

Trifluoromethanesulphonic Acid as a Catalyst for the Ethylation of Benzene

Brian L. Booth,* Mohammed Al-Kinany, and (in part) Khosrow Laali

Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester, M60 1QD

At room temperature and a pressure of ethene of 1 atm, anhydrous trifluoromethanesulphonic (triflic) acid is a more effective catalyst for the ethylation of benzene than AlCl_3 , FSO_3H , and anhydrous H_2SO_4 . It has an activity comparable to that found for a 1 : 1 mixture of FSO_3H – SbF_5 , and under the most favourable conditions the yield of ethylbenzene is *ca.* 38% based on the amount of benzene reacted. Although the initial rate of ethylation is rapid, the reaction effectively ceases after 30–60 min depending on the reaction conditions. The reason for this has mainly been shown to be strong complexation of the triflic acid to polyethylbenzene derivatives in the catalyst layer, but also, in part, to the competing formation of ethyl triflate, which is inactive as an ethylating agent under the conditions used.

The ethylation of benzene is the most important Friedel–Crafts alkylation reaction. The majority of processes for the manufacture of ethylbenzene in this way still use aluminium chloride as a catalyst with chloroethane, water, or HCl as a promoter and an operating temperature of $>80^\circ\text{C}$.¹ The conventional process uses a fairly large amount of catalyst which is present in a heavy catalyst–complex layer, and although the catalyst layer can be recycled, fresh catalyst must be added repeatedly for efficient alkylation and the spent catalyst layer is hydrolysed leading to destruction of the catalyst.^{2,3} A recent Monsanto process operates at higher temperatures and is a homogeneous process which uses much smaller amounts of catalyst. The catalyst is not recycled, but is used only once and the products are hydrolysed after each run.^{2,3}

For some time^{4–6} we have been interested in the special properties of triflic acid as a strong acid catalyst. It is our experience, and that of other workers,^{7,8} that the thermal stability and non-oxidising properties of this superacid, coupled with the low nucleophilicity of the triflate anion, frequently leads to cleaner reactions and higher product yields than those found with other superacid catalysts, including aluminium chloride. Although it is expensive to manufacture, it is not destroyed either during reaction or by hydrolysis and it can be recovered from reaction mixtures by a reasonably simple

procedure. It was of some interest to investigate the efficiency of triflic acid as a catalyst for the ethylation of benzene, and, in particular, whether it offered any significant advantages over the conventional Lewis acid catalysts.

Results and Discussion

Comparison with Other Brønsted and Lewis Acids.—A series of comparative experiments were carried out in which dry ethene was bubbled at a constant rate ($15\text{--}18\text{ cm}^3\text{ min}^{-1}$) at room temperature and atmospheric pressure through a mixture of benzene and various Brønsted and Lewis acids (mole ratio of benzene:acid 6.7:1). The catalyst systems studied included 100% H_2SO_4 ; 100% H_2SO_4 : $\text{CF}_3\text{SO}_3\text{H}$ (mole ratio 1:1); 100% H_2SO_4 : $\text{CF}_3\text{SO}_3\text{H}$ (mole ratio 9.84:1); AlCl_3 in nitromethane; FSO_3H ; FSO_3H : SbF_5 (mole ratio 1:1); anhydrous $\text{CF}_3\text{SO}_3\text{H}$; and anhydrous $\text{CF}_3\text{SO}_3\text{H}$: SbF_5 (mole ratio 1:1). In all cases a mixture of ethylbenzene and polyethylbenzenes was produced and the reactions were monitored at 0.5 h intervals by g.l.c. The results given in Figure 1 show that anhydrous triflic acid ($H_0 = -14.5$)⁹ is a superior catalyst to sulphuric acid, and aluminium chloride, and gives a similar yield of ethylbenzene to that obtained using a 1:1 mixture of FSO_3H and SbF_5 [$H_0 = -21.0$ (25 mol% SbF_5) to -26.5 (90 mol% SbF_5)].¹⁰

