Linear Free Energy Relationships in the Thiophene Series. Part 3.[1] A Kinetic Study of Chlorine-isotopic Exchange between Lithium Chloride and Some 2-Chloro-3-nitro-5-X-thiophenes

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The rate constants for the chlorine-isotopic exchange between lithium chloride-36 and some 2-chloro-3-nitro-5-X-thiophenes (**Ia**—**g**) have been measured in sulpholane solution. The results obtained give a good Hammett correlation (in the range 323—373 K; calculated ρ 5.55—4.68), indicating that the charge developed in the transition state is strongly affected by the electronic effects of substituents. In order to study the effect of solvent on reactivity, the rates of 2-chloro-3,5-dinitrothiophene (**Ig**) have also been measured in acetone, methanol, and propan-2-ol solutions. A comparison has been made between thiophene and benzene derivatives and the MNDO technique has been used to provide a theoretical model of the exchange reaction.

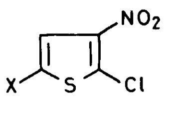
The course of S_NAr reactions in aromatic[2] and heteroaromatic[3] compounds has been extensively studied, both for neutral and anionic reagents, but relatively few papers have appeared[4,5] which deal with reactions between ionic chloride and aromatic chloro-compounds.

In the field of heteroaromatic compounds the only reactivity study has been that of derivatives of 2-chloropyridine,[4c] *i.e.* of six-membered ring compounds. We now report our kinetic data on chlorine-isotopic exchange between lithium chloride-36 and some 2-chloro-3-nitro-5-X-thiophenes (**Ia**—**g**). These represent the first five-membered ring derivatives to be studied by this technique, although many other S_NAr reactions of thiophenes have been reported.[6a–e]

Nitro-activated chlorothiophenes (**I**), compounds which are more reactive towards nucleophiles than the corresponding benzene derivatives, represent a series appropriate to a linear free energy relationship (l.f.e.r.) study. Indeed, no attempts at obtaining l.f.e.r.s have so far been published for chlorine-isotopic exchange reactions. The results of such correlations can be compared with data concerning other nucleophiles, and should furnish information about the structure of the transition state involved in chlorine exchange reactions.

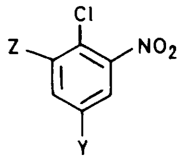
Results and Discussion

Kinetic Data.—Rate constants and activation parameters for the chlorine-isotopic exchange reactions between lithium chloride and thiophene (**Ig**) in several solvents, and thiophenes (**Ia**—**g**) in sulpholane solution, are given in Tables 1 and 2, respectively. In Table 3 the rate constants for the reactions of 1-chloro-2-nitrobenzene (**II**), 1-chloro-2,4-dinitrobenzene (**III**), and 1-chloro-2,4,6-trinitrobenzene (**IV**) are compared with those for thiophenes (**Ia**) and (**Ig**).



(**I**)

a; X = H
b; X = CONH$_2$
c; X = CO$_2$Me
d; X = SO$_2$Me
e; X = Ac
f; X = CN
g; X = NO$_2$



(**II**) Y = Z = H
(**III**) Y = NO$_2$, Z = H
(**IV**) Y = Z = NO$_2$

Table 1. Rate constants[a] for chlorine-isotopic exchange between lithium chloride and 2-chloro-3,5-dinitrothiophene in various solvents

Solvent	T/K	k/dm^3 mol^{-1} s^{-1}
Acetone	272.0	6.60×10^{-2}
Methanol	303.2	3.94×10^{-6}
Propan-2-ol	303.2	6.94×10^{-5} [b,c]
Sulpholane	303.2	1.09×10^{-2} [b,d]

[a] Chemical yield determined by u.v. analysis in methanol solution, $\lambda_{max.}$ 303 nm, ε 2 070 m^2 mol^{-1}. [b] Value calculated from activation parameters. [c] At 323.1 K, $\Delta H^{\neq}$ 85.2 kJ mol^{-1}, and $\Delta S^{\neq}$ −44 J K^{-1} mol^{-1}. [d] *cf.* Table 2.

