

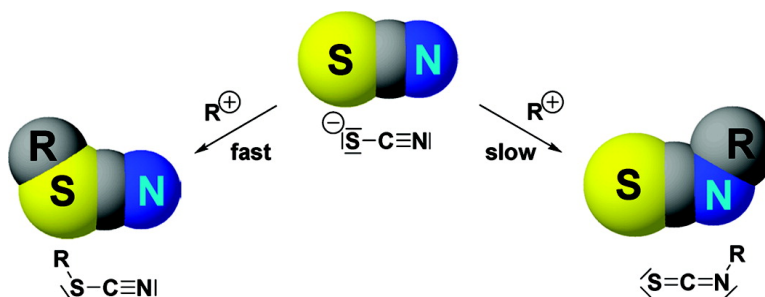
Article

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## Ambident Reactivity of the Thiocyanate Anion Revisited: Can the Product Ratio Be Explained by the Hard Soft Acid Base Principle?

Robert Loos,<sup>†</sup> Shinjiro Kobayashi,<sup>‡</sup> and Herbert Mayr<sup>\*†</sup>

Contribution from the Department Chemie der Ludwig-Maximilians-Universität München, Butenandtstrasse 5-13 (Haus F), D-81377 München, Germany, and Institute for Fundamental Research of Organic Chemistry, Kyushu University, Higashi-ku, Fukuoka 812-8581, Japan

Received July 16, 2003; E-mail: Herbert.Mayr@cup.uni-muenchen.de

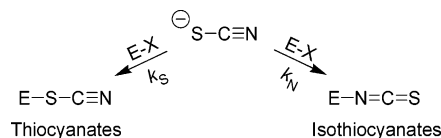
**Abstract:** Laser flash photolysis and stopped-flow methods have been employed to determine the kinetics of the reactions of benzhydrylium ions with both termini of the thiocyanate ion. In contrast to previous investigations which reported sulfur/nitrogen ratios of  $k_S/k_N = 2-10$  for the reactions of carbocations with  $SCN^-$ , values of  $k_S/k_N = 10^3-10^4$  are now derived from absolute rate constants. This discrepancy is explained by the fact that the data determined in this investigation are the first which refer to activation-controlled attack of carbocations at both termini of the thiocyanate ion, while previous reactivity ratios included diffusion-controlled reactions. It is concluded that the selectivities of the reactions of carbocations with the thiocyanate ion cannot be explained by the hard soft acid base principle.

### Introduction

The thiocyanate anion is an ambident nucleophile<sup>1</sup> which may react with electrophiles at sulfur to give thiocyanates or at nitrogen to give isothiocyanates (Scheme 1). Already in 1875, Gerlich<sup>2</sup> and Billeter<sup>3</sup> reported the rearrangement of allyl thiocyanate into allyl isothiocyanate during distillation. This observation laid the foundation for the later conclusion that, in general, isothiocyanates are thermodynamically more stable than the isomeric thiocyanates.<sup>4-6</sup> On the other hand, under conditions of kinetic control, alkylations of  $SCN^-$  usually yield thiocyanates as the main products, indicating faster attack at sulfur than at nitrogen.<sup>6</sup>

The observation that the ratio  $k_S/k_N$  ranges from  $10^2$  to  $10^3$  in  $S_N2$  type reactions<sup>7,8</sup> and from 2 to 10 in  $S_N1$  type reactions<sup>9-13</sup> has been rationalized on the basis of Pearson's

### Scheme 1



hard soft acid base (HSAB) principle:<sup>14</sup> "As the electrophilic character of the reaction center increases, the reactivity of the more basic nitrogen atom, which forms the stronger bond to carbon, increases with respect to that of the more polarizable sulfur atom."<sup>9b,15</sup>

However, no absolute rate constants have been reported for the reactions of carbocations with the thiocyanate ion, and it is not known whether the relative rates for S- and N-alkylation correspond to encounter-limited reactions of this ambident nucleophile or to rate-determining chemical bond formation for reactions that are slower than the diffusion-controlled limit.<sup>16</sup> We report here absolute rate constants for additions of the thiocyanate ion to substituted benzhydrylium ions and show that the rate constant ratios for S- and N-alkylations that are not diffusion-controlled are much larger than previously reported ratios for reactions of carbocations with the thiocyanate ion. These results call for a reevaluation of earlier proposals to rationalize the ambident nucleophilic reactivity of this nucleophile.

### Experimental Section

**Materials.** Commercially available acetonitrile (Aldrich, p.a., H<sub>2</sub>O < 50 ppm) was used without further purification for all laser flash

<sup>†</sup> Universität München.

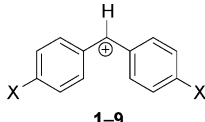
<sup>‡</sup> Kyushu University.

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**Table 1.** Structures of the Benzhydryl Cations 1–9 and Absorption Maxima for the Cations 4–9 Used in This Work


X	Ar <sub>2</sub> CH <sup>+</sup>	λ <sub>max</sub> (CH <sub>3</sub> CN) /nm	λ <sub>max</sub> (CH <sub>2</sub> Cl <sub>2</sub> ) <sup>a</sup> /nm
H	<b>1</b>	435 <sup>b</sup>	
Me	<b>2</b>	464 <sup>b</sup>	
OMe	<b>3</b>	500 <sup>b</sup>	
NPh(CH <sub>2</sub> CF <sub>3</sub> )	<b>4</b>	592	601
NMe(CH <sub>2</sub> CF <sub>3</sub> )	<b>5</b>	586	593
NPh <sub>2</sub>	<b>6</b>	645	672
N-morpholino	<b>7</b>	612	620
NPhMe	<b>8</b>	613	622
NMe <sub>2</sub>	<b>9</b>	605	613

