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Toluene Carbonylation Catalyzed by Mixtures of Water and Trifluoromethanesulfonic Acid

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The effect of water in trifluoromethanesulfonic acid (CF_3SO_3H or triflic acid) on the carbonylation of toluene is reported at room temperature (297 K) and constant CO partial pressure (7.68 MPa = 1100 psig). A method has been developed to measure low concentrations of water in triflic acid by ^1H NMR. The NMR signal increased in value linearly with increasing mole percent of water in the superacid. The first-order rate constant for toluene conversion decreases with increasing water content of the triflic acid when all other experimental variables are held constant. The triflic acid hemihydrate [$(CF_3SO_3H)_2 : H_2O$] is inactive for the carbonylation reaction of toluene. © 1999 Academic Press

INTRODUCTION

The carbonylation of aryl substrates is an important synthesis reaction for aryl aldehydes. Earlier work by Olah *et al.* shows that the carbonylation of aryl substrates proceeds smoothly in strong acids at room temperature (1a; 1c). One reaction of particular interest is the carbonylation of toluene by the action of trifluoromethanesulfonic acid, also known as triflic acid (CF_3SO_3H). This strong acid catalyzes the production of *p*-tolualdehyde in high yields (>95% isomer selectivity) at high conversions of toluene (∼65%) when the acid/substrate ratio is greater than 2 (2). After the reaction, the product mixture must be treated with ice/water to release the products from the acid catalyst (1, 2). The anhydrous triflic acid can be recovered from aqueous solutions by distilling in a Vigreux column under vacuum (15 Torr and 85 C) (3a) or by an alternative method patented by Halder-Topsoe. By this technology, Hommeltoft reports a process for drying triflic acid using a base such as a trialkyl amine (3b). The active agent for the dehydration of the acid is either the trialkyl amine or its salt with triflic acid. Recycling of the acid catalyst may permit the practical use of carbonylation chemistry. It is surprising, however, that little information appears in the literature to describe the effect of small amounts of water on the carbonylation chemistry since it is known that superacids are hygroscopic. Indeed, Olah and co-workers found that the addition of only small amounts of water to triflic acid (<10 mol% or 1.3 wt%) changed the acidity and product selectivity for the isobutane–isobutylene alkylation (4). Thus, one purpose of this study was to document the effects on toluene carbonylation of adding water to triflic acid.

Measuring the water content in strong acids is a daunting task since triflic acid is hygroscopic and the density of the acid is much higher than that of water; therefore accurate measurements of a small amount of water in the acid could be difficult to obtain using traditional methods. For example, the conventional titration method with a base requires a large amount of sample for a reliable measurement when the water content is very low (∼0.1 wt%), and the sample is destroyed by the analysis. A direct approach such as GC/MS may not be possible since wet triflic acid will readily corrode stainless steel and will react with most stationary phases. Therefore, an additional purpose of this study was to develop an analytical technique to measure accurately the water content of the acid well below the 1 wt% level. It is desired that this technique be nondestructive and require only very small amounts of the sample.

Nuclear magnetic resonance of protons is a well-established technique for determining quantitatively the number of protons in a specific environment. The NMR technique is a nondestructive method for which the sample need not come in contact with the metal parts of the spectrometer; thus, corrosion of the instrument by the "wet" acid is avoided. In the present report, we will show that the sensitivity of the NMR technique permits an accurate quantitation of water in wet triflic acid with only a small amount of sample.

EXPERIMENTAL PROCEDURES

Chemicals

Trifluoromethanesulfonic acid was obtained from Alfa Aesar with a water content claimed to be less than 1 mol%.

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We selected a portion of this acid to be purified by distillation under a partial vacuum (14–14.5 Torr; 1.94 kPa) for which the distillate was condensed at 63.5°C (336.6 K). The distilled acid was a colorless, clear liquid and this material was used in preparing the water/acid standards (*vide infra*). Deionized water was used in preparing the standards.

Reagent-grade toluene, obtained from Aldrich, was used after drying over 3-Å molecular sieves. High-purity carbon monoxide, obtained from Matheson Chemicals, was used without further purification. Standards of *o*-, *m*-, and *p*-tolualdehyde were obtained from Aldrich for calibrating the GC/MS.

