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Electrophilic Aromatic Substitution. 10. A Kinetic Study of the Friedel-Crafts *tert*-Butylation Reaction in Nitromethane

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A kinetic study of the reaction between *tert*-butyl chloride and benzene or toluene using aluminum chloride as catalyst was made in solvent nitromethane over the temperature range −27 to 10 °C. The rate law was found to be first order in aromatic hydrocarbon, in *tert*-butyl chloride and in initial catalyst concentration. At −15 °C k_3 for benzene = 6.7 (±1.0) × 10^{-2} M^{-2} s^{-1}; for toluene k_3 = 20 (±2) × 10^{-1} M^{-2} s^{-1} with product isomer percentages meta 4.6 ± 0.3 and para 95.4 ± 0.3. E_a is 76 ± 13 kJ/mol, $\Delta H^\ddagger$ = 74 ± 13 kJ/mol, and $\Delta S^\ddagger$ = 16 ± 46 J/deg mol. Competitive results were k_T/k_B = 25 ± 1, 4.9 ± 0.1% meta, 95.1 ± 0.1% para. The results fit Brown's selectivity relationship. A mechanism involving a rate-determining attack by a *tert*-butyl cation–$AlCl_4^-$ ion pair on the aromatic is proposed.

Although the mechanism of the Friedel–Crafts reaction between *tert*-butyl halides and aromatics has long been a favorite for speculation, this reaction has been difficult to study kinetically. Using gallium bromide or aluminum bromide as a catalyst, Brown found the reaction too rapid for measurement and subject to isomerization in the solvents 1,2,4 trichlorobenzene[1] and in excess aromatic hydrocarbon.[2] After establishing disproportionation[3] as another major side reaction in these solvents, Olah was able to complete a successful competitive kinetic study of the reaction between *tert*-butyl bromide and benzene and toluene through the use of the milder catalyst tin tetrachloride and the more basic solvent nitromethane.[4] Noncompetitive kinetic results[5] were also reported for this system.

Unfortunately the rate law, and particularly the rate order with respect to the arene were not established.[6] Olah's second-order (first in *tert*-butyl bromide and first in aromatic) plot[5] exhibits curvature in the early stages of reaction. Furthermore since the reaction was swamped with aromatic hydrocarbon (1.75 M vs. 0.15 M for *t*-butyl bromide) and the aromatic concentration was not changed, even a totally linear plot would not have determined the aromatic rate order dependence.

Many important mechanistic questions remain unresolved. Is the electrophile a *tert*-butyl cation, ion pair, or polar donor–acceptor complex?[7] Does the reaction involve a rate-determining transition state resembling a π-complex, as suggested?[4] What is the role of the arene? Of the catalyst?[8]

For these reasons we undertook a kinetic study of the *tert*-butylation reaction using our usual vacuum-line techniques.

Experimental Section

The methods, including vacuum-line techniques, for analysis, purification, manipulation, and storage of the reagents benzene, toluene, catalyst aluminum chloride, solvent nitromethane, and internal standard *o*-dichlorobenzene were reported earlier.[9,10] Reagent grade *tert*-butyl chloride (99% pure, GC) was used without further purification. GC product peaks were verified and GC response curves were determined with authentic samples of pure *tert*-butylbenzene and *p*-di-*tert*-butylbenzene. The retention time of *m*-di-*tert*-butylbenzene was established through the *tert*-butylation of *tert*-butylbenzene.

Vacuum-line kinetic procedures were identical with those for isopropylation.[10] Because of the anticipated speed of *tert*-butylation, the gas-tight syringe containing the *tert*-butyl chloride was precooled to reaction temperature in early runs. However this approach proved to be largely unsuccessful in that at −15 °C and below leakage between the Teflon-tipped plunger and glass barrel was observed when injection was attempted. This problem was circumvented by the injection of room temperature *tert*-butyl chloride. The resulting kinetic plots showed good early linearity, probably because of high solution stirring speed and that typically only 20 μL of *tert*-butyl chloride were injected into 10 mL of solution.

As in the case of isopropylation[10] the addition of *tert*-butyl chloride produced a gradual color change from light yellow (benzene) or yellow (toluene) to almost colorless over the reaction period.

