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RESEARCH NOTE

The Formylation of Toluene in Trifluoromethanesulfonic Acid

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The formylation of toluene in trifluoromethanesulfonic acid was studied in a batch reactor to determine the effect on reaction rate of increasing the ratio of trifluoromethanesulfonic acid/substrate at constant temperature. The production rate of *p*-tolualdehyde increased with increasing amounts of acid so that its yield was 99.1% when the acid/substrate was 20 mol/mol (30 min at 298 K). The reaction obeys first-order kinetics in toluene for conversions less than 25%. The rate of formylation increases with increasing CO partial pressures from 500–2000 psig. The reaction rate shows an optimum temperature near 298 K. © 2001 Academic Press

Key Words: **formylation; trifluoromethanesulfonic acid; toluene; carbon monoxide; tolualdehyde.**

INTRODUCTION

Booth and El-Fekky (1) reported that trifluoromethanesulfonic acid (triflic acid, CF_3SO_3H) is an efficient catalyst for the Koch carbonylation reactions. They claim that triflic acid is a more efficient catalyst than 95% sulfuric acid for this reaction as a result of its higher acidity (Hammett acidity function, $H_o = -14.1$ for triflic acid). Moreover, they report that the solubility of CO depends upon the strength of the acid (Table 1). The solubility of CO in the acid/aromatic should influence the reactivity of the carbonylation reaction.

Formylation reactions in triflic acid have been reported for cases when the substrates were alkylbenzenes (2). The high solubility of CO in triflic acid does not ensure high yields of the corresponding aldehydes at low CO pressures of 1–20 atm; however, the tolualdehyde yields do increase with increasing CO pressures (70–125 atm). Formylation of toluene has been reported to yield nearly 100% of the para isomer (2) at the higher CO partial pressures, whereas lower pressures (80 atm) showed about 92% of the para isomer and the remainder was *o*- (5.6%) and *m*-tolualdehyde (2.6%) when the reaction was completed at room temperature in 3.5 h.

Recently we patented a method to prepare aromatic aldehydes using triflic acid as the catalyst (3). This process produced aromatic aldehydes by carbonylation of an arene in the presence of triflic acid at room temperature for reaction times less than 90 min. The preferred embodiments showed that a large excess of triflic acid promoted yields of *p*-tolualdehyde as large as 99.6% for reaction times as short as 30 min at room temperature. In the present communication, we elaborate this technology further to show the effects of reaction temperature, CO partial pressure, and acid/substrate ratio.

EXPERIMENTAL

Chemicals. Anhydrous toluene (Aldrich, 99.8%) and CO (Air Products and Chemicals, CP grade) were used without further purification. Triflic acid (Alfa Aesar, 99%) was freshly distilled in a Pyrex apparatus prior to use (4).

Protocol. A high-pressure autoclave was used for all reactions (Autoclave Engineers). The Hastelloy-C276 reactor vessel was completely dried before each reaction, a fixed amount of triflic acid was introduced to the reactor, and the reactor was sealed. The appropriate amount of toluene was added and the reactor was stirred under a N_2 purge for 2 h. For one set of preliminary reactions, the stirring speed was varied in separate tests between 500 and 2000 rpm. For reactions at temperatures other than room temperature, the reactor was pressurized with He (100 psig) until the desired temperature was attained, and then the reactor was vented and pressurized with the desired pressure of CO. The reaction times were varied in one set of tests to determine the kinetics. At the conclusion of each test, the CO was vented

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TABLE 1

Solubility of CO in Strong Acids (1)

Acid	CO solubility, STP cm^3/l	Remarks
FSO_3H-SbF_5	90	293 K and 160 Torr CO
FSO_3H-SbF_5-SO_3	10	293 K and 160 Torr CO
CF_3SO_3H	155	300 K and 774 Torr
H_2SO_4, 95%	21	300 K and 774 Torr

and the reactor purged with He at 100 psig for 10 min. The contents of the reactor were poured onto 100 cm^3 of ice, the solution was stirred for 30 min, and the two phases were separated. The organic and aqueous phases were neutralized with $NaHCO_3$ and then analyzed by GC–MS as separate samples. The neutralized aqueous phase did not show any hydrocarbons.