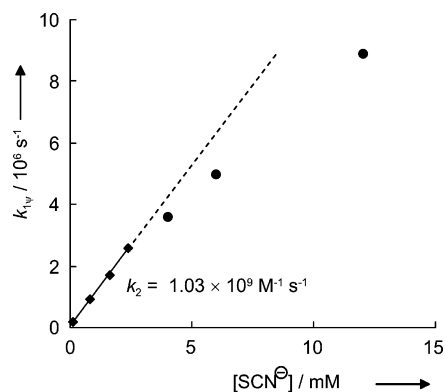
<sup>a</sup> From ref 18. <sup>b</sup> From ref 19.

experiments. For the stopped-flow experiments, acetonitrile (Acros, HPLC-grade) was first distilled from CaH<sub>2</sub>. It was then refluxed for more than 3 days over diphenylketene<sup>17</sup> (1.5 g L<sup>-1</sup>) and freshly distilled prior to the kinetic experiments. Tetra-*n*-butylammonium thiocyanate (Fluka, ≥99%) was used without further purification. The benzhydryl tetrafluoroborates (**4–9**)-BF<sub>4</sub> (see Table 1) were prepared as described in ref 18. Details will be published separately. The benzhydrylium salts (**4–9**)-BF<sub>4</sub> used in this study (Table 1) are colored substances with λ<sub>max</sub> = 586–645 nm in acetonitrile, that is, 7–9 nm shorter than those reported in CH<sub>2</sub>Cl<sub>2</sub><sup>18</sup> (Table 1). An exception is **6**-BF<sub>4</sub> which shows a pronounced hypsochromic shift of 27 nm in acetonitrile relative to CH<sub>2</sub>Cl<sub>2</sub>.

**Laser Flash Kinetics.** The kinetics of the reactions of the benzhydrylium ions with *n*Bu<sub>4</sub>N<sup>+</sup>SCN<sup>-</sup> were studied in acetonitrile at 20 °C. Stock solutions of (**4–8**)-BF<sub>4</sub> and of *n*Bu<sub>4</sub>N<sup>+</sup>SCN<sup>-</sup> in acetonitrile were freshly prepared before the laser flash experiments. Aliquots of these solutions (1.7–299 equiv of *n*Bu<sub>4</sub>N<sup>+</sup>SCN<sup>-</sup>) were transferred into 5-mL flasks and diluted with acetonitrile to yield (1–7) × 10<sup>-5</sup> M solutions of (**4–8**)-NCS with absorbances of approximately 1 at 266 nm. While the combinations of (**4–6**)-BF<sub>4</sub> with *n*Bu<sub>4</sub>N<sup>+</sup>SCN<sup>-</sup> gave colorless solutions of the covalent benzhydryl isothiocyanates, the solutions of **7**-NCS and **8**-NCS remained blue, indicating the presence of a mixture of ionic and covalent material.

The solutions were irradiated immediately after preparation in a rectangular quartz cell with a (3–6)-ns laser pulse (266 nm). The photolysis of (**4–8**)-NCS resulted in the formation of the transient benzhydryl cations **4–8** which were detected by their UV–vis absorbances at λ<sub>max</sub> = 586–645 nm. In the experiments with **7**-NCS and **8**-NCS, which are partially ionic in acetonitrile, particularly in the case of low concentrations of NCS<sup>-</sup>, the laser pulse caused an increase of the benzhydrylium ion concentrations. The decays of these transient optical absorbances were followed at λ<sub>max</sub> of the benzhydryl cations, and in all cases an exponential decay was observed. First-order rate constants *k*<sub>1 $\psi$</sub>  (s<sup>-1</sup>) were obtained by least-squares fitting of the absorbances (averaged from at least four kinetic runs at each nucleophile concentration) to the single-exponential  $A_t = A_0 \exp(-k_{1\psi}t) + C$ .

As shown for the reactions of **4** with SCN<sup>-</sup> in Figure 1, *k*<sub>1 $\psi$</sub>  increases linearly with the concentration of SCN<sup>-</sup> for [SCN<sup>-</sup>] = 0.1–2.5 mM, but shows a smaller increase at higher concentrations of *n*Bu<sub>4</sub>N<sup>+</sup>SCN<sup>-</sup>, probably due to ion pairing. A similar behavior was observed for the reactions of the other benzhydrylium ions with SCN<sup>-</sup>. The second-order rate constants for the reactions of **4–8** with SCN<sup>-</sup> were derived

**Figure 1.** Determination of the second-order rate constant for the reaction of **4** with SCN<sup>-</sup> (acetonitrile, 20 °C).

from the slopes of the linear parts of the *k*<sub>1 $\psi$</sub>  versus [SCN<sup>-</sup>] plots.<sup>20</sup> Complications in the evaluation of the reaction of **8** with SCN<sup>-</sup> are explicitly discussed in the Supporting Information.

**Stopped-Flow Kinetics.** Stopped-flow spectrophotometer systems (Hi-Tech SF-61DX2 controlled by Hi-Tech KinetAsyst2 software) were used for the investigation of the slower reactions (*k*<sub>2</sub> < 10<sup>5</sup> M<sup>-1</sup> s<sup>-1</sup>) of benzhydrylium ions with SCN<sup>-</sup>. The kinetic experiments were performed at 20 °C by mixing equal volumes of solutions of *n*Bu<sub>4</sub>N<sup>+</sup>SCN<sup>-</sup> and of the benzhydrylium tetrafluoroborate in acetonitrile. Thiocyanate concentrations at least 8 times higher than the benzhydryl cation concentrations were usually employed, resulting in pseudo-first-order kinetics with an exponential decay of the benzhydryl cation concentration. First-order rate constants *k*<sub>1 $\psi$</sub>  (s<sup>-1</sup>) were obtained by least-squares fitting of the absorbance/time plots (averaged from at least four kinetic runs at each SCN<sup>-</sup> concentration) to the single exponential  $A_t = A_0 \exp(-k_{1\psi}t) + C$ . Second-order rate constants were derived from plots of *k*<sub>1 $\psi$</sub>  versus [SCN<sup>-</sup>] as described above.

