

Effect of Water during the Quantitation of Formate in Photocatalytic Studies on CO₂ Reduction in Dimethylformamide

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S Supporting Information

ABSTRACT: The effect of the water concentration on the quantitation of formate from dimethylformamide in the presence of electron-donating bases using ion chromatography is reported. This observation has important implications in the area of the photocatalytic reduction of CO₂, where formate levels are often used to calculate catalyst turnover numbers.

In a search for new environmentally friendly energy sources, there is considerable interest in the development of solar-driven photocatalytic systems capable of splitting H₂O into hydrogen and oxygen and also for the reduction of CO₂ into useful fuels.¹ A wide range of both homogeneous and heterogeneous systems have been developed, and their efficiency in the presence of sacrificial agents has been studied as a function of molecular components, sensitizers, and catalysts.² These studies have shown that, based on the conditions and photocatalyst used, a range of products, such as CO, methanol, methane, and formate, can be obtained. While the first three can be determined by gas chromatography, formate is usually measured in aqueous environments using techniques such as conductivity, titrations, and ion chromatography. However, no attention has been paid to the potential affect that sacrificial agents may have on these measurements. Sacrificial agents are present in high concentrations and act as strong bases. Workers in the area typically evaluate the catalyst performance in terms of “turnover number”; defined as the number of product molecules that are formed per catalyst molecule. In these studies, dimethylformamide (DMF) is regularly used as a solvent.¹ The stability of solvents in such systems is crucial. The effect of elevated temperature on DMF stability has been previously reported,³ but because the majority of photochemical reactions are carried out at ambient temperature, this issue is of limited importance. However, sacrificial agents, such as triethylamine (TEA) and triethanolamine (TEOA), are routinely used. Against this background, it is important to consider the effect of a base on DMF in aqueous systems, a reaction reported as early as 1970 by Buncel and Symons, who observed that the addition of 20 mM NaOH to DMF/H₂O mixtures resulted in liberation of dimethylamine and formate depending upon the relative amounts of H₂O present.⁴ Later, Kankaanpera et al. extended this study to dimethylacetamide and selected ureas.⁵ More recently, Øpstad et al. investigated the formation of relatively long-lived radicals

when DMF and dimethyl sulfoxide were treated with small amounts of bases (MeOK and EtOK).⁶

In the present Communication, we evaluate the hydrolysis of DMF in solvent systems that are typically used in reactions involving the photochemical reduction of CO₂ and/or conditions used for quantitation of the amounts of formate formed. Both TEOA and TEA are typically used as electron donors, and 5:1 (v/v) DMF/amine mixtures were prepared as model solvent systems (in the absence of catalyst, typically present at 10⁻⁴ M). Ion-exchange chromatography was previously applied to the determination of anions in selected solvents and so was used herein to quantify formate production in the solvent system (see the experimental details in the Supporting Information, SI).⁷ The results obtained indicate that great care needs to be taken in the determination of the formate levels in DMF/sacrificial agent/H₂O mixtures.

Typically, the ion-chromatographic determination of anions in solvents requires a sample dilution step in the mobile phase or water prior to injection to improve the chromatography, particularly for weakly retained anions, such as formate in this case. Conveniently, in this work, the addition of H₂O as a preinjection dilution step therefore permitted the facile study of DMF hydrolysis in DMF/H₂O mixtures containing organic bases. Before a comprehensive study of DMF hydrolysis was performed, preliminary method validation studies showed the method to be precise (% RSD: 1.33% and <0.01% for the peak area and retention time, respectively; *n* = 8), sensitive (LOD: 1.2 × 10⁻⁷ M formate, S/N = 2) (see Table S1 in the SI) with a linear range of 1.2 × 10⁻⁷ to 2 × 10⁻² M. Selectivity was confirmed by adequately resolving formate from potentially interfering anions, as shown in Figure 1. Intuitively, a dilution of the sample with H₂O would be expected to result in a decreased response for the analyte anion proportional to the dilution factor; however, in this work, the opposite was observed. Another important point is that sample preparation (typically a dilution step) is often performed several hours before injection in instances where many samples are queued for injection in an autosampler. H₂O was added to individual 5:1 DMF/TEOA solvent mixtures prior to injection at levels of 0, 1, 2, 5, 10, 30, 50, 75, 85, and 90% v/v. The resulting samples were injected after fixed periods of time of 0, 2, 5, 8, and 24 h and the levels of formate quantified against a calibration curve. DMF and 5:1 DMF/TEOA were also injected directly, without dilution, to verify the presence of formate, and baseline levels of

