

POLYMERIZATION AND TRANSALKYLATION REACTIONS OF TOLUENE ON Cu(II)-MONTMORILLONITE

T. TIPTON¹ AND L. E. GERDOM²

¹ Civil Engineering Laboratory, Air Force Civil Engineering Support Agency
Tyndall Air Force Base, Florida 32403-5319

² Division of Natural Science, Mobile College, Mobile, Alabama 36663-0220

Abstract—Products resulting from the reaction of toluene with Cu(II)-montmorillonite were analyzed using GC/MS, HPLC/MS, GPC, and FTIR methods. Numerous oligomers of toluene were observed, extending at least as high as the resolution limit (1500 g/mol) of the GPC column. The FTIR spectrum of the nonvolatile components of the extract was very similar to that of liquid toluene. GC/MS data on the volatile components revealed dimers, trimers, and a multitude of transmethylated products. Oligomerization proceeded via both ring-ring (i.e., polyphenyl) and ring-methyl linkages. The primary transmethylated products were tert-butylbenzene and isopropylxylene, indicating a competition between ring- and side-chain methylations. The side-chain substitutions cannot be explained in terms of the aromatic radical cation intermediate which typically forms in arene/clay reactions. A consideration of alkylbenzene reactions observed in various other media suggests that the present transmethylation reactions occur via a benzyl cation intermediate.

Key Words—FTIR, GC/MS, Gel permeation chromatography, Montmorillonite, Polymerization, Toluene, Transalkylation.

INTRODUCTION

Complexation and polymerization reactions of arenes on montmorillonites have been studied extensively in recent years (Laszlo, 1987; Soma *et al.*, 1985; Theng, 1971; Mortland, 1970). Much of this work consisted of *in situ* spectroscopic measurements on clay samples using infrared, Raman, ultraviolet-visible, ESR, NMR, and X-ray diffraction techniques. Only a minor part of this work involved the use of extraction and separation methods to identify reaction products formed in the interlamellar regions of the clays. In some cases, clay-organic reactions are simple enough that direct spectroscopic measurements are sufficient to characterize them (Johnston *et al.*, 1991). However, complex systems can be analyzed more effectively by extracting reaction products from the clay and separating them via gas or liquid chromatography. The present paper explores the use of supercritical fluid extraction, particle-beam HPLC/MS, GC/MS, gel permeation chromatography (GPC), and FTIR spectroscopy to analyze a relatively simple reaction system: toluene on Cu(II)-exchanged montmorillonite.

Numerous investigators have reported some success in removing oligomers from clays using liquid solvents such as methanol, dichloromethane, acetone, hexane, NaOH and HF (Carrado *et al.*, 1990; Soma *et al.*, 1986; Chiou and Shoup, 1985; Sawhney *et al.*, 1984). These solvents are seldom able to remove all organic reaction products from clays. Recently, supercritical fluids have been used increasingly for soil extractions since they are usually more effective than liquid solvents in penetrating microporous materials (Hawthorne and Mil-

ler, 1987). However, the effectiveness of supercritical fluids for removing polymerization products of aromatic compounds from clays does not appear to have been tested until now.

Previous workers have analyzed clay extracts by GPC, HPLC, HPLC/MS, MS, and GC/MS (Carrado *et al.*, 1990; Mortland and Boyd, 1989; Soma *et al.*, 1986; Sawhney *et al.*, 1984; Mortland and Halloran, 1976; Tricker *et al.*, 1975; Fenn *et al.*, 1973). Some of these studies were superficial in that mass spectrometry was performed on unseparated extracts. The presence of complexes and oligomers was established by these studies but little effort was directed toward a detailed identification of products.

Toluene was chosen as the prototype arene for this study because it is a significant soil and groundwater contaminant, and its reactions on montmorillonite have been examined extensively. Toluene is oxidized to a radical cation when sorbed onto Cu(II)-exchanged montmorillonite under very dry conditions (Doner and Mortland, 1969; Soma *et al.*, 1985). This reaction changes the color of the clay from light blue to dark green. The radical cation has been shown by ESR data to be aromatic and planar (Pinnavaia and Mortland, 1971). The changes that take place in the IR, diffuse-reflectance, Raman, and ultraviolet-visible spectra during the formation of the radical cation have been reported in detail (Pinnavaia and Mortland, 1971; Matsunaga, 1972; Soma *et al.*, 1985; Soma *et al.*, 1986).