Product analysis. Liquid samples were analyzed by a Hewlett-Packard GC–MS (Models 5890 Series II Plus and 5972, respectively). Helium (Air Products and Chemicals, 99.995%) was used as the carrier gas and the mixtures were partitioned on a cross-linked polyethylene glycol column (Hewlett-Packard; 30 m long × 0.25 mm ID using a 0.5-μm film thickness).

RESULTS AND DISCUSSION

Effect of Stirring Speed

Tests were completed to identify the stirring speed necessary to eliminate the effects of mass transport on the observed reaction rates. For this series of tests, the impeller speeds were varied between 500 and 2000 rpm for a constant set of reaction conditions. For all tests, the reaction temperature was 298 K, the reaction time was 30 min, and the acid/substrate ratio was 2 mol/mol. In one series of tests the CO partial pressure was 809 psig and for another series the CO partial pressure was 1100 psig. The conversion of toluene was recorded for each of these tests as an indication of the reactor performance (Table 2). These data suggest that the reaction rate was not affected by impeller speed when it was greater than 600 rpm for pressures greater than 800 psig. For the remainder of the tests reported herein the impeller speed was ≥600 rpm.

TABLE 2

Toluene Conversions (%) as a Function of Impeller Speed[a]

	Impeller speeds, rpm				
CO partial pressure, psig	500	600	1000	1300	2000
809	3.8	6.5	8.0	—	8.0
1100	—	20.4	—	20.3	20.6

[a] Conditions: temperature, 298 K; reaction time, 30 min; acid/substrate ratio, 2 mol/mol.

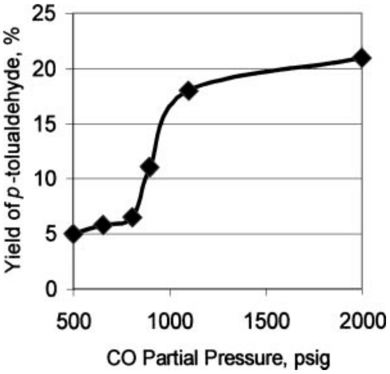


FIG. 1. Effect of CO partial pressure on the yield of *p*-tolualdehyde.

Effect of CO Pressure

The CO partial pressure was changed from 500 to 2000 psig to document the effect of CO partial pressure on the reaction rate (Fig. 1). For all tests, the acid/substrate ratio was 2 mol/mol, the reaction temperature was 298 K, the stirring speed was 600 rpm, and the reaction time was 30 min. The yields of *p*-tolualdehyde increased from 5–6% to 18% when the CO partial pressure increased from 800 to 1100 psig. Further increases in CO partial pressure to 2000 psig caused only small increases in the yield of *p*-tolualdehyde (21%).

Effect of Reaction Time

The kinetics of the reaction were measured at a CO partial pressure of 1100 psig and an acid/substrate ratio of 2 mol/mol at room temperature (Fig. 2). The yields of

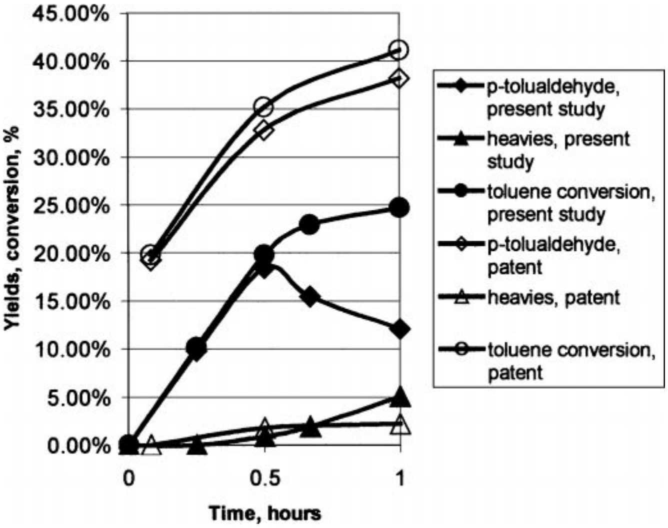


FIG. 2. Yields and toluene conversion as a function of time.

