drogens of the ethanol could be located. All other hydrogen atoms in the complexes could unambiguously be located from difference-Fourier maps.

Parameters refined were the overall scale factors, isotropic secondary extinction parameters, positional parameters of all atoms, anisotropic thermal parameters for non-hydrogen atoms, and isotropic thermal parameters for hydrogens. The weight for each reflection was taken to be $w = \{\sigma(F_o) + 0.01\,|F_o|\}^{-2}$, where $\sigma(F_o)$ is the estimated standard deviation of the observed structure factor (F_o) derived from counting statistics. Scattering factors for non-hydrogen atoms were taken from ref 37; for H the scattering factors of Stewart, Davidson, and Simpson[38] were used. No absorption corrections were applied.

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Registry No. 1 (n = 0), 77877-86-2; 1 (n = 1), 53914-89-9; 1 (n = 1)·quanidium perchlorate, 100840-33-3; 1 (n = 2), 86309-73-1; 1 (n = 3), 86309-74-2; 1 (n = 4), 95216-11-8; 1 (n = 4)·hydrogen tetraphenylborate, 100858-00-2; 1 (n = 5), 95216-12-9; 1 (n = 6), 95216-13-0; **2**, 57659-55-9; **3**, 95216-14-1; **4**, 100840-32-2; **5**, 95216-15-2; **6**, 100857-99-6; **8**, 95216-17-4; 2,6-bis(bromomethyl)pyridine, 7703-74-4; triethylene glycol, 112-27-6; tetraethylene glycol, 112-60-7; pentaethylene glycol, 4792-15-8; hexaethylene glycol, 2615-15-8; heptaethylene glycol, 5617-32-3; octaethylene glycol, 5117-19-1; nonaethylene glycol, 3386-18-3; 1,3-bis(bromomethyl)benzene, 626-15-3; guanidinium sulfate, 594-14-9; guanidinium thiocyanate, 593-84-0.

Supplementary Material Available: Lists of anisotropic thermal parameters for heavy atoms, positional and isotropic thermal parameters for hydrogens, and complete lists of bond lengths and bond angles (47 pages). Ordering information is given on any current masthead page.

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Electrophilic Aromatic Substitution. 9.[1] A Kinetic Study of the Friedel–Crafts Isopropylation Reaction in Nitromethane

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The kinetics of the aluminum chloride catalyzed reaction between isopropyl chloride and benzene or toluene were determined in solvent nitromethane by using vacuum-line techniques. The reaction at 25 °C was first order in isopropyl chloride and in aromatic hydrocarbon and first order in initial catalyst concentration. Noncompetitive results are $k_T/k_B = 2.0 \pm 0.7$ with the following toluene product isomer distribution: % ortho, 45.3 ± 1.5; % meta, 22.7 ± 1.1; % para, 32.0 ± 1.0. For competitive runs k_T/k_B was 2.3 ± 0.1 with the same isomer distribution. Rate constants at 25, 15, 0, −15, and −27 °C yielded $E_a = 78 \pm 4$ kJ/mol, $\Delta H^{\ddagger} = 76 \pm 4$ kJ/mol, $\Delta S^{\ddagger} = -13 \pm 14$ J/mol deg. The results are consistent with a σ complex-like transition state and a predominantly ionic mechanism.

Friedel–Crafts isopropylation has become another focal point in the controversy regarding the mechanisms of electrophilic aromatic substitution reactions. Despite the number of kinetic studies carried out, the order with respect to aromatic has yet to be established, and, furthermore, individual interpretations of various results have led to incompatible conclusions. For example, Brown[3] found the kinetic results of his study in excess aromatic to agree well with his linear free energy relationship (the Brown selectivity relationship) which is based upon a σ-complex mechanism, whereas Olah[4,5] and Nakane[6] found a correlation between their results and a mechanism involving a π-complex-like highest energy transition state. Thus, as a part of our ongoing attempts to assist in the resolution of the controversy, we undertook a kinetic study of the isopropylation reaction using vacuum-line techniques that yielded reproducible results differing substantially from those previously reported for the related ethylation[7] and benzylation[8] reactions. We now report noncompetitive kinetic results for the $AlCl_3$-catalyzed reaction of isopropyl chloride with benzene and toluene as a function of reagent concentrations and temperature, along with competitive kinetic results at 25 °C.

