

REACTIONS OF TRIARYLMETHYL CARBOCATIONS WITH HYDRIDE DONORS AND OTHER NUCLEOPHILES

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The  $N_+$  scale of nucleophilicity, evaluated from reactivities toward carbocations, was initially interpreted in terms of anionic desolvation.<sup>1</sup> The scale also fits diazonium ion capture and deacylations, provided that allowance is made for partitioning of tetrahedral intermediates. However, nucleophilicities, especially towards esters, have often been correlated with basicity,<sup>2</sup> and for different series of reagents they have been rationalized using the hard-soft principle,<sup>3</sup> but the success of the  $N_+$  scale illustrates the importance of desolvation of anionic, and by implication, nonionic, nucleophiles, e.g., amines.

Our aim was to examine nucleophiles which discriminate markedly between carbocations and acyl centers, and we have followed reactions of malachite green ( $MG^+$ ) and tri-*p*-anisylmethyl cation ( $R^+$ ) with  $BH_4^-$ ,  $BH_3CN^-$  and *N*-benzylidihydronicotinamide (1), which are reactive towards carbocations,<sup>4,5</sup> but not in deacylation<sup>6a,b</sup> (Table 1). The reactions were followed using a stopped flow spectrophotometer for reactions of  $R^+$ , and a Gilford spectrophotometer for those of  $MG^+$ .<sup>7,8</sup> We also

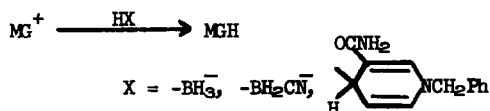


Table 1  
Reactivities of Carbocations with Hydride Donors and Nucleophiles<sup>a</sup>

Reagent	1	$BH_3CN^-$	$BH_4^-$ <sup>b</sup>	$OH^-$ <sup>b</sup>	$PhO^-$ <sup>c</sup>	$PhS^-$	<i>p</i> - $MeC_6H_4S^-$	<i>p</i> - $MeOC_6H_4S^-$	<i>p</i> - $NH_2C_6H_4S^-$
$R^+$ { $k_2$	$2.1 \times 10^5$	9000	$1.3 \times 10^6$	6600	$1.1 \times 10^5$	$1.8 \times 10^8$	$2.4 \times 10^8$	$3.6 \times 10^8$	$1.8 \times 10^8$
{ $\log k_{rel}$	1.5	0.1	2.2	0.0	1.2	4.4	4.6	4.7	4.4
$MG^+$ { $k_2$	27	2.7	32	1.64					
{ $\log k_{rel}$	1.2	0.2	1.2	0.0					

(a) In water at 25.0°;  $k_2$  (l. mole<sup>-1</sup> sec<sup>-1</sup>) is corrected where necessary for reaction with  $OH^-$ ; (b) ref. 7; (c) ref. 8.

measured rate constants of reactions of  $R^+$  with thiophenoxide ions which approach the diffusion controlled limit. The limit of ca.  $10^{10}$  is reached with diazonium ions,<sup>1</sup> but that for a bulky carbocation may be lower. The values of  $\log_{rel}$  (Table 1) differ from  $N_+$  only in the choice of reference reaction and the fitting of the data to give the best overall agreement.<sup>1</sup> The high reactivities of the thiophenoxide ions are consistent with the generally high nucleophilicity of thiolate ions, and the lower solvation of thiolate ion as compared with hydroxide ion, and electronic effects on reactivity are relatively small. As for reactions with phenoxide ions,<sup>6</sup> dispersive and hydrophobic interactions probably assist reactions of both 1 and thiophenoxide ions with carbocations (cf. ref. 7,9), but the difference between the reactivities of  $BH_4^-$  and  $BH_3CN^-$  is due largely to electron withdrawal by the cyano group. However the dihydronicotinamide (1) is very reactive towards the carbocations although there is no coulombic attraction between the reagents.

