

temperature without further change and upon addition of carbon tetrachloride red needles came down which could be further recrystallized from carbon tetrachloride-dichloromethane mixture. Despite repeated attempts at complete purification, the infrared spectrum always showed the presence of traces of nuclear brominated material. We were also unsuccessful in getting a good analysis.

*Anal.* Calcd. for  $C_{22}H_{21}Br_3O_3$ : C, 46.10; H, 3.69; Br, 41.83; mol. wt., 573. Found: C, 46.53; H, 3.59; Br, 42.28; mol. wt. (vapor pressure osmometer), 566.

Ultraviolet and n.m.r. spectra were compatible with assignment to trianisylcarbonium tribromide as are the above data. The infrared spectrum showed no hydroxyl band but the original carbinol could be regenerated upon quenching with water.

4,4'-Dimethoxydiphenylcarbinol was mixed with bromine in dichloromethane in the same equivalent

quantities as in the above experiment. At  $-70$  and  $-30^\circ$  a dark red precipitate was formed rapidly which turned yellow-orange within about 10 min. The solution remained homogeneous at  $0^\circ$ . Cold filtration in a drybox yielded crystals which when warmed on a spatula to room temperature decomposed to products smelling of anisaldehyde and hydrogen bromide. Infrared spectra showed the presence of cleavage products and considerable nuclear brominated material.

4,4'-Dimethoxydiphenylcarbinyl bromide<sup>29</sup> was subjected to the treatment described above for the carbinol. The behavior at  $-70^\circ$  was the same but upon warming to room temperature the only apparent products were hydrogen bromide and ring brominated material.

*Acknowledgment.* We are grateful to Mellon Institute for providing facilities for the preparation of this manuscript.

## Isomerization and Isotopic Exchange of 4,4'-Dimethylbenzhydryl Thiocyanate in Acetonitrile. Partition of Electron-Deficient Intermediates between Thio- and Isothiocyanate<sup>1,2</sup>

Antonino Fava,<sup>3</sup> Antonio Iliceto,<sup>4</sup> Alberto Ceccon, and Paolo Koch

*Contribution from the Istituto Chimico, University of Perugia, and  
Istituto di Chimica Organica, University of Padova, Italy.*

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*In the isomerization and exchange of 4,4'-dimethylbenzhydryl thiocyanate in acetonitrile containing  $NaS^{35}CN$ , only a small fraction of the isothiocyanate formed appears to equilibrate its SCN group with the ionic thiocyanate in solution. Thus isomerization largely proceeds via an ionic path in which the organic moiety and the SCN group do not become separated. An intimate ion pair is postulated. Both isomerization and exchange reactions are subject to positive salt effect of the "normal" type. However, the exchange reaction is much more affected, indicating that it involves a more advanced stage of ionization of the substrate. By studying the relative initial rate of radioactivity intake by the two organic species, thiocyanate and isothiocyanate, it has been established that, in returning to covalent state, the ionic intermediate involved in exchange partitions between thio- and isothiocyanate in the ratio of about 5 to 1. Thus, in the assumption that the intimate ion pair is a precursor of the ionic species involved in exchange, the rate of ionization exceeds the rate of isomerization by a factor of six. From the ratio of the rate of*

*exchange to rate of ionization, the upper limit of the fraction of intimate ion pairs which dissociate is set to 5.4%. Thus, of 100 intimate ion pairs, about 5 undergo further ionization and 95 return to covalent state. Of the latter, about 79 return to thiocyanate and 16 to isothiocyanate.*

### Introduction

In recent papers evidence has been presented concerning the mechanism of isomerization of organic thiocyanates,  $R-SCN \rightarrow R-NCS$ .<sup>5</sup> Solvent, salt, and structural effects indicated large charge separation in the transition state, consistent with an ionization mechanism.<sup>5</sup> The knowledge of the ionization mechanism was further particularized by an experiment in which the isomerization of benzhydryl thiocyanate in acetonitrile solvent was allowed to occur in the presence of  $NaS^{35}CN$ .<sup>6c</sup> The distribution of the label on the ionic thiocyanate, the organic thiocyanate, and isothiocyanate indicated that in the isomerization the "organic" SCN group did not equilibrate with the ionic thiocyanate in solution. As a consequence, for this

(1) Abstracted from the doctoral thesis of P. Koch, University of Padova, 1962.