Apparatus and Standards

NMR calibration. We used a Bruker DRX 500, 500-MHz instrument housed in the Georgia Tech NMR Center. An internal standard was prepared by placing deionized water in a sealed capillary tube. The capillary tubes were obtained from Kimax (Catalog No. 34507) and had dimensions of 0.8–1.1 mm by 90 mm. A number of these capillary tubes containing the water were examined in separate experiments to determine the response of the instrument for the ^{1}H NMR. Ten of these samples that showed relative, integrated intensities between 0.9990 and 1.0004 for the proton resonance were selected. These results indicate that each internal standard presented the same amount of water to the spectrometer. One internal standard was put in each NMR tube containing the water/triflic acid mixture (Fig. 1). The NMR tubes were obtained from Wilmad (5 mm × 177.8 mm) and were sealed with a Teflon cap. The NMR signal of each triflic acid sample was divided by the signal of the internal water standard. Acid/water standards were prepared for 10 mixtures showing water concentrations between 0.1 and 5 wt% (0.8–30.5 mol%). Five of these mixtures were prepared with water concentrations less than 1 wt% (7.7 mol%). Two samples of triflic acid were prepared by distillation of the triflic acid obtained from the Alfa Aesar (*vide supra*).

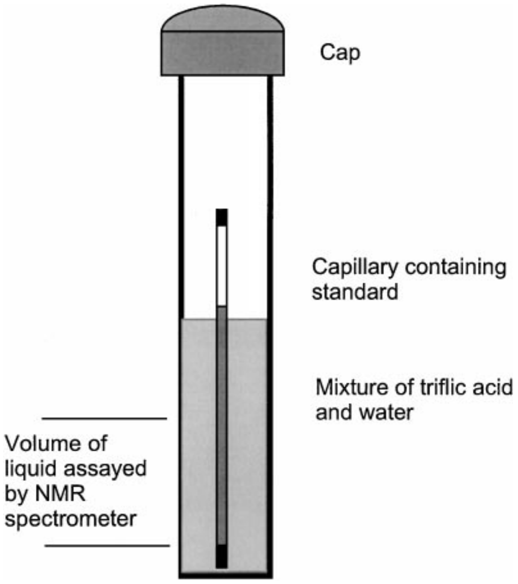

FIG. 1. Schematic diagram of NMR tube with capillary containing standard.

Reactions. The reactions were completed in a stirred autoclave, 50 cm^3, obtained from Autoclave Engineers (Erie, PA). The autoclave was rated to 7000 psig (48.43 MPa) at 400°C (673 K) and it was fabricated from Hastelloy-C to resist the corrosive effects of the water/acid mixtures. The organic products were analyzed in a HP-5890 Series II Plus GC coupled to a HP-5972 mass spectrometer. High-purity helium (99.995%, Air Products and Chemicals) was the carrier gas and the partitioning column was a cross-linked polyethylene glycol column obtained from Hewlett Packard (Part No. 19019 N-233, 30 m long, 0.25 mm i.d., 0.5-mm film thickness).

The reaction conditions for all of the studies were as follows: CO pressure 7.68 MPa; acid/toluene ratio 2 mol/1mol; temperature 297 K; duration of reaction 30 min. At the completion of the reaction, the CO pressure was reduced to 1 atm, the vessel was purged with He, and then ice was added to the reaction mixture to dilute the acid. The organic and aqueous layers were separated and the organic layer was neutralized with sodium bicarbonate until no more CO_2 was observed. The liquid was separated from the solid by filtration and this liquid was diluted in diethyl ether.

To examine the effects of water upon reactivity, we mixed 0.15 mol of freshly distilled triflic acid with known amounts of water varying between 0 and 0.15 mol to produce the desired ratio of acid/water. A small amount of each mixture was examined by ^{1}H NMR to determine the water content. Each mixture was added to 0.077 mol of toluene in the autoclave, the contents were stirred for several minutes, and the reactor was closed and purged with He. Then, CO was added to the desired pressure. To examine the effect of acid/substrate ratio in anhydrous conditions, we added to 0.077 mol of substrate varying amounts of triflic acid (0.038 to 0.15 mol). The reaction conditions for these tests were the same as those for the mixtures of acid and water.

RESULTS AND DISCUSSION

NMR Determination of Water Content in Wet Triflic Acid

Figure 2 shows ^{1}H NMR spectra of the distilled CF_3SO_3H (Fig. 2A), a CF_3SO_3H/H_2O mixture with 7.60 mol% water (Fig. 2B), and the hemihydrate of the acid $[(CF_3SO_3H)_2 : H_2O]$ (Fig. 2C). The signal at 4.670 ppm in each spectrum is the internal water standard while the signal at >10 ppm is the proton resonance from the mixture CF_3SO_3H/H_2O.

