Hydroboration Kinetics. 8.[1] Kinetics and Mechanism of Protonolysis of 9-Borabicyclo[3.3.1]nonane Dimer with Representative Alcohols and Phenols

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The kinetics of protonolysis of 9-borabicyclo[3.3.1]nonane dimer [(9-BBN)$_2$] with representative alcohols and phenol were followed in THF and CCl$_4$ at 25 °C. In carbon tetrachloride the reaction with *tert*-butyl alcohol exhibits first-order kinetics, first order in (9-BBN)$_2$, supporting the conclusion that the reaction proceeds by a dissociation mechanism similar to those observed for the hydroboration of alkenes and alkynes and the reduction of aldehydes and ketones by the reagent. However, in the case of unhindered alcohols, such as methanol and ethanol, there is a competition between the dissociation pathway and a pathway involving direct attack of the alcohol on the dimer. When the reaction was carried out under pseudo-unimolecular conditions (excess ROH) at several different concentrations of the alcohol and the k_{obsd} plotted vs. [ROH], linear plots were realized. From these plots the rate constants for the dissociation pathway (k_1) and the direct attack pathway (k_2) could be evaluated. The k_1 values agree very well with each other in all cases studied and with those reported earlier for the dissociation of (9-BBN)$_2$ in carbon tetrachloride. The k_2 values decrease from methanol to isopropyl alcohol as anticipated for the operation of increasing steric effects. In THF, with both hindered and unhindered alcohols, first-order kinetics are observed, indicating that the dominant pathway involves prior dissociation of (9-BBN)$_2$. In order to understand the effects of structure on the protonolysis reaction, the relative rates of protonolysis of a number of representative alcohols and phenols were determined in THF at 25 °C utilizing competition experiments. The data indicate that increasing steric hindrance in the alcohol decreases the protonolysis rate. Electron-withdrawing substituents enhance, and electron-releasing ones decrease, the rate of protonolysis, suggesting that the dissociated 9-BBN monomer forms a complex with the alcohol which loses H$_2$. Phenols protonolyze (9-BBN)$_2$ considerably slower than do alcohols. Moreover, the opposite electronic effects are observed. Probably in the case of phenols, the complex formation is difficult due to their poorer nucleophilicity, leading to decreased rates of protonolysis.

Recently we established that the hydroboration of alkenes and alkynes with 9-borabicyclo[3.3.1]nonane dimer [(9-BBN)$_2$] proceeds via the dissociation of the dimer followed by the reaction of the monomer with the substrate (eq 1 and 2).[1a-d] These results significantly differed from

$$(9\text{-BBN})_2 \rightleftharpoons 2\ 9\text{-BBN} \qquad (1)$$

$$9\text{-BBN} + \text{alkene} \rightarrow B\text{-alkyl-9-BBN} \qquad (2)$$

our earlier results on the hydroboration of alkenes with disiamylborane dimer, wherein, on the basis of kinetic evidence, a dimer attack mechanism was proposed (eq 3 and 4).[4] In order to understand the behavior of (R$_2$BH)$_2$

$$\text{>C=C<} + (\text{Sia}_2\text{BH})_2 \xrightarrow{\text{slow}} \text{RBSia}_2 + \text{Sia}_2\text{BH} \qquad (3)$$

$$\text{Sia}_2\text{BH} + \text{>C=C<} \xrightarrow{\text{fast}} \text{RBSia}_2 \qquad (4)$$

in reactions with representative nucleophiles, we undertook to study the kinetics of the reactions of (9-BBN)$_2$ with aldehydes and ketones, alcohols, and amines. Very recently we reported our findings on the mechanism of reduction of aldehydes and ketones by (9-BBN)$_2$.[1h] In this paper, we report our observations on the protonolysis of (9-BBN)$_2$ by representative alcohols and phenols.

Results and Discussion

The kinetics of protonolysis of (9-BBN)$_2$ with alcohols were followed by estimating the amounts of H$_2$ evolved as a function of time.[5] The kinetics were followed in CCl$_4$ and THF at 25 °C.

Kinetics of Protonolysis in CCl$_4$. The protonolysis of (9-BBN)$_2$ by *tert*-butyl alcohol exhibits first-order kinetics in CCl$_4$. Changing the initial concentration does not affect the magnitude of the rate constant appreciably.