Experimental Section

Materials. The analysis, purification, drying (where necessary), and storage of the reagents benzene, toluene, catalyst aluminum chloride, and solvent nitromethane are described elsewhere.[8,9] Reagent isopropyl chloride contained approximately 2% n-propyl chloride (GC analysis). Since isopropyl halides undergo Frie-

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del–Crafts alkylation over 1000 times faster than *n*-propyl halides[10] it was used without further purification. *o*-Dichlorobenzene (purity >99.4%, GC) was chosen as the internal standard. Authentic samples of cumene and the cymenes were used to identify product peaks and to determine response curves for GC analysis.

Kinetic Procedure. The general procedure for kinetic studies, GC analysis, and data evaluation is given in a previous paper.[9] The following changes were made. For reactions run at 15, 0, –15, and –27 °C, the syringes used to remove aliquots from the reaction mixture were precooled to the bath temperature in a hexane-containing jar (equipped with a Zip-Lok top for easy access) which was partially immersed in the constant temperature bath. For a kinetic run the reagents were added in the following order: to a clear colorless solution of aluminum chloride in nitromethane, *o*-dichlorobenzene (solution still colorless); benzene and/or toluene (immediate yellow color, more intense with toluene); isopropyl chloride to start the reaction. The solution then gradually lightened in color, with benzene becoming almost colorless after an hour or so.

Analysis. Benzene runs were analyzed with a 20-ft $^1/_8$-in. o.d. stainless steel column packed with 10% diethylene glycol succinate liquid phase on 80/100 mesh Chromasorb W-AW. GC instrument settings were as follows: detector, 250 °C; injection port, 200 °C; oven, 125 °C; N_2 carrier gas flow, 20 mL/min.

A HP5880 gas chromatograph with a 25-m glass capillary OV101 column was used for toluene run analysis. Instrument settings were as follows: detector, 250 °C; injection port, 250 °C; oven, 90 °C; helium carrier gas, 22 cm/sec. Typical retention times (min) were as follows: nitromethane, 3.0; isopropyl chloride, 3.2; toluene, 4.0; *m*-cymene, 9.5; *p*-cymene, 9.7; *o*-dichlorobenzene, 10.0; *o*-cymene, 10.3.

Results

This study was initiated with an investigation of the $AlCl_3$–isopropyl chloride–nitromethane–*o*-dichlorobenzene system. Friedel–Crafts catalysts are known to cause dehydrohalogenation of alkyl halides. However, at 25 °C no HCl gas evolution was observed nor was there a diminution in the isopropyl chloride GLC peak over 1.5 h. The internal standard (*o*-dichlorobenzene) peak was also unaffected over the same time period. We also looked for cumene formation in this system. Both Bovino[11] and Stock[12] observed isopropylation of benzene at room temperature by 2-nitropropane catalyzed by $AlCl_3$ and other strong Friedel–Crafts catalysts. Our nitromethane contained 0.03% 2-nitropropane which had been lowered from 2.8% in the commercially available sample by cryocrystallization.[9] No cumene formation was seen in the purified solvent.

The $AlCl_3$-catalyzed reaction of isopropyl chloride with benzene or toluene proceeds smoothly and homogeneously in nitromethane from –27 to +25 °C. The kinetic results for noncompetitive runs as a function of reagent concentrations[13] and temperature are summarized in Table I. The rate law which best fits this data is given in eq 1 where

$$d[\text{product}]/dt = k_3[AlCl_3]_0[i\text{-PrCl}][ArH] \qquad (1)$$

ArH = benzene or toluene. This was determined by two independent methods. First, the most consistent rate constants were calculated by dividing each initial rate (the slope of the product concentration vs. time plot up to 10% reaction) by $[AlCl_3]_0[i\text{-PrCl}]_0[ArH]_0$. Second, since all reactions were carried out with excess arene (to minimize secondary reactions) and since $AlCl_3$ is a true catalyst in