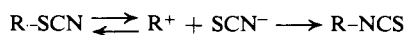
(2) The financial support of Consiglio Nazionale delle Ricerche, Roma, and Shell Internationale Maatschappij, The Hague, Holland, is gratefully acknowledged.

(3) To whom inquiries about this paper are to be addressed: Istituto di Chimica Generale, Università di Pisa, Italy.

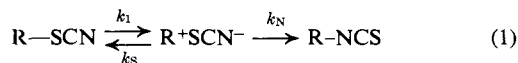
(4) Deceased.

(5) (a) A. Iliceto, A. Fava, and U. Mazzucato, *Tetrahedron Letters*, 11, 27 (1960); (b) A. Iliceto, A. Fava, U. Mazzucato, and P. Radici, *Gazz. chim. ital.*, 99, 919 (1960); (c) A. Iliceto, A. Fava, U. Mazzucato, and O. Rossetto, *J. Am. Chem. Soc.*, 83, 2729 (1961); (d) P. A. S. Smith and D. W. Emerson, *ibid.*, 82, 3076 (1960).

substrate and, *a fortiori*, for substrates giving rise to carbonium ions less stable than benzhydryl, the ionization mechanism could not be the simple dissociation



but it had to comprise an intermediate stage, probably an internal ion pair, through which isomerization took place to the largest extent.



The situation thus brought to light was similar to that which in recent years has been found to apply to many solvolytic and exchange reactions which are accompanied by rearrangement and/or racemization, and which have been studied in considerable detail especially by Winstein's and Goering's groups.<sup>6,7</sup>

With respect to other systems the one under consideration is especially suited to the study of ionization processes and return phenomena,<sup>8</sup> owing to the ambident character of the leaving group,  $\text{SCN}^-$ . Because of this, in fact, covalent return from an ionic intermediate may occur with either "tooth," S or N of  $\text{SCN}^-$ , giving the starting material and the isothiocyanate product, respectively. This feature may be exploited to estimate, under certain assumptions, the rate of ionization of the substrate, as we will see presently.<sup>9</sup>

At the time of our previous paper,<sup>5c</sup> however, a detailed analysis of the ionization process could not be made since two essential pieces of information were missing: namely, (i) the fraction of total radioactivity which entered *via* ionization paths, and (ii) the partition of covalent return between thio- and isothiocyanate, *i.e.*, the value of  $k_S/k_N$  of reaction 1. In this paper we report kinetic data on the isotopic exchange and on the isomerization reactions of 4,4'-dimethylbenzhydryl thiocyanate, as well as data on the partition of radioactivity between thio- and isothiocyanate during isomerization. These allow an estimate of (i) the relative reactivity of the S- to the N-end of  $\text{SCN}^-$  toward the 4,4'-dimethylbenzhydryl cation; (ii) the specific rate of formation of the ionic intermediate through which isomerization obtains, which is a lower limit for the rate of ionization of the substrate; and (iii) the fraction of intimate ion pairs which undergo exchange, which represents an upper limit of the fraction of intimate ion pairs which dissociate.

## Results

*Partition of Radioactivity between Thiocyanate and Isothiocyanate during Isomerization Simultaneous to Exchange.* An indispensable requisite in order to

(6) (a) S. Winstein and A. H. Fainberg, *J. Am. Chem. Soc.*, **80**, 459 (1958), and previous papers in the series; (b) S. Winstein, J. S. Gall, M. Hoio, and S. Smith, *ibid.*, **82**, 1010 (1960); (c) S. Winstein, M. Hoio, and S. Smith, *Tetrahedron Letters*, No. 22, 12 (1960); (d) S. Winstein and J. S. Gall, *ibid.*, No. 2, 31 (1960); (e) S. Winstein, A. Ledwith, and M. Hoio, *ibid.*, No. 10, 341 (1961).

