable to monitor the emission of protonated and deprotonated chromophores, and that they correspond to the protonated species. These spectra were taken in the absence of DIEA and at $[\text{DIEA}] = 0.020$ and 0.030 M . From the results of Figure 3, it can be concluded that the excitation of the complex does not lead to emission, as the complex has a naphtholate like absorption, and no naphtholate

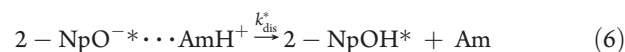
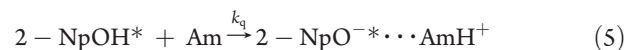
Table 3. Rate Constants for Bimolecular Quenching (k_q) and for Complex Dissociation (k_{dis}^*), for Excited 2-Naphthol-DIEA as a Function of Fluid Density at 35°C

δCO_2 (δ_c)	k_q ($\text{M}^{-1}\cdot\text{s}^{-1}$)	k_{dis}^* (s^{-1})
1.55 ± 0.05	7.0×10^9	22
1.75 ± 0.05	3.0×10^9	19
1.85 ± 0.05	2.0×10^9	16

emission is originated in complex excitation, even at wavelengths where the complex absorbs more than the protonated species. In agreement with this observation, no naphtholate emission is observed in the MP system, as naphtholate emission derives from dynamic quenching, whereas the excitation of the complex can lead to fast backward proton transfer. An extensive investigation of the dynamics and mechanisms of quenching of 2-naphthol by various amines in cyclohexane¹² led the authors to the conclusion that the amines form a proton transfer complex in the ground state with 2-naphthol, and that there is a static and a dynamic component of the quenching, but in a certain concentration range, the quenching can be treated as dynamic, due to the different concentration intervals in which each mechanism is important. This can well be the case for DIEA in scCO_2 : the value of the equilibrium constant for the formation of the ground state complex (which can be interpreted as the static quenching component) is 8–10 times smaller than the corresponding K_{SV} (Tables 1 and 2).

The difference in standard free energy for an electron-transfer reaction between excited 2-NpOH and deprotonated amine was calculated using the half-wave oxidation potentials of the donor and the acceptor,¹⁶ assuming a reaction distance of 0.66 nm (see below for the calculation of molecular radius) and taking the excitation energy of 2-NpOH from spectroscopic data. For all amines a negative value of ΔG° was found indicating that charge transfer is thermodynamically favorable and it might be involved in the proton transfer mechanism.^{10b}

For the system 2-naphthol/DIEA we can calculate the rate constant for complex dissociation in the excited state (k_{dis}^* , eq 6). For this, we use the value of the equilibrium constants and the corresponding value of the quenching rate constant for the excited state of 2-naphthol by DIEA (k_q , eq 5). We further assume that all quenching events in this process lead to proton transfer complex formation.



The kinetic rate constants involving the proton exchange between excited 2-NpOH and DIEA are presented in Table 3 for the different CO_2 densities. The extremely stable complex formation in the excited state results in a long lifetime for this species (ms range, see Table 3), meaning that it does not dissociate during the excited state lifetime.

The quantum yield for the quenching of 2-naphthol by amine (ϕ_Q) is given by the following:

$$\phi_Q = \left(1 - \frac{\tau_f}{\tau_{f_0}}\right) \quad (7)$$

where τ_f and τ_{f_0} are the excited state lifetimes of 2-naphthol in the presence and in the absence of DIEA, respectively. Assuming that

all deactivation processes lead to proton transfer complex formation, then ϕ_Q equals ϕ_{H^+} , the quantum yield for the production of the proton transfer complex. For 0.020 M DIEA in $scCO_2$, $\delta = 1.75 \pm 0.05 \delta_c$, $\tau_f = 11$ ns and $\phi_{H^+} = 0.2$ is obtained, whereas at 0.030 M DIEA, with $\tau_f = 5$ ns, $\phi_{H^+} = 0.6$ is attained.

The critical pressure of CO_2 is 73.77 bar. Our working pressure was always higher than 100 bar. At lower pressures, the concentration of 2-naphthol, and particularly of the amine, cannot reach adequate values for efficient proton transfer to occur in a one phase system.

CONCLUSIONS

We demonstrated the build up of a proton donor–acceptor complex between 2-naphthol and aliphatic amines in $scCO_2$. At moderate temperature, pressure, and amine concentration, a quantum yield as high as 0.6 for 2-naphthol excited state quenching by DIEA can be obtained in a one phase system. This result has implications for carrying out acid–base catalyzed reactions in $scCO_2$. Furthermore, we found that in this solvent, the acidity increase of 2-naphthol upon excitation to the first excited singlet state is as high as in water.

ASSOCIATED CONTENT

S Supporting Information. Equations for the calculation of the equilibrium constant for DIEA, TEA, and MP with 2-NpOH in the ground state, speciation and correction of Stern–Volmer plots for absorption by two species, equilibrium constants, UV–vis and fluorescence emission spectra for the systems: 2-naphthol–DIEA in cyclohexane, 2-naphthol–TEA in $scCO_2$ ($\delta = 1.5 \delta_c$) and 2-naphthol–MP in $scCO_2$ ($\delta = 1.5 \delta_c$), and results of dynamic quenching in cyclohexane are provided. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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