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# Heterogeneous Catalysis by Solid Superacids

## 14. Perfluorinated Resinsulfonic Acid (Nafion-H)-Catalyzed Friedel–Crafts Alkylation of Toluene and Phenol with Alkyl Chloroformates and Oxalates[1]

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Perfluorinated resinsulfonic acid (Nafion-H)-catalyzed Friedel–Crafts alkylation of toluene and phenol with alkyl chloroformates and oxalates was studied, in both liquid- and gas-phase reactions. Alkylations gave good yields in clean reactions without the need for any complex decompositions or workup. No acylation side products were formed in the reactions. The question of C- versus O-alkylation is discussed.

### INTRODUCTION

Compared with the extensive use of a wide variety of alkylating agents carboxylic acid esters have received considerably less attention in Friedel–Crafts alkylations. One of the reasons is that usually Friedel–Crafts alkylation with carboxylic esters in the presence of $AlCl_3$ gives complex reaction mixtures containing alkylation as well as acylation products (*2*). However, if the reaction is catalyzed by protic acids, such as HF (*3*), or weaker Lewis acids, such as $BF_3$ (*4*), high yields of alkylated products are obtained. Previously, we have studied the mechanistic aspects of the $AlCl_3$-catalyzed alkylation of benzene and toluene with esters and haloesters (*5*).

In continuation of our interest in the catalytic activity of solid superacidic catalysts in electrophilic reactions, we now report the results of the perfluorinated resinsulfonic acid (Nafion-H)-catalyzed alkylation of toluene and phenol with esters and haloesters.

### METHOD

All materials used were of >98% purity. Nafion 501 resin, as the potassium salt of the perfluorinated resinsulfonic acid, was obtained from the DuPont Company. The acid form of the salt, (Nafion-H) was prepared by stirring the salt with 20% nitric acid at 20°C for 24 hr, washing with deionized water, and subsequently drying overnight at 105°C.

*Liquid-phase reactions.* Batch reactions were conducted in a 25-ml round-bottomed flask, equipped with a condenser and magnetic stirrer. Alkylation of toluene was conducted by heating under reflux a mixture of toluene (9.2 g), Nafion-H catalyst (1 g), and alkylating agent (10 mmol). Alkylation of phenol was carried out by heating a stirred mixture of phenol (20 mmol), Nafion-H catalyst (0.8 g), and alkylating agent (20 mmol) to a predetermined temperature in a silicon oil bath. Aliquots were taken at various time intervals and analyzed. Attempted isomerizations of phenetole and ethyl phenols over Nafion-H were carried out in the same way, using 3.0 g of the aromatic compound and 600 mg of Nafion-H.

*Gas-phase reactions.* Gas-phase reactions were carried out using a 170 × 12-mm glass tube reactor in which the catalyst was supported by glass wool. The reactor was charged with 1.0 g of the activated dry

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[1] For Part 13, see Ref. (*1*).

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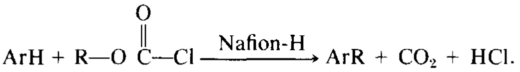
catalyst. During the reaction, a dry $N_2$ stream was passed through, generally at a rate of 5 ml/min. The reactor was electrically heated. The temperature deviation was in the limit of 1°C. The reactants were introduced through a syringe using a syringe pump, equipped with a variable linear rate mechanism. Products emerging from the catalytic reactor were condensed and analyzed by gas–liquid chromatography (glc).

*Analysis*. Products were analyzed using a Varian 3700 gas chromatograph fitted with a flame ionization detector. Peak areas were integrated using CSI auto integrator Model 208E. Product mixtures were separated on 150-ft × 0.1-in capillary column coated with OV 101 at 100°C and 20 psi. Separation of ethyl toluenes was achieved by using 12-ft × $\frac{1}{8}$-in. stainless-steel column, packed with 15% *p*-azoxyanisole on 60- to 80-mesh Chromosorb W. Alkylated compounds were identified by comparison of their retention times with those of authentic samples on the same column. O-Alkylated phenols were analyzed directly. C-Alkylated phenols were analyzed as their trimethylsilyl derivatives. These derivatives were prepared by treating the alkylated phenol with bis-*N,O*-trimethylsilyltrifluoroacetimide (BSTFA).