(7) H. L. Goering and J. T. Doi, *J. Am. Chem. Soc.*, **82**, 5850 (1960), and previous papers in the series.

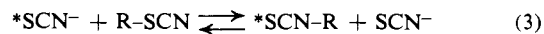
(8) S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck, and G. C. Robinson, *ibid.*, **78**, 328 (1956).

(9) While this work was in progress, two very similar studies have appeared where benzhydryl substrates featuring ambident leaving groups had been exploited to detect return phenomena.<sup>10,11</sup>

(10) H. L. Goering and J. F. Levy, *Tetrahedron Letters*, 644 (1961); *J. Am. Chem. Soc.*, **84**, 3853 (1962).

(11) S. G. Smith, *Tetrahedron Letters*, 979 (1962).

obtain information about the partition between thio- and isothiocyanate of the ionic intermediate involved in exchange is knowing which fractions of the total exchange rate are contributed by direct displacements



Even if such information were available, however, the situation would be quite hard to disentangle if the contributions of paths 2 and 3 are sizeable ones. On the other hand, the analysis of exchange data may become more easily manageable if their contribution is negligible and ionization paths only are involved in exchange. This requirement is met by 4,4'-dimethylbenzhydryl thiocyanate which has been recently shown to undergo essentially unimolecular exchange with ionic thiocyanate in acetonitrile.<sup>12</sup> For this substrate, therefore, all the labeled S atoms which are found on the organic thiocyanate and on the isothiocyanate must have entered by way of ionization processes. Consequently, the ratio of the total number of labeled atoms found on the thiocyanate to that found on the isothiocyanate, extrapolated down to zero time, indicates how covalent return from the ionic intermediate involved in exchange partitions between the two possible routes, *i.e.*, return with the S atom (to give thiocyanate) and return with the N atom (to give isothiocyanate).

Table I reports the specific activities of the ionic thiocyanate,  $A_{\text{NaSCN}}$ , of the organic thiocyanate,  $A_{\text{RSCN}}$ , and of the isothiocyanate,  $A_{\text{RNCS}}$ , which have been observed at various isomerization fractions ranging from 1.5 to 35%. The specific activities are expressed in arbitrary units, having set  $A_{\text{NaSCN}} = 1000$  at time zero. At any time the ratio of the total activities on the isothiocyanate and on the thiocyanate is given by the ratio of the specific activity of each species multiplied by the respective fraction. If  $f$  is the isomerization fraction, *i.e.*,  $f = [\text{R-NCS}]/[\text{R-SCN}]_0$ , the ratio of the total activities is given by  $fA_{\text{RNCS}}/(1-f)A_{\text{RSCN}}$ . This ratio is reported in the last line of Table I and is also plotted against the isomerization fraction,  $f$ , in Figure 1.

As expected, this ratio increases with increasing isomerization. However, the early part of the plot, which is the one of interest, is quite flat so that the extrapolation to zero appears to be safe, even without resorting to experiments at very low isomerization fractions, which on the other hand would be most affected by experimental errors (see Experimental part). The initial ratio appears to be very close to 0.20. It is difficult to make an *a priori* estimate of the accuracy of this result, not only because it is a derived quantity involving several measurements, but also because a correction has to be applied to allow for a zero-time-induced exchange (see Experimental). However, judging from the results of duplicate experiments, the result should be good within a 10% uncertainty. For example, the run at 3.0% isomerization reported in Table I is the average of four independent runs whose maximum deviation from the average was about 5%.

*Salt Effect on Isomerization and Exchange Rates.* A study of salt effect on both the rate of isomerization and the rate of exchange was made, and the results obtained

(12) A. Fava, A. Illiceto, and A. Ceccon, *ibid.*, 685 (1963).