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

temp, °C	reactants, M				initial rate × 10^5, M s^{-1}	10^3k_1, s^{-1}	$10^2k_1/[cat]_0$, M^{-1} s^{-1}	$10^2k_1/[cat]_0[arom]_0$, M^{-2} s^{-1}	10^3k_2, M^{-1} s^{-1}	$10^2k_2/[cat]_0$, M^{-2} s^{-1}
	$[C_6H_6]$	$[C_6H_5CH_3]$	[*i*-PrCl]	$[AlCl_3]$						
25	1.0465		0.0491	0.0846	15 ± 0.3[a]	3.8 ± 0.5[a]	4.6 ± 0.6[a]	4.2 ± 0.6[a]	3.6 ± 0.5[a]	4.3 ± 0.6[a]
	0.9498		0.0455	0.0416	9 ± 5	2.3 ± 0.1	5.5 ± 0.2	5.8 ± 0.2	2.3 ± 0.4	5.5 ± 0.9
	0.5482		0.0517	0.0389	8 ± 1	1.7 ± 0.1	4.1 ± 0.2	7.5 ± 0.4	2.5 ± 0.5	6.4 ± 1.3
	1.0390		0.0930	0.0476	14 ± 3	1.5 ± 0.2	3.2 ± 0.4	3.0 ± 0.4	1.6 ± 0.1	3.4 ± 0.2
	0.5045		0.0459	0.0841	7 ± 4	2.2 ± 0.3	2.6 ± 0.4	5.2 ± 0.8	4.6 ± 0.6	5.4 ± 0.7
	0.9966		0.0451	0.0221	4 ± 1	1.10 ± 0.06	4.9 ± 0.3	5.0 ± 0.3	1.11 ± 0.07	5.0 ± 0.3
	0.3064		0.0422	0.0690	5 ± 2	1.31 ± 0.06	1.9 ± 0.08	6.2 ± 0.3	4.5 ± 0.3	6.5 ± 0.4
							3.8 ± 1.3[b]	5.3 ± 1.4[b]		5.2 ± 1.1[b]
		0.8273	0.0472	0.0229	8 ± 3	2.0 ± 0.1	8.7 ± 0.4	10.5 ± 0.5	2.8 ± 0.3	12 ± 1
		0.3658	0.0478	0.0584	13 ± 2	2.57 ± 0.09	4.4 ± 0.1	12.0 ± 0.4	5.6 ± 0.4	9.6 ± 0.7
		0.7108	0.0479	0.0278	10 ± 2	1.95 ± 0.06	7.0 ± 0.2	9.9 ± 0.3	2.5 ± 0.1	9.0 ± 0.4
		0.4183[c]	0.0562	0.0315	7 ± 2	1.5 ± 0.1	4.7 ± 0.3	10.9 ± 0.7	3.7 ± 0.3	12 ± 1
		0.569	0.0505	0.0331	7.7 ± 0.2	1.70 ± 0.05	5.14 ± 0.15	9.0 ± 0.3	3.02 ± 0.08	9.1 ± 0.2
		0.8276	0.0469	0.0095	(2.1 ± 0.1)	(0.42 ± 0.01)	(4.42 ± 0.01)[d]	(5.3 ± 0.1)[d]	(0.48 ± 0.01)	(5.1 ± 0.1)[d]
							6.0 ± 1.8[b]	10.5 ± 1.1[b]		10.3 ± 1.5[b]
15	0.5316		0.0489	0.0340		0.43 ± 0.01	1.27 ± 0.02	2.39 ± .06		
0	0.5341		0.0461	0.0504		0.104 ± 0.003	0.206 ± .006	0.386 ± 0.011		
–15	0.5824		0.0445	0.0370		0.0084 ± 0.0002	0.0228 ± 0.0005	0.0391 ± 0.0009		
–27	0.5650		0.0481	0.0363		0.00166 ± 0.00004	0.0046 ± 0.0001	0.0081 ± 0.0002		

[a] ± 95% confidence limit. [b] Average ± standard deviation. [c] This reaction was also 0.39 M in cyclohexane. [d] Not included in average. See text for explanation.