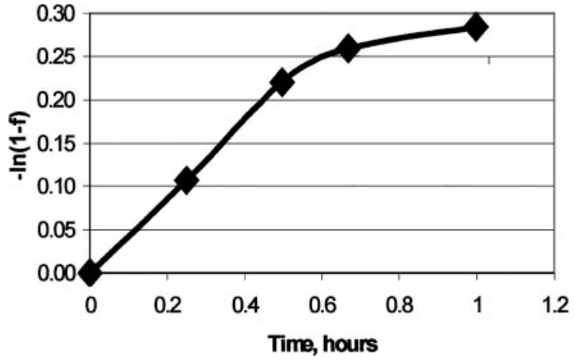


FIG. 3. Reaction kinetics plot at 298 K for the formylation of toluene in triflic acid.

p-tolualdehyde and heavier products (mainly di- and tritolylmethane) are shown in this study as the filled symbols as is the percentage conversion of toluene, whereas the patent data are represented as open symbols. For reaction times shorter than 0.5 h, the selectivity to *p*-tolualdehyde was greater than 90% with *o*-tolualdehyde and heavier products as the only other products that we observed. For longer reaction times, the secondary products, di- and tritolylmethanes, appear in combined yields up to 5%. When the reaction time was 17.5 h (data not shown), the yield of heavier products was 14.6%; whereas, the yield of *o*- + *p*-tolualdehyde was 13.9%. The appearance of these products is not unexpected in that Olah and co-workers (2) observed these products from the reaction of toluene with *p*-tolualdehyde in the presence of triflic acid at room temperature. At 17.5 h, our patent data (3) showed a yield of 52% for the heavy ends and 27.3% for *o*- + *p*-tolualdehyde.

We attempted to fit the toluene conversion data using first-order kinetics, which are irreversible (Fig. 3). These data show that first-order kinetics were obeyed during the first 30 min of reaction, but the data appeared to depart from first-order kinetics when the reaction time was greater than 30 min. The departure from first-order kinetics appeared to coincide with the time when *p*-tolualdehyde was consumed by a secondary reaction to form di- and tritolylmethane (Fig. 2).

Temperature Effects

We studied the effect of reaction temperature in separate tests at 275, 298, and 323 K at a constant acid/substrate ratio of 2 mol/mol and for a reaction time of 30 min at a CO partial pressure of 1100 psig (Table 3). Increasing the temperature from 275 to 323 K resulted in an increase in conversion with an optimum yield of *p*-tolualdehyde at 298 K (18.5%). Apparently, increased reaction temperatures favored the formation of the heavier products. Thus, the best among these three was reaction at room temperature (298 K) since the yield of *p*-tolualdehyde was the highest among these three data sets.

TABLE 3

Effect of Reaction Temperature[a]

Temperature, K	Conversion, %	Yield of *p*-tolualdehyde, %
275	12.0	9.5
298	19.8	18.5
323	25.2	15.2

[a] Conditions: reaction time, 30 min; CO partial pressure, 1100 psig; acid/substrate ratio, 2 mol/mol.

Effect of Acid/Substrate Ratio

Others (2) reported that increasing the acid/substrate ratio showed a beneficial effect on yields. We examined this effect in separate tests for which all other reaction conditions were held constant: temperature = 298 K, reaction time = 30 min, CO partial pressure = 1100 psig. The data for conversion and yield of *p*-tolualdehyde appeared to correlate with the ratio of acid/substrate, mol/mol (Fig. 4). The data from this study and our earlier patent clearly showed that the conversion and yield increased with increasing amounts of acid. Moreover, these data showed that quantitative conversion of the toluene was possible at rather short reaction times, 30 min, and that the reaction was very selective to the *para* isomer (>99%).

The response of this system was similar to that observed by McCaulay and Lin (5) for the isomerization of trimethylbenzenes at 100°C in excess HF (7 mol of HF/mol of substrate) and for which the amount of BF_3 was varied. For tests where the BF_3/substrate ratio was less than unity, the mesitylene content increased linearly with increasing amount of BF_3. For tests where the BF_3/substrate ratio