Aliquot samples were analyzed with a Hewlett-Packard 5880 gas chromatograph and a 25-m OV101 glass capillary column. With instrument temperature settings—injection port 250 °C, oven 115 °C, detector 250 °C—and a helium flow of 22 cm/s, typical retention times (minutes) were found for *tert*-butylbenzene (5.8), *o*-dichlorobenzene (6.6), *m*-di-*tert*-butylbenzene (15.1), *p*-di-*tert*-butylbenzene (18.6). Retention times for toluene runs were longer—*o*-dichlorobenzene (8.5), *m*-*tert*-butyltoluene (10.6), *p*-*tert*-butyltoluene (10.9)—reflecting the lower oven temperature, 100 °C.

Results

Since eventual comparisons between isopropylation and *tert*-butylation kinetic data would be more valid using the same catalyst, we decided to try $AlCl_3$ even though this catalyst caused both isomerization and disproportionation of *p*-*tert*-butyltoluene in nitromethane at 25 °C.[3,4]

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(5) Olah, G. A.; Overchuk, N. A. *J. Am. Chem. Soc.* **1965**, *87*, 5786–5788.

(6) A first-order dependence on aromatic was inferred from the competitive kinetic data, ref 4. However this argument is not valid. See footnote 31 of ref 20.

(7) For low-temperature (−95 °C) *tert*-butylation of toluene, a polar donor–acceptor complex has been proposed. Nakane, R.; Natsubori, A. *J. Am. Chem. Soc.* **1966**, *88*, 3011–3015.

(8) Lebedev found the rate order of aluminum chloride to be solvent dependent and to vary from 0.5 to 2 in the reaction of *tert*-butyl chloride and benzene. Lebedev, N. N. *Zh. Obshch. Khim.* **1958**, *28*, 1151–1160; *Chem. Abstr.* **1958**, 17922e.

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Table I. Rate Constants and Initial Rates for the Aluminum Chloride Catalyzed Reaction of *tert*-Butyl Chloride with Benzene and Toluene in Nitromethane as Solvent

	reactants, M								
temp, °C	$[C_6H_6]$	$[C_6H_5CH_3]$	$[t\text{-BuCl}]$	$[AlCl_3]$	10^5 (initial rate), M s^{-1}	10^2(initial rate)/$[C_6H_6]_0[RCl]_0[AlCl_3]_0$, M^{-2} s^{-1}	10^4k_1, s^{-1}	$10^2k_1/[AlCl_3]_0$, M^{-1} s^{-1}	$10^2k_1/[AlCl_3]_0[arom]_0$, M^{-2} s^{-1}
−15	0.6169		0.0351	0.0101	1.4 ± 0.2[a]	6.4 ± 0.9[a]	4.2 ± 0.7[a]	4.2 ± 0.7[a]	6.8 ± 1.1[a]
	0.3809		0.0393	0.0261	2.9 ± 1.0	7.4 ± 2.5	7.63 ± 0.02	2.92 ± 0.01	7.68 ± 0.02
	0.1992		0.0207	0.0426	0.98 ± 0.10	5.6 ± 0.6	4.80 ± 0.05	1.13 ± 0.01	5.66 ± 0.06
									6.7 ± 1.0[b]
		0.2189	0.0171	0.0231			109 ± 6	47 ± 3	216 ± 12
		0.3918	0.0159	0.0225			167 ± 3	74 ± 1	189 ± 3
									202 ± 19[b]
10	0.2133		0.0179	0.0303			64 ± 2	21.2 ± 0.7	100 ± 3
0	0.2590		0.0172	0.0457			36.2 ± 0.5	7.9 ± 0.1	30.6 ± 0.4
−27	0.424		0.0337	0.0494			1.43 ± 0.06	0.29 ± 0.01	0.68 ± 0.03

[a] ± 95% confidence limit. [b] Average ± standard deviation.

In this same solvent at −15 °C the $AlCl_3$ reaction between *tert*-butyl chloride and toluene proceeds smoothly and homogeneously to completion in 8–17 min (Table I). Over this period of time (and for an additional 4+ h) the *m*- and *p*-*tert*-butyltoluene relative isomer percentages remained almost constant. In a typical reaction the meta product percentage varied from 3.3% (8 s, 9.5% reaction) to 4.5% (19 s, 20% reaction) to 4.9% (1000 s, 99.7% reaction) to 5.1% (4.5 h, 99.8% reaction). Both disproportionation and isomerization appear to be essentially fully quenched at this reaction temperature. No trace of disproportionation products (or secondary products, vide infra) appeared on the gas chromatograms over the 4.5-h contact time with $AlCl_3$.