Reactivity of Thiophenes (**Ia**—**g**) *and Comparison with Benzene Derivatives.*—The chlorine-isotopic exchange reaction proceeds through the addition–elimination mechanism typical of S_NAr; the introduction of electron-withdrawing substituents here causes a large increase in reactivity, *e.g.* $k_{(Ig)}/k_{(Ia)}$ = 2.5×10^6 at 323.1 K. Substituents being equal, chlorothiophenes react at much higher rates than do chlorobenzenes (Table 3). The following sequence of reactivity has been observed for thiophene and benzene derivatives having comparable structures, *viz.* (**IV**) $\geqslant$ (**Ig**) $\gg$ (**III**) > (**Ia**) $\gg$ (**II**).

Thus, thiophene (**Ia**) reacts (in sulpholane solution) much faster than benzene derivative (**II**), although both contain one activating nitro-group. Similarly, thiophene (**Ig**) is much more reactive than compound (**III**); yet both contain two nitro-groups. On the other hand, thiophene (**Ig**) reacts only a little more slowly than does the trinitro-derivative (**IV**), in acetone solution.

This pattern of behaviour conforms to the well known higher reactivity of thiophenes, when compared with benzene

Table 2. Rate constants and activation parameters for chlorine-isotopic exchange between lithium chloride and some 2-chloro-3-nitro-5-X-thiophenes (**Ia**—**g**) in sulpholane solution

Compound	10^4k/dm^3 mol^{-1} s$^{-1\,a}$	$\Delta H^{\neq\,b}$/kJ mol^{-1}	$-\Delta S^{\neq\,b}$/J K^{-1} mol^{-1}	$\lambda_{max.}{}^c$/nm	ε^c/m^2 mol^{-1}	$\sigma_p{}^d$
(Ia)	7.62 (408.1), 12.0 (413.3), 18.7 (418.3), 26.8 (423.1), 41.9 (428.1)	120.2	12.6			0.00
(Ib)	1.59 (333.1), 3.56 (341.6), 6.91 (348.9), 10.8 (353.8), 15.8 (358.8)	86.7	58.3	248	2 070	+0.55
(Ic)	6.86 (323.2), 10.2 (328.1), 14.9 (333.1), 23.0 (338.1), 34.0 (343.1)	71.6	84.9	248	2 280	+0.71
(Id)	8.57 (313.1), 14.4 (318.1), 23.9 (323.1), 39.1 (328.1), 62.9 (333.1)	83.7	36.6	238	2 020	+0.85
(Ie)	10.6 (323.1), 17.0 (328.2), 28.2 (333.2), 43.5 (338.1), 65.9 (343.6)	80.5	53.5			+0.85
(If)	18.4 (308.1), 30.5 (313.1), 47.4 (318.1), 73.9 (323.1), 120 (328.1)	75.2	53.5	243	2 280	+0.92
(Ig)	1 690 (305.7), 2 190 (308.7), 2 860 (311.4), 4 230 (315.9), 5 030 (318.0), 6 990 (321.8), 9 060 (324.9), 10 500 (327.0), 13 300 (329.9)	68.9	34.7	305	852	+1.27

[a] Temperature, K, in parentheses. [b] At 323.1 K. [c] Solvent: methanol; for u.v. determination of chemical yield, used in the method involving isolation of samples of the substrate. [d] Ref. 6*c*.

Table 3. Rate constants for chlorine-isotopic exchange in benzene and thiophene systems

	k/dm^3 mol^{-1} s^{-1}	
Compound	Acetone, 272.0 K	Sulpholane, 313.2 K
(IV)	$1.77 \times 10^{-1\,a,b}$	
(Ig)	6.60×10^{-2}	$4.12 \times 10^{-2\,a}$
(III)	$1.05 \times 10^{-6\,a,b}$	$3.1 \times 10^{-6\,b}$
(Ia)		$1.30 \times 10^{-8\,a}$
(II)		$7.25 \times 10^{-12\,a,b}$

[a] Value calculated from activation parameters [b] Ref. 4*b*.

derivatives, towards nucleophiles. Thus, in methanol solution $k_{(\mathbf{Ia})}/k_{(\mathbf{II})} = 1.1 \times 10^3$ (at 353 K)[6c,7a] and $k_{(\mathbf{Ig})}/k_{(\mathbf{III})} = 4.4 \times 10^2$ (at 273 K)[6c,7b] for reactions with piperidine, and corresponding rate ratios 7.6×10^3 (at 323 K)[7a,c] and 2.4×10^4 (at 293 K)[6e,7a] respectively, obtain for reactions with benzenethiolate.

