

## Regioselectivities of Nitration of Toluene on Bentonite Catalysts by the Use of Alkyl Nitrates

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Regioselectivities of nitration of toluene were investigated on the acid-treated bentonites catalysts by using alkyl nitrates. The reaction was highly *para* selective, compared as composition (*ortho/para* = 1.63) of nitro isomers of nitration of toluene with sulfonitric acid, up to *ortho-to-para* ratios of 0.52, 0.47, 0.41 and 0.41, respectively, when using *n*-propyl nitrate, *iso*-propyl nitrate, cyclohexyl nitrate, *iso*-octyl nitrate on bentonite of sulfuric acid treatment for 1 h. A radical cationic component was proposed to elucidate nitration mechanism according to the calculated and experimental results.

**Key Words:** Bentonite, Alkyl nitrate, Nitrotoluene, Regioselective nitration.

### INTRODUCTION

Electrophilic nitration of aromatic hydrocarbons has been studied extensively. The nitrating agents commonly used are sulfonitric acid, nitric acid-acetic anhydride and nitronium salts *etc.*<sup>1</sup>, which show low regioselectivity. Also, many practical problems remain unsolved. For example, the commercial production of *para*-nitrotoluene accompanied by great large amounts of less desirable *ortho*-nitro isomer is highly desirable. Until quite recently the *ortho* isomer represented a valueless waste product and affected environment seriously. Thus, there is a need for more regioselective control of electrophilic aromatic substitution. Catalysis of organic reactions by inorganic solids<sup>2</sup> is an important new dimension of preparative organic chemistry. Olah *et al.*<sup>3</sup> have surveyed that aluminum chloride could catalyze nitration of aromatics and improve regioselectivity. However, use of standard Lewis acid catalysts is confronted with problems such as their handling and the necessity of using large amounts of solvent. For such reasons and also because of a greater ease of setup and workup, solid catalysts have excited much interest. They include resins such as Nafion-H, modified alumina as well as a number of clays<sup>4-8</sup>. The latter heterogeneous catalysts are inexpensive by comparison with the Nafion-H polymer. They offer a wide range of active sites (*e.g.*, acidic site) for catalysis and most often can regenerate if deactivated during a reaction. Furthermore, they bring other assets. Constraining an organic molecule onto a solid surface has interesting consequences. The adsorbates undergo reduction in dimensionality, from a three-dimensional reaction to a surface. Thereby the frequency

of diffusional encounters increases. The adsorbates also migrate to catalytic sites with an attendant electronic redistribution, hence creating a reduction in the activation energy. The geometric consequence of anchoring onto a solid is to restrict the angles of attack, *i.e.*, to enhance selectivity. For these reasons, we have sought to devise an improved heterogeneous bentonite catalyst for selective nitration reactions. We now report the successful development of such a reaction, utilizing alkyl nitrates as the reagent and acid-treated bentonite as the catalyst.

### EXPERIMENTAL

All of the starting materials were chemical purity grade or above. The analyses of toluene and its nitro isomers were carried out by gas-liquid chromatography with a Shimadzu GC-2014C gas chromatography equipped with a hydrogen flame ionization detector and with a 30 m × 0.25 mm i.d. OV-101 glass capillary column with nitrogen as a carrier gas using *n*-dodecane as internal standard.

An acidic bentonite used for nitration catalyst was prepared by mixing 10 g commercial Na based bentonite and 800 mL 30 % of aqueous sulfuric acid solution. The resulting clay suspension was vigorously stirred under reflux for 1 h. Then the acid-treated bentonite was washed thoroughly with deionized water until without  $\text{SO}_4^{2-}$  and dried at 100 °C in air. The acidic bentonite was calcined in air at 300 °C for at least 12 h prior to use.

Followed by employing the above acidic bentonite as selective nitration catalyst, to 200 mL toluene was added 5 g alkyl nitrate and 8 g acidic bentonite. The reaction mixture

was vigorously stirred and refluxed for 16 h under a dry nitrogen atmosphere. At the end of the reaction, the mixture was cooled to room temperature and filtered. The filtrate was analyzed by gas-liquid chromatography.