The oxidation of toluene on Cu(II)-exchanged montmorillonite leads to the formation of partially extractable polymer products. The only analysis of these prod-

ucts that was previously attempted consisted of mass spectral measurements on an unseparated extract (Tricker *et al.*, 1975). Dimers and trimers of toluene were identified but no specific compound identifications were made. Elsewhere, it was reported that the reactions of toluene on montmorillonite are anomalous with respect to those of other methyl-substituted benzene compounds but no details were given (Soma *et al.*, 1985).

The present study used gas and liquid chromatography to separate products of the reaction of toluene with Cu(II)-exchanged montmorillonite. GPC was used to obtain a broader picture of the oligomer distribution. FTIR spectroscopy was used along with mass spectrometry to identify the products.

EXPERIMENTAL

The SAz-1 Cheto montmorillonite was collected from Apache County, Arizona, and distributed by the Source Clays Repository of the Clay Minerals Society at the University of Missouri. The procedure used for preparation of the Cu(II)-exchanged form of this clay (Cu-SAz1) has been described elsewhere (Johnston *et al.*, 1991). We obtained the toluene sample from Aldrich Chemical Company (HPLC grade).

Reaction of liquid toluene with Cu-SAz1 was performed in a 2-ml supercritical fluid extraction cell (Suprex Model EX-60002). This cell consisted of a stainless steel cylinder capped with a pair of frits. The cylinder was encased in a threaded stainless steel housing which could be interfaced with a pair of 1/16-in stainless steel tubes via Valco fittings. The cell was sealed by compression after it was loaded to capacity with toluene and clay. This cell had several advantages over a conventional refluxing apparatus: (1) volatile reaction products could not escape from the cell during the reaction; (2) the liquid fraction of the product mixture could be easily separated from the clay by applying pressure through the frits in the extraction cell; (3) the liquid residue could be injected into a GC without prior vaporization of excess unreacted contaminant; and (4) the cell could be conveniently plumbed into a supercritical fluid extractor or attached to an HPLC pump for liquid extraction.

The extraction cell was loaded with 800 mg of Cu-montmorillonite (Cu-SAz1) and 1.5 ml of toluene, and heated to 160°C for periods ranging from 0.5 hr to 15 hr. The elevated pressure of the cell (resulting from heating a closed vessel) did not have any noticeable effect on the composition or quantity of the product mixture. After the cell had cooled to room temperature, the liquid residue was blown into a glass vial with compressed air. This residue was analyzed along with subsequent extracts obtained using additional solvents.

A supercritical fluid extractor (Suprex Model SFE/

50) filled with CO₂ solvent was used to extract some of the clay samples. Adding 0.2 ml of methanol to the cell prior to the introduction of CO₂ greatly enhanced the efficiency of the extractions. The extractions were programmed at 50°C and 150 atm for 10 min; 60°C and 200 atm for 10 min; and 70°C and 250 atm for 10 min. For the present application, supercritical fluid extraction (SFE) did not have a significant advantage over extraction with liquid acetone. The extractable products were so soluble in liquid acetone that efficient extractions could be done simply by attaching the SFE cell to an HPLC pump and running a few ml of solvent through the cell. However, SFE is much cleaner and more efficient than Soxhlet extraction, and would be the preferred method if an extremely efficient liquid solvent were not available.

The extracts were separated into their components using either GC or HPLC. Both of these techniques were combined with mass spectrometry to identify the components. A spectral library (McLafferty and Stauffer, 1988) aided in the identifications.

GC/MS spectra were recorded on a Hewlett-Packard Model 5980A GC, coupled with a Model 5970 mass selective detector. A 1.0- μ l sample was injected via the splitless mode into a 30-m long, 0.25-mm i.d. capillary column coated with 1 μ m of 5 percent phenyl polymethylsiloxane (J&W Scientific). The oven was held at 40°C for 4 min, ramped to 250°C at 10°C/min, and held at 250°C for 10 min. The carrier gas was helium, and the column head pressure was 15 psi above atmospheric pressure.