Concentrations and rate constants for the individual kinetic experiments are given in the Supporting Information.

**Equilibrium Measurements.** Equilibrium constants at 20 °C were derived from UV–vis absorbances of the benzhydrylium ions in the presence of variable concentrations of *n*Bu<sub>4</sub>N<sup>+</sup>SCN<sup>-</sup>. Details of the calculation of the equilibrium constants *K*<sub>S</sub> and *K*<sub>N</sub> from laser flash, stopped-flow, or conventional UV–vis experiments are described in the Supporting Information.

**Product 6-NCS from 6-BF<sub>4</sub> and *n*Bu<sub>4</sub>N<sup>+</sup>SCN<sup>-</sup>.** A solution of *n*Bu<sub>4</sub>N<sup>+</sup>SCN<sup>-</sup> (301 mg, 1.00 mmol) in 1 mL of dry CH<sub>2</sub>Cl<sub>2</sub> was added to a blue solution of **6**-BF<sub>4</sub> (588 mg, 1.00 mmol) in 50 mL of dry CH<sub>2</sub>Cl<sub>2</sub> at room temperature. The color of the mixture faded immediately, but when the solvent was removed in vacuo, a green-blue residue remained, which was stirred with dry diethyl ether for 10 min and filtered to remove the insoluble *n*Bu<sub>4</sub>N<sup>+</sup>BF<sub>4</sub><sup>-</sup>. Evaporation of the ether yielded 419 mg of a green-blue residue of bis(4-diphenylaminophenyl)methyl isothiocyanate (**6**-NCS) contaminated by traces of *n*Bu<sub>4</sub>N<sup>+</sup>BF<sub>4</sub><sup>-</sup> and minor amounts of unidentified byproducts. Attempted chromatographic purification (silica gel) resulted in a quantitative conversion into the corresponding benzhydryl.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 5.86 (s, 1H), 7.00–7.27 (m, 28H). <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>): δ 63.88 (d, Ar<sub>2</sub>CH), 123.05, 123.27, 124.69, 127.48, 129.32 (5 d), 132.52, 147.40, 147.85 (3 s). A signal for the isothiocyanate group could not be observed, in accord with Kessler's report that isothiocyanates give rise to broad <sup>13</sup>C NMR signals whereas thiocyanates show sharp and easily detectable signals.<sup>21</sup> IR (KBr): 2060 (broad) [–NCS], 1589, 1507, 1491, 1330, 1314, 1279,

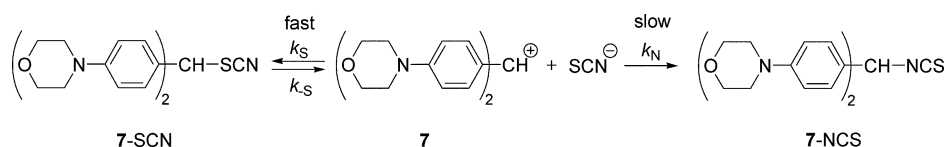
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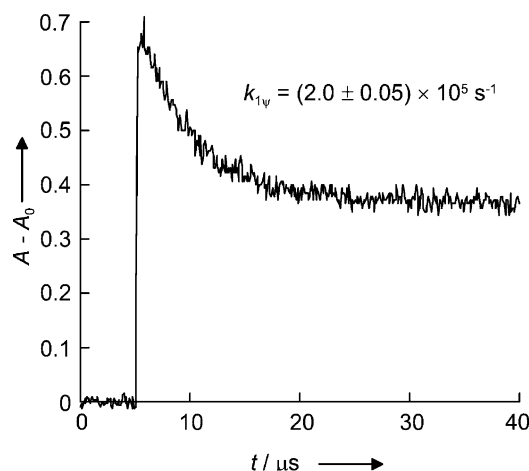
## Scheme 2



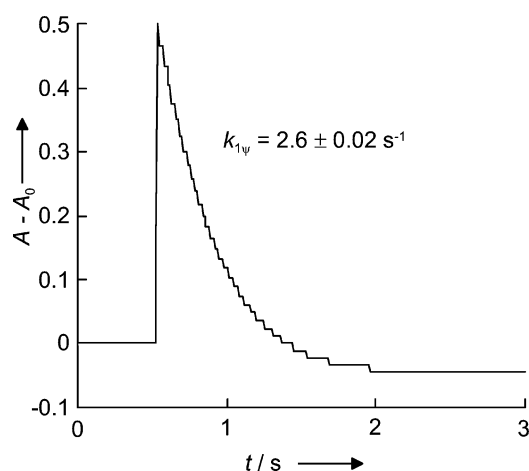
1175, 754, 696  $\text{cm}^{-1}$ . MS (FAB<sup>+</sup>):  $m/z$  501 (basis peak,  $\text{Ar}_2\text{CH}^+$ ). MS (FAB<sup>-</sup>):  $m/z$  58 (basis peak,  $\text{SCN}^-$ ).

## Results and Discussion

Irradiation of 7-NCS in acetonitrile (in the presence of a large excess of  $n\text{Bu}_4\text{N}^+\text{SCN}^-$  to shift the ionization equilibrium toward covalent 7-NCS) with a (3–6)-ns laser pulse at  $\lambda = 266$  nm resulted in the formation of the benzhydrylium ion 7 with  $\lambda_{\text{max}} = 612$  nm.<sup>22</sup> When this photolysis experiment was performed in a 6.14 mM solution of  $n\text{Bu}_4\text{N}^+\text{SCN}^-$  in acetonitrile, an exponential decay of almost 40% of the carbocation was observable within 30  $\mu\text{s}$  (Figure 2), while the remaining transient disappeared within 0.2 s.



**Figure 2.** Fast decay of the absorbance of 7 (0.05 mM) in the presence of 6.14 mM  $n\text{Bu}_4\text{N}^+\text{SCN}^-$  in acetonitrile (20 °C) – the averaged  $k_{1\psi}$  value from several experiments is given in the Supporting Information.