The differences in S_NAr reactivity between thiophene and benzene derivatives depend on many factors. One such factor is the difference in the electron-withdrawing efficiencies of a nitro-group when substituted in a thiophene ring or in a benzene ring. This derives partly from the unusual kind of transmission of electronic effects operating in five-membered rings.[6a,b,f] Moreover, nitro-groups seem to be more conveniently arranged in a thiophene ring in being more nearly coplanar. *X*-Ray crystallographic analysis of thiophene (**Ig**) shows that the 5-nitro-group is coplanar with the ring, the 3-nitro-group being only a little out of plane.[8] In contrast, corresponding (though not recent) evidence suggests that in compound (**III**) both the 4-nitro-group (*ca.* 15°) and the 2-nitro-group (*ca.* 40°) are rotated with respect to the benzene ring,[9] which would result in reduced activation by the nitro-substituents.

Intrinsic geometric differences between five- and six-membered rings are also responsible for a higher reactivity in thiophene derivatives; the latter offer reduced inhibition of resonance, with respect to corresponding benzene derivatives, and a reduced *F*-strain on the approach of a nucleophile,[10] as well as a lower activation energy consequent on the quasi-tetrahedral arrangement around the (2-C) atom in thiophene.[11] Moreover, there is chemical evidence[12] (see also evidence from MO calculations, below) that the sulphur atom in compound (**I**) is able to accommodate a significant negative charge in the rate-determining transition state. Finally, the lower resonance stabilisation energy of thiophene allows the necessary perturbation of aromatic π-orbitals in S_NAr to be achieved more easily in thiophene derivatives than in the corresponding benzene derivatives.[6a]

The kinetic behaviour of thiophene (**Ig**) in several solvents (Table 1) shows that the reactivity decreases in the sequence: acetone > sulpholane > propan-2-ol > methanol.[4b] The exchange reaction is thus much slower in protic solvents than in dipolar aprotic solvents, as expected on the basis of the predictable variation of ion-solvent interactions for a small anion with a high charge density. This variation affects the nucleophilicity of chloride ion, and accounts for the wide range of rates observed.[13]

As has been observed similarly with benzene derivatives, chloronitrothiophenes (**Ia**—**g**) undergo reaction with lithium chloride more slowly than they do with other nucleophiles. The exchange reactions (k_{Cl}) in sulpholane solution can be compared with piperidino-dechlorinations (k_N) and benzenethiolate dechlorinations (k_S), although the data for the latter were obtained in methanol solution, in which the nucleophilicities of both piperidine and benzenethiolate anion are much lower than they would be in sulpholane solution. The reactivity ratios observed for thiophene (**Ia**) are $k_S:k_N:k_{Cl}::1.5 \times 10^7: 3.6 \times 10^4: 1$ (at 323 K), and for thiophene (**Ig**) $:: 1.3 \times 10^7: 1.4 \times 10^3: 1$ (at 293 K). The nucleophilicity order observed is thus $C_6H_5S^- >$ piperidine $> Cl^-$.

Theoretical Modelling of the Exchange Reactions.—In order to gain further insight into the factors governing the reactivity of our substrates in the chlorine exchange reaction, SCF LCAO MO calculations were carried out in the MNDO approximation, with the standard parametrisation of Dewar and Thiel.[14] The calculations showed * that the optimised geometries (bond lengths, bond angles) of compounds (**Ig**) and (**III**) were generally in good agreement with the crystallographic data for these compounds, although the two sets of data refer to different phase states. However, calculated angles of twist of the nitro-groups suggested that the 3-nitro-group in (**Ig**) and the 2-nitro-group in (**III**) were virtually coplanar; this is at variance

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* Details are given in Supplementary Publication No. SUP 56041 (5 pp). (Details of Supplementary Publications are in Instructions for Authors in *J. Chem. Soc., Perkin Trans. 2*, 1984, Index Issue.