HPLC/MS spectra were obtained using a Hewlett-Packard Series 1050 HPLC, coupled with a mass selective detector (Model 5987A) via a particle-beam interface (Model 59980A). Initial runs were performed using a 250-mm length, 4.6-mm i.d. stainless steel column containing reverse phase 5- μ m C₁₈ packing (Alltech). For these runs, a preliminary separation of the extract was effected via vacuum distillation at 150°C. Three carrier solvents were tested: 80 percent methanol/20 percent water, 80 percent acetonitrile/20 percent water, and 100 percent acetone. Additional runs were made using a 300-mm length, 7.8-mm i.d., 10-nm pore gel-permeation column (Waters ULTRA-STYRAGEL®) with toluene solvent. All HPLC/MS runs were made using an injection volume of 100 μ l. Preliminary HPLC chromatograms were collected using detection at 254 nm.

FTIR data were recorded on a Nicolet 740 FTIR spectrometer using a 2-mm source aperture, a KBr beamsplitter, and an MCT-A detector. Normally, the infrared samples were incorporated into KBr pellets or sandwiched between two KBr plates. Additional FTIR data were recorded on samples which were eluted from a GC (Hewlett-Packard Model 5890-II) and condensed onto a copper mirror cooled by a cryostat (Air Products Displex Model CSA-202).

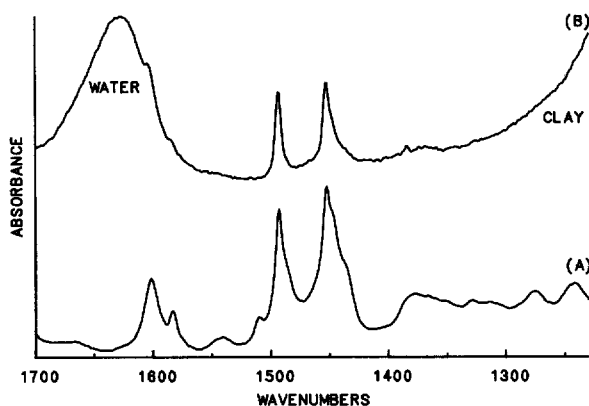


Figure 1. FTIR KBr-pellet spectra of (A) an acetone extract of toluene/Cu-SAz1, and (B) toluene/Cu-SAz1 prior to extraction.

RESULTS AND DISCUSSION

Extraction

None of the supercritical fluid mixtures or liquid solvents that were tested were able to remove all of the products of the reaction of toluene with Cu-SAz1. The incompleteness of the extraction was evidenced by residual infrared bands in the clay spectra and by the difference in color between the extracted clay and the unreacted clay. The clay changed from blue to green on exposure to toluene but became gray rather than blue after extraction. The reactivity of the gray form of the clay toward further treatments with toluene was minimal, indicating that the Cu(II) ions had probably been reduced.

The extract of the reacted clay was a brown oily substance. The mass ratio of the extract to the dry Cu-SAz1 was about 2 percent for a freshly prepared sample heated for 2.0 h in a sealed cell at 160°C. However, the reactivity of the Cu-SAz1 starting material virtually

vanished when it was allowed to age for several months. Similar behavior has been reported for Fe(III)-montmorillonite (Pinnavaia *et al.*, 1974).

The amount of organic material that remained on the clay after extraction could not be accurately weighed because the clay mass was too sensitive to changes in relative humidity. This quantity was also difficult to estimate spectroscopically because the high-boiling components of the extract had to be pulverized before their infrared absorption could be observed.

FTIR

Figure 1 compares the spectrum of a toluene/Cu-SAz1 sample recorded prior to extraction with the spectrum of the extract. All of the organic bands that appear in the former also appear in the latter (the band at 1630 cm^{-1} and the steep increase in absorption near 1200 cm^{-1} are due to water and Cu-SAz1 respectively). These bands do not have proportional intensities because not all of the organic products were extractable. Some new bands can be observed in the spectrum of the extract because the reaction products were much more concentrated in this sample than in the clay sample from which the extract was obtained. Figure 1B contains fewer bands than a previously published spectrum of toluene on a dry Cu(II)-montmorillonite film (Pinnavaia and Mortland, 1971) because bands due to physisorbed toluene and the radical cation of toluene vanished on re-exposure of the clay to ambient conditions.

