Structural Effects on Concurrent First- and Second-Order Processes in Borderline Nucleophilic Substitution. The Isotopic Exchange between Substituted Benzhydryl Thiocyanates and Ionic Thiocyanate in Acetonitrile and Acetone[1]

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Abstract: A kinetic study has been carried out of a typical borderline nucleophilic substitution, the isotopic exchange between substituted benzhydryl thiocyanate and ionic thiocyanate, for which, under certain specified conditions,[3] the rate law is: rate $= k_1[\mathrm{R{-}SCN}] + k_2[\mathrm{R{-}SCN}][\mathrm{NaSCN}]$. The structural effect has been separately determined for the first- and the second-order rate contributions in a wide range of electron-attracting power of the substituents in the phenyl rings (from 4,4′-dimethyl to 4,4′-dinitro). The first-order rate coefficient, k_1, is excellently correlated by a linear-free-energy relationship (σ^+) characterized by a high negative value of ρ (-4.5). On the contrary, the second-order rate coefficient shows extremely poor correlation and gives rise in the Hammett plot to a shallow U-shaped curve. From the magnitude of the structural effect, the first-order path is argued to involve an electron-deficient species past the intimate ion-pair stage, and the free carbonium ion is suggested as the more likely intermediate. As to the second-order path, it is suggested to be a one-step displacement on the substrate, rather than a two-step process involving a carbonium–leaving group ion pair in fast equilibrium with the substrate. The arguments used to rule out the latter mechanism are based, besides the structural effect, on the estimation of the ionization rate. Other facets of direct nucleophilic substitution reactions which are discussed include the solvent effect and its change with structure, and the role that ion pairs of the nucleophile may play in determining the over-all second-order rate for different substrates.

In a recent communication on nucleophilic substitution at saturated carbon atoms by charged nucleophiles we have pointed out the difficulties usually encountered in establishing the reaction mechanism in the "borderline" region and have indicated how at least some of these difficulties can be circumvented or minimized.[3] Our approach was primarily designed to provide a "clean" reaction order with respect to the nucleophile, *i.e.*, freed from the ambiguities which may arise from "mass law" effect, salt effects, and incomplete dissociation of the salt used to supply the nucleophile.

The reaction under study was the exchange of SCN groups between *para*-substituted benzhydryl thiocyanates and ionic thiocyanate in acetonitrile.[3]

$$\mathrm{R{-}SCN} + {}^{*}\mathrm{SCN}^- \rightleftarrows \mathrm{R{-}{}^{*}SCN} + \mathrm{SCN}^-$$

$$\mathrm{R} = 4\text{-X-}\mathrm{C_6H_4CHC_6H_4}\text{-}4\text{-X}'$$

$$\mathrm{X, X'} = \mathrm{H, H;\ CH_3,\ CH_3;\ H, Cl;\ H, NO_2}$$

These displacement reactions of typical borderline substrates can have no difficulty arising from the mass law effect since the concentration of the nucleophile is constant throughout any given kinetic experiment. Our experiments were run in the presence of a high concentration (0.099 to 0.090 *M*) of an electrolyte, $\mathrm{NaClO_4}$, having the same cation as the ionic reactant, NaSCN, which in turn was varied over a 10-fold range, 0.001 to 0.01 *M*, but was still very dilute with respect to the total electrolyte present.

This procedure had the twofold purpose of swamping out salt effects while keeping constant the ion-pair dissociation fraction of the ionic reactant. Thus all ambiguities stemming from salt effects and their specificity could be minimized as well as those arising from incomplete, and variable, dissociation of $\mathrm{Na^+\text{-}SCN^-}$.

Under the described conditions the rate data were found[3] to fit an equation of the type to be expected for concurrent first- and second-order processes

$$\mathrm{rate}/[\mathrm{RSCN}] = k_1 + k_2[\mathrm{NaSCN}]_s \qquad (1)$$

where $[\mathrm{NaSCN}]_s$ is the stoichiometric concentration.

From the limited data available it was apparent that changes in the electron-withdrawing power of the substrate affected both rate constants, k_1 and k_2, although to vastly different extents. To wit, while for the most electron-releasing substrate in the series (4,4′-dimethyl) the second-order term did not contribute appreciably to the rate and for the most electron attracting (4-$\mathrm{NO_2}$) the first-order term was negligible, the two processes were found to compete comparably in the two substrates of intermediate electron-donating capacity (4-Cl and unsubstituted). These findings were taken as a clear-cut demonstration of the simultaneous operation of the unimolecular and bimolecular mechanism for nucleophilic substitution and of the gradual transition from one mechanistic extreme to the other which can be induced by relatively mild structural variations.[3]

The kinetic study has now been extended to some additional benzhydryl thiocyanates and to another solvent, acetone. These new results, together with those previously reported, allow a more complete picture to be given of borderline nucleophilic substitution.

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(3) A. Fava, A. Iliceto, and A. Ceccon, *Tetrahedron Letters*, 685 (1963).