**Table I.** Partition of Radioactivity between Thio- and Isothiocyanate during Isomerization Carried Out in the Presence of NaS<sup>35</sup>CN<sup>a</sup>

100f <sup>b</sup>	1.5	2.0	2.5	3.0	6.5	10.2	18.3	22.6	26.7	34.3
100F <sup>c</sup>	3.13	3.68	4.47	5.44	10.3	17.2	27.5	31.3	36.8	43.9
A <sub>NaSCN</sub> <sup>d</sup>	974	969	963	957	944	915	850	812	776	716
A <sub>RNCS</sub> <sup>d</sup>	59.6	55.5	51.3	50.2	46.4	51.0	62.0	58.0	68.4	70.5
A <sub>RSCN</sub> <sup>d</sup>	4.26	5.24	6.43	7.80	15.2	26.4	42.4	50.5	59.3	75.0
A <sub>RNCS</sub> f / A <sub>RSCN</sub> (1 - f)	0.21	0.22	0.20	0.20	0.21	0.21	0.33	0.33	0.42	0.49

<sup>a</sup> Temp., 0.2 ± 0.1°; solvent, acetonitrile; [NaS<sup>35</sup>CN] = 1.0 × 10<sup>-2</sup> M; [R-SCN] = 5.0 × 10<sup>-2</sup> M. <sup>b</sup> Fraction of isomerization. <sup>c</sup> Apparent fraction of exchange, corrected for zero-time-induced exchange. It is obtained as the ratio of the (calculated) specific activity of the combined organic species to the (calculated) specific activity at infinite time, A<sub>∞</sub>: [A<sub>RNCS</sub>f + A<sub>RSCN</sub>(1 - f)]/A<sub>∞</sub> = F. <sup>d</sup> Corrected for zero-time-induced exchange.

for two salts, NaSCN and NaClO<sub>4</sub>, are reported in Tables II and III. As the data show, both isomerization and exchange reactions are positively affected by

**Table II.** Salt Effects on the Rate of Isomerization of 4,4'-Dimethylbenzhydryl Thiocyanate<sup>a</sup>

10 <sup>2</sup> [NaSCN]	...	2.10	3.98	6.00
10 <sup>2</sup> k <sub>i</sub> , sec. <sup>-1</sup>	8.97 <sup>b</sup>	9.56	10.43	11.07
10 <sup>2</sup> [NaClO <sub>4</sub> ]	...	2.02	4.04	6.06
10 <sup>2</sup> k <sub>i</sub> , sec. <sup>-1</sup>	8.97 <sup>b</sup>	9.45	9.73	10.14

<sup>a</sup> Solvent, acetonitrile; temp., 25.0 ± 0.1°; [R-SCN] = 0.15 M. <sup>b</sup> The value measured in this work is slightly higher than that previously obtained, 8.79 × 10<sup>-6</sup>.

**Table III.** Salt Effect on the Initial Rate of Exchange of 4,4'-Dimethylbenzhydryl Thiocyanate with NaS<sup>35</sup>CN<sup>a</sup>

10 <sup>2</sup> [NaSCN]	0.108	1.05	2.91
10 <sup>6</sup> k <sub>ex</sub> , sec. <sup>-1</sup>	0.817	1.21	1.87
10 <sup>2</sup> [NaClO <sub>4</sub> ] <sup>b</sup>	...	0.305	1.00
10 <sup>6</sup> k <sub>ex</sub> , sec. <sup>-1</sup>	0.817	0.896	1.12
			1.74

<sup>a</sup> Because of the isomerization, the exchanging system is not a stable one. Since the isothiocyanate, once formed, does not undergo further exchange, the exchange rate decreases with time. Therefore initial rates only were measured. Solvent, acetonitrile; temp., 0.2 ± 0.1°; [R-SCN] = 0.05 M. <sup>b</sup> [NaS<sup>35</sup>CN] = 1.0 × 10<sup>-3</sup> M.

electrolytes although to quite different extent. Within the limited concentration range investigated, the salt effect is of the linear type, which has been called "normal" by Winstein.<sup>13</sup> The values of the coefficient *b* of the Winstein's equation<sup>13</sup> for normal salt effects are the following: for isomerization at 25°, NaClO<sub>4</sub>, 2; NaSCN, 4. For isotopic exchange at 0° the values are: NaClO<sub>4</sub>, 38; NaSCN, 48.