[(9-BBN)$_2$], *M*	[*t*-BuOH], *M*	$k_1 \times 10^4$, s^{-1}
0.200	0.800	1.53
0.100	1.50	1.60
0.100	2.00	1.57

The first-order rate constant is in good agreement with those obtained earlier for the hydroboration of alkenes[1a] and alkynes[1d] and the reduction of hexanal,[1h] indicating that the reaction proceeds by a rate-limiting dissociation of (9-BBN)$_2$ followed by a rapid reaction of the monomer with *tert*-butyl alcohol (eq 5 and 6).

$$(9\text{-BBN})_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\ 9\text{-BBN} \qquad (5)$$

$$9\text{-BBN} + t\text{-BuOH} \rightarrow t\text{-BuO-9-BBN} + \text{H}_2 \qquad (6)$$

With unhindered alcohols, the situation was different. With methanol, for example, the reaction was faster than that with *tert*-butyl alcohol. The rate data did not fit into the integrated rate expressions of either first or second order. Doubling the initial concentration of methanol increased the rate of protonolysis, but not to the extent of doubling the initial rate. We thought that this may be

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[1] For previous studies in this series, see: (a) Brown, H. C.; Scouten, C. G.; Wang, K. K. *J. Org. Chem.* **1979**, *44*, 2589–2591. (b) Brown, H. C.; Wang, K. K.; Scouten, C. G. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 698–702. (c) Wang, K. K.; Brown, H. C. *J. Org. Chem.* **1980**, *45*, 5903–5906. (d) Wang, K. K.; Scouten, C. G.; Brown, H. C. *J. Am. Chem. Soc.* **1982**, *104*, 531–536. (e) Nelson, D. J.; Brown, H. C. *Ibid.* **1982**, *104*, 4907–4912. (f) Nelson, D. J.; Blue, C. D.; Brown, H. C. *Ibid.* **1982**, *104*, 4913–4917. (g) Wang, K. K.; Brown, H. C. *Ibid.* **1982**, *104*, 7148. (h) Brown, H. C.; Wang, K. K.; Chandrasekharan, J. *Ibid.* **1983**, *105*, 2340.

[2] Postdoctoral research associate on Grant CHE 79-18881 of the National Science Foundation.

[3] Graduate research assistant on Grant CHE 76-20846 of the National Science Foundation.

[4] Brown, H. C.; Moerikofer, A. W. *J. Am. Chem. Soc.* **1963**, *85*, 2063–2065.

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Table I. Kinetic Data[a] for the Protonolysis of $(9\text{-BBN})_2$ by Unhindered Alcohols in CCl_4 at 25 °C

alcohol	k_1, 10^{-4} s^{-1}	k_2, 10^{-5} M^{-1} s^{-1}
methyl	1.45	7.0
ethyl	1.44	3.3
isopropyl	1.42	1.0

[a] The rate constants were obtained under pseudo first-order conditions and the k_{obsd} were plotted *vs.* the initial concentration of the alcohol. The linear plots had correlation coefficients better than 0.995.

Table II. Kinetic Data for the Protonolysis of $(9\text{-BBN})_2$ with Representative Alcohols and Phenol in THF at 25 °C

compound	k_1, 10^{-4} s^{-1}
methanol[a]	15.4
1-hexanol[a]	14.1
tert-butyl alcohol	14.2
2,3-dimethyl-2-butanol	15.2
tri-*n*-octylcarbinol	14.0
2,2,4-trimethyl-3-pentanol	15.0
phenol[b]	11.4

[a] Data from ref 5. [b] Shows slight intermediate behavior.

due to a competition between the direct attack reaction pathway (eq 7 and 8) and the dissociation mechanism.

$$(9\text{-BBN})_2 + CH_3OH \xrightarrow{k_2} B\text{-}CH_3O\text{-}9\text{-BBN} + 9\text{-BBN} + H_2 \quad (7)$$

$$9\text{-BBN} + CH_3OH \rightarrow B\text{-}CH_3O\text{-}9\text{-BBN} + H_2 \quad (8)$$

The rate equation for the overall process will be eq 9. This

$$-\frac{d[(9\text{-BBN})_2]}{dt} = k_1[(9\text{-BBN})_2] + k_2[CH_3OH][(9\text{-BBN})_2] \quad (9)$$

simple equation eludes easy methods of integration. Consequently, we evaluated k_1 and k_2 by the following method. When the reaction is done with excess methanol, it will follow pseudo-first-order kinetics with the rate constant (eq 10)

$$k_{obsd} = k_1 + k_2[CH_3OH] \quad (10)$$

The plot of k_{obsd}, determined for several different initial concentrations of methanol, vs. $[CH_3OH]$ should be a straight line with slope k_2 and intercept k_1.