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Table II. Linearity of Second-Order Isopropylation Kinetic Plots at 25° C

reactants, M		extent of reaction, %[a]	no. of pts	*r*-coef[b]
[C_6H_6]	[$C_6H_5CH_3$]			
1.0465		85	14	0.988
0.9498		81	13	0.956
0.5482		67	12	0.963
1.0390		29	9	0.997
0.5045		66	11	0.987
0.9966		40	9	0.998
0.3064		18[c]	10	0.996
	0.8273	90	13	0.989
	0.3658	64	12	0.994
	0.7108	81	17	0.996
	0.4183	53	12	0.995
	0.569	36	15	0.998
	0.8276	69	16	0.999

[a] The extent of the reaction for which the first- and second-order plot was linear. [b] Linear correlation coefficient. [c] Only the first ten points, through 18%, were analyzed.

this system, the reactions are expected to be pseudo-first-order in isopropyl chloride. This was the case. All the first-order plots were linear (Table II) with slopes that passed through the origin within experimental error. If these calculated k_1 values (slopes) are divided by $[AlCl_3]_0$ or by $[AlCl_3]_0$ and $[ArH]_0$, the results are more consistent for the latter case. Both calculations are presented in Table I.

Finally, because the aromatic *is* used up to some extent, we have also included the more correct rate constants, $k_2/[AlCl_3]_0$, where k_2 is the second-order rate constant, first order in isopropyl chloride and in aromatic hydrocarbon.

Some comments concerning the scatter in our data are in order. Isopropylation, as is typical of other Friedel–Crafts reactions, is greatly affected by moisture. Every precaution possible was taken to exclude moisture; but the fact is the sampling process may, on occasion, have brought moisture into the system.[9]

The effect of moisture is seen in the results of the last toluene run at 25 °C shown in Table I. A very small aluminum chloride sample was inadvertently used. Our nitromethane solvent after drying with molecular sieve and P_2O_5 has 0.005% water or 0.000 03 mol of water in 10 mL. Thus the water concentration of 0.003 M was roughly a third of the catalyst concentration, 0.0095, and probably was a large part of the reason why this run proceeded at half the expected pace.

It is possible that our data is influenced by a solvent dielectric or polarity effect produced by increasing the aromatic concentration from typically 0.4 to 0.8 M. To check this effect, the concentration of nonpolar species was "doubled" by adding an approximately equal concentration of cyclohexane to a toluene run (Table I). The resulting initial rate and rate constants show aromatic concentration may be varied in this range without inducing solvent effects.

Even though the arene–isopropyl chloride ratio was deliberately kept in the range 10–20, small amounts of secondary products would sometimes appear on the chromatogram when late reaction points were analyzed. These were always less than 5% of the primary products and were not analyzed. In most cases the first- and second-order plots were linear through at least 65% reaction (Table II). Occasionally early curvature was observed, even before secondary products were apparent. The reason for this is unknown, but it probably means a small amount of moisture had entered the system in spite of our efforts.

Through glass capillary chromatography, *o*-, *m*-, and *p*-cymene product concentrations were easily followed during toluene reactions. All three cymene isomer percentages remained constant throughout each run (e.g., at 6.5% reaction, 43.8% ortho, 23.5% meta, 32.7% para; at 70.7% reaction, 44.1% ortho, 23.4% meta, 32.5% para) and from run to run. For *all* noncompetition toluene runs the average isomer percentages (± standard deviation) were as follows: ortho, 45.3 ± 1.5; meta, 22.7 ± 1.1; para, 32.0 ± 1.0.

Table III. Results of the Aluminum Chloride Catalyzed Competitive Isopropylation of Benzene and Toluene in Nitromethane at 25 °C

reactants, M				k_T/k_B
[C_6H_6]	[$C_6H_5CH_3$]	[*i*-PrCl]	[$AlCl_3$]	
0.3821	0.3303	0.0412	0.0400	2.3 ± 0.1
0.0869	0.7158	0.0457	0.0291	2.2 ± 0.4
0.4152	0.0416	0.0444	0.1313	2.4 ± 0.2
				2.3 ± 0.1[a]

[a] Average ± standard deviation.