The corresponding reaction with benzene proved to be somewhat more complicated. Considerable *m*- and *p*-di-*tert*-butylbenzene formation occurred after the first few percent of reaction. This was observed throughout the entire temperature range, 10 to −27 °C, even though a tenfold excess of benzene to *tert*-butyl chloride was used.

It appears these products are due mainly to secondary *tert*-butylation rather than disproportionation. When a mixture of $AlCl_3$, *tert*-butylbenzene, and internal standard *o*-dichlorobenzene in nitromethane was stirred for 100 s at 10 °C, only 0.2% disproportionation product *p*-di-*tert*-butylbenzene was formed. Under the same reaction conditions, a normal benzene run at 10 °C (Table I) was over 48% complete in 100 s.

Since each secondary product molecule is produced by two *tert*-butyl chloride molecules, the GC data were easily adjusted for secondary *tert*-butylation once the GC hydrogen flame detector response of the secondary products was determined.

As expected, the corrected data proved to be more linear; pseudo-first order plots–ln ($[t\text{-BuCl}]_0/[t\text{-BuCl}]$) vs. time—consistently exhibited linear correlation coefficients of 0.997 or better over 48–81% reaction for both benzene and toluene.

The data are internally consistent with the rate law (eq 1). This is apparent from initial rates analyses and from the constancy of k_3 as shown by dividing k_1 by the initial concentration of both $AlCl_3$ and benzene or toluene.

$$\frac{d[\mathit{product}]}{dt} = k_3[AlCl_3]_0[t\text{-BuCl}][\text{arom}] \qquad (1)$$

Strictly speaking, the reaction is first order in arene. However, because it is present in tenfold excess, it remains essentially unchanged and can be treated accordingly.

In summary, the noncompetitive absolute rate data for −15 °C reactions are as follows: $k_B = 6.7\ (\pm 1.0) \times 10^{-2}\ M^{-2}\ s^{-1}$; $k_T = 2.0\ (\pm 0.2)\ M^{-2}\ s^{-1}$; $k_T/k_B = 30 \pm 7$; % meta, 4.6 ± 0.3% and % para 95.4 ± 0.3% (± standard deviation). From these values the slope, *b*, in the Brown selectivity relationship is calculated to be 1.38 ± 0.1, well within the range of the Brown–Stock slope[11] of 1.31 ± 0.10 (± standard deviation).

A competitive study at −15 °C yielded similar results (Table II). As in the noncompetitive reactions, benzene but not toluene secondary *tert*-butylation occurred. This was included in the calculation of $k_T/k_B = 25 \pm 1$.

Finally, benzene reaction rate data at 10, 0, −15 (average results), and −27 °C, were plotted in the usual fashion, i.e. ln ($k_1/[AlCl_3]_0[C_6H_6]_0$) vs. $1/T$. From the slope −9.1 (±3.2) × 10^3 and intercept 32 ± 12 (± 95% confidence limits) of the resulting straight line (−0.994 linear correlation coef-

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Table II. Competitively Determined Rate Constant Ratios and Product Isomer Percentages for the $AlCl_3$-Catalyzed Reaction between *tert*-Butyl Chloride and Benzene and Toluene in Nitromethane at -15 °C

$[C_6H_6]$, M	$[C_6H_5CH_3]$, M	[*t*-BuCl], M	$[AlCl_3]$, M	k_T/k_B	% meta	% para	b[a]
0.3588	0.2961	0.0372	0.0079	25 ± 1[b]	4.89 ± 0.14[b]	95.11 ± 0.14[b]	1.35 ± 0.03[b]

[a] Calculated slope for the Brown selectivity relationship. [b] Standard deviation.

Table III. Absolute Rate Data for the $AlCl_3$-Catalyzed Isopropylation and *tert*-Butylation Reactions with Benzene in Nitromethane

RCl	rate constant,[a] $M^{-2}\ s^{-1}$	relative rate	$\Delta H^{\ddagger}$, kJ/mol	$\Delta S^{\ddagger}$, J/deg mol
C_3H_7	5.1×10^{-2} [b]	107	76 ± 4[c]	−13 ± 14[c]
C_4H_9	(5.5)[d,e]		74 ± 13	16 ± 46

[a] At 25 °C. [b] Reference 10. [c] ± standard deviation. [d] This work. [e] Calculated.