## RESULTS AND DISCUSSION

### *Alkylation of Toluene with Alkyl Chloroformates*

Earlier studies have shown that Nafion-H is able to catalyze alkylation of aromatic compounds with olefins (*6*), alcohols (*6*), and alkyl halides (*7*) in a flow system at 130–200°C. The high volatility of the lower alkyl halides and the low reactivity of alcohols under the relatively mild conditions make it difficult to carry out similar alkylations in batch reactions. For such reactions, it was found that alkyl chloroformates are particularly suitable as alkylating agents. They combine sufficiently high boiling points as to allow atmospheric pressure batch reactions with high reactivity. A further advantage in using alkyl chloroformates is that the by-products, $CO_2$ and HCl, are volatile:



$$\mathrm{ArH + R{-}O{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}Cl \xrightarrow{\text{Nafion-H}} ArR + CO_2 + HCl.}$$

As can be seen from Table 1, yields are dependent both upon the reaction temperature (generally limited by the boiling point of the used alkyl chloroformate) and upon the nature of the alkyl group of the ester. For comparison, it was further shown (see Table 1) that even less reactive carboxylic acid alkyl esters alkylate effectively under the same reaction conditions. Ethyl acetate, although found to be capable of alkylating toluene, deactivates the catalyst very readily, probably by ketene formation from the acetic acid formed as a by-product (*8*). In contrast, diethyl oxalate is found to have a good alkylating ability even under milder conditions, giving, upon heating under reflux for 12 hr, up to 50% ethyl toluenes.

Under the reaction conditions employed, secondary isomerization of the formed alkyl toluenes is minor, but intramolecular isomerization of the intermediate σ-complexes results in increased *meta* sub-

TABLE 1

Nafion-H-Catalyzed Liquid-Phase Alkylation of Toluene with Esters and Haloesters[a]

| Alkylating agent | Temp (°C) | Percentage conversion | Percentage isomer distribution | | |
|---|---|---|---|---|---|
| | | | *ortho* | *meta* | *para* |
| $\mathrm{MeO\overset{\displaystyle O}{\overset{\|}{C}}Cl}$ | 70–72 | 2 | 48 | 26 | 26 |
| $\mathrm{EtO\overset{\displaystyle O}{\overset{\|}{C}}Cl}$ | 90 | 24 | 46 | 26 | 28 |
| $\mathrm{i\text{-}prO\overset{\displaystyle O}{\overset{\|}{C}}\text{-}Cl}$ | 110 | 80 | 42 | 21 | 37 |
| $CF_3CO_2Et$ | 82 | 5.5 | 49 | 24 | 27 |
| $CCl_3CO_2Et$ | 110 | 20 | 44 | 28 | 28 |
| $(COOEt)_2$ | 110 | 50 | 48 | 24 | 28 |

[a] Reaction time, 12 hr.

stitution. In most cases (Table 1), the isomer distribution shows an *ortho*:*para* ratio of ca. 2, which is the statistical ratio and is characteristic of an electrophilic substitution with a reactive alkylating agent.

In all the alkylations less than 2% dialkylation was observed, as a substantial excess of toluene over the ester (10: 1 molar ratio) was used.

Due to the higher reactivity of alkyl chloroformates, as compared to that of alcohols in the same flow system over Nafion-H catalyst, higher yields of alkylation of toluene were obtained. A 59% conversion of *methyl chloroformate* was observed in the alkylation of toluene at 200°C (Table 2) as compared to about 10% conversion using methyl alcohol (*9*). As found in preceding work (*7, 9*), yields depend significantly upon the reaction temperature and contact time.