The FTIR spectra of two components of the toluene/Cu-SAz1 extract are compared to the spectrum of pure liquid toluene in Figure 2. Assignment of the toluene monomer spectrum has been discussed elsewhere (Pinnavaia and Mortland, 1971; La Lau and Snyder, 1971). Figure 2B was obtained by injecting the extract into a GC and collecting a portion of the effluent on a cryogenically cooled mirror. The product was identified as (methylphenyl) phenylmethane (i.e., benzyltoluene). The other component (Figure 2C) is the residue resulting from vacuum distillation of the extract at 150°C. The close resemblance of this spectrum to that of benzyltoluene suggests that the residue consisted of toluene polymers.

GC/MS

GC/MS analyses were performed on three samples: (1) an acetone extract of a Cu-SAz1 sample exposed to toluene vapor for 8 days at room temperature in a desiccator containing P_2O_5 ; (2) a portion of the toluene solution resulting from heating Cu-SAz1 together with toluene in a sealed cell at 160°C for 2 hr; and (3) an acetone extract of the reacted Cu-SAz1 used in the preparation of sample 2.

A representative GC/MS spectrum (sample 2) is shown in Figure 3, and assignments for all three of the above samples are given in Tables 1 and 2. Sample 1

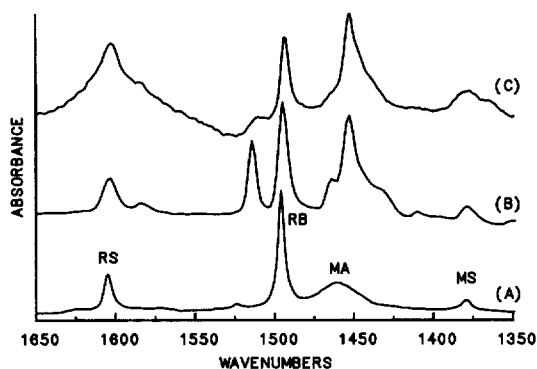


Figure 2. FTIR spectra of (A) liquid toluene, (B) a toluene dimer mixture extracted from toluene/Cu-SAz1, and (C) the residue from a 150°C vacuum distillation of a toluene/Cu-SAz1 extract. Approximate descriptions of the toluene vibrations shown on this plot are (La Lau and Snyder, 1971): RS = C-C ring stretch, RB = ring H-C-C bend, MA = methyl asymmetric bend, and MS = methyl symmetric bend.

Table 1. GC/MS data for extracts of toluene/Cu-SAz1 (excluding compounds listed in Table 2).

MW	Sample ¹	Assignment	Retention time (min)
		Oxidation products:	
108	1	benzaldehyde	12.78
108	1, 3	methylphenol	14.49 14.83
		Cyclization products:	
174	2, 3	trimethyltetralin	18.10
188	2, 3	pentamethylindan	18.42 19.12
250	3	phenyl-trimethyltetralin	? 26.89 27.16
264	2, 3	phenyl-pentamethylindan	? 26.51 26.71 27.08 27.33
		Oligomers:	
170	2, 3	trimethylnaphthalene	22.74
182	1, 2, 3	dimethylbiphenyl	22.30
182	1, 2, 3	o-benzyltoluene	22.46
182	1, 2, 3	p-benzyltoluene	22.51
196	3	monomethylated dimer	22.98 24.59
196	2, 3	monomethylated dimer	23.45 23.55 23.71 23.84
196	2	monomethylated dimer	23.94
210	2, 3	dimethylated dimer	23.98 24.07 24.26 24.37
210	2, 3	dimethylated dimer	24.51 25.34
210	3	dimethylated dimer	24.67 25.05 25.21 25.44
224	2, 3	trimethylated dimer	24.44
224	3	trimethylated dimer	24.79 25.14 25.88
238	3	tetramethylated dimer	25.79 25.98 26.23 26.40
252	3	pentamethylated dimer	26.93 27.73
272	1	pentamethylated trimer	31.34 31.62
272	1, 3	pentamethylated trimer	32.67 32.80 33.89
286	3	monomethylated trimer	33.75 34.42
286	2, 3	monomethylated trimer	34.16
		Unassigned peaks:	
?	2		23.36
?	3		15.94 16.90 17.48 17.77
			27.90 28.33 30.10 31.39