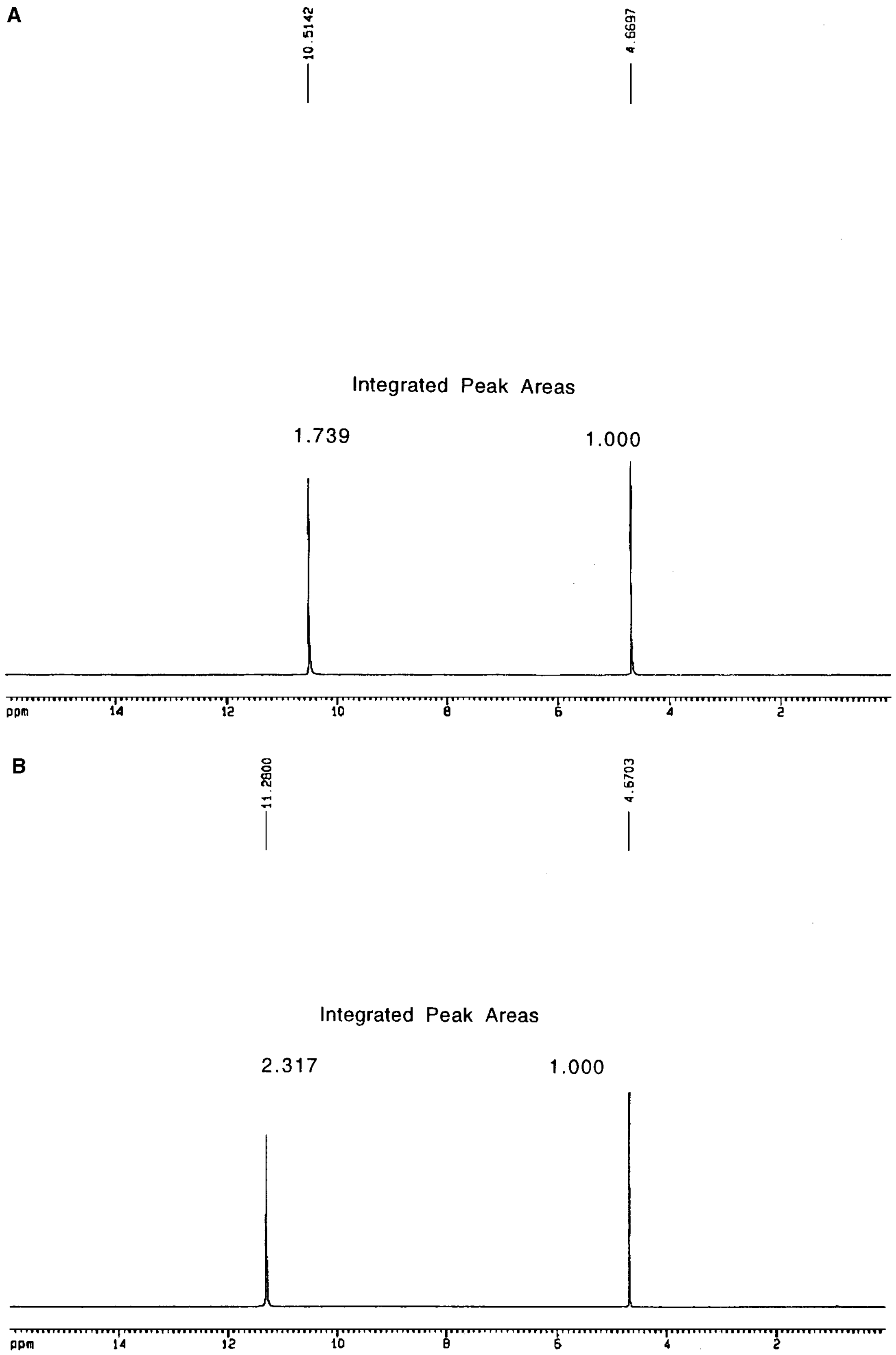

FIG. 2. (A) ^{1}H NMR of distilled triflic acid and standard. Peak at 4.669 ppm is the water standard; peak at 10.5142 ppm is the triflic acid. Numbers above the peaks are the integrated peak areas. (B) ^{1}H NMR of triflic acid/water (7.6 mol%) and standard. Peak at 4.670 ppm is the water standard; peak at 11.28 ppm is the triflic acid/water mix. Numbers above the peaks are the integrated peak areas. (C) ^{1}H NMR of triflic acid hemihydrate and standard. Peak at 4.670 ppm is the water standard; peak at 11.57 ppm is the triflic acid/water mix. Numbers below the peaks are the integrated peak areas. (D) ^{1}H NMR of triflic acid in deuterated chloroform. Peak at 10.5246 ppm is the distilled triflic acid.