Taking the average $k_2/(AlCl_3)_0$ value of 10.3 (±1.5) × 10^{-2} for toluene reactions and 5.2 (± 1.1) × 10^{-2} for benzene reactions (Table I) yields k_T/k_B of 2.0 ± 0.7. For the sake of comparison and because much of Olah's and Nakane's data are for competitive reactions, k_T/k_B was also determined competitively. As seen in Table III, the average value is 2.3 ± 0.1. For competitive runs the product isomer percentages were as follows: ortho, 45.3 ± 1.0; meta, 22.8 ± 0.3; para, 31.9 ± 0.7. In each case the slope value, *b*, of the Brown selectivity relationship $\log p_f = bS_f$ may be calculated.[14] The values for direct and competitive data sets, 1.30 and 1.44, respectively, are both within the experimentally determined limits of Brown and Stock, 1.31 ± 0.20 (95% confidence limits).

Rate constants were evaluated at 25, 15, 0, −15, and −27 °C (see Table I) in order to obtain the usual Arrhenius/Eyring activation parameters. A regression analysis of the ln *k* vs. 1/*T* plot yielded a slope of −9.4 (±1.0) × 10^3, an intercept of 29 (±4) and a linear correlation coefficient of −0.998 (± 95% confidence limits). These values were used to calculate $E_a = 78 \pm 4$ kJ/mol, $\Delta H^\ddagger = 76 \pm 4$ kJ/mol, $\Delta G^\ddagger = 80 \pm 1$ kJ/mol, and $\Delta S^\ddagger = -13 \pm 14$ J/mol deg (± standard deviation).

Discussion

Although liquid-phase isopropylation kinetic studies abound (Table IV), the reaction order with respect to the aromatic had not been determined previously. The competitive method has been used to infer first-order dependence,[4,6] but this is based on erroneous reasoning.[1] For their direct kinetic study Brown and Choi[3] proposed a rate law (eq 2). The rate did not depend upon isopropyl

$$\frac{d[HBr]}{dt} = k[i\text{-PrBr–GaBr}_3]_0^2$$

bromide, but this is reasonable in view of the fact that it was used in considerable excess over the catalyst and in weakly basic aromatic solvent the catalyst apparently is completely converted to the 1:1 complex.[16] However, since excess aromatic was the reaction medium, its order could not be ascertained. In the other direct kinetic study re-

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(14) p_f = partial rate factor for the para position of toluene = (k_T/k_B)(% para/100)(6); S_f = selectivity factor = ((2 × % para)/% meta). For example, see: Brown, H. C.; Smoot, C. R., *J. Am. Chem. Soc.* **1956**, *78*, 6255–6259.

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Table IV. Friedel–Crafts Liquid-Phase Isopropylation of Benzene and Toluene

C_3H_7X	catalyst	solvent	temp, °C	k_T/k_B	% ortho	% meta	% para	"b"[a]	ref
Br	$GaBr_3$	toluene	25	1.82[c]	29.6	25.2	45.2	1.25	3, 10
Br	$AlCl_3$	CH_3NO_2	25	2.03[c]	46.7	14.7	38.6	0.93	4
Br	$AlCl_3$	CH_3NO_2	25	1.65[b]	47.7	18.2	35.1	0.92	5
F	BF_3	CH_3NO_2	25	2.18[c]	43.2	22.3	34.5	1.33	6
Cl	$AlCl_3$	CH_3NO_2	25	2.0[b]	45.3	22.7	32.0	1.30	this work
Cl	$AlCl_3$	CH_3NO_2	25	2.3[c]	45.3	22.8	31.9	1.44	this work
F	BF_3	n-hexane	25	0.69[c]	45.6	21.0	33.4	0.28	6
F	BF_3	cyclohexane	25	0.70[c]	45.1	21.5	33.4	0.30	6
OSOCl	SbF_5	CH_3NO_2	30	2.4[c]	42.3	20.3	37.4	1.29	15
$O_2SC_6H_5$	$AlCl_3$	CH_3NO_2	30	2.6[c]	45.2	21.5	33.2	1.46	15
OSO_2F	$AlCl_3$	SO_2	−78	1.1[c]	43.3	23.4	33.3	0.75	15
p-$OSO_2C_6H_4CH_3$	$AlCl_3$	CH_3NO_2	30	2.5[c]	46.4	21.8	31.8	1.46	15
OSO_2CF_3	$AlCl_3$	SO_2	−78	1.6[c]	43.8	21.8	34.4	1.04	15
OSO_2CF_3		aromatic (ex)	25	2.9[c]	46.5	19.1	34.4	1.40	15
$OOCCF_3$	$AlCl_3$	CH_3NO_2	30	2.6[c]	45.1	22.0	33.0	1.49	15

[a] Calculated slope for Brown selectivity relationship. [b] Direct (noncompetitive) kinetic study. [c] Competitive kinetic study.