¹ See text.

produced the poorest GC/MS spectrum since the reaction temperature was much lower than for the other two samples. Benzaldehyde was the only significant component of this sample that was not also present in the heated samples. Its formation was likely enhanced by the long exposure of the sample to ambient air. The remainder of sample 1 consisted almost entirely of dimers ($m/z = 182$) and trimers ($m/z = 272$) of toluene. The dimer components were composed of dimethylbiphenyl, o-benzyltoluene, and p-benzyltoluene. The presence of both dimethylbiphenyl and benzyltoluene indicates that there were two competing reaction pathways. One, and possibly both, of these pathways continued at least to the trimer stage, as evidenced by the close resemblance of some of the observed spectra to that of bis-(methylphenyl) phenylmethane (Elder *et al.*, 1981). The uncertainty in the trimer identifications is due to the lack of library data for these compounds and the possible similarity in the spectra of bis-(methylphenyl) phenylmethane and trimethylterphenyl. The presence of dibenzyltoluene was ruled out since cleavage of the benzyl-phenyl bond produces an easily recognizable ion-fragment pattern (Elder *et al.*, 1981). The trimerization pathway was therefore: toluene > (meth-

ylphenyl) phenylmethane > bis-(methylphenyl) phenylmethane; and/or toluene > dimethylbiphenyl > trimethylterphenyl. The latter pathway agrees with that of toluene polymerization with $AlCl_3/CuCl_2$ and is analogous to that of benzene polymerization on Cu(II)-montmorillonite (Kovacic and Ramsey, 1969; Soma *et al.*, 1985). Evidently, polymerization of toluene pro-

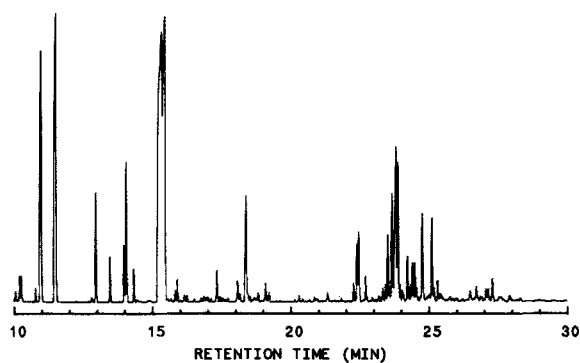


Figure 3. GC/MS chromatogram of the toluene solution resulting from heating Cu-SAz1 together with toluene in a sealed cell at 160°C for 2 hr. The assignment of this chromatogram is given in Tables 1 and 2.

Table 2. Retention times (min) of transmethylation products of toluene: $C_6H_{(5-N)}(CH_3)_NCH_{(3-n)}(CH_3)_n$.

N	n = 0	n = 1	n = 2	n = 3
0				13.46 (3)
1	11.01 (2) ¹ 11.55 (2)	13.50 (2)	14.01 (2) 14.36 (2)	15.37 (2, 3)
2	12.99 (2) 13.50 (2)	14.10(2)	15.50 (2)	17.37 (2, 3)
3	15.93 (2)			
4	18.69 (2)			
5				

¹ Multiple entries indicate separate isomers. The sample number is given in parentheses (see text).

ceeds by at least two different mechanisms depending on the reaction conditions. A previous study of toluene on Cu(II)-montmorillonite reported the presence of oligomers but did not give any further details (Tricker *et al.*, 1975).

No tetramers of toluene were observed in any of the samples even when the upper temperature limit of the GC was raised to 350°C from the usual 250°C. Nevertheless, liquid chromatography data (discussed below) indicate that polymerization occurred beyond the trimer stage.