Results

The initial[4] first-order rates of exchange are reported in Table I. It will be noticed that the rate has been measured over a range of concentrations in some cases, but at a single concentration in other ones. In acetonitrile it appears that with 4-methylbenzhydryl thiocyanate the exchange occurs by the first-order process exclusively ($10^6k_1 = 2.02 \pm 0.05$; $10^4k_2 = -0.07 \pm 0.08$) while with the 3-chloro compound the first- and second-order processes are competitive ($10^6k_1 = 0.32 \pm 0.04$; $10^4k_2 = 1.83 \pm 0.07$). In acetone the unsubstituted compound appears to exchange by way of a second-order process exclusively ($10^6k_1 = -0.1 \pm 0.09$; $10^4k_2 = 3.59 \pm 0.07$).

Table I. First-Order Rate Coefficients for Isotopic Exchange between Substituted Benzhydryl Thiocyanates ($XC_6H_4CHC_6H_4$-X')SCN and NaSCN at Constant Electrolyte Concentration[a]

Substituents X	X′	Temp, °C	Solvent	$10^3 \times$ [NaSCN], M	10^6rate/ [RSCN], sec^{-1}
4-NO_2	4-NO_2	70.0	Acetonitrile	9.95	3.02
			Acetone	10.2	7.80
H	4-NO_2		Acetone	8.47	2.59
H	3-Cl		Acetonitrile	1.99	0.72
				3.98	1.03
				5.11	1.28
				8.16	1.86
			Acetone	8.16	1.30
H	4-Cl			10.4	4.33
H	H			1.02	0.35
				3.57	1.24
				5.37	1.94
				7.35	2.47
				10.2	3.29
				18.4	6.51
				26.4	9.50
H	4-CH_3	25.0	Acetonitrile	0.93	2.03
				5.11	1.93
				8.05	2.05
				9.95	1.96
		35.0		10.1	7.68
4-CH_3	4-CH_3	10.0		4.96	11.14
		20.0		5.78	38.25

[a] Adjusted to 0.100 M with $NaClO_4$.

On the basis of these results and those previously reported,[3] it was deemed unnecessary to verify the change of rate with changing concentration of nucleophile in the other cases. Thus, all substrates having electron-attracting substituents are assumed to react by a second-order process in acetone. The same assumption was made for the 4,4′-dinitro substrate in acetonitrile, since the mononitro substrate was proved to do so.[3] On the other hand the 4-methyl and 4,4′-dimethyl substrates, which react by a first-order process at 25 and 0°, respectively, were assumed to maintain the same kinetics over a range of temperatures.

No data are reported in Table I for 4-methyl and 4,4′-dimethyl substrates in acetone. In this solvent, these strongly electron-releasing substrates display a very complex behavior which appears to be determined to a large extent by the incursion of "salt-assisted" ionization paths.[6] Those phenomena are currently under study and will be reported in a later paper.[7]

The values of k_1 and k_2 obtained by fitting the data of Table I and those previously reported[3] by means of eq 1 are summarized in Table II.

Table II. First- and Second-Order Rate Constants for Isotopic Exchange between Substituted Benzhydryl Thiocyanates and NaSCN in Acetonitrile and Acetone at Constant Electrolyte Concentration at 70°[a]

	Acetonitrile		Acetone,
Substituents	10^6k_1, sec^{-1}	10^4k_2, sec^{-1} M^{-1}	10^4k_2, sec^{-1} M^{-1}
4-NO_2, 4′-NO_2	. . .	3.02	7.71
4-NO_2, H	. . .	2.47	3.06
3-Cl, H	0.32	1.87	1.59
4-Cl, H	4.66	5.80	4.15
H, H	7.11	8.56	3.59
4-CH_3, H	410[b]	. . .	. . .
4-CH_3, 4′-CH_3	7300[c]	. . .	. . .

[a] [NaSCN] + [$NaClO_4$] = 0.1 M. [b] Extrapolated from data at 25 and 35°. Arrhenius energy of activation 23.9 kcal/mole. [c] Extrapolated from data at 0, 10, and 20°. Arrhenius energy of activation 20.9 kcal/mole.

Discussion

The results given here and those reported previously by us[3] and by Casapieri and Swart[8] as well as those recently reported by Winstein and collaborators[9] and by Pocker and collaborators[10] have established quite clearly that for nucleophilic substitution in the borderline region, the rate equation comprises one first-order and one second-order term, suggesting two competing reaction paths. The probable nature of the two paths can be inferred on the basis of the structural and solvent effects.