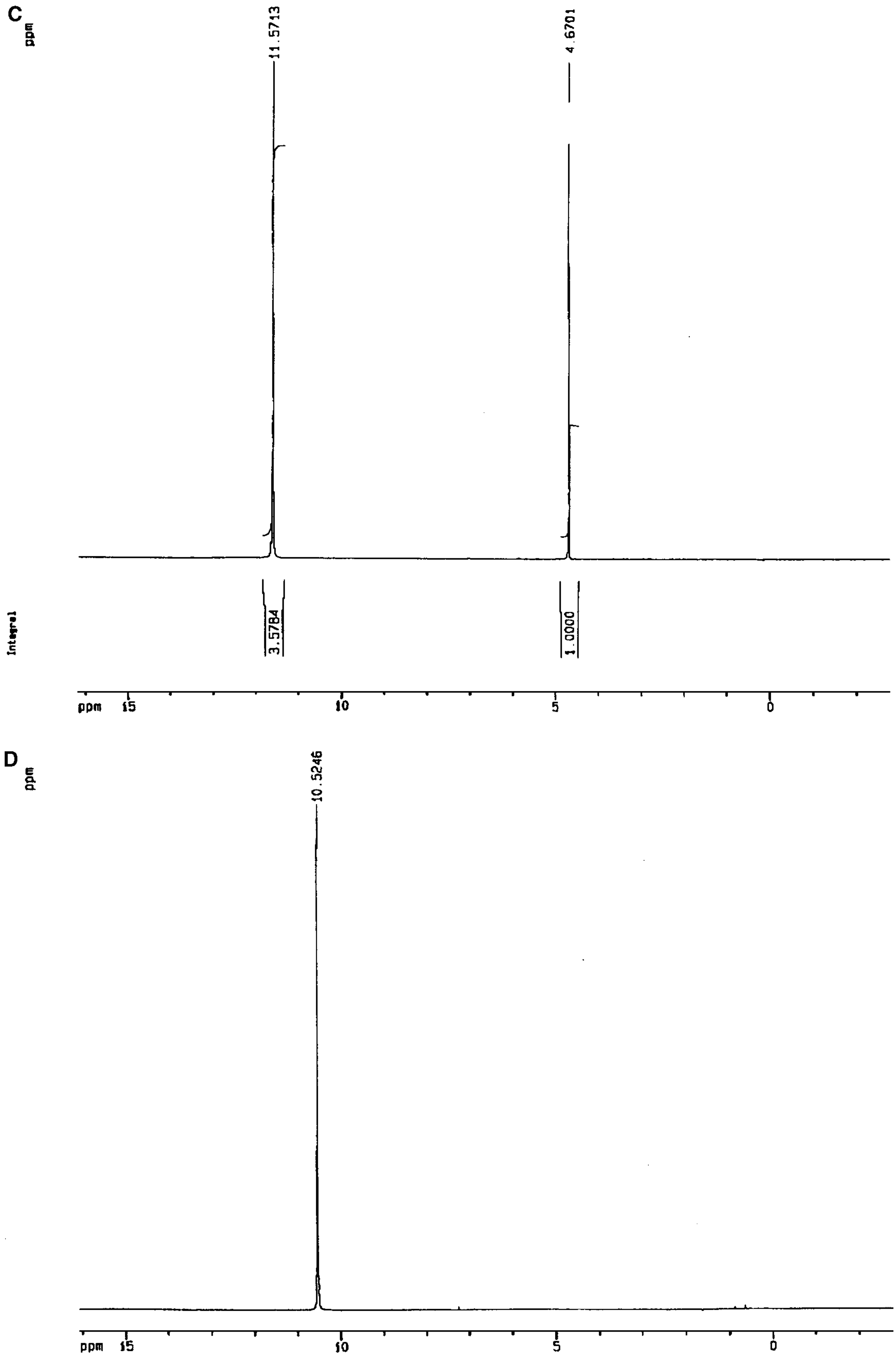

FIG. 2—*Continued*

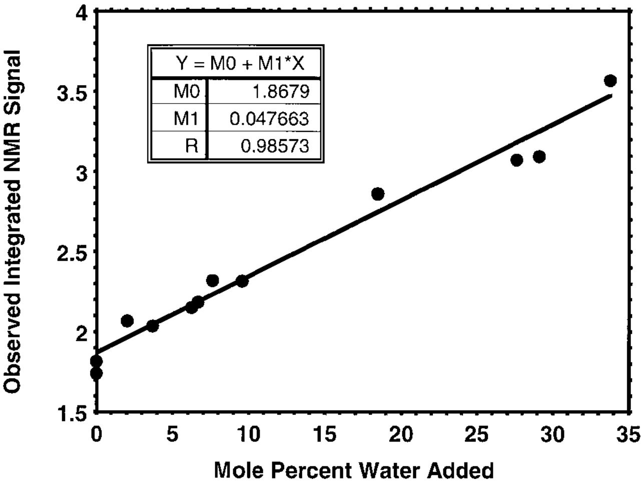

FIG. 3. ^{1}H-NMR signal as a function of mole fraction water.

These assignments are confirmed with separate measurements of the pure acid (10.53 ppm, Fig. 2D) diluted in deuterated chloroform (1% sample in chloroform) to calibrate the chemical shift. A total of 12 samples were measured in this manner and we recorded for each the ratio of the integrated NMR signals for the peaks at >10 ppm to that for the internal standard at 4.67 ppm.