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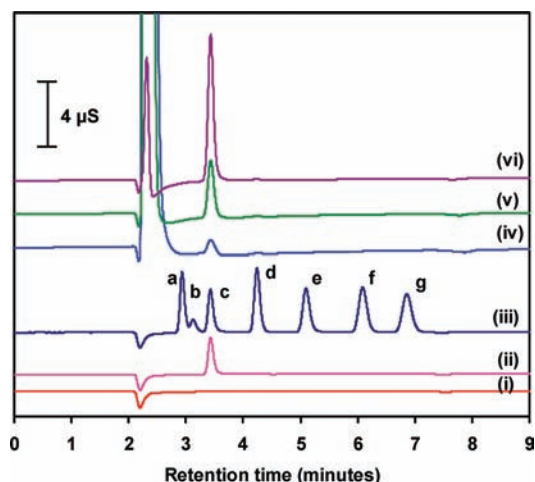


Figure 1. Increase in the formate levels with the water concentration for 5:1 DMF/TEOA solutions stored for 2 h: (i) blank, H₂O; (ii) 10⁻⁴ M formate; (iii) standard 10⁻⁴ M anion mixture; (iv) DMF/TEOA + 30 vol % H₂O; (v) DMF/TEOA + 50 vol % H₂O; (vi) DMF/TEOA + 75 vol % H₂O. Chromatographic conditions as described in the Supporting Information. Peak assignment: (a) fluoride; (b) acetate; (c) formate; (d) chloride; (e) nitrite; (f) nitrate; (g) bromide. The void is the result of a change in the absorbance related to the detection of unretained components of the injection.

up to 10⁻⁴ M formate were found, as shown in Figures S1 and S2 in the SI under these conditions. As illustrated in Figures 1 and 2, formate concentrations increased both with an increase

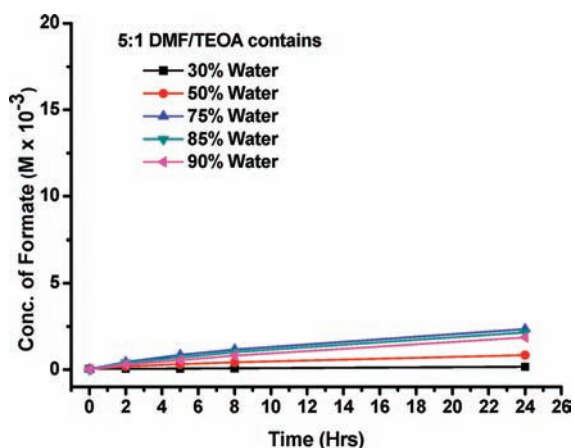


Figure 2. Effect of time and the water concentration (30–90% v/v) on the formate concentration in a 5:1 DMF/TEOA solution.

in the concentration of water, especially above water concentrations of 30 vol %, and with time (see Figure S3 in the SI). Concentrations of water <30 vol % resulted in relatively modest variations in the formate levels (10⁻⁴ M). Figure 2 shows that the formate concentration increased significantly as the water content increased from 30 to 75 vol %; however, for solutions containing 75–90 vol % H₂O, a marginal decrease in the amount of formate formed was observed. For example, after dilution of a DMF/TEOA sample by 50% with H₂O, the formate levels increased from their baseline level of 10⁻⁵ M to 1.88 × 10⁻⁴ M after 2 h and 4.29 × 10⁻⁴ M after 8 h, representing a 10-fold increase in the formate levels. Conversely, the addition of 75 vol % H₂O increased the

formate levels to 4.35 × 10⁻⁴ M after 2 h and 1.16 × 10⁻³ M after 8 h, representing a 40-fold increase.