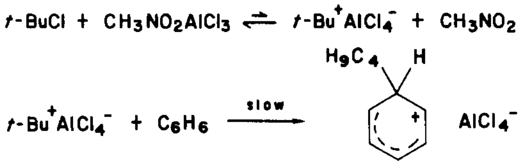
ficient), the usual kinetic parameters were calculated: $E_a = 76 \pm 13$ kJ/mol, $\Delta H^{\ddagger} = 74 \pm 13$ kJ/mol, $\Delta G^{\ddagger} = 69.4 \pm 0.2$ kJ/mol, and $\Delta S^{\ddagger} = 16 \pm 46$ J/deg mol (± standard deviation).

Discussion

To our knowledge this is the first complete noncompetitive kinetic study of the Friedel–Crafts *tert*-butylation reaction.

Even though both the isopropylation and *tert*-butylation reactions in nitromethane follow the same rate law (eq 1), they differ mechanistically. This can be seen from their respective enthalpy and entropy of activation values (Table III). Whereas $\Delta H^{\ddagger}$ remains the same, there is an increase of about 30 J/deg mol in $\Delta S^{\ddagger}$ for *tert*-butylation. Thus a considerable portion of the higher rate of reaction of *tert*-butyl chloride is directly due to entropy factors. Because product isomer percentages are essentially unaltered by the form of the isopropyl compound, it was argued that the isopropylation reaction proceeds through a rate-determining attack of the aromatic by an isopropyl cation–anion ion pair.

Since the entropy of activation is more favorable for *tert*-butylation and in fact is positive, it seems that almost the same mechanistic picture applies but there must be solvent release in the transition state.[12] A likely mechanism involves the rate-determining reaction between the *t*-$Bu^+AlCl_4^-$ ion pair and aromatic. The entropy of activation would be more favorable here than in the analogous isopropylation reaction if the *tert*-butyl cation were more fully developed *and solvated* than the isopropyl moiety.



It most be noted that there is no spectroscopic evidence for the existence of either cation[13] or ion pair in nitromethane. However, the kinetically active species may not be present in concentrations detectable by UV, IR, or NMR.

The literature values for competitively determined k_T/k_B ratios and product isomer percentages are given in Table IV. The somewhat differing meta/para product percentages probably reflect the occurrence of small amounts of isomerization.

This reaction clearly fits Brown's selectivity relationship and must therefore resemble a σ-complex in its rate-determining transition state. This adds further support to the evidence that most electrophilic substitution reactions *which involve the aromatic in the rate-determining step* fit Brown's relationship. This has proven to be true for benzylation in excess aromatic,[17] acylation,[9,18] sulfonylation,[18] formylation with 1,1-dichloromethyl methyl ether,[19] isopropylation,[10] and benzylation with *p*-nitrobenzyl chloride in nitromethane,[20] all reported earlier as exceptions.

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Registry No. *tert*-Butyl chloride, 507-20-0; benzene, 71-43-2; Toluene, 108-88-3; alumimum chloride, 7446-70-0; nitromethane, 75-52-5.

Table IV. The Literature Values of Competitively Determined Rate Constant Ratios and Product Isomer Percentages for the *tert*-Butylation Reaction with Benzene and Toluene

t-C_4H_9X	catalyst	solvent	temp, °C	k_T/k_B	% meta	% para	b[a]	ref
Br	$SnCl_4$	CH_3NO_2	25	16.6	6.4	93.6	1.34	4
$C_6H_5SO_2$	$AlCl_3$	CH_3NO_2	30	16.5	6.9	93.2	1.37	14
SO_2Cl	$AlCl_3$	CH_3NO_2	25	16.1	8.7	91.3	1.47	15
Cl	$AlCl_3$	CH_3NO_2	−15	25	4.9	95.1	1.35	this work
$C_4H_9^+$	gas phase		37.5	55.5	5.4	94.6	1.6	16

[a] Calculated slope for the Brown selectivity relationship.

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(13) Giacomello and Cacace report over 65% ortho (4-position) substitution in the gas-phase reaction between *tert*-butyl cations and *m*-xylene. Ortho substitution is not observed in analogous solution reactions. Whether this is due to steric effects or fast product isomerization is not known. Giacomello, G.; Cacace, F. *J. Chem. Soc., Chem. Commun.* **1975**, 379–380.

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