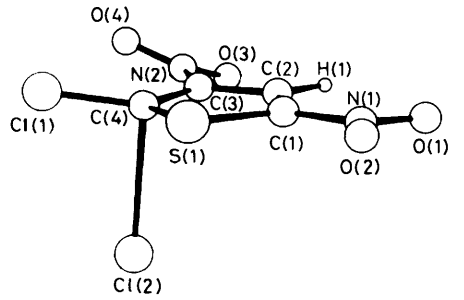

Figure 1. Calculated geometry of the transition state with 2-chloro-3,5-dinitrothiophene

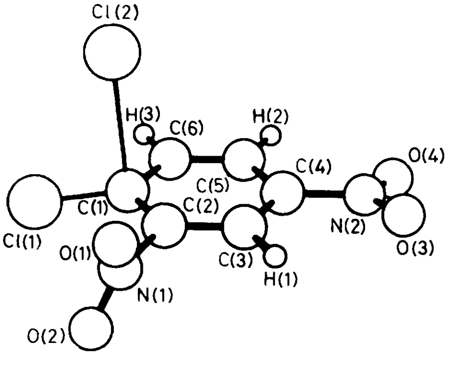

Figure 2. Calculated geometry of the transition state with 1-chloro-2,4-dinitrobenzene

with the geometries[15] found for these compounds in the crystalline state, where other interactions may be involved.

Calculations* of charge distributions of the substrate molecules (**Ig**) and (**III**) show that high polarity, normally associated with nitro-groups, is here confirmed, with high positive charges occurring at the N atoms and corresponding negative charges at the O atoms. In (**Ig**) a large positive charge (+0.32e) on the S atom and a small positive charge (+0.05e) on the Cl atom are noteworthy. Population analysis reveals that the charge on the S atom is due mainly to low occupancy of the sulphur $2p_z$AO, which is compensated for by the high negative charges on the 3- and 5-C atoms. In contrast, the nitro-groups in (**III**) are (overall) more negative, and the C atoms bearing nitro-groups are less negative, than those in (**Ig**).

According to the frontier orbital concept,[16] a nucleophilic reagent will attack a molecule in an orbitally controlled process at a position for which the square of the LUMO coefficient is at a maximum. Evaluation of these coefficients shows that attack by chloride will be predicted to occur at the carbons bearing the Cl atoms, *viz.* that the reaction observed will be a chloride exchange, as shown by experiment. The electron-accepting properties of both compounds are indicated by the negative values of the LUMOs, *viz.* −2.4 eV for (**III**) and −2.7 eV for (**Ig**). Moreover, the numerical value of the LUMO coefficients at the reacting position of (**Ig**) (+0.614) is substantially greater than that of (**III**) (−0.554). Both these factors would predict an enhanced reactivity for the thiophene compound (**Ig**) over that of the benzenoid compound (**III**), under comparable conditions.

Theoretical modelling of the exchange reactions was looked at next, recognizing that the inability to take solvation into account restricts its application. Useful results nevertheless emerged. The Cl^- ion was set at fixed distances from the C atom being attacked, and all other geometrical parameters were then allowed to relax. The resulting minimum energy reaction path was found to involve the attacking ion approaching the ring at a right angle, for both (**Ig**) and (**III**). As the incoming ion approaches the reaction centre the neighbouring nitro-groups are twisted (rotated) out of the plane of the ring. At a point corresponding to the maximum on this surface, *viz.* at the transition state (TS1), the angles of twist were 20° for (**Ig**), and *ca.* 70° for (**III**), suggesting that in particular the benzenoid derivative undergoes major geometrical changes during this reaction. The calculated TSs are shown diagrammatically in Figures 1 and 2. Structural details and charge distributions for the intermediate species are given elsewhere. In substrates (**Ig**) and (**III**), and in the more simply substituted thiophene (**Ia**), the TSs were found to correspond to structures for which the distance between the attacking chloride ion (Cl-2) and the pertinent C atom (C-4 in Figure 1, or C-1 in Figure 2) is *ca.* 270 pm (see Figure 3).