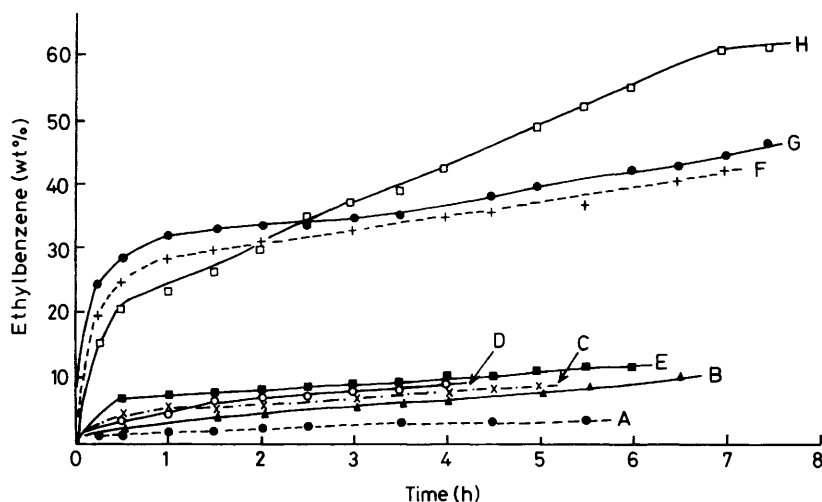


Figure 1. Yield of ethylbenzene (wt%) as a function of time from the ethylation of benzene at 22°C (ethene flow rate $15\text{--}18\text{ cm}^3\text{ min}^{-1}$, benzene to catalyst mole ratio 6.7:1). Catalysts: A, 100% H_2SO_4 ; B, H_2SO_4 – $\text{CF}_3\text{SO}_3\text{H}$ (9.84:1); C, H_2SO_4 – $\text{CF}_3\text{SO}_3\text{H}$ (1:1); D, FSO_3H ; E, AlCl_3 in nitromethane; F, FSO_3H – SbF_5 (1:1); G, $\text{CF}_3\text{SO}_3\text{H}$; H, $\text{CF}_3\text{SO}_3\text{H}$ – SbF_5 (1:1)

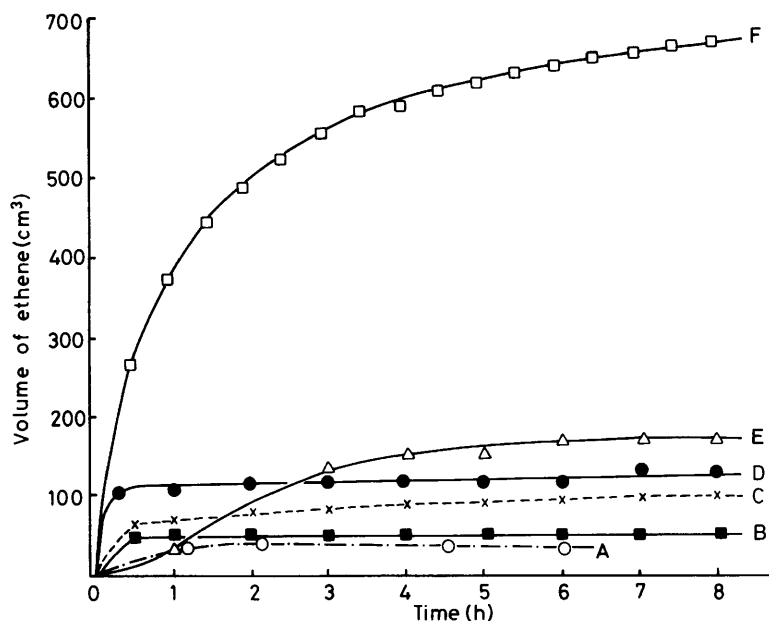


Figure 2. Uptake of ethene as a function of time in the ethylation of benzene at 22 °C (1 atm ethene, benzene:catalyst mole ratio 6:1). Catalysts: A, 100% H₂SO₄; B, FSO₃H; C, AlCl₃ in nitromethane; D, 98% CF₃SO₃H; E, H₂SO₄-CF₃SO₃H (1:1); F, CF₃SO₃H

Moreover, the product distribution found with triflic acid is similar to that reported for the industrial ethylation of benzene using AlCl₃ as catalyst.³ This contrasts with the low yield of ethylbenzene obtained with fluorosulphonic acid alone, despite the fact that it has a similar acid strength ($H_0 = -15$)¹¹ to that of triflic acid. A possibility that the low yield using fluorosulphonic acid may be due to competing fluorosulphonation of ethylbenzene and polyethylbenzenes was considered but no evidence was found for such products in the product mixture. The catalyst which gave the highest yield of ethylbenzene was a 1:1 mixture of CF₃SO₃H and SbF₅ (H_0 ca. -18.5).¹² This gave a 92% conversion of benzene to ethylbenzene containing ca. 62% of ethylbenzene after 7.5 h.

Unlike the AlCl₃ catalyst system where a small amount of water promotes catalysis, the triflic acid system cannot tolerate even traces of water and it is essential to dry the ethene and benzene rigorously. This can be seen from the results obtained on measuring the uptake of ethene in a closed system using anhydrous and 98% triflic acid with an acid to benzene ratio of 1:6 at room temperature (Figure 2). Similarly, addition of 100% sulphuric acid to anhydrous triflic acid caused a marked decrease in catalytic activity (see Figure 1) despite reports in the patent literature¹³ that such mixtures catalyse the alkylation of C₄-C₆ isoparaffins by C₃-C₅ alkenes.

At 22 °C with a benzene to triflic acid ratio of 6:1, the yield of ethylbenzene was 32% after 1 h and this rose slowly to 40% over a further 4 h. Under these conditions the rates of isomerization and transalkylation of the polyethylbenzene by-products are slow. So, for example, the composition of the diethylbenzenes changed only from *o*-(46.5%), *p*-(30.0%), and *m*-(23.5%) after 1 h to *o*-(45.0%), *p*-(30.5%), and *m*-(24.5%) after 5 h.