**Figure 3.** Slow decay of the absorbance of 7 in the presence of 0.409 mM  $n\text{Bu}_4\text{N}^+\text{SCN}^-$  in acetonitrile (20 °C) – the averaged  $k_{1\psi}$  value from several experiments is given in the Supporting Information.<sup>23</sup>

At 15 times lower concentration of  $n\text{Bu}_4\text{N}^+\text{SCN}^-$  (0.409 mM), the decay of absorbance due to the fast reaction was

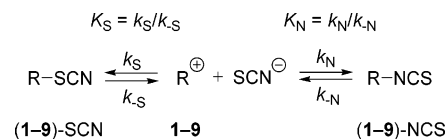
(22) At low  $\text{SCN}^-$  concentrations, 7-NCS is partially ionic, and the laser pulse caused an increase of the degree of ionization.

almost negligible, and the exponential decay caused by the slow reaction is shown in Figure 3.

This behavior can be explained by Scheme 2. Fast attack of 7 at the sulfur terminus of  $\text{N}\equiv\text{C}-\text{S}^-$  ( $k_S = 1.3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ) results in the formation of the thiocyanate 7-SCN. Because of the low thermodynamic stability of this adduct, equilibrium is reached after 40% conversion. The consecutive slow reaction with  $k_N = 6.2 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  results in the formation of the thermodynamically more stable isothiocyanate 7-NCS.

This interpretation is in accord with the results of stopped-flow experiments. Combination of 0.1–0.7 mM solutions of  $n\text{Bu}_4\text{N}^+\text{SCN}^-$  with 0.015 mM solutions of 7-BF<sub>4</sub> in acetonitrile resulted in 6–14% consumption of the carbocation during mixing (3 ms, reversible formation of 7-SCN), and the decay of the absorbance of the remaining 7 occurred with almost the same rate constant ( $k_N = 5.3 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ ) as determined for the slow reaction in the laser flash experiment (formation of 7-NCS). At lower concentrations of  $\text{SCN}^-$ , the reaction did not proceed with quantitative formation of 7-NCS and reached equilibrium.

## Scheme 3



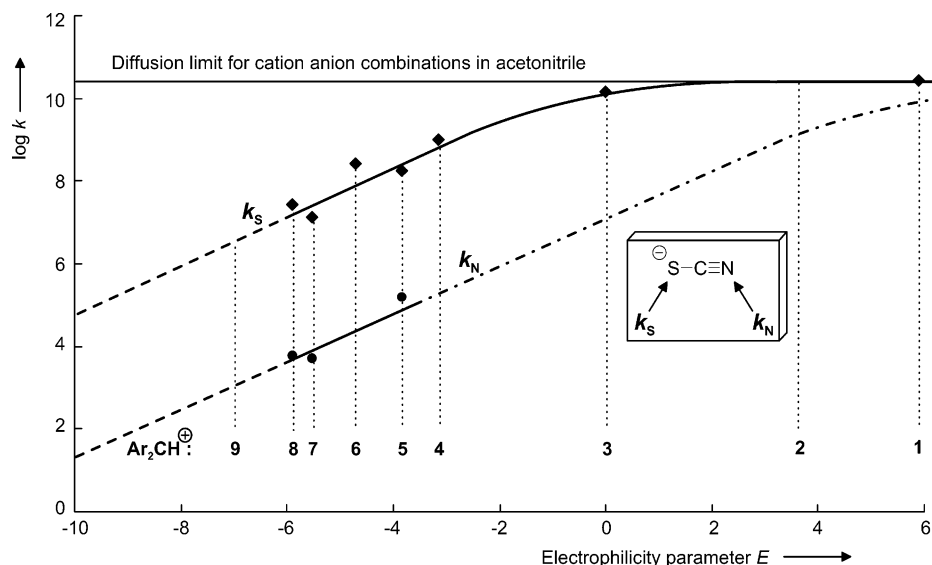
Analogous observations were made for the reactions of  $\text{SCN}^-$  with other benzhydrylium ions (Scheme 3). In the case of 8,  $k_S$  was determined with laser flash photolytically generated carbocations, and  $k_N$  was obtained with the stable salt 8-BF<sub>4</sub> in stopped-flow experiments. Despite its slightly smaller electrophilicity parameter  $E$ , the benzhydrylium ion 8 reacts somewhat faster with  $\text{SCN}^-$  in acetonitrile than does 7 ( $k_S$  and  $k_N$ ).<sup>24</sup>

In line with this interpretation, the fast decays ( $2 \times 10^8$  to  $3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ) of the laser flash photolytically generated benzhydrylium ions 1–6 in solutions of  $n\text{Bu}_4\text{N}^+\text{SCN}^-$  in acetonitrile are assigned to the formation of the thiocyanates (1–6)-SCN ( $k_S$ , Table 2). Because the equilibrium for the formation of the thiocyanates (1–6)-SCN is far on the side of the covalent products, the direct observation of two separate processes was usually not possible. Only in the case of 5 was the rate of formation of 5-NCS observable, when a low  $\text{SCN}^-$  concentration was used to avoid the almost complete conversion of 5 into 5-SCN by the fast process.

We have not succeeded in determining rate constants for reactions of  $\text{SCN}^-$  with less electrophilic benzhydrylium ions, because even in the case of 9, which is only 1 order of

(23) The fact that the absorbance measured 2 s after the laser pulse is smaller than before the laser pulse (Figure 3) indicates that part of the benzhydrylium system is irreversibly destroyed, possibly because of homolytic C–NCS cleavage and dimerization of the resulting radicals.

(24) An analogous reversal of electrophilicity of 7 and 8 in acetonitrile and water as compared to dichloromethane has previously been observed in the München laboratory for reactions with other nucleophiles.



**Figure 4.** Rate constants for the reactions of the benzhydrylium ions **1–9** with the thiocyanate ion at the S and N terminus (20 °C, acetonitrile). Dashed (---): Reactions do not take place because of an unfavorable equilibrium constant. Dash-dotted (· · · ·): Not observable because of the faster quantitative reaction at sulfur.