The First-Order Path. The data of Table II show that k_1 of eq 1 is very markedly affected by structural changes in the substrate, the rate being enhanced by electron-releasing substituents in the aryl rings. Application of the Hammett equation (Figure 1, solid line) shows that the k_1 values are excellently correlated by a linear-free-energy relation using σ^+ substituent constants.[11] At 70° in acetonitrile the value of the reaction constant results: $\rho = -4.5$ (correlation coefficient 0.996).[12] This high negative value of ρ indicates a highly polar transition state. It is significant that this value is considerably more negative than that obtained for the isomerization reaction of the same substrates: R-SCN → R-NCS, for which a value of $\rho = -3.40$ had been found under the same conditions.[5] Since isomerization is likely to occur by way of intimate ion pairs,[13,14] it appears that the first-order

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[4] Under the conditions of the exchange, isomerization of R-SCN to R-NCS takes place,[5] so that the exchanging system is not a stable one. However, the rate of isomerization is slow enough to make the McKay plots linear up to 30 to 40% of exchange. Thus, the estimation of initial rates is quite accurate.

[5] A. Iliceto, A. Fava, U. Mazzuccato, and O. Rossetto, *J. Am. Chem. Soc.*, 83, 2729 (1961).

[6] S. Winstein, E. C. Friedrich, and S. Smith, *ibid.*, **86**, 305 (1964).

[7] Some relevant observations have been presented at the Symposium on Organic Reaction Mechanisms, Cork, Ireland, July 1964.

[8] (a) P. Casapieri and E. R. Swart, *J. Chem. Soc.*, 4342 (1961); (b) *ibid.*, 1254 (1963).

[9] (a) A. F. Diaz and S. Winstein, *J. Am. Chem. Soc.*, **86**, 5010 (1964); (b) S. Winstein, R. Appel, R. Baker, and A. Diaz, Special Publication No. 19, The Chemical Society, London, 1965, p 109.

[10] Y. Pocker, W. A. Mueller, F. Naso, and G. Tocchi, *J. Am. Chem. Soc.*, **86**, 5011 (1964).

[11] Y. Okamoto and H. C. Brown, *J. Org. Chem.*, **22**, 485 (1957).

[12] H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

[13] A. Fava, A. Iliceto, A. Ceccon, and P. Koch, *J. Am. Chem. Soc.*, 87, 1045 (1965).

[14] A. Fava, U. Tonnellato, and L. Congiu, *Tetrahedron Letters*, 1657 (1965).

term of eq 1 corresponds to an exchange path involving an ionic intermediate which has proceeded past the "intimate ion-pair" stage in the ionization–dissociation process. Since in a solvent of relatively high polarity such as acetonitrile solvent-separated carbonium–thiocyanate ion pairs are unlikely to be present in any significant amount, the dissociated carbonium ion appears as the more likely intermediate involved in the first-order exchange.[15]

The Second-Order Path. The stoichiometry of this path indicates that its rate-determining transition state contains one nucleophile and one substrate molecule. It is therefore a bimolecular path to which the SN2 label can be attached in its original significance.[16] However, in view of the character of the substrates, there may be some question about the timing of the bond-making and bond-breaking processes. Two alternatives may be reasonably considered: (a) a one-step process in which bond breaking and making are included in the same transition state, (b) a two-step process in which bond breaking is preliminary to bond formation.

The first of these alternatives is the usual form of the SN2 mechanism in which formation of the new bond and rupture of the old one are synchronous, although they may not necessarily be of equal extent in the transition state. In the second alternative, which is similar, but not equal, to the SN2C+ mechanism,[17] a preequilibrium step leads to a carbonium–thiocyanate ion pair

$$\text{R-SCN} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \text{R}^+\text{SCN}^- \qquad (2)$$

which subsequently reacts with the nucleophile[18]

$$\text{R}^+\text{SCN}^- + {}^*\text{SCN}^- \xrightarrow{k_2'} \text{R}^{+*}\text{SCN}^- + \text{SCN}^- \qquad (3)$$

In this mechanism the observed first-order rate coefficient is composite.

$$k_{ex} = \frac{k_1 k_2'[\text{SCN}^-]}{k_{-1} + k_2'[\text{SCN}]}$$

Obviously, if the rate is linearly dependent (eq 1) on nucleophile concentration, the condition $k_{-1} \gg k_2' \times [\text{SCN}^-]$ must hold, and the observed rate constant is $k_2 = k_2'(k_1/k_{-1}) = Kk_2'$ where K is the equilibrium constant for ion-pair formation (eq 2).

We shall now offer evidence against this latter mechanism (b) based on the estimation of the specific rate of ion-pair formation (k_1 of eq 2). If mechanism b applied, the observed first-order specific rate of exchange, k_{ex}, would approach but never exceed k_1. Actually a necessary condition for second order to be observed is that $k_1 \gg k_{ex}$. Therefore, if it can be shown that this inequality does not hold, mechanism b would also be refuted. (As we shall see presently this proof can be achieved for some of the more electron-attracting substrates used in this work.)