Since xylenes were found to isomerize only to a limited degree under conditions similar to those used in the present study (*10*), it can be assumed that the isomer distribution reflects that of the alkylation process itself. As can be seen from Table 2, the *ortho*:*para*-xylene ratio is scarcely dependent upon the reaction conditions and stays in the range of 2. This, again, indicates a highly reactive alkylating species as was the case in the Nafion-H catalyst batch reaction with methyl chloroformate (Table 1).

*Ethyl chloroformate* gave higher alkylation yields than methyl chloroformate under similar conditions. The low *ortho*:*para* ratio

TABLE 2

Nafion-H-Catalyzed Gas-Phase Alkylation of Toluene with Alkyl Chloroformates ($\mathrm{RO}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{—Cl}$)

| *R* | Feed rate (ml/min) | Temp (°C) | Percentage alkylation | Percentage isomer distribution | | |
|---|---|---|---|---|---|---|
| | | | | *ortho* | *meta* | *para* |
| $CH_3$– | 0.022 | 200 | 59 | 46 | 26 | 28 |
| | 0.044 | 200 | 51 | 50 | 22 | 28 |
| | 0.088 | 200 | 38 | 49 | 20 | 31 |
| | 0.176 | 196 | 27 | 53 | 20 | 27 |
| | 0.044 | 183 | 44 | 53 | 19 | 28 |
| | 0.044 | 166 | 22 | 54 | 18 | 28 |
| | 0.044 | 142 | 10 | 56 | 17 | 27 |
| $CH_3CH_2$– | 0.022 | 197 | 69 | 25 | 48 | 27 |
| | 0.044 | 197 | 64 | 30 | 42 | 28 |
| | 0.088 | 197 | 46 | 34 | 38 | 28 |
| | 0.176 | 197 | 32 | 39 | 33 | 28 |
| | 0.046 | 176 | 43 | 38 | 32 | 30 |
| | 0.044 | 157 | 36 | 41 | 28 | 31 |
| | 0.044 | 139 | 23 | 40 | 27 | 33 |
| $(CH_3)_2CH$– | 0.022 | 192 | 76 | 4 | 66 | 30 |
| | 0.044 | 192 | 86 | 4 | 65 | 31 |
| | 0.088 | 192 | 91 | 4 | 65 | 31 |
| | 0.176 | 190 | 91 | 5 | 63 | 32 |
| | 0.044 | 180 | 95 | 4 | 65 | 31 |
| | 0.044 | 162 | 68 | 5 | 62 | 33 |
| | 0.044 | 143 | 51 | 5 | 61 | 34 |
| $CH_3CH_2CH_2$– | 0.044 | 178 | 93(3)[a] | 12(28) | 49(36) | 39(36) |

[a] Values in parentheses correspond to *n*-propyl derivative.

(~1) is a result of the isomerization of ethyl toluenes, which was observed to take place under similar conditions (*11*). The isomer distribution at 197°C is very close to the aluminum chloride-catalyzed equilibrium isomer distribution of ethyl toluenes in the liquid phase (*o* : *m* : *p* = 9 : 64 : 27) (*12*). At lower temperatures the *ortho* : *para* ratio increases due to a decrease in the rate of isomerization (*11*).

*Isopropyl chloroformate* expectedly shows the least dependence in its alkylation reactions upon the reaction temperature and contact time. There seems to be an optimum in the reaction conditions. At lower temperature, the reactions are too slow, whereas at higher temperatures, the yield decreases due to competing dealkylation, which becomes more predominant. Under the most favorable conditions, a 95% yield of isopropyl toluenes was obtained at 180°C with a feed rate of 0.04 ml/min.

We have previously shown that, in the gas phase, transalkylation of toluene by cymenes takes place over Nafion-H (*11*), and that the isomeric cymene distribution is *o* : *m* : *p* = 4 : 67 : 29. Similar isomer distribution is obtained in the present study (Table 3), indicating fast isomerization, even at relatively low temperatures.