The formation of formate in DMF/H₂O mixtures is mediated by the presence of the organic base, which was confirmed by the injection of 30:70 DMF/H₂O in the absence of either TEOA or TEA at different times over a 24 h period. The peak area for the baseline levels of formate already present in the aqueous DMF remained constant, as shown in SI (Figure S2), most likely because a source of OH⁻ anions (organic base) was absent. It is highly unlikely that significant amounts of formate are formed on the column because the peak areas obtained are independent of the flow rate used. Further verification of the presence of formate in aqueous DMF mixtures incorporating an organic base was confirmed by ¹³C NMR spectroscopy. The spectrum of a sample of 5:1 DMF/TEOA containing 75 vol % H₂O is shown in Figure 3. Peaks for DMF, TEOA, and both degradation products of DMF hydrolysis (formate and dimethylamine) are clearly visible.

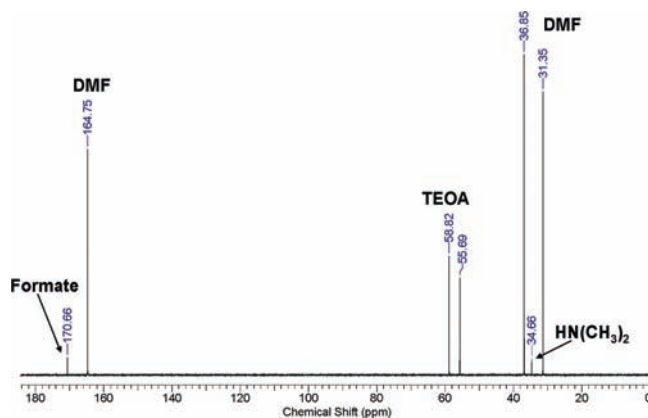


Figure 3. ¹³C NMR (D₂O, 600 MHz) of a 5:1 DMF/TEOA mixture containing 75 vol % H₂O.

TEA has also been used as an electron donor in the photoreduction of CO₂, and therefore it is pertinent to study its role in the hydrolysis of DMF, leading to erroneously high levels of formate being produced, which affects calculations of the catalyst turnover numbers.

The quantitative determination of formate in DMF/TEA mixtures incorporating <30 vol% H₂O was difficult because of broad chromatographic peaks, and so concentrations of water were restricted to 50 vol % and higher (see Figures S4–S6 in the SI). Figure S6 in the SI shows a 30-min-old 5:1 DMF/TEA mixture including 60 vol % H₂O, spiked with formate. An increase in the peak area after spiking permitted the subsequent unequivocal quantitation of formate from external calibration curves. It is fortuitous that both TEOA and TEA have markedly different *K_b* values of 5.78 × 10⁻⁷ and 5.18 × 10⁻⁴, respectively. Equimolar concentrations of TEA relative to TEOA should lead to greater OH⁻ production because TEA is the stronger base, resulting in increased DMF hydrolysis as described previously. Figure 4 shows the formate concentration increasing in the order 50 < 60–90 < 70 < 80 vol % H₂O, and also the amount formed increased with time.

As much as 10⁻² M formate was produced from a 5:1 DMF/TEA/H₂O mixture containing 80 vol % H₂O prepared 7 h prior to injection. The relative rate of formate production can be evaluated (see Figures S4–S6 in the SI). For example, 1.88 × 10⁻⁴ M formate was formed in DMF/TEOA containing 50 vol