**Table 2.** Rate ( $k_S$ ,  $k_N$ ) and Equilibrium ( $K_S$ ,  $K_N$ ) Constants for the Reactions of Benzhydrylium Ions with the S and N Terminus of the Thiocyanate Anion ( $\text{SCN}^-$ ) at 20 °C<sup>a</sup>

$\text{Ar}_2\text{CH}^+$	$E^b$	$k_S/\text{M}^{-1}\text{s}^{-1}$	$K_S/\text{M}^{-1}$	$k_N/\text{M}^{-1}\text{s}^{-1}$	$K_N/\text{M}^{-1}$
<b>1</b>	5.90	$2.7 \times 10^{10}$ (LF) <sup>d</sup>			
<b>3</b>	0.00	$1.4 \times 10^{10}$ (LF) <sup>d</sup>			
<b>4</b>	-3.14	$1.0 \times 10^9$ (LF)			
<b>5</b>	-3.85	$1.7 \times 10^8$ (LF)	$2.4 \times 10^3$ (LF) $5.1 \times 10^3$ (SF)	$1.5 \times 10^5$ (SF)	
<b>6</b>	-4.72	$2.5 \times 10^8$ (LF)	$2.8 \times 10^4$ (LF)		
<b>7</b>	-5.53	$1.3 \times 10^7$ (LF)	$2.0 \times 10^2$ (LF)	$6.2 \times 10^3$ (LF) $5.3 \times 10^3$ (SF)	$5.5 \times 10^3$ (SF) <sup>f</sup> $9.6 \times 10^3$ (UV)
<b>8</b>	-5.89	$2.7 \times 10^7$ (LF) <sup>e</sup>		$5.9 \times 10^3$ (SF)	$3.2 \times 10^3$ (SF) <sup>f</sup> $3.7 \times 10^3$ (UV)

<sup>a</sup> (LF) indicates laser flash experiments; (SF) indicates stopped-flow experiments; (UV) indicates standard UV-vis experiments. <sup>b</sup> Electrophilicity parameter from ref 18. <sup>c</sup> Because  $K_S$  and  $K_N$  determined by different methods differed by a factor of 2, this error has to be assumed for all equilibrium constants. <sup>d</sup> From ref 25. <sup>e</sup> Of little precision, see the Supporting Information for details. <sup>f</sup> Approximate equilibrium constants obtained by dividing the rate constant for the forward reaction  $k_N$  through the rate constant for the reverse reaction  $k_{-N}$  derived from the plot of  $k_{1\psi}$  versus  $[\text{SCN}^-]_0$ , see the Supporting Information.

magnitude less electrophilic than **8** (Table 1), the equilibrium constant for the formation of the covalent adduct **9**-NCS is so small that the rate of this process could not be measured.

All rate and equilibrium constants which could be determined for the reactions of benzhydrylium ions with  $\text{SCN}^-$  are listed in Table 2, which shows that some values have been obtained by two different methods. Whereas  $k_N$  (**7** +  $\text{SCN}^-$ ) determined by laser flash and stopped-flow experiments differed by less than 17%,  $K_S$  (**5** +  $\text{SCN}^-$ ) was determined to be 2 times smaller by the laser flash than by the stopped-flow experiments. Because of the problems to determine absolute concentrations of  $\text{Ar}_2\text{CH}^+$  under the conditions of the laser flash experiments (destruction of the benzhydrylium system, see ref 23), the equilibrium constants determined by the laser flash experiments are considered to be less accurate.

In numerous publications, we have demonstrated that the rates of the reactions of carbocations with nucleophiles can be described by eq 1, where electrophiles are characterized by a single parameter  $E$ , while nucleophiles are characterized by the

nucleophilicity parameter  $N$  and the slope parameter  $s$ .<sup>18,26–30</sup> Equation 1 is better suited for practical applications than the equivalent equation  $\log k = Nu + sE$ , where the nucleophile-dependent parameters  $s$  and  $N$  are combined ( $Nu = sN$ ).<sup>18,26</sup>

$$\log k (20 \text{ }^\circ\text{C}) = s(N + E) \quad (1)$$

Assuming that the reactions of benzhydrylium ions with  $\text{SCN}^-$  also follow this relationship, we arrive at Figure 4, which plots all available rate constants for these reactions against the electrophilicity parameters  $E$  of the benzhydrylium ions.<sup>18,26d</sup>

Although the reactions of  $\text{SCN}^-$  with carbocations of  $-10 < E < -6$  (dashed lines) are predicted by Figure 4 to proceed fast, such reactions are not observable because of the unfavorable thermodynamics of adduct formation. On the other hand, carbocations with  $E > -3$  react fast with the S terminus of  $\text{SCN}^-$  to yield  $\text{Ar}_2\text{CH}-\text{SCN}$  almost quantitatively, and the remaining equilibrium concentration of  $\text{Ar}_2\text{CH}^+$  is so small that the rate of its reaction with the N terminus of  $\text{SCN}^-$  ( $k_N$ , dash-dotted line) cannot directly be observed.