When the integrated intensities of the samples are divided by the signals of the internal standard in each capillary tube, we found that this ratio of integrated NMR signals increased linearly as a function of mole percent of water for the 12 samples in the range of 0–33 mol% water (Fig. 3). This correlation may be inverted to give the desired target variable (mole percent of water) as a function of the measured variable (ratio of NMR integrated peak areas : unknown to internal standard).

$$\text{mol\% } H_2O = 21.0\ (\text{NMR ratio}) - 39.2 \qquad [1]$$

As an example of the application of this technique, we examined the sample as received from Alfa Aesar and found that it contained 0.39 mol% water (0.05 wt%). This determination agrees well with the water content claimed by the vendor (<1 mol%). Thus, the present technique provides a reliable estimate of the water concentration in aqueous mixtures of triflic acid when the water content is ≤33 mol%.

Several comments are appropriate to the use of these equations. First, the ratio of integrated NMR signals of CF_3SO_3H/H_2O depends on the size (diameter) of both the NMR tube and the capillary tube since the relative amount of the sample to the “internal” water standard varies with the size of the tubes. Moreover, both the sample tube and the capillary containing the internal standard must be longer than the coil length of the NMR instrument. Finally, the capillary tube should be placed in the NMR tube so that the capillary is completely in the coil area. Thus, it would be unwise to use these correlations as a means to interpret NMR data from other instruments without calibrating these instruments using the techniques we described above. Equation [1] was correlated on the range of the ratio of NMR signals between 1.80 and 3.40 and thus should not be extrapolated beyond this range. The present method seems not to be applicable to samples of the CF_3SO_3H/H_2O system with water content >33.3 mol%.

The phase diagram for triflic acid and water shows that triflic acid hydrates ($CF_3SO_3H nH_2O$, $n = 0.5$, 1, 2, 4, and 5) have been identified (5, 6, 7). One of these hydrates is the hemihydrate, which shows a water content of 33.3 mol%. The phase diagram does not ensure that these hydrates exist as discrete molecules under the conditions of the analysis or the reaction. However, we can imagine that as water is added to triflic acid, hydronium ions are created in a one-to-one ratio to the moles of water added. The integrated NMR signal will double when the number of hydrogens is doubled. This result is observed when one considers the absolute values of the NMR signal for the anhydrous acid (signal ∼1.70; 1 equivalent of protons: CF_3SO_3H) and for the mixture containing 33.3 mol% water {signal ∼3.50, two equivalents of protons: $1/2[(CF_3SO_3H)_2 : H_2O]$}. Thus, the ratio of the ^{1}H NMR peaks should increase in a linear fashion as shown in Fig. 3.

Toluene Carbonylation Studies

The conversion of toluene after 30 min of reaction at room temperature decreases as the mol percent of water in the original acid increases (Fig. 4). The conversion for the anhydrous acid was 20.4% under standard conditions and the yield to *p*-tolualdyde was 18.5% in this base case. When just 1.5 mol% water was added to the acid, the conversion of toluene decreased to 14% and the conversion was zero for a water concentration of 33 mol% (i.e., the hemihydrate is not active). The response of the data suggested a nonlinear behavior in the conversion with water content of the acid; the fastest decrease in the conversion appeared with the addition of the first 2 mol% water.

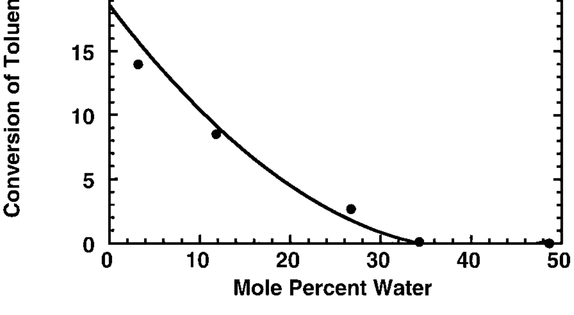

FIG. 4. Conversion of toluene versus mole percent water.

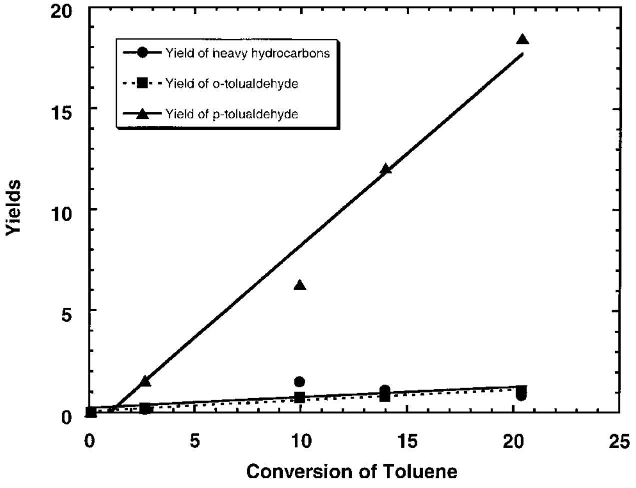

FIG. 5. Yields versus toluene conversion.