Sample 2 contained a variety of compounds that were not present in sample 1. Sample 2 was collected primarily for the purpose of identifying volatile compounds that would normally have escaped from the reaction vessel prior to the GC/MS analysis. Most of these volatile products resulted from side-chain and ring substitutions of the methyl group into toluene (Table 2). It might be expected that benzene would be present as a byproduct of the observed reactions but we detected no more than a trace of it. Two different product distributions are represented in Table 2, corresponding to samples 2 and 3. Sample 2 contained

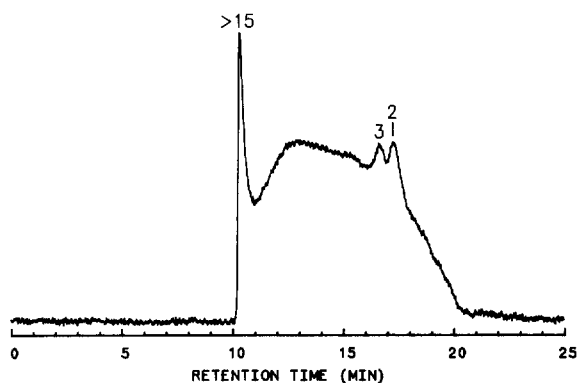


Figure 4. GPC chromatogram of the acetone extract of a Cu-SAzi sample heated together with toluene in a sealed cell at 160°C for 2 hr. The labeling of the peaks signifies the number of toluene monomer units per oligomer.

products which were multiply methylated in both the side chain and the ring, with a propensity for the former. The major transmethylation products were isopropylxylene and tert-butyltoluene. Sample 3 exhibited side-chain substitutions exclusively. The results for sample 3 can be attributed partly to a sample preparation procedure which favored components that were nonvolatile and relatively difficult to extract.

Additional transmethylation products were observed in the oligomer components of sample 2. Dimer derivatives containing as many as three extra methyl substituents were observed along with a monomethylated trimer. It was not possible to distinguish between ring- and side-chain alkylation products in these cases because reference standards were not available.

The disproportionation of toluene has been studied extensively but only ring substitutions of the methyl group have previously been reported (Uguina *et al.*, 1991; Aneke *et al.*, 1979; Schriesheim, 1961). A recent study of the alkylation of toluene by methanol on alumina-pillared montmorillonite revealed the formation of xylenes and trimethylbenzenes but no side-chain products (Horio *et al.*, 1991). Similarly, the reaction of anisole on pillared bentonite yielded transmethylated ring-substituted products but no side-chain substituted products (Carrado *et al.*, 1990).

The radical cation mechanism, which accounts for many arene reactions on clays, does not explain side-chain alkylation. However, there is evidence from the literature that a benzylic cation can be produced from primary alkylbenzenes via hydride abstraction by a Lewis acid species (Buchanan *et al.*, 1985). Cyclization, transalkylation, and side-chain oxidation of alkylbenzenes have been explained in terms of a benzylic cation mechanism (Buchanan *et al.*, 1985). The high acidity of the interlayers of dry clays provides a favorable environment for benzylic cation formation.

Further evidence of a possible benzylic cation mechanism was obtained through the identification of ring-closure products such as trimethyltetralin in sample 2. Previous work on the molten salt catalysis of bond-cleavage reactions of arenes indicates that ring closure can proceed via the benzylic cation mechanism (Buchanan *et al.*, 1983; Buchanan *et al.*, 1985). The side chains of multimethylated toluene molecules could combine via ring closure, although the details of such reactions are not clear from present data.

Sample 3 contained a wider variety of compounds than either of the other samples but all of the additional compounds observed in the GC/MS spectra were either closely related to those already discussed, or could not be identified. These unidentified compounds comprised only about 4 percent of the total ion intensity. A significant portion of sample 3 consisted of material that was insufficiently volatile to pass through the GC column. This material was analyzed later using liquid chromatography (see below).