## RESULTS AND DISCUSSION

The reaction procedure was applied to toluene substrate. The alkyl nitrates nitrating reagents selected involve *n*-propyl nitrate, *iso*-propyl nitrate, cyclohexyl nitrate and *iso*-octyl nitrate. In the presence of acid-treated bentonite, the regioselectivity for reaction shown in Table-1. The results clearly indicate that *para*-selective nitration of toluene is heightened although the reaction leads to lower yield. For the chosen alkyl nitrates, *para*-selectivities are in the order cyclohexyl nitrate > *iso*-octyl nitrate > *iso*-propyl nitrate > *n*-propyl nitrate. The *ortho/para* ratios follow the expected trend from 0.41 to 0.52 in accord with decreasing steric hindrance. With respect to the nitration of toluene, Table-2 shows a comparison of nitration of toluene with various nitrating reagents. The *para* selectivity is rather poor. In the present study we also found that alkyl nitrates did not act as nitrating agents in the absence of acidic bentonite catalyst. This apparent paradox may be explained by this catalyst offering the best compromise between reactivity and selectivity. We have not striven to optimize the procedure as to yields or selectivity. Undoubtedly, these will be further improved.

TABLE-1  
REGIOSELECTIVITIES OF NITRATION OF TOLUENE  
WITH ALKYL NITRATES ON ACIDIC BENTONITE

Alkyl nitrate	Nitrotoluene (%)			<i>ortho</i> / <i>para</i>	Yield (%)
	<i>ortho</i>	<i>meta</i>	<i>para</i>		
<i>n</i> -Propyl nitrate	34	1	65	0.52	22
<i>iso</i> -Propyl nitrate	32	Trace	68	0.47	14
Cyclohexyl nitrate	29	Trace	71	0.41	13
<i>iso</i> -Octyl nitrate	29	1	70	0.41	13

TABLE-2  
NITRATION SELECTIVITY OF TOLUENE WITH  
VARIOUS NITRATING REAGENTS<sup>1</sup>

Reagent	Nitrotoluene (%)			<i>ortho</i> / <i>para</i>
	<i>ortho</i>	<i>meta</i>	<i>para</i>	
HNO <sub>3</sub> -Ac <sub>2</sub> O	63	3	34	1.85
NO <sub>2</sub> <sup>+</sup> BF <sub>4</sub> <sup>-</sup>	65.4	2.8	31.8	2.06
HNO <sub>3</sub> -H <sub>2</sub> SO <sub>4</sub>	59.5	4	36.5	1.63
AgNO <sub>3</sub> -BF <sub>3</sub>	59	4	37	1.59
CH <sub>3</sub> COONO <sub>2</sub>	61	2	37	1.65
C <sub>6</sub> H <sub>5</sub> COONO <sub>2</sub>	59.6	4.3	36.1	1.65

PM3 calculations carried out for the toluene, toluene radical cation, alkyl nitrates and active nitrating agents. Electronic structure parameters were listed in Fig. 1 and Table-3. Fig. 1 revealed that the frontier electron density C4 of *para*-carbon involved control in a soft-soft situation and  $E_{\text{LUMO}}(\text{NO}_2^+) < E_{\text{HOMO}}(\text{Ar})$ , it is possible to for electron-transfer from toluene to  $\text{NO}_2^+$ . And then there are some active centers to provide strong driving force for electron transfer, such as surface radical sites of the O<sub>3</sub>SiO-silyloxy type resulting from dehydrative activation of a bentonite catalyst<sup>5</sup>.