The yields of *o*- and *p*-tolualdehyde and heavy hydrocarbons (i.e., di- and tritolymethane) also change with water content of the acid. The *o*- and *p*-tolualdehyde decreased in a manner similar to the toluene conversion with increasing water content; however, these yields were very small as were the yields of di- and tritolymethane. We plotted the yields versus toluene conversion (Fig. 5) to show the correlation of yields of tolualdehyde with conversion.

To understand better the effect of water upon the chemistry, data of toluene conversion, f, were converted into rate constants, k, using the integrated rate equation for an isothermal batch reactor under first-order kinetics for toluene consumption

$$-\ln(1-f)/t = k, \qquad [2]$$

where k is the observed first-order rate constant. The usefulness of this kinetic rate law is supported by the recent work of Sood (2), who showed that the carbonylation reaction followed first-order kinetics in toluene when the conversion was less than 25%. Nonlinear kinetics in toluene was observed for higher conversion as a result of secondary reactions between the product aldehydes and toluene to form di- and tritolymethane.

This rate constant increased with increasing values of the triflic acid mole fraction: x_{HOTf}. Under anhydrous conditions, this effect may be exploited to achieve nearly total conversion of substrate to *p*-tolualdehyde at room temperature and constant CO partial pressure (7.68 MPa) (8). In order to understand better the effect of water upon the carbonylation chemistry, Fig. 6 shows data for two separate tests in which the mole fraction of triflic acid was changed by (i) varying the amount of the anhydrous acid (squares) or (ii) adding varying amounts of water to constant amounts of the anhydrous acid (circles). Apparently, the response of the rate constants was different for changing the acid/substrate ratio either (i) by the addition of water or (ii) under anhydrous conditions when $x_{\mathrm{HOTf}} < 0.67$. The rate constants appear to describe a single curve when $x_{\mathrm{HOTf}} > 0.67$. For toluene carbonylation, very high acid strength is required to catalyze the desired reaction to the desired *p*-tolualdehyde (1).

This result can be understood in terms of the reaction mechanism given below:

$$\mathrm{CO(gas)} \Leftrightarrow \mathrm{CO(dissolved\ in\ acid/hydrocarbon)}:$$

$$x_{[\mathrm{CO}]} = hP_{\mathrm{CO}} \qquad [3]$$

$$\mathrm{CO(dissolved)} + \mathrm{HOTf} \Leftrightarrow \mathrm{COH^+OTf^-}: x_{[\mathrm{COH^+OTf^-}]}$$

$$= K_2\gamma_{\mathrm{CO}}\gamma_{\mathrm{HOTf}}/\gamma_{\mathrm{COH^+OTf^-}}x_{[\mathrm{CO}]}x_{[\mathrm{HOTf}]} \qquad [4]$$

$$\mathrm{Toluene} + (\mathrm{COH^+OTf^-}) \rightarrow \mathrm{tolualdehyde{-}H^+} + \mathrm{OTf^-}:$$

$$R = k_3 a_{\mathrm{TOL}} a_{\mathrm{COH^+OTf^-}} \qquad [5]$$

$$\mathrm{Tolualdehyde{-}H^+OTf^-} + \mathrm{H_2O}$$

$$\rightarrow \mathrm{tolualdehyde} + \mathrm{H_3O^+} + \mathrm{OTf^-}. \qquad [6]$$

Carbon monoxide must be dissolved into the reaction mixture for the reaction to occur. We model this step using Henry's law for which the mole fraction of dissolved CO is linearly related to the partial pressure of CO gas by the constant, h, in Eq. [3]. The constant, h, is a function of temperature and the acidity of the liquid (9). The protonation of CO by a strong acid to form the formyl ion [$\mathrm{HCO^+}$] is necessary for the reaction to proceed (1, 4). We show this step to be a reversible reaction characterized by the equilibrium constant K_2 in Eq. [4]. Here we use the solution model to express activities in terms of mole fractions and activity coefficients. We assumed that γ_{CO}, γ_{HOTf}, and γ_{COHOTf} were functions of temperature and acidity of the reaction