HPLC/MS and GPC

The GC/MS method discussed in the previous section was effective only for compounds with molecular weights of 300 atomic mass units or less. Therefore, HPLC/MS data were collected to characterize the non-volatile components of the toluene/Cu-SAz1 extracts. Initial HPLC/MS runs, performed using a reverse phase C₁₈ column, were unsuccessful because no suitable solvent could be found which could compensate for the low sensitivity of the HPLC/MS instrument. Subsequent runs were made using a gel permeation column designed to separate compounds with molecular weights in the range of 50 to 1500 mass units.

A typical GPC chromatogram of a toluene/Cu-SAz1 extract is shown in Figure 4. The numbering of the peaks in this figure signifies the number of monomer units in the observed toluene oligomers. The retention times ranged from 10.4 min for polymers to 21 min for monomers. Toluene does not appear in this chromatogram because toluene was used as the solvent and its signal was ratioed out. Nearly all of the extract was soluble in toluene even though toluene was not very effective in extracting reaction products from the clay. An approximate calibration of the chromatogram was obtained with polystyrene standards. A more reliable assignment of the 17.3 min (dimer) and 16.6 min (trimer) peaks was made via GC/MS analyses of the HPLC effluent. The lack of structure in the range of 11 min to 16 min of the chromatogram prevented an extrapolation of the dimer and trimer assignments to the rest of the chromatogram. Nevertheless, it is clear that a broad distribution of oligomers was present, extending probably to at least 15 monomer units. Similar results were reported for polymerization of phenol on Fe(III)- and Cu(II)-montmorillonite (Soma *et al.*, 1986).

CONCLUSIONS

The present study of the reaction of toluene with Cu-SAz1 has revealed a surprisingly diverse array of isomeric oligomers and isomeric alkylated oligomers. Present evidence in combination with previous results indicates that transalkylation is an important reaction pathway accompanying the polymerization of arenes on clays. The observed reaction products are consistent with a reaction scheme involving both aromatic radical cations and benzyl cations. The benzyl cation mechanism may be operative only for primary alkylbenzenes since the aromatic radical cation mechanism appears to explain the products obtained from numerous other arene/clay reactions.

ACKNOWLEDGMENT

We wish to thank Dr. H. Mayfield for assistance in running the GC/MS and GC/HPLC samples.