Effect of Ethene Flow Rate.—The effect of changing the ethene flow rate over the range 3–6, 15–18, and 25–28 cm³ min⁻¹ on the product distribution using triflic acid as catalyst at room temperature is shown in Figure 3. With a flow rate of 3–6 cm³ min⁻¹ there was no detectable reaction during the first 30 min, and thereafter the reaction proceeded slowly to give a 37% yield of ethylbenzene after 4 h; little formation of polyethylated

products occurred during the first 90 min of the reaction. When the ethene flow rate was increased to 15–18 cm³ min⁻¹, onset of ethylation occurred almost immediately and the yield of ethylbenzene was 18% after 0.5 h rising to >32% after 1 h. Higher ethylated products started to appear after 0.5 h, but even after 1 h ethylbenzene accounted for 90% of the ethylation products. With a flow rate of 25–28 cm³ min⁻¹, higher ethylated products were observed even during the early stages of reaction and after only 0.5 h the mixture contained 29% ethylbenzene, 7% diethylbenzenes, and traces of triethylbenzenes.

Effect of Variation in the Triflic Acid: Benzene Mole Ratio.—Using a closed system at room temperature and 1 atm pressure of ethene, a set of experiments was carried out in which the triflic acid:benzene ratio was varied over the range 2:1 to 1:20. In all cases the rates of ethylation were followed by measurement of the uptake of ethene, and representative samples of the organic/catalyst layers were analysed (after quenching with water) at 0.5 h intervals. The trends observed are shown in Figure 4. In all the reactions, except that using an acid:benzene ratio of 1:20, the rate of ethene uptake is rapid during the first 0.5 h, but after this the rate of reaction slows down considerably and after 1 h it effectively stops. The total uptake of ethene increases with an increase in the acid:benzene ratio and at high acid:benzene ratios rapid ethylation is accompanied by the formation of high yields of polyethylbenzenes. Also, under these conditions there is appreciable intramolecular isomerization and transalkylation, as demonstrated previously by Roberts.¹⁴ Thus, the most favourable conditions for ethylbenzene formation at room temperature are an acid:benzene ratio in the range of 1:5 to 1:10. Under these conditions the rate of ethylation is quite rapid, formation of higher ethylation products is low, and the rates of intramolecular isomerization and transalkylation are slow.

Why Does the Reaction Stop?—It is apparent that a common feature of all these ethylation reactions with triflic acid as catalyst is that there is an initial rapid uptake of ethene during the first 0.5–1.0 h and then the reaction effectively stops despite

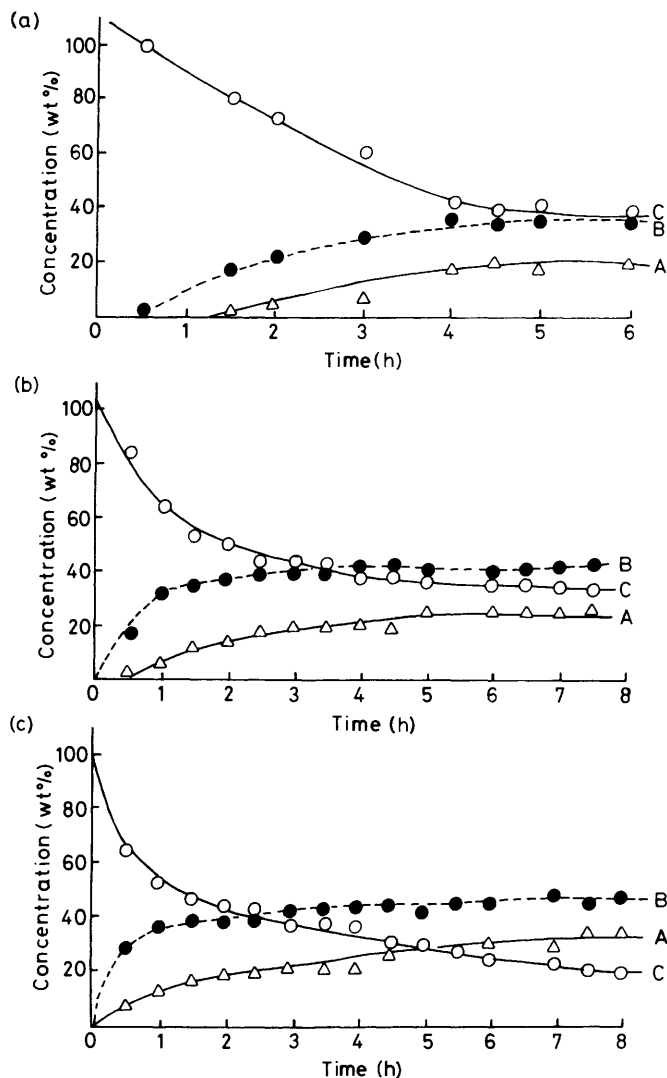


Figure 3. Effect of ethene flow rate on the rate of formation of ethylbenzene and polyethylbenzenes in the ethylation of benzene catalysed by triflic acid at 22 °C (benzene: acid mole ratio 5:1) (a) Flow rate 3–6 cm³ min⁻¹; (b) 15–18 cm³ min⁻¹; (c) 25–28 cm³ min⁻¹. A, Polyethylbenzenes; B, ethylbenzene; C, benzene

the fact that an appreciable amount of unchanged benzene remains in the reaction mixture.