The striking difference in the *b* values characterizing the two reactions is worth noticing.

### Discussion

The data in Table I show that the specific radioactivity of the isothiocyanate is always much lower than that of the ionic thiocyanate (the experiments at the lower isomerization fractions are the more significant). This finding implies that the species involved in isomerization does not undergo a kinetically fast exchange with the ionic thiocyanate since, if it did, the isothiocyanate would have equilibrated its activity with that of the ionic thiocyanate. In turn, this implies that the main species involved in isomerization is not the free carbonium ion since the mixing of the "organic" with

the ionic SCN groupings would have occurred inevitably upon formation of the dissociated carbonium ion. Thus, also for this strongly electron-releasing

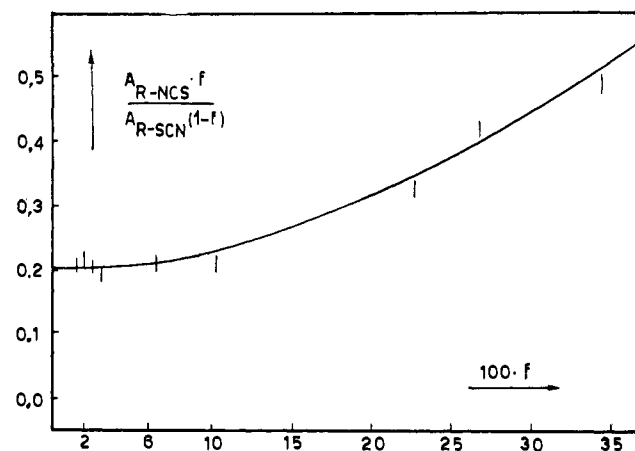
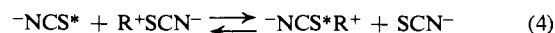


Figure 1. Ratio of total activities, isothiocyanate/thiocyanate, in isomerization of 4,4'-dimethylbenzhydryl thiocyanate in acetonitrile in the presence of Na<sup>+</sup>S<sup>35</sup>CN<sup>-</sup>.

substrate, isomerization essentially proceeds by way of a precursor of the carbonium ion, probably an "internal" ion pair, as depicted in eq. 1.

The comparison of the rate of exchange with the rate of isomerization and of the salt effects thereon is most interesting. At 0° the specific exchange rate is 8.17 × 10<sup>-7</sup> sec.<sup>-1</sup>, that is, about one-fourth as large as the rate of isomerization at the same temperature, 36 × 10<sup>-7</sup> sec.<sup>-1</sup>.<sup>5c</sup> Since the exchange rate is independent of the nucleophile concentration,<sup>12</sup> the participation of the internal ion pair involved in isomerization in a slow *direct* displacement (4) with the ionic thiocyanate can be ruled out.



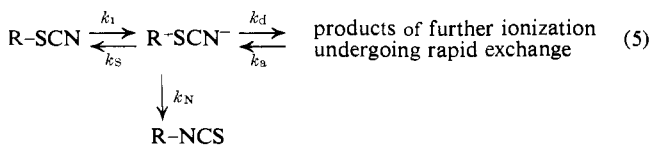
On the other hand, the strikingly greater response to salt effect of the exchange than of the isomerization reaction points out that the former involves a more advanced stage of ionization of the substrate. The data do not provide any evidence about which particular intermediate is involved in exchange, apart from the indication that it entails greater charge separation than that involved in isomerization. Since, however, exchange follows inevitably upon formation of the dissociated carbonium ion, the exchange rate sets an upper limit to the rate of formation of this species.