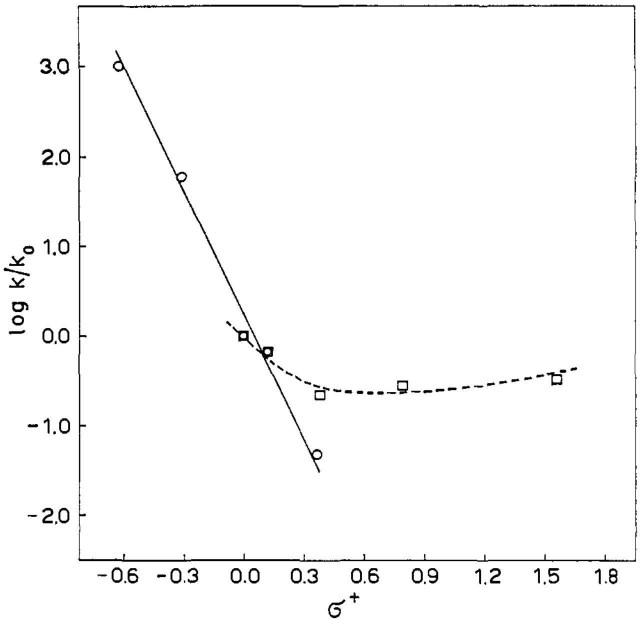

Figure 1. Plot of log k/k_H *vs.* σ^+ for isotopic exchange between benzhydryl thiocyanates and ionic thiocyanate in acetonitrile at 70°. The solid line correlates the first-order rate coefficients (circles) and the broken line correlates the second-order ones.

In previous papers,[5,13] we have shown that the isomerization of benzhydryl thiocyanates occurs through the intermediacy of an intimate ion-pair species, R^+SCN^-.

$$\text{R-SCN} \underset{k_S}{\overset{k_1}{\rightleftarrows}} \text{R}^+\text{SCN}^- \xrightarrow{k_N} \text{R-NCS} \qquad (4)$$

In this scheme the specific rate of ionization, k_1, is related to the specific rate of isomerization, k_i, as follows

$$k_1 = k_i\frac{k_S + k_N}{k_N} = k_i(1 + k_S/k_N) \qquad (5)$$

and k_1 can be evaluated from experimentally determined values of k_i provided the ratio k_S/k_N can be estimated. The latter is the relative reactivity of the two "teeth," S and N, of the ambident nucleophile SCN^- toward R^+, and can be expected to depend upon the nature of the carbonium ion. This ratio has been found to have a value of 5 in the case of 4,4′-dimethylbenzhydryl carbonium ion,[13] and more recent work in this laboratory indicates that it decreases somewhat with decreasing stability of the carbonium ion. For instance, for 4-chlorobenzhydryl values of k_S/k_N ranging between 2 and 3 have been found in different solvents.[22] Thus for the scope of our discussion the value of k_1 for various substrates can be set within the limits of about two to six times k_i, the lower factors applying to the more

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(15) The suggestion that the first-order exchange involves a free carbonium ion has already been advanced for several benzhydryl substrates by us,[3,13] by Winstein,[9] and by Pocker.[10]

(16) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 315.

(17) E. Gelles, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 2918 (1954); C. A. Bunton, "Nucleophilic Substitution at a Saturated Carbon Atom," Elsevier Publishing Co., Amsterdam, 1963, p 9.

(18) This special kind of SN2 mechanism has been suggested by Winstein[19] and by Hine[20] as one which would be kinetically indistinguishable form the one-step process. More recently Sneen has suggested that the reaction of ionic azide with 2-octyl methanesulfonate in aqueous dioxane may occur by the rate-determining attack of azide on a preformed ion pair.[21]

(19) S. Winstein, A. Ledwith, and M. Hojo, *Tetrahedron Letters*, **No. 10**, 341 (1961).

(20) J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 138.

(21) H. Weiner and R. A. Sneen, *J. Am. Chem. Soc.*, 87, 292 (1965).

(22) U. Tonnellato, L. Congiu, and A. Fava, to be published.

electron-attracting substrates.[23] In acetonitrile the values of k_i can be obtained either directly or by interpolation from the data reported in a previous paper.[5] In acetone the isomerization rates necessary to carry out the analysis have been determined.

With the available data the proof that the inequality $k_2[\mathrm{NaSCN}]_s > k_1$ holds can be reached only for the more electron-attracting substrates (up to 4-NO_2 in acetonitrile, and up to 3-chloro in acetone). These two examples will be worked out in detail.

(a) 4-Nitrobenzhydryl Thiocyanate in Acetonitrile. The second-order exchange rate coefficient is $k_2 = 2.47 \times 10^{-4}\ M^{-1}\ \mathrm{sec}^{-1}$. The maximum concentration of nucleophile at which the exchange rate was measured is 0.01 *M*. Therefore $k_{\mathrm{ex}} = k_2[\mathrm{NaSCN}]_s = 2.47 \times 10^{-6}\ \mathrm{sec}^{-1}$. With the aid of the Hammett relation the isomerization rate can be estimated to be[5] $k_i = 1.1 \times 10^{-7}\ \mathrm{sec}^{-1}$. If k_S/k_N is assumed to be 2, a rather conservative guess for this substrate, $k_1 = 3.3 \times 10^{-7}$ and $k_{\mathrm{ex}}/k_1 = 7$, *i.e.*, the exchange rate considerably exceeds the ionization rate. By similar computations, k_{ex}/k_1 is estimated to be about 3000 for 4,4′-dinitrobenzhydryl thiocyanate, but only about 0.1 for 3-chlorobenzhydryl thiocyanate. More electron-releasing substrates give still lower ratios.