One obvious explanation for the observed behaviour is that free triflic acid is removed from the reaction mixture by reaction with the ethylated benzenes formed to produce arenium triflates which will be present in the catalyst layer. Roberts¹⁵ has shown that toluene and higher methylated benzenes are fully protonated in triflic acid. While his conditions are not typical of those prevalent in the majority of the experiments carried out in our work, it is clear from solvent extraction studies that appreciable amounts of polyethylbenzenes, particularly hexaethylbenzene, are present as arenium salts in the catalyst layer. So, for example, a typical analysis of the organic layer from the ethylation of benzene after 1 h using an acid:benzene ratio of 1:3 at room temperature shows unchanged benzene (53 wt%), ethylbenzene (35 wt%), diethylbenzenes (*o*, 5.3 wt%; *m*, 2.6 wt%; *p*, 3.5 wt%), with only traces of tri-, tetra-, and pentaethylbenzenes. Analysis of the catalyst layer after quenching with water shows no benzene, ethylbenzene, or diethylbenzenes, but triethylbenzenes (1.3 wt%), tetraethylbenzenes (1.1 wt%), and pentaethylbenzenes (0.5 wt%). The main components in the catalyst layer (after hydrolysis) are hexaethylbenzene (72 wt%), 4-ethylidene-1,1,2,3,5,6-hexaethylcyclohexa-2,5-diene (1, 22 wt%), and an isomer believed to be 2-ethylidene-1,1,3,4,5,6-hexaethylcyclohexa-3,5-diene (2, 3 wt%); both (1) and (2) arise from heptaethylbenzenium triflate. Mixtures of hexa- and heptaethylbenzenium tetrachloroaluminates have been identified previously by Olah¹⁶ in the red catalyst layer from the reaction of benzene and chlorobenzene with AlCl₃. Heptaethylbenzenium hexafluoroantimonate has been prepared previously¹⁶ by addition of hexaethylbenzene to an equimolar quantity of ethyl hexafluoroantimonate, or by ethylation of hexaethylbenzene with ethyl chlorosulphonate in the presence of HF-SbF₅.¹⁷ Olah has demonstrated that when a solution of heptaethylbenzenium salt in sulphur dioxide is quenched with water, extraction with pentane gives a 2:1 mixture of (1) and hexaethylbenzene.¹⁶ A similar mixture is also reported to be formed on hydrolysis of the product mixture from the reaction between tetraethylbenzene and chloroethane in the presence of aluminium chloride,¹⁸ and from the ethylation of benzene using HF-BF₃.¹⁹ These observations agree closely with our own findings that a mixture of anhydrous triflic acid and hexaethylbenzene (mole ratio 5.85:1) rapidly absorbs ethene to form a deep orange solution. On quenching with water a mixture of hexaethylbenzene (14%), compound (1) (79%), and compound

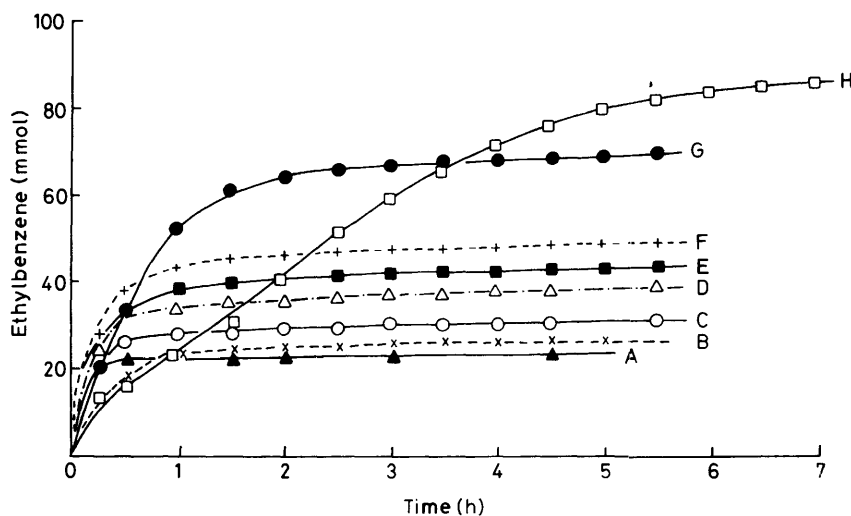


Figure 4. Effect of variation of the benzene to triflic acid mole ratio on the rate of formation of ethylbenzene at 22 °C and an ethene flow rate of 15–18 cm³ min⁻¹. A, acid:benzene 2:1; B, 1:1; C, 1:2; D, 1:3; E, 1:5; F, 1:6; G, 1:10; H, 1:20