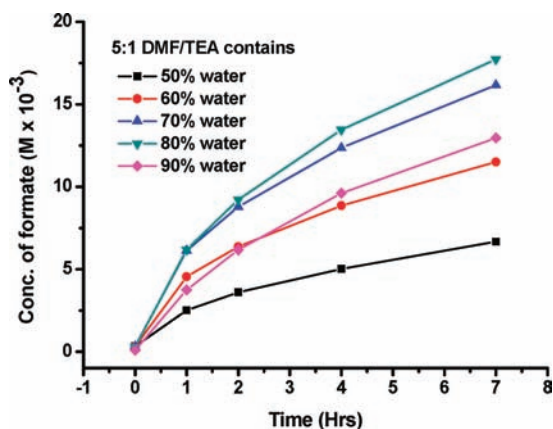


Figure 4. Effect of time and the water concentration (50–90% v/v) on the formate concentration in a 5:1 DMF/TEA solution.

% H₂O after 2 h, whereas when the relatively weak organic base was replaced with the stronger base TEA, formate production increased to 3.61×10^{-3} M.

¹³C NMR was again used to confirm the presence of formate in aqueous DMF/TEA mixtures. Figure S7 in the SI shows characteristic peaks for formate (170.6 ppm) and dimethylamine (35.5 ppm) as well as DMF (164.8, 36.9, and 31.4 ppm) and TEA (46.0 and 9.1 ppm). The ¹³C NMR spectrum in D₂O of a sample of 5:1 DMF/TEA (in the absence of added H₂O) was obtained at various times (0–72 h); see Figure S10 in the SI. Peaks for DMF, TEA, and the degradation products of DMF hydrolysis, both formate and dimethylamine, were observed. Fourier transform infrared (FTIR) spectroscopy also confirmed the presence of formate, as illustrated in Figure S8 in the SI. Overlaid FTIR spectra of DMF/H₂O, formate, and DMF/TEA/H₂O (see Figure S8 in the SI) show that there are vibrational bands for C=O at 1581 cm^{-1} and a C–O band at 1351 cm^{-1} , which are indicative of the presence of formate in the DMF/TEA/H₂O mixture.

This study shows that caution should be exercised when determining the catalyst turnover numbers for photocatalytic systems for CO₂ reduction based upon the formate levels when DMF is used as a solvent. The results obtained show that when the water content is high, spontaneous formation of formate is observed. Because in photocatalytic experiments, in general, rather low water concentrations are used, i.e., < 30%, this observation is less critical for photocatalytic processes. However, during analysis of the samples obtained, problems may occur. In the presence of the organic bases TEA and TEOA, formate concentrations in the range of 10^{-2} to 10^{-3} M can be found. At lower water concentrations, that process is much less prevalent. The results also show that the amount of formate increases with time, adding another measure of uncertainty. This indicates that when using DMF as a solvent in photocatalytic studies, care should be taken concerning the amount of water present. The observations are most important for the choice of the analytical procedure used to analyze the photocatalytic mixtures. When aqueous analytical methods such as titrations, ion chromatography, or conductivity are used, the DMF/amine photocatalytic samples obtained after irradiation need to be diluted with water to allow accurate measurement. At that stage, serious problems arise and the formate concentrations measured may be overestimated.

■ ASSOCIATED CONTENT

📄 Supporting Information

Experimental details, analytical performance criteria (Table S1), chromatograms of DMF, 5:1 DMF/TEOA, and an anion mixture (Figure S1), formate determination in DMF in the absence of base (Figure S2), effect of time on formate production in 5:1 DMF/TEOA solutions (Figure S3), effect of the water concentration on the formate levels in 5:1 DMF/TEA solutions (Figure S4), effect of time on formate production in 5:1 DMF/TEA solutions (Figure S5), qualitative identification of formate in 5:1 DMF/TEA via spiking (Figure S6), ¹³C NMR of a 5:1 DMF/TEA mixture containing 80 vol % H₂O (Figure S7), IR spectrum of a 5:1 DMF/TEA mixture containing 80 vol % H₂O (Figure S8), ¹³C NMR of DMF in D₂O (Figure S9), ¹³C NMR (600 MHz) of 5:1 DMF/TEA in D₂O (Figure S10), and mechanism for the hydrolysis of DMF (Figure S11). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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