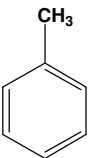
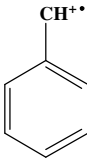
	q	f		q	f
	-0.2599	0.0471		-0.1397	0.1205
	-0.0843	0.6125		0.1806	0.5534
	-0.3855	0.3944		-0.1197	0.3501
	-0.3717	0.2539		-0.1298	0.1574
	-0.1986	0.5965		0.1195	0.6505

Fig. 1. Atomic charges (q) and frontier reaction factors (f) calculated by PM3 method for the toluene and toluene radical cation

Indeed, experiment results bear out the explanation of a high *para* preference for reactions in which the radical cation pathway, reported by Perrin<sup>9</sup> in a thought-provoking article in 1977, is expected to predominate. A plausible nitration mechanism on bentonite catalyst with alkyl nitrates could account for the regioselective results (Fig. 2).

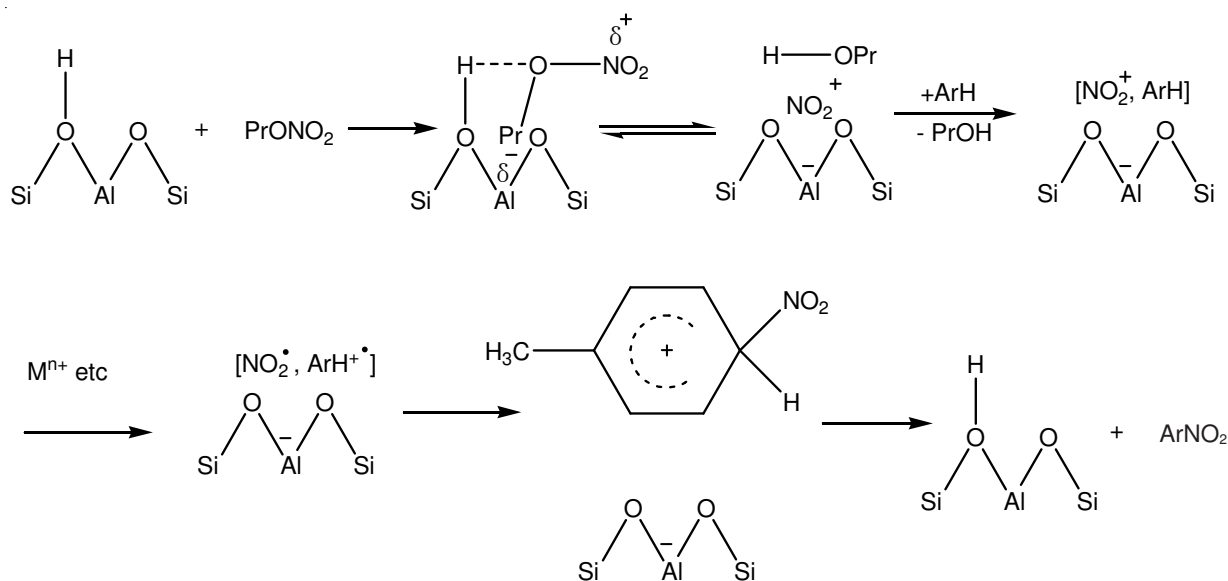


Fig. 2. A plausible mechanism of nitration of toluene with alkyl nitrates over acidic bentonite catalyst

TABLE-3  
FRONTIER ORBITAL ENERGY CALCULATED BY PM3  
METHOD FOR THE RELATED SUBSTRATES

Substrate	E <sub>NLUMO</sub> (ev)	E <sub>LUMO</sub> (ev)	E <sub>H(S)OMO</sub> (ev)	E <sub>NHOMO</sub> (ev)
NO <sub>2</sub> <sup>-</sup>	3.6899	-0.0362	-10.3219	-12.9385
NO <sub>2</sub> <sup>+</sup>	-10.2400	-11.9850	-20.8480	-22.5893
C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	0.4454	0.3763	-9.4419	-9.7220
C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> <sup>+</sup>	-5.0492	-6.3391	-15.4882	-15.5184

### Conclusion

Impressive regioselectivity of nitration of toluene can be achieved by using alkyl nitrate as nitrating reagents in the acidic bentonite catalyst.

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