Indeed, the first-order rate constants obtained for several different initial concentrations of methanol yielded a straight line, when plotted against $[CH_3OH]$, with slope 7.0×10^{-5} M^{-1} s^{-1} (k_2) and intercept 1.45×10^{-4} s^{-1} (k_1). Similar plots were established for ethanol and isopropyl alcohol (Figure 1). It should be noted that the k_1 values (Table I) are essentially the same for all three alcohols studied and agree very well with the rate constant for the dissociation of $(9\text{-BBN})_2$ in noncomplexing solvents such as hexane, CCl_4, and cyclohexane.[1] As expected, k_2 decreases in the order methanol > ethanol > isopropyl alcohol.

This observation presents a clear-cut kinetic evidence for the occurrence of the dimer attack mechanism in the reaction of unhindered alcohols with $(9\text{-BBN})_2$. Increasing the nucleophilicity of the substrate thus tends to favor direct attack on the dimer.

Kinetics in THF. The protonolysis of $(9\text{-BBN})_2$ in THF with hindered alcohols and phenol exhibits first-order kinetics (Table II), showing that the reaction proceeds by the dissociation mechanism. The kinetics of protonolysis of $(9\text{-BBN})_2$ by a few unhindered alcohols in THF were reported earlier.[5] The rates are very close to that observed for *tert*-butyl alcohol. Obviously in THF, the dimer attack mechanism is relatively unimportant. In view of the remarkable capability of THF to dissociate $(9\text{-BBN})_2$ into 9-BBN monomer,[1g] we believe that the dissociation mechanism predominates over any possible dimer attack pathway.

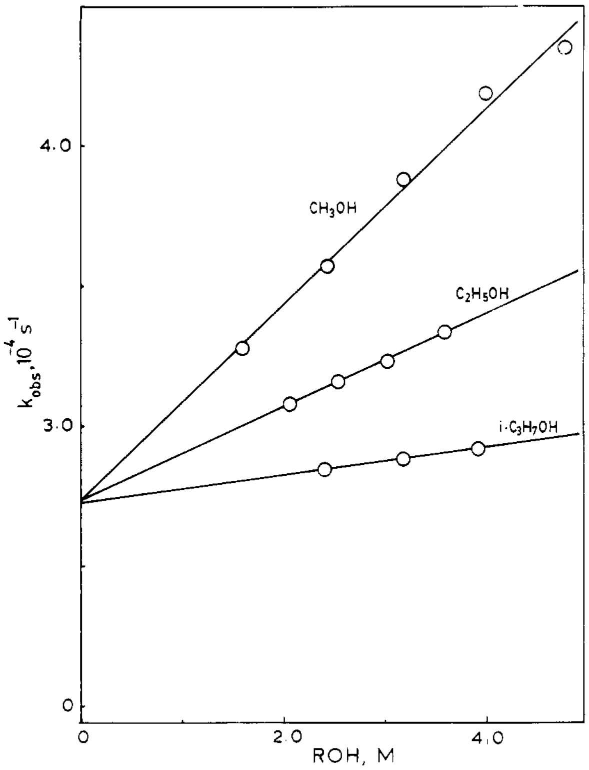

Figure 1. Plots of k_{obsd} vs. [ROH] for the protonolysis of $(9\text{-BBN})_2$ (0.200 M) with methanol, ethanol, and isopropyl alcohol in CCl_4 at 25 °C.

Structural Effects. The kinetic study does not reveal the mechanistic details beyond the dissociation of $(9\text{-BBN})_2$. We therefore undertook to determine the relative rates of the reaction of representative alcohols and phenols with $(9\text{-BBN})_2$ in THF at 25 °C by the competitive method. However, we faced a major difficulty. Our preliminary studies indicated that the *B*-alkoxy-9-BBN product exchanges rapidly with alcohols (eq 11). Consequently,

(11)

we could not set up competition experiments involving two alcohols in which the relative reactivity would be determined by an analysis of the products. Fortunately, we discovered a practical solution. It proves possible to compare the relative rate of protonolysis of $(9\text{-BBN})_2$ by an alcohol with that of the hydroboration of an alkene of suitable reactivity, such as 1-decene, using the competition method. Thus equimolar quantities of an alcohol and an alkene were allowed to react with an insufficient amount of 9-BBN and the amount of H_2 evolved was measured by a gas buret. From the hydrogen evolved, the amount of alcohol reacted could be calculated. From this quantity, the amount of alkene reacted was deduced. The relative rates were then obtained by using the Ingold–Shaw expression.[6] The data are summarized in Table III.