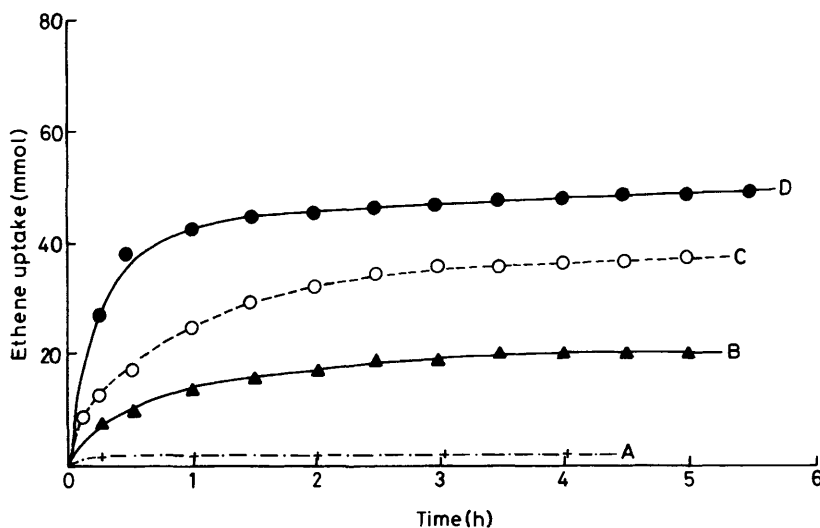
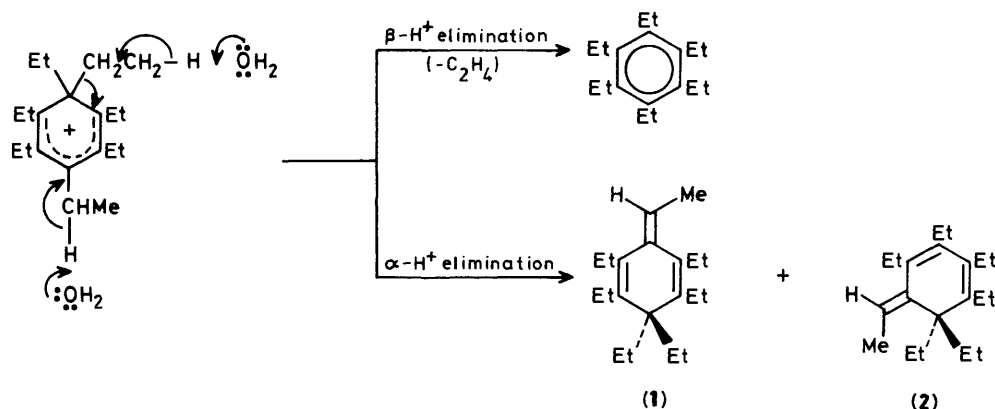


Figure 5. Effect of adding hexaethylbenzene and ethylidenehexaethylcyclohexadiene on the rate of ethene uptake during ethylation of benzene (72 mmol) at 22 °C with triflic acid catalyst (12 mmol). A, Hexaethylbenzene (0.15 mmol) and ethylidenehexaethylcyclohexadiene (0.64 mmol) present before addition of triflic acid; B, hexaethylbenzene (2.03 mmol) present before addition of triflic acid; C, hexaethylbenzene (2.03 mmol) added 5 min after addition of triflic acid; D, no hexaethylbenzene or ethylidenehexaethylcyclohexadienes added

(2) (6%) is formed. All three products can arise from hepta-ethylbenzenium triflate by the competing pathways shown in Scheme 1.

The effect of adding hexaethylbenzene and the ethylidenehexaethylcyclohexadiene isomers on the rate of ethylation was examined in a series of experiments carried out at room temperature using a mole ratio of triflic acid to benzene of 1:6. The rate of ethylation was followed by measurement of ethene uptake and the results are shown in Figure 5. It can be seen from these results that addition of hexaethylbenzene (17 mol% of total acid) after 5 min slowed down the initial rate of reaction considerably. When hexaethylbenzene (2.03 mmol, 17 mol% of total acid) was present from the start of the reaction, the rate of ethene uptake is very slow, and when both hexaethylbenzene (1.25 mol% of total acid) and the ethylidenehexaethylcyclohexadiene isomers (5.3 mol% of total acid) are present at the start, the reaction is almost completely inhibited. In 1958 von Doering²⁰ reported that methylation of trimethylbenzenes is inhibited by the addition of methylidenehexamethylcyclohexadiene and HCl in amounts equivalent to slightly more than the AlCl_3 catalyst. More recently, Mamedov and Pinsker²¹ have shown that penta- and hexa-ethylbenzenes, as well as

compound (1), are active poisons for the AlCl_3 -catalysed ethylation of benzene. The triflic acid catalysed reactions appear to differ in some respects from the AlCl_3 -catalysed reactions in that only small amounts (< 10 mol% of the triflic acid present) of ethylidenehexaethylcyclohexadienes are sufficient to inhibit the reaction almost completely. Thus, inhibition is not simply due to removal of triflic acid by formation of the arenium ions $(\text{C}_6\text{Et}_6\text{H})^+\text{OTf}$ and $(\text{C}_6\text{Et}_7)^+\text{OTf}$. Our results suggest that the arenium ions probably exist in the catalyst layer as aggregates of the type $(\text{C}_6\text{Et}_6\text{H})^+\text{OTf}$, $(\text{TfOH})_n$ and $(\text{C}_6\text{Et}_7)^+\text{OTf}$, $(\text{TfOH})_n$ in which each triflate anion is tightly hydrogen bonded to several molecules of triflic acid. From studies of acid-base equilibria in non-hydroxylic solvents, it has been known for some time that there is a strong hydrogen bonding stabilization of sulphate anion by an excess of sulphonic acid molecules.²² Recently, Farcasiu²³ has estimated on the basis of n.m.r. evidence that as many as 3–4 triflic acid molecules may be associated with the anion of the complex $(\text{C}_6\text{Me}_6\text{H})^+\text{OTf}$ in a hydrocarbon solvent. Clearly, if this is the case, then formation of hexa- and hepta-ethylbenzenium triflates in amounts equivalent to only 25–30% of the total acid would be sufficient to stop the ethylation reaction. There is, however, another way

in which triflic acid could be removed from the ethylation mixture, and that is by formation of ethyl triflate. This possibility has been examined.