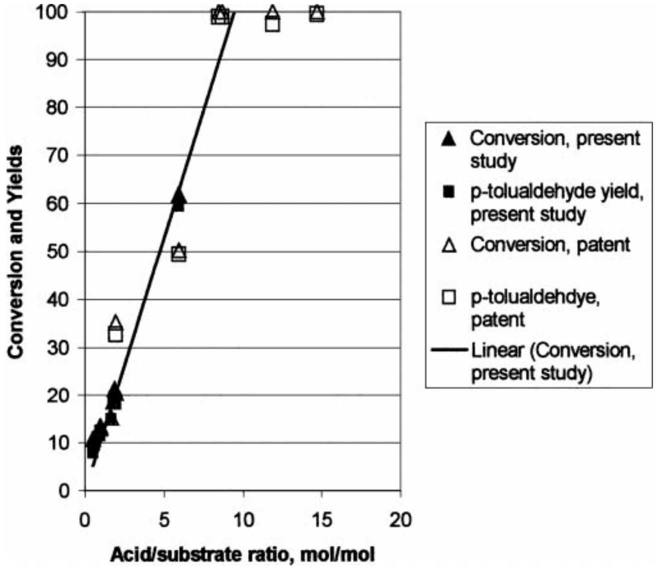


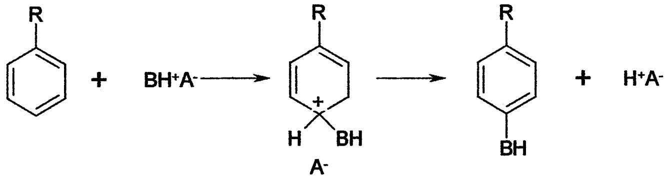
FIG. 4. Effect of acid/substrate ratio.

was greater than unity, the mesitylene content was 100%. Those authors attributed the high yields of mesitylene to the superacidity of a mixture of BF_3 with HF. They attributed the large yield of mesitylene to the very high relative stability of BF_3/HF/mesitylene complexes. Similar results were reported by those authors in the same paper for the isomerization of xylenes and tetramethylbezenes in excess acid/substrate ratio. In those studies, the *meta* isomer was favored at high acid/substrate ratio. Olah reported similar results for the isomerization of di*iso*propylbenzene in large excesses of superacid (either HF or triflic acid) (6). In a manuscript to be published, we show how high acid/substrate ratios, 20–50 mol/mol, favored the isomerization of dimethylbiphenyl to the *meta* isomers (i.e., 3,3′- and 3,4′-dimethylbiphenyl) in preference to the other four isomers. Our data shows that the yield of a single isomer of tolualdehyde also occurs when the acid/substrate ratio is very large, ~10 mol/mol. We suggest that the high yield/selectivity to the *p*-tolualdehyde is also due to the formation of a stable HOTf/*p*-tolualdehyde complex or some intermediate that leads ultimately to *p*-tolualdehyde.

The practical application of this technology requires a viable catalytic process similar to the one we described recently for the synthesis of dimethylbiphenyl from toluene (7). The continuous regeneration of the triflic acid from an aqueous solution was a key element in this process. Future advances to lower the cost of this acid regeneration technology (8) will improve the viability of this method to produce aryl aldehydes with control of the regioselectivity.

DISCUSSION

Elements of this reaction mechanism have been discussed by Olah (2) and others. They agree that the reaction follows an electrophilic substitution mechanism suggested by the following scheme:



The electrophilic agent BH^+A^- is synthesized by the action of a superacid, H^+A^-, on a substrate, B by the following equilibrium:

$$H^+A^- + B \overset{K}{\Leftrightarrow} BH^+A^-. \qquad [1]$$

The value of the equilibrium constant, *K*, is determined by the strength of the acid. For substrates such as CO, a superacid is needed to produce the electrophile. We showed evidence that the carbonylation rate of toluene was lower in mixtures of triflic acid and water than in neat acid (4). These results suggest that the value of the equilibrium constant, *K*, was lower in aqueous mixtures of triflic acid and we speculated that the solubility of CO in toluene was lower in the water/acid mixtures. Indeed, we hypothesized that the reaction scheme for CO and toluene was

$$\mathrm{CO(gas)} \Leftrightarrow \mathrm{CO(dissolved\ in\ acid/hydrocarbon)} \qquad [2]$$

$$\mathrm{CO(dissolved)} + \mathrm{H^+OTf^-} \Leftrightarrow \mathrm{COH^+OTf^-} \qquad [3]$$

$$\mathrm{CH_3C_6H_5} + \mathrm{COH^+OTf^-} \rightarrow \mathrm{CH_3C_6H_4CHO{-}H^+OTf^-} \qquad [4]$$

If this scheme is an accurate model for toluene carbonylation then we expect that the reaction rate should demonstrate saturation-type kinetics for increasing partial pressures of CO. The data in Fig. 1 do show such saturation kinetics as indicated by increasing conversion of toluene at lower CO pressures (~500 psia) in a batch reactor for fixed reaction time and fixed amounts of acid and toluene. At higher CO pressures (~1100 psia), the conversion of toluene does not change much as suggested by saturation-type kinetics.