Steric Effects. The reactivity of alcohols toward the protonolysis of 9-BBN decreases sharply with increasing steric requirements of the alkyl groups. The same effect is observed for ortho-substituted phenols.

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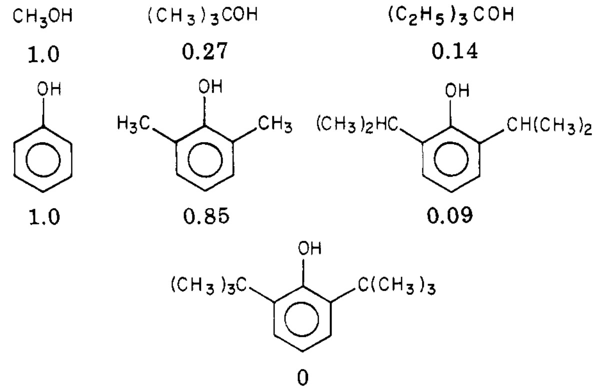
(6) Ingold, C. K.; Shaw, F. R. *J. Chem. Soc.* **1927**, 2918–2926.



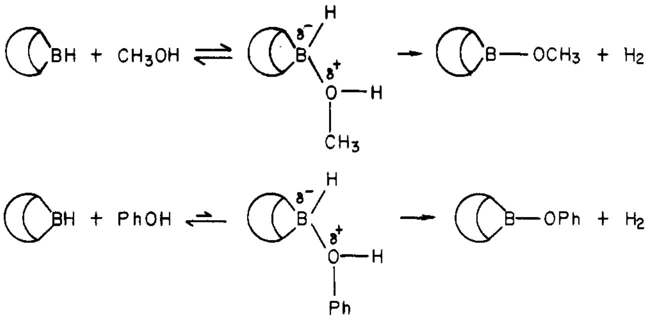
However, there is a puzzle. The reactivity of phenol is comparable to that of triethylcarbinol, yet the steric requirements of the phenyl group must be far lower than those of the triethylmethyl group. Obviously, electronic effects must play a very important role in this reaction.

Electronic Effects. Benzyl alcohol is considerably more reactive than methanol.

$$\underset{1.00}{CH_3OH} \quad \underset{4.32}{Ph\text{-}CH_2OH} \quad \underset{0.13}{Ph\text{-}OH}$$

Presumably, this is a reflection of the *-I* effect of the phenyl substituent, increasing the acidity of the O–H bond. However, this cannot be the sole determining factor. Phenol is far more acidic than benzyl alcohol, yet its rate of protonolysis is far slower. How can we account for the far lower reactivity of phenols in the protonolysis of 9-BBN?

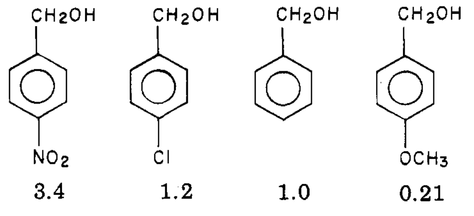
One possible explanation is that the protonolysis proceeds through a prior coordination of the oxygen atom of the alcohol with the boron.



The observed rates would then be a complex function of the relative ability of the oxygen atom of the alcohol or the phenol to coordinate with the boron and the relative acidity of the contained proton. The much lower donor properties of the oxygen atom in phenol would result in a markedly decreased formation of the complex, which could lead to a decreased rate of formation of H_2.

We examined the effect of substituents, both in benzyl alcohol and in phenol, to understand their effect. Somewhat surprisingly, we observed opposite effects.

In benzyl alcohol electron-withdrawing substituents increase, and electron-releasing ones decrease, the rate of protonolysis.

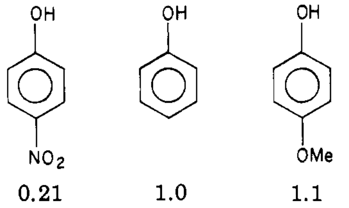


Presumably, in alcohols, which are better nucleophiles, the limiting factor must be the acidity of the O–H bond. Consequently, the strong acid, *p*-nitrobenzyl alcohol, reacts faster.