It has been shown that no reaction occurs at room temperature over 16 h when ethyl triflate (4 mmol) is added to hexaethylbenzene (1 mmol) in benzene. Addition of triflic acid (6 mmol) to the mixture caused slow transekylation to occur to give, after 2 h at room temperature, ethylbenzene (15%), diethylbenzenes (5%), triethylbenzenes (5%), tetraethylbenzenes (5%), and pentaethylbenzene (4%) in addition to unchanged benzene and hexaethylbenzene. Significantly, no evidence was obtained for the formation of the ethylidenehexaethylcyclohexadiene derivatives (1) and (2) indicative of heptaethylbenzenium ion formation. This established that under the conditions of our experiments ethyl triflate does not behave as an ethylating agent. The next objective was to establish whether ethyl triflate was formed under typical ethylation conditions, and, if so, in what amounts. I.r. spectroscopy was of no value for

this purpose, and ^1H n.m.r. spectroscopy of the reaction mixture was far too complex to be useful. Attempts to use g.l.c. for the quantitative estimation of ethyl triflate was unsuccessful in our hands as extensive decomposition occurred even at room temperature on all the columns used (*i.e.*, FFAP, Carbowax, APL, PEGA, and SE30).

A control experiment established that ethyl triflate reacted quantitatively with pyridine at room temperature to form *N*-ethylpyridinium triflate with no evidence for the formation of ethene and pyridinium triflate by *E2* elimination. In a separate experiment, a mixture of hexaethylbenzene (14%) and the two ethylidenehexaethylcyclohexadiene isomers (1) and (2) (86%) treated with 1 mol equiv. of triflic acid was quenched with pyridine at $0-2^\circ\text{C}$ to give a white precipitate which, within the detection limits of the technique, was found to be only pyridinium triflate by ^1H n.m.r. spectroscopy. G.l.c. analysis of the organic products showed hexaethylbenzene (70.5%), compound (1) (27.8%), and compound (2) (1.7%). Thus, in contrast to the behaviour of water (*vide supra*), the stronger base pyridine reacts with heptaethylbenzenium triflate to give mainly hexaethylbenzene by elimination of ethene. In a separate experiment, the formation of ethene was confirmed by g.l.c. analysis of the gaseous products.

As neither hexa- nor hepta-ethylbenzenium triflates react with pyridine to form *N*-ethylpyridinium triflate, it is assumed that none of the other benzenium ions present under ethylation conditions will give the *N*-ethyl derivative on quenching with pyridine. Thus, any *N*-ethylpyridinium triflate produced must come from ethyl triflate present in the reaction mixture. Consequently, several ethylation reactions were carried out at room temperature using triflic acid: benzene mole ratios of 1:2, 1:5, and 1:10, respectively. Under each set of conditions the product mixture was analysed at 30 min intervals by quenching with pyridine, and determining the ratio of *N*-ethyl to *N*-H pyridinium salts so formed. The results are given in Figure 6. In all cases the increase in *N*-ethylpyridinium triflate is matched by a corresponding decrease in pyridinium triflate. This is exactly as expected as the only way a proton can be lost from the system is by formation of ethyl triflate; all other products *i.e.* free and complexed triflic acid, ethylated benzenium ions, and heptaethylbenzenium triflate will act as proton sources on quenching with pyridine. Under all three sets of conditions the rate of formation of ethyl triflate is rapid during the first hour and then slows down appreciably. This trend is similar to that observed for the ethene uptake, and is compatible with the assumption that ethyl triflate formation and the ethylation of benzene proceed *via* a common intermediate, possibly the $(\text{MeCH}_2)^+\text{OTf}^-$ ion pair. Hence, ethyl triflate formation is a contributing factor in inhibiting ethylation under these conditions, and accounts for approximately one-third of the total acid concentration.