REFERENCES

- Aneke, L. E., Gerritsen, L. A., van den Berg, P. J., and de Jong, W. A. (1979) The disproportionation of toluene over a HY/ β -AlF₃/Cu catalyst: *J. Catal.* **59**, 26–36.
- Buchanan, A. C., III, Chapman, D. M., and Smith, G. P. (1985) Redox vs. Lewis acid catalysis. The chemistry of 1,2-diarylethanes in SbCl₅-rich molten salt media: *J. Org. Chem.* **50**, 1702–1711.
- Buchanan, A. C., III, Dworkin, A. S., and Smith, G. P. (1983) Molten salt catalysis. Selective bond cleavage reactions for some α , -diphenylalkanes in SbCl₅ melts: *J. Am. Chem. Soc.* **105**, 2843–2850.
- Carrado, K. A., Hayatsu, R., Botto, R. E., and Winans, R. E. (1990) Reactivity of anisoles on clay and pillared clay surfaces: *Clays & Clay Minerals* **38**, 250–256.
- Chiou, C. T. and Shoup, T. D. (1985) Soil sorption of organic vapors and effects of humidity on sorptive mechanism and capacity: *Environ. Sci. Technol.* **19**, 1196–1200.
- Doner, H. E. and Mortland, M. M. (1969) Benzene complexes with copper(II) montmorillonite: *Science* **166**, 1406–1407.
- Elder, V. A., Proctor, B. L., and Hites, R. A. (1981) Organic compounds found near dump sites in Niagara Falls, New York: *Environ. Sci. Technol.* **15**, 1237–1243.
- Fenn, D. B., Mortland, M. M., and Pinnavaia, T. J. (1973) The chemisorption of anisole on Cu(II) hectorite: *Clays & Clay Minerals* **21**, 315–322.
- Hawthorne, S. B. and Miller, D. J. (1987) Extraction and recovery of polycyclic aromatic hydrocarbons from environmental solids using supercritical fluids: *Anal. Chem.* **59**, 1705–1708.
- Horio, M., Suzuki, K., Masuda, H., and Mori, T. (1991) Alkylation of toluene with methanol on alumina-pillared montmorillonite: *Appl. Catal.* **72**, 109–118.
- Johnston, C. T., Tipton, T., Stone, D. A., Erickson, C., and Trabue, S. L. (1991) Chemisorption of p-dimethoxybenzene on copper-montmorillonite: *Langmuir* **7**, 289–296.
- Kovacic, P. and Ramsey, J. S. (1969) Polymerization of aromatic nuclei. XIV. Polymerization of toluene with aluminum chloride-cupric chloride: *J. Polym. Sci., A-1*, **7**, 111–125.
- La Lau, C. and Snyder, R. G. (1971) A valence force field for alkyl benzenes: Toluene, p-xylene, m-xylene, mesitylene, and some of their deuterated analogues: *Spectrochim. Acta* **27A**, 2073–2088.
- Laszlo, P. (1987) Chemical reactions on clays: *Science* **235**, 1473–1477.
- Matsunaga, Y. (1972) The diffuse reflection spectra of bentonites colored with various aromatic compounds and related ion-radical salts: *Bull. Chem. Soc. Japan* **45**, 770–775.
- McLafferty, F. W. and Stauffer, D. B. (1988) *The Wiley/NBS Registry of Mass Spectral Data*: 5th Ed., Wiley-Interscience, New York.
- Mortland, M. M. (1970) Clay-organic complexes and interactions: *Advan. Agron.* **22**, 75–114.
- Mortland, M. M. and Boyd, S. A. (1989) Polymerization and dechlorination of chloroethenes on Cu(II)-smectite via radical-cation intermediates: *Environ. Sci. Technol.* **23**, 223–227.
- Mortland, M. M. and Halloran, L. J. (1976) Polymerization of aromatic molecules on smectite: *Soil Sci. Soc. Amer. J.* **40**, 367–370.
- Pinnavaia, T. J. and Mortland, M. M. (1971) Interlamellar metal complexes on layer silicates. I. Copper (II)-arene complexes on montmorillonite: *J. Phys. Chem.* **75**, 3957–3962.
- Pinnavaia, T. J., Hall, P. L., Cady, S. S., and Mortland, M. M. (1974) Aromatic radical cation formation on the in-

- tracrystal surfaces of transition layer lattice silicates: *J. Phys. Chem.* **78**, 994–999.
- Sawhney, B. L., Kozloski, R. K., Isaacson, P. J., and Gent, M. P. N. (1984) Polymerization of 2,6-dimethylphenol on smectite surfaces: *Clays & Clay Minerals* **32**, 108–114.
- Schriesheim, A. (1961) Toluene disproportionation: *J. Org. Chem.* **26**, 3530–3533.
- Soma, Y., Soma, M., and Harada, I. (1985) Reactions of aromatic molecules in the interlayer of transition-metal ion-exchanged montmorillonite studied by resonance Raman spectroscopy. 2. Monosubstituted benzenes and 4,4-disubstituted biphenyls: *J. Phys. Chem.* **89**, 738–742.
- Soma, Y., Soma, M., and Harada, I. (1986) The oxidative polymerization of aromatic molecules in the interlayer of montmorillonites studied by resonance Raman spectroscopy: *J. Contaminant Hydrology* **1**, 95–106.
- Theng, B. K. G. (1971) Mechanisms of Formation of Colored Clay-Organic Complexes. A Review: *Clays & Clay Minerals* **19**, 383–390.
- Tricker, M. J., Tennakoon, D. T. B., Thomas, J. M., and Graham, S. H. (1975) Novel reactions of hydrocarbon complexes of metal-substituted sheet silicates: Thermal dimerisation of trans-stilbene: *Nature* **253**, 110–111.
- Uguina, M. A., Sotelo, J. L., and Serrano, D. P. (1991) Toluene disproportionation over ZSM-5 zeolite—Effects of crystal size, silicon-to-aluminum ratio, activation method and pelletization: *Appl. Catal.* **76**, 183–198.

(Received 8 April 1992; accepted 3 June 1991; Ms. 2205)