Table III. Relative Rates for the Protonolysis of $(9\text{-BBN})_2$ by Representative Alcohols and Phenols in THF at 25 °C

	relative rate	
compound	1-decene = 100	methanol = 100
p-nitrobenzyl alcohol	1360	1470
p-chlorobenzyl alcohol	465	502
benzyl alcohol	400	432
1-decene	100	108
methanol	92.6	100
p-methoxybenzyl alcohol	84.0	90.7
ethanol	62.9	67.9
isopropyl alcohol	43.7	47.2
cyclopentanol	42.9	46.3
cyclohexanol	41.7	45.0
cycloheptanol	35.3	38.1
tert-butyl alcohol	24.7	26.7
2,3-dimethyl-2-butanol	15.7	17.0
p-methoxyphenol	13.4	14.5
triethylcarbinol	12.5	13.5
o-cresol	12.5	13.5
phenol	12.1	13.1
2,6-dimethylphenol	10.2	11.0
p-nitrophenol	2.6	2.8
o-*tert*-butylphenol	1.1	1.2
2,6-diisopropylphenol	1.1	1.2
2.6-di-*tert*-butylphenol	0	0

On the other hand, in phenols, the effect is exactly opposite.



Presumably in phenols, the dominating factor is the ability of the oxygen atom to coordinate with boron. Here the weaker basic properties of the *p*-nitro derivative results in a slower rate.

Thus the observed electronic effects strongly suggest that hydrogen production proceeds through the prior formation of a complex between the hydroxyl group and the 9-BBN monomer.

Experimental Section

Detailed procedures for the manipulation of boron reagents have been outlined in Chapter 9 of ref 7. All glassware, syringes, and needles were dried for several hours in an oven at 140 °C. Syringes were assembled while hot and cooled as assembled units. The glassware was also assembled hot and cooled under a stream of dry nitrogen. The liquid alcohols and phenols were purified by distillation and dried over molecular sieves. The solid alcohols and phenols were recrystallized from suitable solvents and dried in vacuo before use.

Kinetics of Protonolysis. The protonolysis of $(9\text{-BBN})_2$ was followed by measuring the volume of H_2 evolved as a function of time. A detailed procedure was reported earlier.[5] In the present studies, the reactions were done in CCl_4 and THF at 25 °C.

Relative Rates. The relative rate of protonolysis by an alcohol was compared with that of hydroboration of a suitable alkene by using the competition method. An oven-dried, nitrogen-cooled, round-bottom flask was equipped with a water condenser and connected to a gas buret through a dry ice–acetone trap. Into

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(7) Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. "Organic Syntheses via Boranes"; Wiley-Interscience: New York, 1975; Chapter 9.

the flask 10 mL of THF, 5.0 mmol of an alcohol, and 5.0 mmol of a suitable alkene, say 1-decene, were introduced. The reaction flask was surrounded by a bath at 25 °C. After the system reached equilibrium, 2.5 mmol of $(9\text{-BBN})_2$ in THF was added and the amount of H_2 gas evolved was measured. After the reaction was complete, the number of mmol of H_2 evolved was calculated, after correcting for the temperature and pressure, which corresponds to the amount of alcohol reacted. From this, the amount of alkene reacted was computed. From the initial and final amounts of alcohol and alkene, the relative rate was calculated by using the Ingold–Shaw expression:[6]

$$\frac{k_{\text{alcohol}}}{k_{\text{alkene}}} = \frac{\ln\,[\text{alcohol}]_{\text{initial}} - \ln\,[\text{alcohol}]_{\text{final}}}{\ln\,[\text{alkene}]_{\text{initial}} - \ln[\text{alkene}]_{\text{final}}}$$

In the case of less reactive alcohols and phenols, *cis*-2-nonene was used for the competition experiment.

Acknowledgment. We thank the National Science Foundation for Grants CHE 76-20846 and CHE 79-18881.