The data in Table I and Figure 1, referring to the distribution of the label during isomerization, indi-

(13) A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **78**, 2763 (1956).

cate that the labeled SCN groups partition between thiocyanate and isothiocyanate approximately in the proportion 5 to 1. Thus, the ionic intermediate involved in exchange returns to covalent state five times more often with the S- than with the N-end of SCN<sup>-</sup>.

From this piece of information it follows that, if isomerization and exchange are related, in the sense that the intermediate involved in isomerization is a precursor of that involved in exchange (eq. 5)



$k_S/k_N = 5$ , and the specific rate of ionization,  $k_i$ , is about six times the specific rate of isomerization,  $k_i$ .

$$k_i = \frac{k_S + k_N}{k_N} k_i = 6k_i \quad (6)$$

This method of obtaining the ionization rate constant is very similar to that recently proposed by Goering in his study of the equilibration of the carboxyl oxygen atoms during solvolysis of benzhydryl *p*-nitrobenzoate-carbonyl-O<sup>18</sup>.<sup>10,14</sup>

The main difference between our and Goering's methods is that the carboxylate leaving group is symmetrical, while the thiocyanate is not. This feature makes the carboxylate system somewhat superior; in fact, the equality (apart from the isotopic label) of the two "teeth" of the ambident leaving group in the carboxylate system guarantees that the partition of internal return between the two "teeth" is always equal to unity independently of reaction conditions, so that in every case the equilibration rate measures total return. In the thiocyanate system instead, the  $k_S/k_N$  ratio may be dependent on temperature and reaction medium.<sup>15</sup> Therefore, an exact knowledge of total return under different reaction conditions requires the measurement, beside the isomerization rate (which does not pose special problems), of  $k_S/k_N$  ratio under each particular condition, which is a lengthy task at best, and may often become an impossible one.

From the specific rate of ionization, obtained above, and the rate of exchange, it is now possible to evaluate the fraction of intimate ion pairs which undergo exchange, thus setting an upper limit to the fraction of intimate ion pairs which dissociate. This fraction is

(14) Both our and Goering's methods of estimating the ionization rate are based upon the assumption that the ion-pair intermediate, through which isomerization (equilibration) obtains, is not preceded by another intermediate which returns to covalent state with the S (ether-O) atom exclusively. If this (not very likely) possibility is taken into account, the rate derived above (eq. 6) sets a lower limit to the ionization rate.

(15) Kornblum and his associates<sup>16</sup> have shown that medium charges may cause large variations of the ambident reactivity of phenoxide or naphthoxide ions vs. the benzyl carbon. Moreover, A. F. has recently shown that in the reaction of thiocyanate ion vs. the benzyl carbon the relative reactivity of the S atom increases slightly in going towards more polar solvents; thus, at 70°  $k_S/k_N$  is equal to 960 and 660 in acetonitrile and methyl ethyl ketone, respectively.<sup>17</sup> Although the evidence above<sup>16,17</sup> concerns reactions of the SN2 type, work in progress in this laboratory seems to indicate that the ambident reactivity of SCN<sup>-</sup> towards carbonium ions is medium dependent as well. However, in the solvolysis of 4,4'-dimethylbenzhydryl chloride or bromide in 65% aqueous acetone containing 0.2 M NH<sub>4</sub>SCN, Taft<sup>18</sup> has obtained the same value,  $k_S/k_N = 5$ , which we have obtained in the present work in acetonitrile. Evidently systematic work is desirable in order to clarify this point.

given by

$$\frac{k_{ex}}{k_i} \frac{k_S + k_N}{k_N} \quad (7)$$

Since the effect of reaction conditions on  $k_S/k_N$  is not known, the fraction 7 above can be calculated only for the conditions under which the ratio  $k_S/k_N$  has been measured (acetonitrile, 0°; [NaSCN], 0.01 M).