Table V. Enthalpies and Entropies of Activation of Friedel–Crafts Isopropylation Reactions

system	$\Delta H^‡$, kJ/mol	$\Delta S^‡$, J/(deg mol)
$GaBr_3$–C_3H_7Br–$C_6H_5CH_3$[a,b]	33	−81
$AlCl_3$–C_3H_7Cl–CH_3NO_2[a,c]	76 ± 4[d]	−13 ± 14[d]

[a] Solvent. [b] Reference 3. [c] This work. [d] ± standard deviation.

ported,[5] the aromatic was present in excess and was not varied. Furthermore, the second-order plot shows curvature at short reaction times and thus is not firm evidence of first order with respect to aromatic. Our data does establish first-order aromatic dependence.

Our study indicates that in nitromethane, isopropylation proceeds homogeneously and at a moderate rate and under kinetic control, i.e., no isomerization or disproportionation (transalkylation). Indeed one would expect competitive and direct kinetic results to be in agreement; and even though different isopropyl halides and in one case a different catalyst was used, the results in nitromethane solvent are in reasonable agreement (Table IV). In fact both Nakane's and our results fit the selectivity relationship. On the other hand, Olah's competitive and noncompetitive results yield selectivity relationship slope values of 0.93 and 0.92, well outside the Brown–Stock limits of 1.31 ± 0.20 (95% confidence limits). However, the fact remains that these results are reasonably close to the other data. Considering the difficulties encountered in getting reproducible kinetic data and in separating product isomer peaks chromatographically (Olah reports an experimental uncertainty of ±5 relative percent for the ortho and para isomers and "in certain instances as high as 20 relative percent for the meta isomer",[4] we suggest that the differences in the studies *are* largely experimental error. We think it also follows that the isopropylation data in nitromethane is supportive of a σ rather than a π complex mechanism.

The available enthalpies and entropies of activation for isopropylation are summaried in Table V. For the alkylation reactions in excess aromatic involving methyl, ethyl, and isopropyl bromide,[3] the constancy and magnitude of $\Delta S^‡$ (all about −20 cal/deg mol) is consistent with a displacement mechanism involving a rate-determining interaction between a polarized alkyl bromide–catalytic halide complex and the aromatic. The large increase in the entropy of activation for isopropylation in nitromethane is indicative of a mechanistic change, probably to a predominately ionic mechanism. This is supported by product toluene isomer distribution (Table IV) which appears to be independent of the isopropyl compound and catalyst used. Since a polarized alkyl halide–catalytic halide complex will be expected to show larger steric requirements than the isopropyl cation, the lower ortho product isomer percentage found by Brown (Table IV) is reasonable.

Clearly, Nakane's data for isopropylation in hydrocarbon solvents are unusual. Since there are five possible substitution positions in toluene and six in benzene, the limiting k_T/k_B ratio should be 5/6 or 0.83 regardless of mechanism. Nakane reports the observation of a Tyndall effect when BF_3 gas was quickly dissolved in n-hexane solution containing benzene, toluene, and isopropyl fluoride. This effect was not observed when BF_3 was introduced slowly. However, it does agree with our experience with Friedel–Crafts reactions in nonpolar solvents.[7] In the ethylation reaction in hexane, k_T/k_B was as expected (~4) until layer separation occurred at which point k_T/k_B became less than one. Because of the low concentrations of reagents we found the onset of inhomogeneity difficult to detect. Possibly Nakane's results were biased by a similar phase separation. When it happened in our ethylation reaction system, there was evidence of disproportionation of the toluene product which would decrease the apparent k_T value.

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Registry No. $AlCl_3$, 7446-70-0; isopropyl chloride, 75-29-6; benzene, 71-43-2; toluene, 108-88-3; nitromethane, 75-52-5.