Registry No. $(9\text{-BBN})_2$, 70658-61-6; CH_3OH, 67-56-1; PhOH, 108-95-2; $(CH_3)_3COH$, 75-65-0; $(C_2H_5)_3COH$, 597-49-9; *p*-nitrobenzyl alcohol, 619-73-8; *p*-chlorobenzyl alcohol, 873-76-7; benzyl alcohol, 100-51-6; 1-decene, 872-05-9; *p*-methoxybenzyl alcohol, 105-13-5; ethanol, 64-17-5; isopropyl alcohol, 67-63-0; cyclopentanol, 96-41-3; cyclohexanol, 108-93-0; cycloheptanol, 502-41-0; 2,3-dimethyl-2-butanol, 594-60-5; *p*-methoxyphenol, 150-76-5; *o*-cresol, 95-48-7; 2,6-dimethylphenol, 576-26-1; *p*-nitrophenol, 100-02-7; *o*-*tert*-butylphenol, 88-18-6; 2,6-diisopropylphenol, 2078-54-8; 2,6-di-*tert*-butylphenol, 128-39-2; tri-*n*-octylcarbinol, 17687-72-8; 2,2,4-trimethyl-3-pentanol, 5162-48-1.

Nucleophilic Attacks on Activated 9-Methylenefluorenes. Application of the Ritchie Equation to Low-Lying LUMO Substrates

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Rate constants (k_{nuc}) for nucleophilic attacks on 9-(dinitromethylene)-, 9-(dicyanomethylene)-, and 9-(nitromethylene)fluorene (FDN, FDCN, and FN, respectively) have been determined. The slope of the plots of log k_{nuc} vs. N_+ values are 1.23 ($r = 0.998$) for FDN and 1.29 ($r = 0.983$) for FDCN. These results indicate the need for incorporating a selectivity parameter in the Ritchie equation. FN displays an ambidentic behavior. In aqueous medium, CN^- reacts with FN at position 9 of the fluorene ring, whereas in Me_2SO and DMF, position α becomes more reactive. The final product of the reaction of CN^- at C-α is the corresponding vinyl cyanide. MeO^- in MeOH reacts with both sites with a ca. fivefold preference for position 9. The reactivity order of the three substrates is FDN > FDCN > FN. This order does not correlate with the pK_a of the activating groups, i.e., dinitromethane, malononitrile, and nitromethane. However, it does correlate with their deprotonation rate constants, indicating that the anomalous behavior of nitro-activated carbon acids in deprotonation reactions is not necessarily associated with a pyramidal nature in the transition state. It is suggested that the difference between substrates which obey the Ritchie equation and those which follow the Swain–Scott equation stems from the dissimilarity in the energies of their LUMOs. The first class of compounds is characterized by low LUMOs (LL) whereas high-energy LUMOs (HL) are typical of the second class. This results in a difference in the nature of the transition state of these reactions. On the basis of current theories it is suggested that the transition state of nucleophilic reactions with LL substrates is characterized by a relatively large extent of nucleophile–electrophile electron transfer as compared to reactions with HL substrates. This hypothesis is supported by the observed correlation between the thermodynamic ability to transfer electrons in solution and the nucleophilicity order $N_3^- > OH^- > CN^-$ which characterizes the N_+ scale. It is noteworthy that this order is the reverse of that typical for reactions with HL substrates where the Swain–Scott n scale is operative.

In spite of numerous theoretical studies and the wealth of experimental data gathered, nucleophilic reactions do not cease to attract the attention of organic chemists. Several years ago Ritchie established a new empirical nucleophilicity scale based on the reactions of nucleophiles with malachite green.[1] The reactivity was correlated by a single parameter equation ($\log k/k_0 = N_+$) which was found later to be applicable to other substrates such as diazonium ions,[1] carbonyl compounds,[2] electron-deficient aromatics,[3] and with some modification also activated olefins.[4] Ritchie noted that reactions which obey his equation display a different behavior pattern from that observed with reactions correlating with the Swain–Scott equation[5] ($\log k/k_0 = sn$). He suggested[1] that this difference could originate from the fact that in the first class of reactions, the nucleophile–electrophile bond formation is not coupled with the departure of the nucleophuge as is the case for substrates obeying the Swain–Scott equation.

We point out that there is an additional feature which is not common to these two reaction classes and that is the energy of the LUMO of the electrophiles. While the first class of substrates is highly electrophilic and posses low-lying LUMOs (LL), the LUMOs of the second class are generally σ^* orbitals and therefore of relatively much higher energy (HL for high LUMO). Since it is generally accepted that frontier orbital interaction, namely, HOMO(nucleophile)–LUMO(electrophile), determines the energetics and the course of the reaction,[6] it is highly likely

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