Earlier studies of the Nafion-H-catalyzed alkylation of toluene with 1-propanol (*6*) or 1-chloropropane (*7*) resulted exclusively in the formation of isopropyl toluenes. In the present study with *n*-propyl chloroformate about 3% of the formed propylated toluene was found to be *n*-propyl toluenes, whereas the balance were cymenes. This indicated that although the major reaction path is through the intermediacy of the isopropyl cation, some of the reaction proceeds through a different mechanism, i.e., a nucleophilic attack of toluene on the carbon of the protonated (complexed) *n*-propyl chloroformate.

TABLE 3

Nafion-H-Catalyzed Gas-Phase Alkylation of Toluene with Alkyl Oxalates $(COOR)_2$

| *R* | Feed rate (ml/min) | Temp (°C) | Percentage alkylation | Percentage isomer distribution | | |
|---|---|---|---|---|---|---|
| | | | | *ortho* | *meta* | *para* |
| $CH_3-$ | 0.022 | 189 | 12 | 50 | 18 | 32 |
| | 0.044 | 188 | 5 | 56 | 15 | 29 |
| | 0.044 | 194 | 10 | 55 | 17 | 28 |
| | 0.044 | 224 | 18 | 55 | 17 | 28 |
| $CH_3-CH_2-$ | 0.022 | 198 | 69 | 15 | 57 | 28 |
| | 0.044 | 198 | 57 | 17 | 52 | 31 |
| | 0.088 | 199 | 45 | 22 | 44 | 34 |
| | 0.176 | 199 | 33 | 27 | 38 | 35 |
| | 0.044 | 181 | 47 | 25 | 37 | 38 |
| | 0.044 | 164 | 38 | 28 | 33 | 39 |

### *Alkylation of Toluene with Alkyl Oxalates*

Dimethyl oxalate was found to have an alkylating ability comparable to that of methyl alcohol (*9*) in alkylations over Nafion-H catalyst (Table 3). As is the case with methylation with methyl alcohol, a high *ortho* : *para* ratio is obtained, indicating a highly reactive alkylating species.

Previous work (*6*) showed that 3–5% ethylbenzene was formed in the alkylation of benzene with ethyl alcohol over Nafion-H at 190–210°C. It was also found (*7*) that only 5.2% ethyltoluenes were formed when ethyl chloride was used as the ethylating agent over Nafion-H at 195°C. The present study shows that the alkylating ability of diethyl oxalate is much higher than that of ethyl alcohol or ethyl chloride. A 70% conversion of diethyl oxalate was observed in its ethylation of toluene over Nafion-H at 198°C (Table 3).

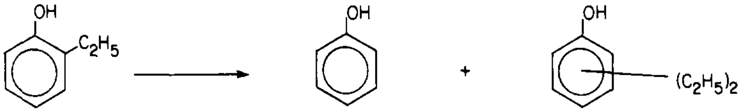
It has been shown in our previous work (*6*) that the Nafion-H catalyst has a limited thermal stability and must generally be used below 200°C. At temperatures above 200°C, the catalytic activity is irreversibly decreased. It is apparent from the data in Table 3 that, whereas upon increasing the temperature from 188 to 194°C, the yield of xylene formation increases from 5 to 10%, raising the temperature further to 224°C increases the yield only to 18%. The nonlinear increase of yield with temperature is again attributed to the thermal deactivation of the catalyst.

### *Alkylation of Phenol*

The experimental results regarding the alkylation of phenols and anisoles, cited in the literature, point to a controversy on the question whether anisole (phenetoles, etc.) serves as an intermediate in the ring methylation (alkylation) of phenol. When alkylation of phenol is carried out over alumina (*13*), alkoxybenzenes were reported to be intermediates in the ring alkylation process. By using the same catalyst, Kannan and Pillai (*14*) suggested that O- and C-alkylations are parallel reactions.

In our previous study of the alkylation of phenol over Nafion-H (*15*), methyl alcohol was used as the alkylating agent. The alkylation reactions were carried out at 200°C. At these temperatures, isomerization of anisole and phenetole to cresols and ethyl phenols took place. Consequently, it could not be unequivocally decided whether O- and C-alkylations were parallel reactions or not. At temperatures below 130°C, methyl alcohol was practically unreactive as an alkylating agent under the conditions employed.