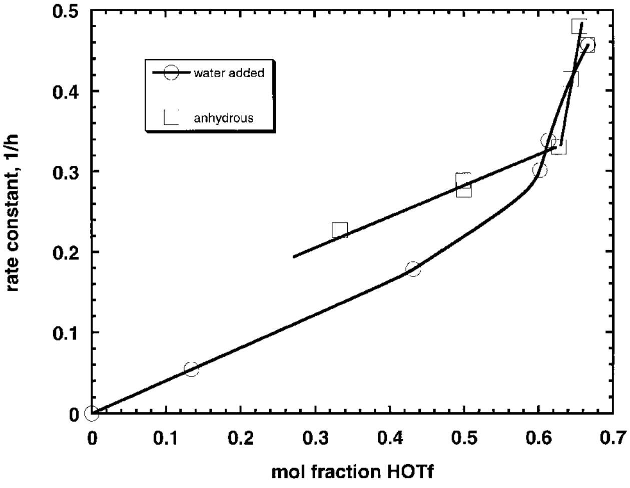

FIG. 6. Observed rate constant as a function of mole fraction of triflic acid. (a) Squares are results under anhydrous conditions. (b) Circles are results for mixtures of acid/water. Reaction conditions: $T = 297$ K; $p = 7.68$ MPa; 0.077 mol of toluene; variable amounts of water added to reaction mixture, initially.

mixture; whereas K_2 was only a function of temperature. The rate-determining step was assumed to be the electrophilic substitution reaction described by Eq. [5] and characterized by rate constant k_3. For this rate equation, we use the activities of toluene and COH^+OTf^- to express the effect of concentration upon rate. Water added to the reaction mixture released the tolualdehyde by Eq. [6], which has been practiced in the literature (1) and was recently confirmed by Sood (2).

Considering the fact that the reaction rate of toluene carbonylation increases with increasing values of the acid/substrate ratio, which is well documented in the literature (1, 2), we use an empirical relationship for the reaction rate:

$$R = k_3 x_{\text{toluene}} g(\text{mol HOTf/mol toluene}). \qquad [7]$$

This rate expression accounts for the reaction order (first order in the toluene mole fraction, $x_{[\text{toluene}]}$,) and varies according to some function, g, of the ratio moles of HOTf/moles of toluene. Here $x_{[\text{toluene}]}$ is defined as [mole toluene/(mole toluene + mole acid + mole of water + mole of hemihydrate)].

The mechanism given in Eqs. [3]–[5] may be used to develop a rate equation assuming that Eq. [5] is the rate-determining step. The mole fraction of COH^+OTf^- may be eliminated in Eq. [5] considering the equilbria (Eqs. [3] and [4]) to give

$$\begin{aligned} R &= k_3 \gamma_{\text{toluene}} h P_{\text{CO}} K_2 (\gamma_{\text{CO}} \gamma_{\text{HOTf}} / \gamma_{\text{COH}^+\text{OTf}^-}) x_{[\text{HOTf}]} x_{[\text{toluene}]} \\ &= k x_{[\text{toluene}]}, \qquad [8] \end{aligned}$$

where k is the observed first-order rate constant shown in Eq. [2]. Upon comparing Eqs. [7] and [8], we observe that the function g in Eq. [7] is

$$k = k_3 g;\ g = h P_{\text{CO}} K_2 (\gamma_{\text{toluene}} \gamma_{\text{CO}} \gamma_{\text{HOTf}} / \gamma_{\text{COH}^+\text{OTf}^-}) x_{\text{HOTf}}.$$

Thus, we suggest that the product $(h P_{\text{CO}} K_2 \gamma_{\text{toluene}} (\gamma_{\text{CO}} \gamma_{\text{HOTf}} / \gamma_{\text{COH}^+\text{OTf}^-}) x_{[\text{HOTf}]})$ increases with increasing mole fraction HOTf. In the present case we assume that h, γ_{toluene}, γ_{CO}, γ_{HOTf}, and γ_{COHOTf} may be functions of x_{HOTf}.

Equations [7] and [8] will be used to interpret the data of Fig. 6. For one set of tests, we changed the acid/substrate ratio by mixing known amounts of water (0–0.077 mol) into fixed amounts of acid and substrate (0.15 mol acid; 0.077 mol substrate). Here, the water was added in just such amounts so as to make a mixture of triflic acid and its hemihydrate. One result of adding water to the triflic acid was to reduce the effective amount of the acid catalyst by a reaction to form the triflic acid hemihydrate since the hemihydrate was inactive for the toluene carbonylation reaction (Fig. 3). Thus the amount of the effective acid catalyst, $N_{[\text{HOTf}]}$, is

$$N_{[\text{HOTf}]} = N_{[\text{HOTf}]\text{o}} - 2N_{[\text{H2O}]},$$

where $N_{[\text{HOTf}]\text{o}}$ is the number of moles of triflic acid prior to reacting with water and $N_{[\text{H2O}]}$ is the number of moles of water added to the triflic acid. The data were correlated against the mole fraction of triflic acid remaining unreacted with water.