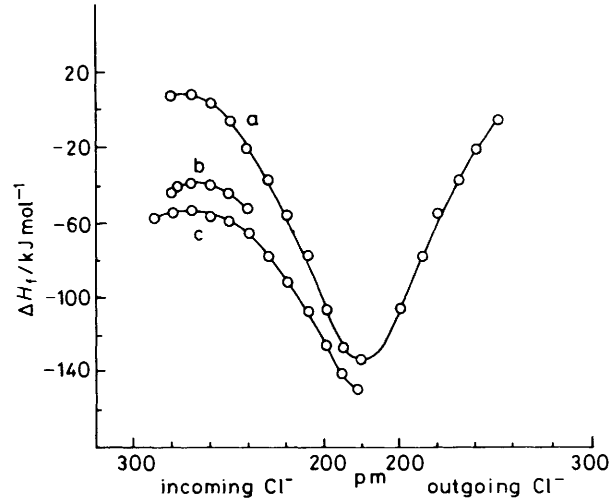

Figure 3. Calculated total energy of the system chloride + substrate as a function of C–Cl bond distance, for a, 2-chloro-3,5-dinitrothiophene; b, 2-chloro-3-nitrothiophene, and c, 1-chloro-2,4-dinitrobenzene

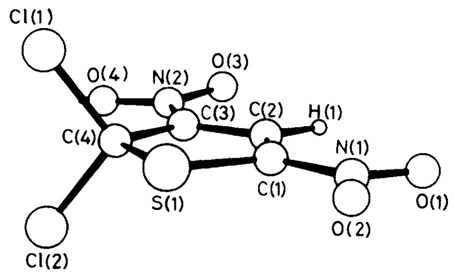

Figure 4. Calculated geometry of the σ-complex with 2-chloro-3,5-dinitrothiophen

After passing over this maximum the energies rapidly decrease to a minimum, corresponding to the formation of σ-complexes, in each of which the two C–Cl bond lengths are the same, being *ca.* 181.5 pm for derivative (**Ig**) (Figure 4) and *ca.* 184.6 pm for derivative (**III**) (Figure 5). At all stages leading to the formation of the σ-complex derived from compound (**Ig**), the thiophene ring retains its essential planarity, and the twist angles of the nitro-groups suffer only small changes. There are two orientations of a 2-nitro-group for which the two Cl atoms

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* Details are given in Supplementary Publication No. SUP 56041.

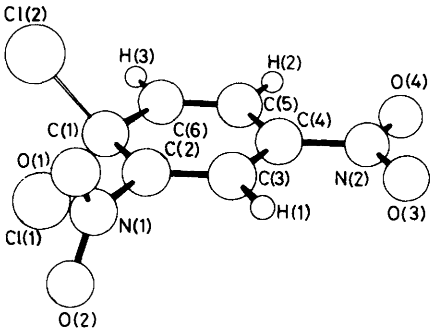

Figure 5. Calculated geometry of the σ-complex with 1-chloro-2,4-dinitrobenzene

in the σ-complex will be equivalent, *viz.* when the nitro-group is coplanar with, or when it is orthogonal to, the aromatic ring. Within the accuracy expected for torsional angles predicted by the MNDO method, these two orientations of the nitro-group are found in the σ-complexes derived from thiophene (**Ig**) (*viz.* coplanar) and from compound (**III**) (*viz.* orthogonal), respectively.

The charge densities calculated for the model σ-complexes reveal interesting differences for the benzene and thiophene systems. Overall, the ring atoms retain only a small proportion of the unit negative charge introduced by the chloride ion. The sum of charges for the thiophene (**Ig**) σ-complex is -0.187e, and for the benzene (**III**) σ-complex is -0.162e. More significant are the changes in electron distribution calculated for conversion of initial states into σ-complexes. Thus, for thiophene (**Ig**) both the 3-nitro and the 5-nitro groups can accommodate some negative charge, equivalent to 0.144e and 0.143e, respectively. The ring S-atom can accommodate electron density (equivalent to 0.321e) in the partially empty $2p_z$AO. For the σ-complex derived from substrate (**III**) it is the 2-, 4-, and 6-C atoms which chiefly accommodate the negative charge introduced, to the extent of 0.203e, 0.204e, and 0.140e, respectively. For the σ-complex from thiophene (**Ig**), also, the C atoms bearing nitro-groups are seen to be good acceptors of negative charge, *viz.* 0.276e and 0.139e at the 3-C and 5-C atoms, respectively. The 4-nitro-group of (**III**) develops an additional negative charge, equivalent to 0.148e, in the σ-complex, but the corresponding charge for the 2-nitro-group is only 0.061e. This must be due to a substantial reduction in conjugation, resulting from out-of-plane rotation of this group (see above).