Interpolation of the data of Table III gives  $k_{ex} = 1.16 \times 10^{-6} \text{ sec.}^{-1}$ . In the absence of salt,  $k_i = 3.6 \times 10^{-6} \text{ sec.}^{-1}$ .<sup>5c</sup> Using a  $b$  value of 4.0, a specific rate of isomerization  $k_i = 3.7 \times 10^{-6} \text{ sec.}^{-1}$  can be estimated in the presence of 0.01 M NaSCN.<sup>19</sup> Therefore the fraction 7 above is 5.3%.<sup>20</sup> That is, of 100 intimate ion pairs, about 5 undergo further ionization (perhaps up to carbonium ion) and 95 return to covalent state. Of the latter, about 79 return to thiocyanate and the rest, 16, to isothiocyanate. Since acetonitrile is a nonsolvolytic medium, the above may be stated by saying that total return is at least 94.7% internal and at most 5.3% external.

Obviously, if this is the situation in acetonitrile for a substrate such as 4,4'-dimethylbenzhydryl, in less polar solvents, or for less electron-releasing substrates, internal return will predominate over external return even more completely. From this, the general conclusion may be drawn that the isomerization of organic thiocyanates is an essentially intramolecular process, in the sense that the two fragments, carbonium and thiocyanate ions, tend to remain tied up within the same solvent cage.

A short comment may be warranted about the value of the competition factor, S vs. N, of the two "teeth" of the ambident nucleophile, SCN<sup>-</sup>, towards the 4,4'-dimethylbenzhydryl carbonium ion. The value found in this work (5) agrees well with those, ranging from 2 to 9, which have been obtained by Taft and Cannell<sup>21</sup> from the product ratio, thiocyanate/isothiocyanate, in reactions of carbonium-ion forming substrates (either formed in deamination or in solvolysis).

The comparison of the reactivity ratio, S to N, in reactions with carbonium ions, on the one hand, and with substrates which react by the direct displacement mechanism, SN2, is interesting. Here, typical competition factors range into 10<sup>3</sup> for primary substrates such as benzyl<sup>17</sup> and 10<sup>2</sup> for secondary ones (isopropyl).<sup>22</sup> Thus it appears that as bond breaking in the transition state is more advanced, the reactivity of the nitrogen increases with respect to that of the sulfur atom. This trend of the ambident reactivity with changing the substrate is consistent with the generalization early expressed by Kornblum<sup>23</sup> and can be easily rationalized on the basis of the more recent discussions by Edwards

(16) (a) N. Kornblum, P. J. Berrigan, and W. J. Le Noble, *J. Am. Chem. Soc.*, **85**, 1141 (1963); N. Kornblum, R. Seltzer, and P. Haberfeld, *ibid.*, **85**, 1148 (1963).

(17) A. Fava, A. Iliceto, and S. Bresadola, in press.

(18) R. W. Taft, Jr., private communication.

(19) The temperature coefficient of salt effect has been neglected.

(20) The greater sensitivity of  $k_{ex}$  over  $k_i$  with respect to salt effects suggests that fraction 7 increases strongly with salt. However, in order to calculate (7) at various electrolyte concentrations, it would be necessary to know the magnitude of the salt effect on  $k_S/k_N$ , which is unknown at present.

(21) L. G. Cannell and R. W. Taft, Jr., 129th National Meeting of the American Chemical Society, Dallas, Texas, April 8-13, 1956, abstracts of papers, p. 40N.

(22) U. Tonellato, A. Levorato, and A. Fava, unpublished.

(23) N. Kornblum, R. A. Smiley, R. K. Blackwood, and D. C. Iffland, *J. Am. Chem. Soc.*, **77**, 6269 (1955).

and Pearson<sup>24</sup> and by Hudson<sup>25</sup> on the factors which determine nucleophilicity: 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.