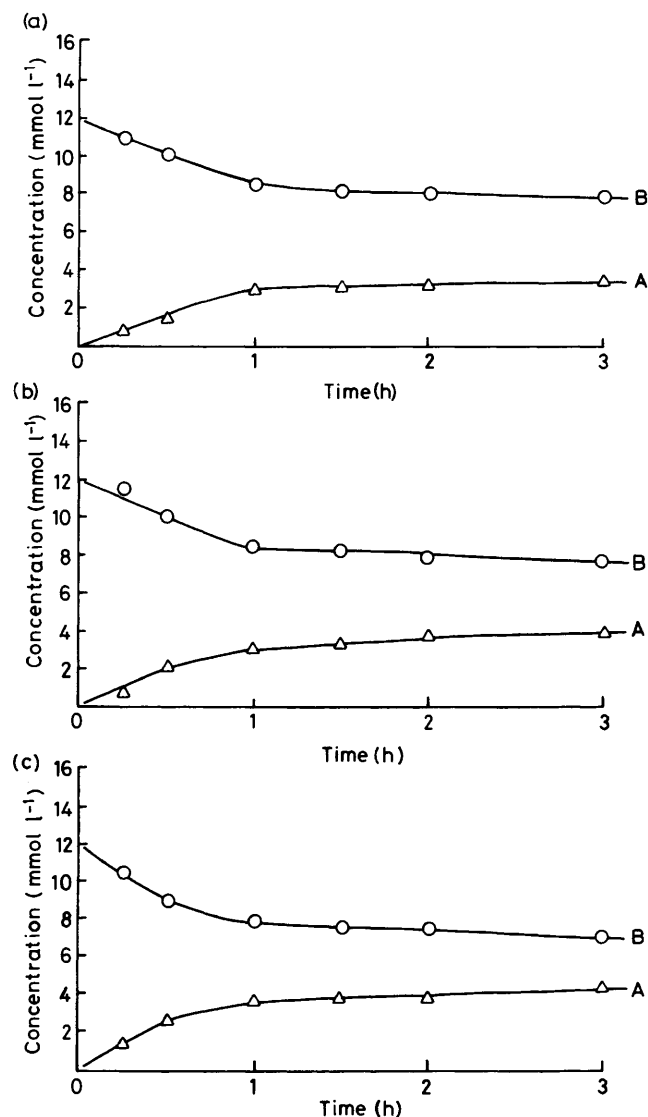


Figure 6. Formation of pyridinium triflate and *N*-ethylpyridinium triflate as a function of time on quenching the products of ethylation of benzene at 22°C and 1 atm ethene with pyridine. (a) Benzene:triflic acid mole ratio 1:2; (b) 5:1; (c) 10:1. A, *N*-ethylpyridinium triflate; B, pyridinium triflate

Conclusions

From this investigation it appears that triflic acid is a very effective catalyst for the ethylation of benzene and at room temperature it gives a similar product distribution to that obtained using AlCl_3 at elevated temperatures. Reaction in the liquid phase suffers from the problem that polyethylbenzenes, which are concentrated in the catalyst layer, remove triflic acid from the reaction mixture as does the formation of ethyl triflate. Fresh catalyst must, therefore, be added if the catalyst layer is to be recycled. A possible way round this problem may be to use conditions similar to the Monsanto process where polyethylbenzene formation would be minimized. Although the triflic acid would only be used once, unlike AlCl_3 , it can be recovered. We have shown that by removal of the water from an aqueous solution of triflic acid, followed by addition of fuming sulphuric

acid and distillation at atmospheric pressure, 90% of the triflic acid can be recovered in the anhydrous state suitable for re-use as a catalyst for ethylation.

Experimental

Benzene (research grade 99.9%) was purified according to the standard literature procedure,²⁴ and dried over 3A or 4A molecular sieves. Ethene (BOC CP grade 99.9%) was passed through a 1 m column packed with activated 3A or 4A molecular sieves. Triflic acid and fluorosulphonic acids were commercial samples purified by double distillation under dry nitrogen at atmospheric pressure immediately before use. Anhydrous sulphuric acid was prepared by the 'foggy and fair' method.²⁵

¹H N.m.r. spectra were recorded on a Perkin-Elmer R34 instrument (220 MHz), and g.l.c. analyses were carried out using a Pye Unicam 104 instrument fitted with a 30 m glass capillary column packed with 10% FFAP. The g.l.c. instrument was calibrated by the normalization method using a standard mixture of benzene, ethylbenzene, *o*-, *m*-, and *p*-diethylbenzenes, 1,3,5-triethylbenzene, and hexaethylbenzene; sampling and analysis errors were estimated to be within ± 0.5 to 1.0%.

General Procedures.—(a) *Closed system.* A 25-cm³ three-necked flask fitted with a thermometer and a septum cap was connected to a gas burette. The apparatus was evacuated and filled with dry ethene, and this sequence was repeated several times. Then the required amount of dry benzene was injected into the flask and the ethene absorption was recorded. Triflic acid was then injected with efficient stirring and cooling to keep the temperature in the range 22 ± 1 °C. Aliquots (15 μ l) of the mixed organic and catalyst layers were removed every 30 min, and were quenched with water (5 cm³). The sample was then extracted with hexane (0.4–0.6 cm³) and analysed by g.l.c. Reaction products were identified by comparison of their retention times with those of authentic samples where possible, and identification was confirmed by g.l.c./m.s. analysis.

(b) *Open system.* The apparatus used was similar to that described above except that one neck of the 25-cm³ flask was connected to an oil bubbler. Another neck was connected to a cylinder of ethene through a bubbler, a flow controller (VCD 1000), and a tube containing freshly activated molecular sieves. The apparatus was flame-dried under a stream of dry nitrogen and then flushed with dry ethene. Dry benzene was then introduced into the flask and ethene was bubbled through the benzene at the required flow rate with stirring and cooling. Triflic acid was introduced quickly by means of a syringe and the mixture was stirred vigorously. An aliquot (10 μ l) was removed after 15 min and thereafter every 30 min. The product mixture in each case was analysed by g.l.c. as described in the previous experiment.