(b) 3-Chlorobenzhydryl Thiocyanate in Acetone. At the concentration of nucleophile used, 0.082 *M*, the value of $k_{\mathrm{ex}} = k_2[\mathrm{NaSCN}]_s$ is $1.30 \times 10^{-6}\ \mathrm{sec}^{-1}$. The isomerization rate under the same conditions has been measured and found to be $k_i = 3.6 \times 10^{-7}\ \mathrm{sec}^{-1}$. Assuming $k_S/k_N = 2$, the ratio k_{ex}/k_1 is about 1.2, *i.e.*, the exchange rate is slightly higher than the ionization rate.

By similar computations, k_{ex}/k_1 is estimated to be about 150 for 4-nitrobenzhydryl thiocyanate, but only about 0.3 for the unsubstituted compound.

The considerations above show that mechanism b can be ruled out at least for the more electron-attracting substrates. For the more electron-releasing and the intermediate substrates, however, it still remains a possibility.

A second line of evidence against mechanism b may be based upon the structural effect on k_2: in mechanism b, $k_2 = k_2'K$; consequently the observed structural effect arises from combination of the effects on k_2' and *K*. Since k_2' is the rate coefficient for direct displacement on preformed ion pairs, it seems reasonable to assume for the transition state of reaction 3 a structure approaching that of an ion triplet, $SCN^-R^+SCN^-$. *If this is so*, the attainment of the transition state would require, with respect to the ion-pair initial state, only a minor reorganization of charge distribution on the organic moiety, and consequently k_2' may be expected to suffer only minor structural effects. On the other hand *K*, being the equilibrium constant for an ionization reaction, is expected to be very strongly affected by structural changes (with negative ρ).[25] Therefore k_2 should be affected by structural changes of the substrate in the same direction as *K*, though less strongly.[27] *This appears not to be the actual case;* application of the Hammett equation to k_2 values (in acetonitrile) yields the points reported as squares in the plot of Figure 1. The dotted line connecting the points is drawn mainly to stress what appears to be the more relevant feature of the structural effect, namely its smallness. In fact the values of ρ, which go from negative to positive, stay relatively small throughout the range of available substituents, being about -1.8 at the electron-releasing end and $+0.2$ at the electron-attracting end of the plot. A similar, though more symmetrical, behavior is observed in acetone, where ρ is -0.95 and $+0.58$ at the two ends, respectively.

The curvature of the Hammett plot is a rather common feature of nucleophilic substitutions in aralkyl and aroyl halides and esters and it occurs with both charged and uncharged nucleophiles.[28] This behavior has been given an excellent discussion as early as 1951 by Swain in terms of the change of transition-state character which may be induced by the substituent itself.[29] As the structure of the substrate is so modified by substituents that the relative importance of bond making and breaking at the transition state is continuously changed, the reaction constant, ρ, of the Hammett equation will continuously change as well.

The gradual change of transition-state character for the second-order path with varying structure is very clearly shown by the effect that a solvent change, from acetonitrile to acetone, has on the k_2 values for the various substrates. From the data in Table II the following ratios of $k_2(\mathrm{acetonitrile})/k_2(\mathrm{acetone})$ can be obtained: 4,4′-dinitro, 0.39; 4-nitro, 0.81; 3-chloro, 1.18; 4-chloro, 1.4; unsubstituted, 2.4.

The rate ratio, acetonitrile/acetone, appears to increase smoothly in going from the electron-attracting to the electron-releasing end of the reaction series. It is interesting to remark that while the ratio is <1 at the electron-attracting extreme, 4,4′-dinitro, which is the type of solvent effect usually observed for S_N2 substitution, at the other extreme the ratio is well above unity. Here the *direction* of the solvent effect is that which is usually observed for S_N1 substitutions, although there are differences in degree. For a reaction that occurs by way of a carbonium ion-pair intermediate, such as the racemization of *p*-chlorobenzhydryl thiocyanate, the rate ratio, acetonitrile/acetone, both containing $NaClO_4$ 0.1 *M*, has a value of about 6.[22]

In dealing with charged nucleophiles, however, as in

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[23] This method of estimating the ionization rate is based on the assumption that in the ionization process (eq 4), the ion pair from which isomerization obtains is not preceded by another ion pair which gives covalent return exclusively to thiocyanate. This possibility cannot be excluded *a priori* for such a hypothetical kind of ion pair cannot, by definition, be detected by means of isomerization experiments. It might, in principle, be detected by means of stereochemical experiments where the concomitant racemization and isomerization of an optically active thiocyanate are determined. Work in progress in these laboratories, however, gives no indication that racemization might occur at an ionization level prior to that from which isomerization obtains. Instead, all available evidence indicates that racemization and isomerization occur by way of one and the same intermediate.[24] This evidence, however, does not rule out the possible preliminary formation of an ion-pair intermediate which returns exclusively to thiocyanate with virtually complete retention of configuration.