However, when anisole or phenetole was heated for 6 hr to 130°C, in the presence of Nafion-H, it was recovered unchanged. Similarly, when alkyl phenols or cresols were treated in the same way, no significant isomerization took place. In the reaction of *o*-ethyl phenol, only minor traces of phenol and the diethyl phenols, the product of disproportionation, were detected.



These findings lead to the conclusion that any C- or O-alkylation in the liquid phase, under similar experimental conditions, must derive from competing direct alkylation (Table 4).

Contrary to the liquid-phase studies carried out at temperatures below 130°C, at higher temperatures in the gas phase, phenetole and anisole are readily rearranged over Nafion-H catalyst. When anisole vapors were passed over Nafion-H at 205°C, a 56% rearrangement was observed (*15*). Phenetole, as expected, underwent rearrangement even more readily. Only

TABLE 4

Liquid-Phase Alkylation of Phenol with Alkyl Esters over Nafion-H Catalyst

| Alkylating agent | Temp (°C) | Time (hr) | Percentage conversion of ester | $C_6H_5OR$ | $RC_6H_4$–OH | Percentage alkyl phenol | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | *ortho* | *meta* | *para* |
| $(COOCH_3)_2$ | 100 | 0.5 | 3.5 | 57.2 | 42.8 | 26.8 | 6.4 | 66.8 |
| | | 1 | 4.5 | 71.9 | 28.1 | 30.5 | 5.9 | 63.6 |
| | | 3 | 8.1 | 85.1 | 14.9 | 13.8 | 8.7 | 77.5 |
| $(COOC_2H_5)_2$ | 130 | 1 | 13.7 | 62.8 | 37.2 | 71.0 | 7.3 | 21.7 |
| | | 2 | 19.9 | 77.5 | 22.5 | 74.0 | .7 | 25.3 |
| | | 4 | 25.2 | 70.2 | 29.8 | 70.4 | 2.5 | 27.1 |
| | | 6 | 33.2 | 65.2 | 34.8 | 69.3 | 1.9 | 28.8 |
| $ClCOOC_2H_5$ | 100 | 1 | 5.8 | 29.1 | 70.9 | 64.8 | 12.2 | 23.0 |
| | | 3 | 25.4 | 23.1 | 76.9 | 63.6 | 12.7 | 23.7 |
| | | 6 | 24.7 | 22.5 | 77.5 | 63.6 | 12.8 | 23.6 |

traces of unreacted phenetole were detected after passing its vapors over Naifon-H at 202°C at a similar space velocity as in the case of anisole (Table 5). Besides O → C-ethyl migration, some loss of ethyl groups was also observed in these experiments, most probably due to dealkylation, followed by deprotonation, giving ethylene.

In preceding studies, only traces (~1%) of *m*-cresol were formed by the rearrangement of anisole over Nafion-H and in the methylation of phenol with methyl alcohol (*9*). At the same time, the observed *para* : *ortho* isomer ratio was ~2.

In the present study, when methyl chloroformate was used as the alkylating agent (Table 6), under conditions similar to those used in the previous study (*9*), the *para* : *ortho* isomer ratio was 1 : 1. By decreasing the temperature from 200 to 140°C, the*para* : *ortho* ratio increased to 1.5 : 1, and the amount of *m*-cresol increased from 2.8 to 34.2%.

Anisole (40%) was formed when methyl chloroformate was reacted with phenol over Nafion-H at 200°C. A comparable relative amount of anisole was left unchanged in the rearrangement of anisole over Nafion-H catalyst under similar conditions. The yield of anisole in the methylation of phenol is slightly temperature dependent. By lowering the temperature from 200 to 140°C, the yield of anisole formed increased from 40 to 52%.

When phenol was alkylated with diethyl oxalate or ethyl chloroformate only 1–2% phenetole was formed at 200°C (with a feed rate of 0.044 ml/min). This is in agreement with the relative ease with which phenetole underwent disproportionation (Table 5). At lower temperatures, the yield of phenetole increased due to the slower rate of its disproportionation.