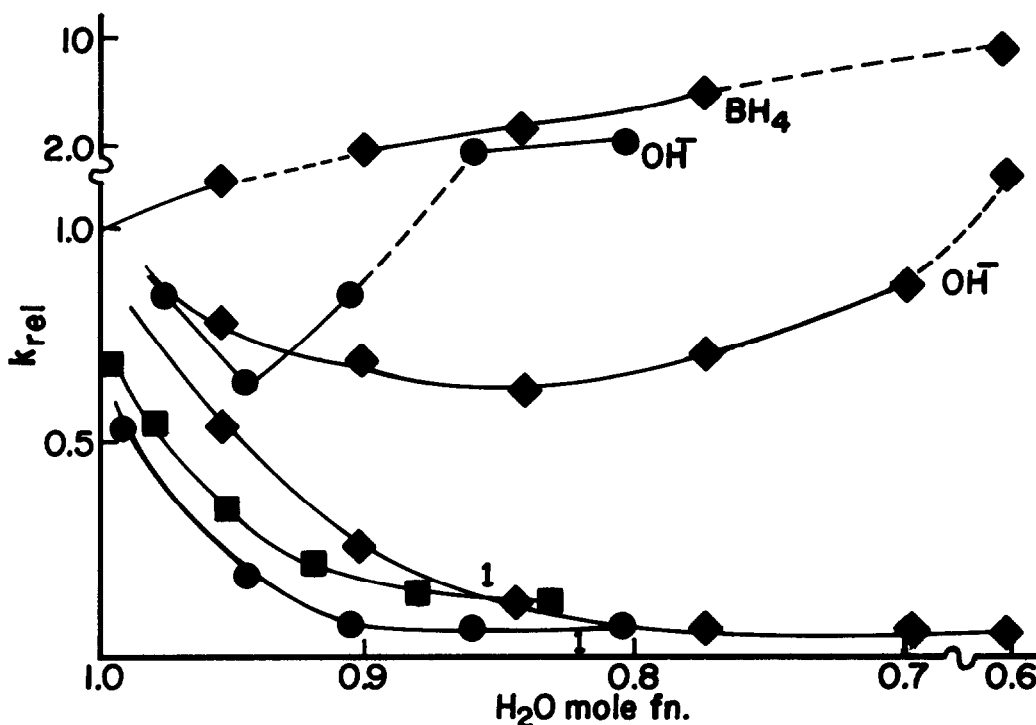
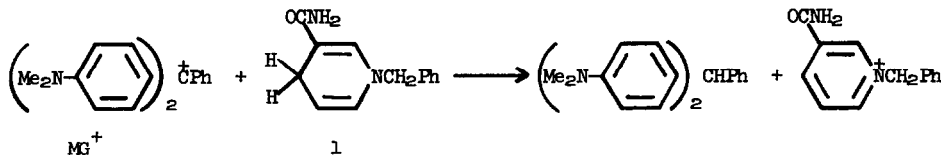


Figure 1. Solvent effects upon reactions of  $MG^+$  at  $25.0^\circ$ .

●  $t\text{-BuOH-H}_2\text{O}$ ; <sup>1,2</sup> ■ dioxane- $H_2O$ ; ◆  $MeCN-H_2O$ .

Solvent effects on hydride transfer to  $MG^+$  (Figure 1) are readily understandable in terms of qualitative solvent theory,<sup>10</sup> and anionic solvation.<sup>11</sup> Reaction with  $BH_4^-$  is markedly speeded by addition of organic solvent, but that of 1 is slowed, possibly because solvation of the

forming pyridinium ion in the transition state assists reaction, so that although the dihydronicotinamide (1) is almost as reactive as  $\text{BH}_4^-$  in water, the differential solvent effect makes  $\text{BH}_4^-$  very much more reactive in aqueous MeCN.



The rate minima for reaction of  $\text{OH}^-$  with  $\text{MG}^+$  in aqueous acetonitrile or t-butanol are understandable in terms of the effects of organic solvents on water structure,<sup>13</sup> because there are strong interactions between water and the highly solvated hydroxide ion which is acting as a nucleophile or a general base, so that solvent effects are completely different from that on reaction of  $\text{BH}_4^-$ . For reactions of  $\text{MG}^+$  the solvent isotope effects,  $k_{\text{OH}^-}/k_{\text{OD}^-} = 1.10$  and  $k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}} = 1.50$ , in the ranges observed earlier for attacks on carbocations,<sup>14</sup> whereas inverse solvent hydrogen isotope effects are often found for nucleophilic attack by  $\text{OH}^-$ , so that the evidence is consistent with hydroxide ion giving general base catalysis of the attack of  $\text{H}_2\text{O}$  on the carbocation<sup>1</sup> (cf. ref. 15, 16 for catalysis of reactions with  $\text{R}^+$  by tertiary amines).

An all embracing nucleophilicity scale appears to be a chimera, even for reactions in a single solvent, although strong hydration of anionic nucleophiles often presents such a large barrier to reaction that there is a close correlation between nucleophilicity and anionic solvation,<sup>11</sup> and it may obscure other structural effects. For anion-cation recombination no existing covalencies are broken, and desolvation may then be the major barrier to reaction, but proton transfers are important in reactions of some amines and probably of water,<sup>1,15,16</sup> and C-H or B-H bonds are broken in hydride transfers. Although the  $\text{N}_+$  scale can be applied to attack of some nucleophiles on carbonyl compounds there is little or no correlation between the reactivities of  $\text{OH}^-$ ,  $\text{BH}_4^-$  and the dihydronicotinamide (1) towards carbonyl compounds and carbocations, in that 1 is reactive towards carbonyl groups only under biological conditions, and the borohydrides are relatively ineffective deacylating agents. But there is also little correlation between the reactivity of these nucleophiles towards carbocations and their kinetic or equilibrium basicity. For example carbocations compete very effectively with  $\text{H}^+$  for cyanoborohydride ion<sup>4b,17</sup> and we find that considerable amounts of  $\text{RH}$  are formed when a solution of  $\text{ROH} + \text{BH}_4^-$  is added to excess dilute  $\text{H}_2\text{SO}_4$ .

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