[24] A. Fava, *Acta Cient. Venezolana*, **15**, 223 (1965); see also ref 14.

[25] For example, the substituent effect on the equilibrium constant for carbonium ion formation from benzhydrols in sulfuric acid is characterized by a value of $\rho = -6.67$.[11,26]

[26] H. G. Kuivila and A. R. Hendrikson, *J. Am. Chem. Soc.*, **74**, 5068 (1952).

[27] This argument is recognized to have limited value since a whole spectrum of ion-pair intermediates as well as an ion-triplet transition state can be envisioned, having various degrees of covalent character, which would give rise to a spectrum of substituent effects.

[28] Reference 20, pp 171 and 294; see also A. Streitwieser, Jr., *Chem. Rev.*, **56**, 591 (1956).

[29] C. G. Swain and W. P. Langsdorf, Jr., *J. Am. Chem. Soc.*, **73**, 2813 (1951).

the case at hand, there may be another factor contributing to the nonlinearity of the Hammett plot which, to our knowledge at least, has never been given adequate consideration in this connection. This is the reactivity of ion pairs of the nucleophile. In fact, whatever the detailed mechanism of the second-order path is, the observed second-order rate coefficient, k_2, is composite

$$k_2 = k_{\mathrm{I}}\alpha + k_{\mathrm{IP}}(1 - \alpha) \qquad (6)$$

where α is the degree of dissociation of the ionic reactant and k_{I} and k_{IP} are the rate constants for displacement by the free ion, SCN^-, and by the ion pair, Na^+SCN^-. For the k_2 values to be directly comparable among themselves, it is necessary that the ratio $k_{\mathrm{I}}/k_{\mathrm{IP}}$ be independent of substrate or that either one of the two terms of the right-hand side of eq 6 always predominates.

In direct nucleophilic substitution reactions it is frequently assumed that the reactivity of ion pairs can be neglected with respect to that of free ions. Indeed, on the basis of this assumption, it has been proposed that the ion-pair dissociation constant of the nucleophilic salt may be obtained from kinetic data.[8b,30] This assumption may be justified in those extreme cases where, bond formation being the predominant factor, the reaction center is strongly discriminating; however, it is unlikely to hold in substitutions where heterolysis of the bond of carbon to leaving group is a conspicuous feature. As the extent of bond breaking in the transition state increases, the reaction center will become less discriminating and the nucleophilicity of the ion pair will approach that of the free ion. Thus the contribution of the $k_{\mathrm{IP}}(1 - \alpha)$ term may become very substantial as the substrate moves toward the electron-releasing end, the more so for more polar solvents.

With the available information, it is impossible to make even a rough estimate of the importance of this factor in the present case. However, the data of Lichtin,[31] showing that the reactivity of bromide ion toward 4-nitrobenzyl bromide in liquid SO_2 is not very much greater than that of bromide ion pairs, suggest that this may be a very substantial factor in determining the rising of the left-hand side of the Hammett plot and its curvature in the case at hand.

From what precedes, it should be clear that we apply the concept of the gradual change of transition-state character to the bimolecular reaction, without adopting the view of a unity of mechanism in nucleophilic substitution. In fact, though quite general, the factors discussed above are likely to be relatively minor ones and it would not be justified to hold them responsible for the substantial changes in ρ which are sometimes observed, especially in solvolytic reactions. In many such cases a gross change in mechanism, from the unimolecular to the bimolecular, sets in also which is not sudden, of course, since the two mechanisms may operate concurrently for a range of substrates.

This point may be illustrated with reference to our own results. If instead of separating the contributions by the two paths, the over-all rates are considered at a fixed concentration of nucleophile, say 0.01 M, the following first-order specific rates ($\times\ 10^6$) would have been measured for the various substrates: 4,4′-dimethyl, 7300; 4-methyl, 410; unsubstituted, 15.7; 4-chloro, 10.5; 3-chloro, 2.19; 4-nitro, 2.47; 4,4′-dinitro, 3.02. Reported on a Hammett plot, these data yield the solid line of Figure 2. The dotted line in the same figure reports the data for another concentration of nucleophile, 0.1 M. These curves, which obviously derive from a change in mechanism along the series, are very similar to those frequently observed for substitutions, either solvolytic or by added nucleophiles, of benzyl derivatives under conditions of facile ionization.[32] A specific example which has been somewhat debated is that of benzyl tosylates in aqueous acetone or dioxane.[33,11] Considering our results, we are naturally inclined to consider the latter as a typical case where the nonlinearity of the Hammett plot reflects a change in mechanism along the series.