Because of the paucity of rate constants in the nondiffusion-controlled range, determinations of the parameters  $N$  and  $s$  according to eq 1 are problematic. The plot of  $\log k_S$  for the reactions of the sulfur terminus of  $\text{SCN}^-$  with the benzhydrylium ions **4–8** versus the electrophilicity parameters  $E$  yields  $N(\text{SCN}^-) = 17.94$  and  $s(\text{SCN}^-) = 0.60$ . Despite the low correlation coefficient ( $r^2 = 0.82$ ), this regression line appears to be reliable because the slope  $s$  is similar to that of other anionic nucleophiles.<sup>29,30</sup> With the assumption that the same

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**Table 3.** Experimental and Calculated Rate Constants for the Reaction of the Sulfur and Nitrogen Terminus of the Thiocyanate Ion with Benzhydrylium Ions **4–8** (20 °C, Acetonitrile)

Ar <sub>2</sub> CH <sup>+</sup>	<i>E</i>	<i>k<sub>S</sub></i> (calc) <sup>a</sup>	<i>k<sub>S</sub></i> (exp)	<i>k<sub>N</sub></i> (calc) <sup>b</sup>	<i>k<sub>N</sub></i> (exp)
<b>4</b>	−3.14	7.6 × 10 <sup>8</sup>	1.0 × 10 <sup>9</sup>		
<b>5</b>	−3.85	2.8 × 10 <sup>8</sup>	1.7 × 10 <sup>8</sup>	9.3 × 10 <sup>4</sup>	1.5 × 10 <sup>5</sup>
<b>6</b>	−4.72	8.6 × 10 <sup>7</sup>	2.5 × 10 <sup>8</sup>		
<b>7</b>	−5.53	2.8 × 10 <sup>7</sup>	1.3 × 10 <sup>7</sup>	9.1 × 10 <sup>3</sup>	5.3 × 10 <sup>3</sup>
<b>8</b>	−5.89	1.7 × 10 <sup>7</sup>	2.7 × 10 <sup>7</sup>	5.5 × 10 <sup>3</sup>	5.9 × 10 <sup>3</sup>

<sup>a</sup> From eq 1 with *N* = 17.94, *s* = 0.60. <sup>b</sup> From eq 1 with *N* = 12.13, *s* = 0.60.

*s*-parameter (*s* = 0.60) holds for the attack at nitrogen (*k<sub>N</sub>*), the corresponding nucleophilicity parameter *N*(SCN<sup>−</sup>) = 12.13 is obtained by least-squares fitting. Table 3 shows that the observed and calculated (eq 1) rate constants for S- and N-attack agree within a factor of 2–3. One can, therefore, assume that the nucleophilicity parameters for S- and N-attack derived above can also be used for estimating the rate constants for the reactions of both termini of SCN<sup>−</sup> with other carbocations of known *E* parameters.

**Table 4.** Activation Free Enthalpies, Reaction Free Enthalpies, and Intrinsic Barriers for the Reactions of Benzhydrylium Ions with Sulfur and Nitrogen of SCN<sup>−</sup> (in kJ mol<sup>−1</sup>, 20 °C)

X	Ar <sub>2</sub> CH <sup>+</sup>	Δ <i>G</i> <sup>‡</sup>	Δ <sub>r</sub> <i>G</i> <sup>o</sup> <sup>a</sup>	Δ <i>G</i> <sub>0</sub> <sup>‡</sup>
Sulfur-attack of SCN <sup>−</sup>				
NMe(CH <sub>2</sub> CF <sub>3</sub> )	<b>5</b>	25.6 ± 1.7 <sup>b</sup>	−20.8 ± 1.7	35.2 ± 2.5
NPh <sub>2</sub>	<b>6</b>	24.6 ± 1.7 <sup>b</sup>	−24.9 ± 1.7	36.0 ± 2.5
<i>N</i> -morpholino	<b>7</b>	31.8 ± 1.8 <sup>b</sup>	−12.9 ± 1.7	37.9 ± 2.6
Nitrogen-attack of SCN <sup>−</sup>				
<i>N</i> -morpholino	<b>7</b>	50.9 ± 0.3 <sup>c</sup>	−22.3 ± 1.7	61.6 ± 1.0
NPhMe	<b>8</b>	50.6 ± 0.3 <sup>c</sup>	−20.0 ± 1.7	60.2 ± 1.0

<sup>a</sup> Uncertainty of factor 2 estimated for the equilibrium constants *K<sub>S</sub>* (taken from stopped-flow measurement for **5**) and *K<sub>N</sub>* (taken from conventional UV–vis measurements). <sup>b</sup> Uncertainty of factor 1.5 estimated for the rate constants *k<sub>S</sub>*. <sup>c</sup> Uncertainty of factor 1.1 estimated for the rate constants *k<sub>N</sub>*.

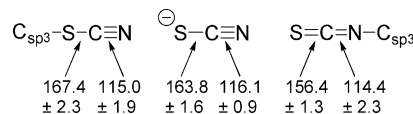
The formation of thiocyanates by kinetically controlled reactions and their rearrangement to isothiocyanates implies that attack at sulfur occurs with a lower intrinsic barrier than attack at nitrogen. The availability of rate and equilibrium constants allows us to employ the Marcus equation (eq 2) for calculating the magnitude of the intrinsic barriers of the rate-determining step.<sup>31–35</sup>

$$\Delta G^\ddagger = w_R + \Delta G_0^\ddagger + 0.5\Delta_r G^\circ + ((\Delta_r G^\circ)^2/16\Delta G_0^\ddagger) \quad (2)$$

When the work term *w<sub>R</sub>* is neglected, the experimental values for Δ*G*<sup>‡</sup> and Δ<sub>r</sub>*G*<sup>o</sup> (calculated from the rate and equilibrium constants in Table 2) can be used to calculate the intrinsic barriers (Δ*G*<sub>0</sub><sup>‡</sup>) for the reactions of benzhydrylium ions with both termini of SCN<sup>−</sup> (Table 4).