The solubility of CO at different CO partial pressures can also be illustrated by the effect of mixing upon the observed yields in a batch reactor. For a reaction scheme where one reactant, CO, must be absorbed into a liquid phase containing the catalyst, we expect that the agitation of the reaction mixture may have an effect on the observed yields. Indeed, the observed conversion of toluene was a function of stirring speed at lower CO partial pressures (~800 psia), but the conversion was not a function of stirring speed at a higher CO partial pressure (~1100 psia) for the same stirring speeds. Thus, the preliminary data of toluene carbonylation appear to fit into a scheme where CO must be absorbed into the liquid phase and then protonated by the acid catalyst.

The yields of products *versus* time in the batch reactor showed that *p*-tolualdehyde attained a maximum yield (~18%) when the reaction time was 0.5 h, the temperature was 25°C, and the acid/substrate ratio was 2. At this time, the yield of ditolylmethane appeared to increase significantly. Olah (2) suggested that ditolylmethane was the product of a reaction between protonated tolualdehyde and toluene to form ditolylmethanol, which then became protonated and formed ditolylmethane by a subsequent dehydration step followed by hydride addition. We showed that this reaction could be effectively suppressed by the addition of a large excess of triflic acid, >10 mol of acid/mol of toluene (Fig. 4). The reaction to form the diaryl species is a second-order reaction for which the reaction rate depends upon the concentrations of toluene and protonated aldehyde. The concentrations of both species decrease with increasing acid/toluene ratio (>2) and it is speculated that the concentration of dissolved COH^+ increases with increasing acid/toluene ratio. Thus, the rate of the bimolecular reaction should decrease and the rate of tolualdehyde formation should be favored by increasing acid/toluene ratios. Therefore, the yield of the tolualdehyde should be favored when the acid/toluene ratio is increased to large values.

The reaction kinetics appear to obey first-order kinetics in toluene when the toluene conversion is less than 25% and then other kinetics at higher conversions. The first-order toluene kinetics is consistent with a reaction rate that we suggested earlier (4),

$$\text{rate} = kx_{\text{toluene}}, \qquad [5]$$

where x_{toluene} is the mole fraction of toluene and k is the observed rate constant. The observed rate constant was related to the intrinsic rate constant for the carbonylation reaction, k'; the product of the Henry's law constant for CO solubility in the acid/toluene mixture, h; the CO partial pressure; the equilibrium constant for the protonation of CO, K; and activity coefficients for the reactants and products using the model described in Eqs. [2]–[4]. We can imagine that the Henry's law constant will increase with increasing acid/toluene ratio and with increasing CO partial pressure, but this function will not be monatonic as the solution has only a finite capacity to hold dissolved CO. The model equations described elsewhere (4) showed first-order dependence on toluene when the reaction rate was small for the series reaction to form ditolylmethane. When this subsequent reaction cannot be ignored, we expect that the overall conversion of toluene obeys different kinetics. One important consequence of the further reaction to form ditolylmethane is the formation of water. The elimination of water will certainly reduce the acid strength of the solution and thereby inhibit the reaction rate in a way that we showed earlier (4).

This model would also predict a complicated effect of temperature upon reaction yields. For example, increasing the temperature would increase the intrinsic rate constant, k', in a manner predicted by the Arrhenius equation, but we expect that the Henry's law constant would decrease with increasing temperature. The response of the equilibrium constant, K, with increasing temperature is not known. Since toluene is used to form tolualdehyde and to form ditolylmethane, the conversion of toluene could increase while the yield of tolualdehyde may decrease with increasing temperature. Thus, the model could predict an optimum temperature for the carbonylation reaction to form *p*-tolualdehyde which is what we observed (Table 2).

SUMMARY

The formylation of toluene was completed in triflic acid to show high yields (~99% on toluene disappearance) when the CO pressure was at least 1000 psig and the reaction temperatures were no more than 300 K. For reaction times of less than 30 min, only small amounts of the di- and tri-tolylmethanes were observed. This reaction path may be commercially viable for the production of aryl aldehydes provided that one may find an inexpensive method to regenerate the triflic acid.

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