### Experimental

*Materials and Methods.* All products and solvents were commercial reagent grade. The organic thiocyanate, 4,4'-dimethylbenzhydryl thiocyanate, was reported previously.<sup>5b</sup> Labeled NaSCN (S<sup>35</sup>) was obtained as previously reported.<sup>26</sup>

The procedures used to measure the rate of isomerization and of isotopic exchange have both been reported.<sup>5c</sup>

*Tracer Experiments.* To separate the isothiocyanate from the thiocyanate and measure their activities, essentially the same procedure was used which has been described.<sup>5c</sup> Some major modification, however, has considerably improved the separation. In the first place, owing to the fact that small fractions (down to 1.5%) of isothiocyanate had to be separated, it was found expedient to apply a carrier technique. The acetonitrile solution which had been subjected to simultaneous isomerization and exchange (10 ml. of initially 0.05 M R-SCN and 0.01 M NaS<sup>35</sup>CN) was poured in cyclohexane which contained a known amount of isothiocyanate carrier (usually 0.45 mmole).

The cyclohexane was extracted with water containing some inactive NaSCN. The washings were discarded, while the first aqueous extract was oxidized to finally yield BaSO<sub>4</sub>.

The cyclohexane layer was dried on sodium sulfate and then treated with 3-dimethylamino-1-propylamine, a difunctional amine (primary and tertiary). After 15 min. at 7°, the solution was extracted with 0.1 M aqueous perchloric acid. The perchlorate of N-benzhydryl-N'-(3-dimethylamino-1-propyl)thiourea precipitated out of the aqueous medium as an amorphous mass adhering to the walls of the separatory funnel.

(24) J. O. Edwards and R. G. Pearson, *J. Am. Chem. Soc.*, **84**, 16 (1962).

(25) R. F. Hudson, *Chimica*, **16**, 173 (1962).

(26) A. Fava and A. Iliceto, *Ric. Sci.*, **25**, 54 (1955).

The dried cyclohexane layer was treated a second time with amine for 30 min. at room temperature, and the aqueous acid extract was disregarded. The cyclohexane layer was treated to obtain BaSO<sub>4</sub>.<sup>5c</sup>

The first aqueous acid extract and the amorphous precipitate was treated with NaOH and extracted with cyclohexane, which was subjected to a second aqueous perchloric acid extraction. After repeated washings with cyclohexane, the thiourea perchlorate was dissolved in ethanol and refluxed with AgNO<sub>3</sub>. Silver sulfide was subsequently oxidized to yield BaSO<sub>4</sub>.<sup>5c</sup> Radioactivity counting was effected on thick-layer BaSO<sub>4</sub> samples. To obtain convenient levels of activity even at the lowest isomerization fraction, the labeled ionic thiocyanate had a rather high specific activity (20 mc./g., which in our counting systems gave about 700,000 c.p.m. per thick-layer sample of BaSO<sub>4</sub> of about 0.6-cm.<sup>2</sup> area).

The procedure outlined above gave zero-time separations which, although excellent in ordinary exchange work, were not equally good in this particular work which called for the measurement of very small exchange fractions. The zero-time-induced exchange was found to be (average of five independent experiments) 1.55 ± 0.18%. The radioactivity entering the organic substrate by way of the zero-time exchange was found to be mostly on the thiocyanate (93.4%), although some (6.6%) was found on the isothiocyanate carrier. Apparently the activity entering the substrates by way of the separation-induced exchange partitions between thio- and isothiocyanate differently from the homogeneous exchange. The total separation-induced exchange fraction, 1.55 ± 0.18, can be thought of as made up of two contributions, 1.45 ± 0.18 and 0.101 ± 0.011, relative to thio- and isothiocyanate, respectively. The induced exchange and its mode of partitioning was accounted for and the specific activities reported in Table III are corrected accordingly. Since at the lowest isomerization fractions the fraction of exchange is on the order of 3 to 6%, the correction to be applied for the induced exchange is a sizeable one. Thus, it did not seem wise to perform separation at isomerization fractions lower than 1.5%, where the induced exchange already amounts to about 50% of the total exchange.