Preparation of 4-Ethylidene-1,1,2,3,5,6-hexaethylcyclohexa-2,5-diene and 2-Ethylidene-1,1,3,4,5,6-hexaethylcyclohexa-3,5-diene Isomers (1) and (2).—Freshly distilled triflic acid (2.0 cm³, 24 mmol) was added to dry hexaethylbenzene (1.0 g, 4.1 mmol) to form a deep orange solution, and the mixture was stirred at room temperature under an atmosphere of ethene whereupon the colour changed to a deep clear yellow after 10 min. Stirring was continued for a further 3 h after which the reaction mixture was poured into ice-water (400 cm³) and shaken vigorously until the solution turned colourless. The solution was extracted with ether, and the extract was washed with water until neutral to litmus, dried (MgSO₄), and evaporated under reduced pressure to give a thick oil (0.4 g), shown by g.l.c. to contain hexaethylbenzene (15%), compound (1) (76.7%), and compound (2) (5.9%) plus small amounts (*ca.* 1%) of two unidentified

compounds with higher retention times. Addition of a small amount of ethanol to the oil precipitated some of the hexaethylbenzene, and a repeat of this procedure several times gave a sample which contained hexaethylbenzene (14%), compound (1) (79%), and compound (2) (7%). The ethylidenehexaethylcyclohexadiene isomers gave the following spectra: δ_{H} (220 MHz, Me₄Si ext. ref., CDCl₃) 0.52 (t, 3 H, *J* 7.5 Hz), 0.95 (t, 6 H, *J* 7.0 Hz), 1.0 (t, 6 H, *J* 7.0 Hz), 1.52 (q, 2 H, *J* 7.5 Hz), 1.87 (d, 3 H), 2.09 (q, 2 H, *J* 7.5 Hz), 2.15 (q, 2 H), 2.42 (q, 2 H), 2.58 (q, 2 H), and 5.42 (q, 1 H) p.p.m.; δ_{C} 9.49, 14.05, 14.39, 15.50, 15.93, 51.92, 113.39, 134.09, 134.69, 134.79, 139.05, and 139.96 p.p.m.; *m/z* (g.l.c./m.s.) 274 (*M*⁺) and 245 (*M* – Et)⁺ 100%.

Quenching with Pyridine: General Procedure.—Using the apparatus and procedure described above for the closed system, a series of experiments were carried out using a 1:2, 1:5, and 1:10 mole ratio of triflic acid to benzene. For each ratio six reactions were carried out at 22 ± 1 °C: these were quenched by the careful addition of dry pyridine (1.0 cm³, 12.4 mmol) after the different reaction times 0.25, 0.5, 1.0, 1.5, 2.0, and 3.0 h, respectively. After quenching the product mixtures consisted of an upper organic layer and a colourless, thick oil which contained a white, gelatinous precipitate. The upper layer was separated and shown by g.l.c. to contain pyridine, benzene, and ethylated benzenes, and in each case the composition of the mixture agreed well with that found for quenching with water under similar conditions. The lower layer was washed with benzene (2 \times 5 cm³) and dry ether (4 \times 15 cm³) before dissolution in dry acetone (2 cm³). The ¹H n.m.r. spectrum (220 MHz) of the acetone solution showed it to be a mixture of pyridinium triflate [δ_{H} 8.3 (t, 1 H, *J* 7.5 Hz, 4-H), 8.85 (app. t, 2 H, 2 H, 3-H), and 9.07 (d, 2 H, *J* 5 Hz, 2-H) p.p.m.] and *N*-ethylpyridinium triflate [δ_{H} 1.70 (t, 3 H, *J* 7.5 Hz, Me), 4.85 (q, 2 H, CH₂), 8.25 (t, 1 H, *J* 7.5 Hz, 4-H), 8.71 (app. t, 2 H, 3-H), and 9.18 (d, 2 H, *J* 5 Hz, 2-H) p.p.m.]. The ratio of the two compounds was calculated from the relative intensities of the doublet signals for the 2-H protons. The method was tested with known ratios of the two salts and the error was found to be of the order of $\pm 0.7\%$.

Recovery of Triflic Acid.—The aqueous acid solution obtained on quenching the products of an ethylation reaction (triflic acid taken 5.2 g, 3 cm³) with water, followed by separation of the organic layer, was washed with diethyl ether (3 \times 25 cm³) to remove any traces of organic material. The water was then distilled off, and fuming sulphuric acid was added carefully and mixed thoroughly with the pot residue. The mixture was then heated at atmospheric pressure to give anhydrous triflic acid (2.7 cm³, 4.7 g, 90% yield), b.p. 162–166 °C, and triflic acid monohydrate (0.7 g, b.p. 214–216 °C) which solidified on cooling to a white solid, m.p. 34 °C, (lit.,²⁶ m.p. 34 °C).

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