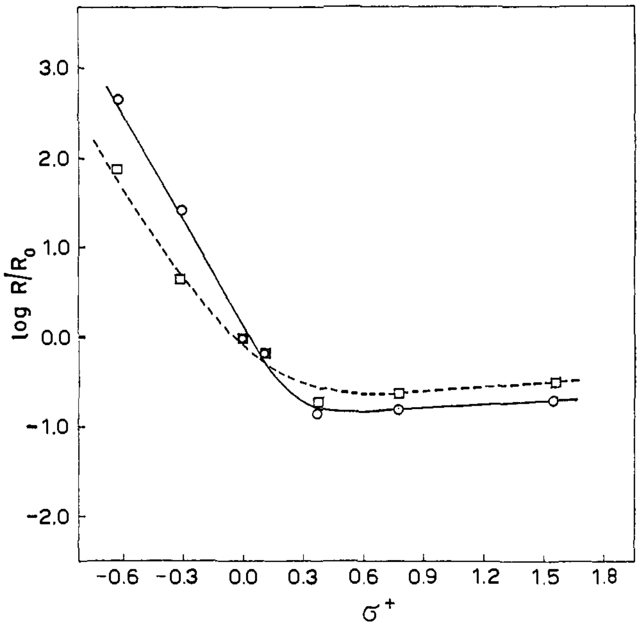

Figure 2. Plot of log R/R_{H} *vs.* σ^+ for isotopic exchange between benzhydryl thiocyanates and ionic thiocyanate in acetonitrile at 70°. The two lines correlate rates calculated for [NaSCN] = 0.01 M (circles, solid line) and for [NaSCN] = 0.1 M (squares, broken line).

To further elucidate the nature of the second-order path, it may be well to mention here the main conclusions of a stereochemical study recently accomplished in these laboratories using optically active 3-chlorobenzhydryl thiocyanate.[34] These are: (1) the rate of racemization of 4-chlorobenzhydryl thiocyanate in acetone or acetonitrile increases when sodium thiocyanate is substituted for sodium perchlorate by an amount equal to $2k_2[\mathrm{NaSCN}]_s$, where k_2 is the second-order rate coefficient for isotopic exchange measured under identical conditions. Thus, the second-order exchange path involves net inversion of configuration.[35] (2) At a NaSCN concentration of

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[30] W. M. Weaver and J. D. Hutchison, *J. Am. Chem. Soc.*, **86**, 261 (1964).

[31] N. N. Lichtin and K. N. Rao, *ibid.*, **82**, 2417 (1961).

[32] For a recent example, see H. Hill and A. Fry, *ibid.*, **84**, 2763 (1962).

[33] F. T. Fang, J. K. Kochi, and G. S. Hammond, *ibid.*, **80**, 563 (1958); G. S. Hammond, C. E. Reeder, F. T. Fang, and J. K. Kochi, *ibid.*, **80**, 568 (1958); G. S. Hammond, J. Peloquin, F. T. Fang, and J. K. Kochi, *ibid.*, **82**, 443 (1960).

[34] U. Tonnellato and A. Ceccon, *Gazz. Chim. Ital.*, **96**, 71 (1966).

[35] This result agrees with that reported by Winstein and collaborators for racemization and radiochloride exchange in a closely related system, namely *p*-chlorobenzhydryl chloride and tetrabutylammonium chloride in acetone.[19]

0.1 *M*, the racemization rate in acetone or acetonitrile is considerably greater than the ionization rate (estimated as above from the isomerization rate and the k_S/k_N ratio). Since in mechanism b the value of k_1 (eq 3) sets the upper limit of all processes occurring through the intermediacy of ion pairs (see, however, ref 23), exchange, and racemization through exchange, must occur largely by way of direct displacement on the substrate. Thus, also this piece of evidence favors mechanism a against b for the 4-chlorobenzhydryl substrate both in acetone and in acetonitrile and, *a fortiori*, for other more electron-attracting substrates.

Experimental Section

Solvents and Materials. Acetonitrile was first dried over Drierite, refluxed over phosphorous pentoxide, and distilled. From redistillation over potassium carbonate the fraction bp 81.5–81.6° was collected. Commercial reagent grade acetone was refluxed over potassium permanganate and distilled. From redistillation over potassium carbonate the fraction bp 56.4–56.5° was collected.

Labeled NaSCN (^{35}S) was obtained as previously described.[36]

3-Chlorobenzhydryl Bromide. Friedel-Crafts reaction of 3-chlorobenzoic acid chloride with benzene gave 3-chlorobenzophenone. This was reduced with $LiAlH_4$ and the alcohol converted to the bromide with HBr in ether. The product was distilled under reduced pressure: bp 158–159° (0.4 mm). *Anal.* Calcd for $C_{13}H_{10}ClBr$: Br, 29.92. Found: Br, 28.84.