The experimental results indicate that in the gas phase reactions, two processes are taking place: alkylation and competing dealkylation. Although almost all the alkylating agent is consumed in the reaction,

TABLE 5

Disproportionation of Phenetole over Nafion-H Catalyst in the Gas Phase

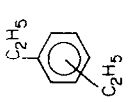
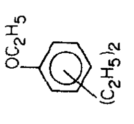
| Feed rate (ml/min) | Temp (°C) | Percentage composition | | | | | | Percentage recovered ethyl groups |
|---|---|---|---|---|---|---|---|---|
| | | PhOH | PhOEt | Ethyl phenols | Ethyl phenols (*ortho* : *meta* : *para*) |  |  | |
| 0.044 | 202 | 55.7 | 0.1 | 36.6 | (40.7 : 36.9 : 22.4) | 1.0 | 6.5 | 51.7 |
| 0.088 | 202 | 53.7 | 2.5 | 34.3 | (48.4 : 22.4 : 29.2) | 0.5 | 9.0 | 55.8 |
| 0.176 | 202 | 54.0 | 6.8 | 27.9 | (46.2 : 19.7 : 34.1) | 0.5 | 10.8 | 57.3 |
| 0.044 | 175 | 45.1 | 28.6 | 18.1 | (48.6 : 13.8 : 37.6) | 3.2 | 5.0 | 63.1 |
| 0.044 | 160 | 39.1 | 42.1 | 12.5 | (51.2 : 11.2 : 37.6) | 3.4 | 2.9 | 67.2 |

TABLE 6

Gas-Phase Alkylation of Phenol with Diethyl Oxalate[a] and Alkyl Chloroformate[b] over Nafion-H Catalyst (1.0 g)

| Alkylating agent | Feed rate (ml/min) | Temp (°C) | (Percentage conversion based on alkylating agent) | (Percentage O-alkylation) | Percentage alkyl phenols | | |
|---|---|---|---|---|---|---|---|
| | | | | | *ortho* | *meta* | *para* |
| $(COOC_2H_5)_2$ | 0.044 | 200 | 62 | 1.0 | 45.3 | 32.7 | 22.0 |
| | 0.088 | 200 | 60 | 9.6 | 49.3 | 24.7 | 26.0 |
| | 0.176 | 200 | 60 | 14.2 | 52.5 | 18.0 | 29.5 |
| | 0.044 | 176 | 58 | 15.9 | 50.8 | 15.9 | 33.3 |
| | 0.044 | 160 | 55 | 20.5 | 55.5 | 13.1 | 31.4 |
| $ClCOOC_2H_5$ | 0.044 | 200 | 65 | 2.0 | 50.6 | 23.7 | 25.7 |
| | 0.088 | 200 | 60 | 7.8 | 50.2 | 23.6 | 26.2 |
| | 0.176 | 200 | 61 | 12.7 | 52.7 | 19.3 | 28.0 |
| | 0.044 | 160 | 57 | 12.8 | 47.8 | 19.3 | 32.9 |
| $ClCOOCH_3$ | 0.044 | 200 | 78 | 29.7 | 68.2 | 2.8 | 30.0 |
| | 0.044 | 180 | 67 | 50.4 | 65.5 | 10.8 | 23.7 |
| | 0.044 | 160 | 55 | 49.8 | 48.6 | 24.2 | 27.2 |
| | 0.044 | 140 | 40 | 52.2 | 37.9 | 34.2 | 27.9 |

[a] Diethyl oxalate : phenol = 1 : 4 (mole/mole).

[b] Alkyl chloroformate : phenol = 1 : 2 (mole/mole).

only ca. 60% of alkylated phenols were recovered. This finding is attributed to the competing dealkylation processes.

It is well known that the tendency to cleave or transfer of methyl groups attached to aromatic rings is smaller than that of ethyl groups. This explains why, at higher temperatures, the yield of alkylation of phenol with methyl chloroformate is higher than that with ethyl chloroformate (Table 6).

## ACKNOWLEDGMENT

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