The rate constant data for the acid/water mixtures (circles, Fig. 6) fall below the curve for the effect of acid/substrate ratio under anhydrous conditions (squares, Fig. 6) when $x_{\text{HOTf}} < 0.67$. Thus, we conclude that the effect of adding water is more than just converting triflic acid to inert triflic acid monohydrate. These data for the anhydrous acid (squares, Fig. 6) show that the rate constant is described by two straight lines, with a higher slope for $x_{\text{HOTf}} > 0.67$. This change in slope suggests that the factor $(h P_{\text{CO}} K_2 \gamma_{\text{toluene}} \gamma_{\text{CO}} \gamma_{\text{HOTf}} / \gamma_{\text{COHOTf}})$ increases with increasing triflic acid mole fraction. The partial pressure of CO, P_{CO}, was constant in all of these tests. We expect that the Henry's law constant, h, and the chemical equilibrium constant for Eq. [2], K_2, should not change much as a function of x_{HOTf}, but the activity coefficients for toluene, dissolved CO, protonated CO, and HOTf may change with x_{HOTF}. The data for the acid/water mixtures show that the factor $(h P_{\text{CO}} K_2 \gamma_{\text{toluene}} \gamma_{\text{CO}} \gamma_{\text{HOTf}} / \gamma_{\text{COHOTf}})$ is a different function of x_{HOTF} when x_{HOTf} is less 0.67. This result may be a consequence of the lower acid strength of the mixture when water is added to triflic acid to form the hemihydrate, a much weaker acid. Olah *et al.* showed that the addition of even a small amount of water (ca. 1 mol%) to triflic acid reduced the acid strength by as much as 1 order of magnitude when measured by the Hammett (see Ref. 10) acidity function ($H_o = -14$ to -13). Further addition of water to triflic acid (ca. 15 mol% water) reduced the H_o to -11 (4), which is an order of magnitude lower than that ascribed to 100% H_2SO_4. The observation that the hemihydrate is inactive for the carbonylation reaction suggests that the reaction is promoted only by a superacid. The decrease in acid strength should reduce the Henry's law constant since Booth and El-Fekky (8) showed that CO is much more soluble in triflic acid (155 cm^3/liter acid) than in 95% sulfuric acid (21 cm^3/liter acid) at 300 K and a CO partial pressure of 205 kPa. Our expectation is that the CO solubility will decrease as the strength of the mixed acid (HOTf + acid hemihydrate) decreases. The observed reaction rate, k, should decrease as x_{HOTf} decreases even though the CO partial pressure remains constant. We observed this result.

SUMMARY

The present work suggests a method to measure low concentrations of water in triflic acid. This technique is based on the observation that the intensity of the ^1H NMR signal for wet triflic acid is proportional to the amount of water in the sample. This analytical tool was used to characterize the water content of several acid/water mixtures to catalyze the carbonylation of toluene at room temperature. Data of first-order rate constants showed that the water inhibited the carbonylation reaction (i) directly by converting HOTf to an inert species, such as the inactive acid hemihydrate, and (ii) indirectly, perhaps by lowering the CO solubility in the toluene/acid mixture at fixed temperature and CO partial pressure.

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REFERENCES

1. (a) Olah, G. A., Ohannesian, L., and Arvanaghi, M., *Chem. Rev.* **87**, 671 (1980); (b) Booth, B. L., El-Fekky, T. A., and Noori, G. F. M., *J. Chem. Soc. Perkins I*, 181 (1980); (c) Olah, G. A., Laali, K., and Farooq, O., *J. Org. Chem.* **50**, 1483–1486 (1985).
2. Sood, D. S., Ph.D. Thesis, Georgia Institute of Technology, Atlanta, GA, 1998.
3. (a) Goeppart, A., Louis, B., and Sommer, J., *Catal. Lett.* **56**, 43–48 (1998); (b) Hommeltoft, S. I., European Patent 687658A1 (29.05.95), and U.S. Patent 5,759,357; “Process for the Recovery of a Strong Acid from an Aqueous Solution,” 1998.
4. Olah, G. A., Batamack, P., Deffieux, D., Torok, B., Wang, Q., Molanar, A., and Surya Prakash, G. K., *Appl. Catal. A Gen.* **146**, 107 (1996).
5. DeLaplane, R. G., Lundgren, J. O., and Olovsson, I., *Acta Crystallogr. Sect. B* **31**, 2202 (1975).
6. Spencer, J. B., and Lundgren, J. O., *Acta Crystallogr. Sect. B* **29**, 1923, (1973).
7. DeLaplane, R. G., Lundgren, J. O., and Olovsson, I., *Acta Crystallogr. Sect. B* **31**, 2208 (1975).
8. Booth, B. L., and El-Fekky, T. A., *J. Chem. Soc. Perkins I*, 2441–2446 (1979).
9. Kenvin, J. C., Schiraldi, D. A., Sood, D. S., and White, M. G., “Proceedings, 11th International Symposium on Homogeneous Catalysis, Edinburgh, Scotland, July 1998.”
10. Hammett, L. P., and Paul, M. A., *J. Am. Chem. Soc.* **56**, 830 (1934).