3-Chlorobenzhydryl Thiocyanate. Reaction of the bromide with KSCN in acetone[5] afforded a thick oil which in our hands did not crystallize. After removal of volatiles, it was sublimed at 50° and 0.01 mm. No further purification was attempted. *Anal.* Calcd for $C_{14}H_{10}NClS$: N, 5.37; Cl, 13.65; S, 12.32. Found: N, 5.31; Cl, 13.43; S, 12.50.

4,4′-Dinitrobenzhydryl Bromide. Diphenylmethane was nitrated to give 4,4′-dinitrodiphenylmethane, mp 183° (lit.[37] 183°). The bromide was obtained by reaction with bromine in CCl_4 in the presence of benzoyl peroxide, according to the method of Wragg, *et al.*[38] To improve the bromination yield it was found useful to increase the reaction time from 0.5 hr at reflux, as suggested by Wragg, *et al.*,[38] to 1.5 hr.

After evaporation of the solvent, the residue was fractionally crystallized from acetone–petroleum ether. The first crop of crystals melted at 181°, contained no bromine, and appeared to be essentially pure 4,4′-dinitrodiphenylmethane. The second crop melted at 84–86° and had a high bromine content, 25.1%. It was fractionally crystallized from CCl_4, the first fraction, mp 92–93° (lit.[38] 90.5°), giving a satisfactory bromine analysis. *Anal.* Calcd for $C_{13}H_9N_2O_4Br$: Br, 23.7. Found: Br, 24.4.

4,4′-Dinitrobenzhydryl Thiocyanate. The bromide was treated with KSCN in acetone.[5] After evaporation of the solvent, the residue was extracted with water–cyclohexane. The organic layer was washed, dried over Na_2SO_4, and evaporated. The residue was crystallized from acetone–light petroleum; mp 135–36°. *Anal.* Calcd for $C_{14}H_9N_3O_4S$: N, 13.33; S, 10.16. Found: N, 13.20; S, 10.23.

All other products used in this and in the previous work[3] have been described.[5,39]

Kinetics. Isotopic Exchange. In the "slow" runs, taking place at 70°, the solutions of organic thiocyanate, sodium thiocyanate, and sodium perchlorate were mixed at room temperature in the appropriate volumetric ratio to give the desired concentration of reactants. The two salts were so adjusted as to give a total 0.1 *M* concentration of electrolyte, while the ionic thiocyanate was varied between 0.001 and 0.01 *M*. Three-milliliter portions of the solution were sealed in ampoules and put in a thermostat from which they were withdrawn at appropriate time intervals. For the "fast" runs, taking place at, or below, room temperature, the solutions of the organic and of the ionic reactants were mixed at the temperature of the experiment by inverting the Y-shaped reaction vessel. Samples were pipetted out at appropriate time intervals. The work-up and counting procedures have been described.[5] The rate constants reported in Table I are uncorrected for expansion.

Isomerization. The rates of isomerization in acetone, necessary to estimate the ionization rate (eq 5), have been measured by infrared spectrophotometry as previously described.[5]

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

(37) N. Staedel, *Ann.*, **283**, 151 (1895).

(38) A. H. Wragg, T. S. Stevens, and D. H. Ostle, *J. Chem. Soc.*, 4057 (1958).

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Anionic Rearrangement of Hydrazines. II.[1] Isomers of Bis(organosilyl)hydrazines[2]

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Abstract: Eight new bis(organosilyl)hydrazines have been prepared, comprising four sets of 1,1 and 1,2 isomers. Isomeric structural assignments are made based mainly on a new method involving the splitting between the infrared N–H stretching modes, which is greater for 1,1- than for 1,2-hydrazines. Structures are also assigned for the known bis(trimethylsilyl)hydrazines, reversing the assignment made previously.[1,3,4]

Rearrangement of silylhydrazines in the presence of *n*-butyllithium was first observed in our laboratories in 1964.[1] Work following this original discovery shows that the anionic rearrangement of organosilylhydrazines is a remarkably general and suprisingly rapid reaction.[5] The experimental evidence and conclusions drawn from it will be explained in succeeding papers in this series.

The rearrangement reaction was first noted for bis(trimethylsilyl)hydrazine,[1] and many of the later rear-

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(1) For part I see R. E. Bailey and R. West, *J. Am. Chem. Soc.*, **86**, 5369 (1964).

(2) Research sponsored by Air Force Office of Scientific Research (SRC), O.A.R., U.S.A.F., Grant No. AF-AFOSR 1061-66.

(3) (a) U. Wannagat and H. Liehr, *Angew. Chem.*, **69**, 783 (1957); (b) *Z. Anorg. Allgem. Chem.*, **297**, 129, 133 (1958); (c) U. Wannagat and C. Krüger, *Monatsh. Chem.*, **93**, 613 (1964).

(4) H. Bock, *Z. Naturforsch.*, **17b**, 423 (1962).

(5) R. West and R. E. Bailey, Abstracts, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965, p 4M.