While the intrinsic barriers for N-attack are around 61 kJ mol<sup>−1</sup>, those for S-attack are smaller by approximately 25 kJ mol<sup>−1</sup> (35–38 kJ mol<sup>−1</sup>, Table 4). This behavior mirrors the

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**Scheme 4.** Average Bond Lengths (in pm) of Organic Thiocyanates, “Free” Thiocyanate Anions, and Organic Isothiocyanates Derived from Crystal Structures – For Details, See the Supporting Information

different nucleophilicities of thiolates and amines. Bernasconi has demonstrated that the extraordinarily high nucleophilicity of thiolates as compared with amines and oxyanions is only partially due to the high carbon basicity of thiolates.<sup>36</sup> An additional factor is the exceptionally low intrinsic barrier of thiolate additions, which was tentatively assigned to a product-stabilizing factor which develops ahead of C–S bond formation.<sup>36a</sup> It was emphasized that this phenomenon is untypical<sup>37a</sup> because most other breakdowns of rate–equilibrium relationships which were analyzed by the “Principle of Non-Perfect Synchronization” were explained by product-stabilizing factors (e.g., resonance, solvation) whose development lags behind bond formation in the transition state.<sup>37</sup>

The different intrinsic barriers for S- and N-attack at thiocyanate are also related to the structural reorganizations of the SCN moiety during the two types of reaction. Scheme 4 shows that the formation of alkyl isothiocyanates from thiocyanate anions is accompanied by a considerably larger change of the C–S-bond length (ca. −7.5 pm) than the formation of alkyl thiocyanates (ca. +3.5 pm). The small changes of the C–N bond lengths in both reactions are within the standard deviations. As a consequence, the lower intrinsic barriers for S-attack, which are responsible for the preferential formation of the thiocyanates Ar<sub>2</sub>CH–SCN from benzhydrylium ions and SCN<sup>−</sup>, may also be derived from the “Principle of Least Nuclear Motion”.<sup>38</sup>

**Analysis of Literature Data.** Our observations that the carbocations **5**, **7**, and **8** react 10<sup>3</sup>–10<sup>4</sup> times faster with the S terminus of SCN<sup>−</sup> than with the N terminus differ dramatically from literature reports which give *k<sub>S</sub>*/*k<sub>N</sub>* = 2–10 in S<sub>N</sub>1 type reactions<sup>9–13</sup> (see above and Table 5). For that reason, we will now discuss previous reports on the selectivities of thiocyanate additions on the basis of our new experimental data.

Our results do not affect the interpretation of the preferential formation of trityl isothiocyanates from trityl halides with alkali thiocyanates in acetone<sup>42</sup> and of ferrocenyl(phenyl)methyl isothiocyanate from ferrocenyl(phenyl)methyl tetrafluoroborate and potassium thiocyanate in dichloromethane.<sup>43</sup> Although Figure 4 predicts that Ph<sub>3</sub>C<sup>+</sup> (*E* = 0.51)<sup>29</sup> and Fc(Ph)CH<sup>+</sup> (*E* = −2.64)<sup>26d</sup> should react faster at sulfur than at nitrogen, both thiocyanates are produced by reversible reactions. The fast

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**Table 5.** Ratios  $k_S/k_N$  for  $S_N1$  Type Reactions of Carbocations with  $SCN^-$ 

electrophile	$E$	solvent	$k_S/k_N$	ref
4,4'-dimethylbenzhydryl cation ( <b>2</b> )	3.63	acetonitrile	5	9b
4,4'-dimethylbenzhydryl cation ( <b>2</b> )	3.63	acetone/water (95:5 vv)	8.3	9c
4-chlorobenzhydryl cation	$\sim 6^a$	aqueous acetic acid (0.1–100% vv)	3.3–4.2	13
benzhydryl cation ( <b>1</b> )	5.90	acetone/water (35:65 vv)	9	10
phenyl cation <sup>b</sup>	unknown	0.035 M sulfuric acid	2.2–2.4	12
<i>tert</i> -butyl cation <sup>c</sup>	8.5–9 <sup>d</sup>	aqueous nitrous acid	1.9–2.5	10
benzyl cation <sup>e</sup>	$\gg 9^f$	pD 2 sulfate buffer	4.4	11
isobutyl cation <sup>g</sup>	$\gg 10$	aqueous nitrous acid	5.3	10

<sup>a</sup> From ref 39. <sup>b</sup> From decomposition of  $Ph-N_2^+BF_4^-$ . <sup>c</sup> From solvolysis of *tert*-BuCl or diazotization of *tert*-butylamine or from rearranged isobutyl cation produced by diazotization of isobutylamine. <sup>d</sup> From ref 40. <sup>e</sup> From acid-catalyzed decomposition of *N*-benzyl-*N*-nitrososulfamate. <sup>f</sup> Estimated from  $E \approx 9.0$  for the phenylmethylmethyl cation (from ref 41). <sup>g</sup> The nonrearranged part from the diazotization of isobutylamine.

isomerization of trityl thiocyanate into the isothiocyanate via an ionization recombination process has previously been shown by Fava and co-workers.<sup>15,42</sup>

Kessler and co-workers reported that tropylium isothiocyanates ( $E(C_7H_7^+) = -3.72$ )<sup>26d</sup> rapidly topomerize via contact ion pairs,<sup>21,44,45</sup> which is also in line with our observation of the coexistence of ionic and covalent isothiocyanates for carbocations of  $-6 < E < -3$ .

Why does the exchange of 4,4'-dimethylbenzhydryl thiocyanate (**2**-SCN) with  $S^{35}SCN^-$  in acetonitrile give a  $k_S/k_N$  ratio of 5,<sup>9b</sup> much smaller than that observed in this work with the benzhydrylium ions **5**–**8** ( $k_S/k_N = 10^3$ – $10^4$ )? Figure 4 shows that for the 4,4'-dimethylbenzhydrylium ion **2** ( $E = 3.63$ ),  $k_S$  is diffusion-controlled and a  $k_S/k_N$  ratio of approximately 10 can directly be derived from Figure 4. The observed  $k_S/k_N$  ratio of 8.3 for the isomerization of **2**-SCN,<sup>9c</sup> which precedes its solvolysis in 95% aqueous acetone, is on the same order of magnitude as predicted by Figure 4.

When reactions in solvents with a higher content of water are considered, Figure 4 cannot directly be used for the data analysis, because anions are less nucleophilic in water than in dipolar aprotic media.<sup>46,47</sup> The dimethoxy-substituted benzhydrylium ion **3** was the only electrophile for which we were able to determine the kinetics of the reaction with  $nBu_4N^+SCN^-$  in a 2:1 (vv) mixture of  $H_2O$ /acetonitrile by laser flash photolysis. The second-order rate constant of  $2.0 \times 10^9 M^{-1} s^{-1}$  almost reaches the value for diffusion control in water (ca.  $5 \times 10^9 M^{-1} s^{-1}$ ),<sup>48</sup> which implies that for all more electrophilic carbocations ( $E > 0$ ) sulfur-attack should be diffusion-controlled also in water. This was also concluded earlier by Kresge and co-workers for the reaction of strong electrophiles (laser flash generated protonated *p*- and *o*-quinone methides) with the thiocyanate ion in water.<sup>49</sup>

Nitrous acid deamination of 4-chlorobenzhydrylamine in aqueous acetic acid solutions containing thiocyanate ions yields

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mainly 4-chlorobenzhydryl thiocyanate and isothiocyanate, from which  $k_S/k_N \approx 3.8$  has been derived.<sup>13</sup> Because the 4-chlorobenzhydryl cation ( $E \approx 6$ )<sup>39</sup> is considerably more electrophilic than **3**,  $k_S$  must be diffusion-controlled, and the small  $k_S/k_N$  ratio is in accord with Figure 4. The small ratio  $k_S/k_N = 9$  observed for the solvolytically generated parent benzhydrylium ion (**1**) in 35% aqueous acetone<sup>10</sup> can also be explained by diffusion-controlled attack of sulfur at **1** ( $E = 5.90$ ).

The phenyl cation<sup>12</sup> produced by dediazonation of the benzene diazonium ion or the *tert*-butyl cation<sup>10</sup> ( $E = 8.5$ – $9$ ) produced in aqueous nitrous acid containing  $SCN^-$  reacted with formation of R-SCN and R-NCS in a 2:1 ratio. Both cations are considerably more electrophilic than the parent benzhydrylium ion **1** ( $E = 5.90$ ), which implies diffusion control of  $k_S$  according to Figure 4. The same is true for the benzyl cation ( $E \gg 9$ ,  $k_S/k_N = 4.4$ ) generated from *N*-benzyl-*N*-nitrososulfamate in a pD 2.0 sulfate buffer<sup>11</sup> and the isobutyl cation ( $E > 10$ ) produced by dediazonation of isobutylamine. The higher  $k_S/k_N$  ratio of 5.3 observed by the dediazonation of isobutyl-diazonium ion in aqueous solutions of  $SCN^-$  has been attributed to a transition state,<sup>10</sup> where the thiocyanate ion is involved in the breaking of the C–N bond of the diazonium ion. This interpretation is strongly supported by the finding that the methyldiazonium ion under the same conditions yielded exclusively the methyl thiocyanate.<sup>10</sup>

As a consequence, all  $k_S/k_N$  ratios so far reported for the reactions of carbocations with  $SCN^-$  refer to cases in which at least  $k_S$  corresponds to diffusion control. The systems reported in this investigation, which give  $k_S/k_N = 10^3$ – $10^4$ , are the first where both thiocyanate termini undergo activation-controlled reactions with carbocations.<sup>50</sup> As shown in Figure 4, it is only few carbocations ( $-6 < E < -3$ ) which allow one to observe this phenomenon, because more stable carbocations ( $E < -6$ ) do not react at all while less stable carbocations ( $E > -3$ ) react quantitatively at sulfur. The same phenomena that control the selectivities of intermolecular reactions and are responsible for the change from constant selectivity relationships to the domain of the reactivity selectivity principle<sup>16,51–55</sup> are thus found also to control the ambident reactivity of the thiocyanate ion.

## Conclusions

In agreement with previous investigations, we find isothiocyanates R-NCS to be more stable than thiocyanates R-SCN. As a consequence, the exclusive formation of isothiocyanates is observed in reactions of benzhydryl cations with thiocyanate ions which are reversible under the reaction conditions. Because

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the rearrangement of 2-SCN into 2-NCS has been reported to occur with a half-life of 4 h in acetonitrile at 20 °C,<sup>9a</sup> one can conclude that under these conditions thermodynamic reaction control can be expected for reactions of SCN<sup>-</sup> with carbocations of  $E < 3$ .

The interpretation of the thermodynamically controlled reactions thus fully agrees with previous analysis. In contrast, a reinterpretation of the kinetically controlled reactions is needed. The high preference of S- over N-attack which has previously been observed in S<sub>N</sub>2 type reactions of SCN<sup>-</sup> ( $k_S/k_N = 10^2$ – $10^3$ )<sup>7,8</sup> is also found for activation-controlled reactions of SCN<sup>-</sup> with carbocations, as shown for the combinations of SCN<sup>-</sup> with **5**, **7**, and **8** ( $k_S/k_N = 10^3$ – $10^4$ , Table 2). Thus, the change from alkyl halides (soft) to carbocations (hard) does not necessarily imply a decrease of the  $k_S/k_N$  ratio, as predicted by the HSAB principle. The previously reported small  $k_S/k_N$  ratios of 2–10 for the reactions of SCN<sup>-</sup> with carbocations exclusively refer to reactions which yield R-SCN with equal, diffusion-controlled rate constants  $k_S$  (see Figure 4). Because of high  $k_N$  values ( $k_N > 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ), small  $k_S/k_N$  ratios result. Because activation-controlled attack at both termini of SCN<sup>-</sup> can only be observed for a very small group of carbocations ( $-6 < E < -4$ , Figure

4), which react reversibly with SCN<sup>-</sup>, it is understandable that this phenomenon has not previously been observed. One can assume, however, that analogous phenomena may also rule the reactions of carbocations with other ambident nucleophiles, for example, CN<sup>-</sup>, OCN<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, or enolates, and it appears necessary to reanalyze the reported selectivities on the basis of absolute rate constants.

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**Supporting Information Available:** Details of the kinetic and equilibrium measurements and the bond lengths analysis (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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