The stabilisation energies of the σ-complexes were calculated to be *ca.* 142 kJ mol^{-1} for compound (**Ig**) and *ca.* 90 kJ mol^{-1} for compound (**III**), but these values, though presumably qualitatively correct, are unlikely to be precise, since such calculations neglected solvation and desolvation phenomena.

The calculated parameters can be used to provide estimates of the position of the TSs along the reaction co-ordinates. For example, the electronic charges on the S atom in compound (**Ig**) in the IS, the TS, and the σ-complex, are 0.317e, 0.270e, and 0.086e, respectively; this suggests, on a linear basis, that the TS here occurs *ca.* 20% along the reaction path leading to the σ-complex. Similarly, using charges on incoming and outgoing Cl atoms, the involvement of an 'early' TS for this exchange reaction is indicated. Yet, these heteroatoms are particularly prone to being involved in solvation, which phenomenon was not allowed for in the calculations (see above). It may be of significance that the apparent location of the TSs, using as criteria the electron distributions at atoms unlikely to be directly involved in significant solvation, *viz.* the C atoms of the ring, then appears at *ca.* 30—70% along the reaction path leading to the formation of the σ-complexes. Results from the analysis of our kinetic data (see below) indeed suggests that a 'late' TS is likely to be involved in the chloride-exchange process.

The Hammett Relationship.—Because of the large differences in reactivities of the various chlorothiophenes (**I**) studied here, the kinetic data have been collected over a wide range of experimental temperatures (305—428 K). The susceptibility constants have therefore been calculated in the range 323—373 K by using log k values computed from activation parameters. The choice of the temperature range has been made so as to obtain log k values near to the experimental temperature range for as many compounds as possible. σ_p^- Values for thiophene derivatives, as previously determined by two of us,[6c] have been used here and gave excellent correlations (r 0.9934—0.9963, c.l. > 99.95%) at each temperature.

The calculated susceptibility constants, as observed elsewhere,[17] smoothly decrease with increasing temperature, *viz.* $\rho_{323.1} = +5.55$ and $\rho_{373.1} = +4.68$. The high ρ values here calculated, together with the better correlation obtained by use of σ_p^- constants instead of σ_p constants, indicate[2b,17] that a large negative charge develops in the transition state, and that this is strongly affected by the electronic effects of the substituents present. For this reaction series, as for other S_NAr processes using anionic nucleophiles, the high ρ value seems to suggest a late transition state, in contrast with predictions made by other workers.[18]

Comparisons of ρ values for chloride-exchange reactions and other S_NAr of chlorothiophenes are made difficult because they have been studied for different solvent systems. Thus, piperidino-dechlorinations[6c] (ρ +3.42 at 293.15 K) and benzenethiolate dechlorinations[6e] (ρ +4.06 at 293.15 K) had been measured in methanol solution (a protic solvent of moderate polarity), whilst chloride-exchange was measured in sulpholane (a dipolar aprotic solvent), and it is well known that different solvation and desolvation phenomena concerning the nucleophile, the substrate, and the transition states, strongly affect the reactivities.

Nevertheless it is evident that for the above reactions the ρ values observed are significantly lower than that for chloride exchange (ρ +5.55 at 323.1 K). In particular, a comparison of the two anionic nucleophiles, benzenethiolate and chloride, shows up a remarkable difference in the substituent effects for the two reactions. It must be concluded that the reactivity of the poor and hard nucleophile chloride is affected more by the electronic effects of substituents than is the strong and soft nucleophile benzenethiolate.

Experimental

Materials.—Compounds (**Ia** and **c**—**g**) were prepared and purified according to published procedures.[6c] Solvents were purified as previously reported.[4b]

Kinetic Measurements.—Two methods were used for the determination of rate constants. The method[19a] involving isolation and counting of a sample of the substrate for each kinetic point was employed for compounds (**Ic**—**e** and **g**); the u.v. maxima used for determination of chemical yield are given in Table 2. The method[19b] in which inorganic chloride is isolated and estimated as silver chloride was required for compounds (**Ia** and **f**). The two procedures are known[20] to give results which are in excellent agreement with each other. Rate constants for the very reactive substrates (**If** and **g**) were determined by the single-point technique using sealed ampoules; for each temperature 2—4 single rate determinations were carried out, usually for 40—75% of exchange, with reaction times as low as 30 s.

Details of the calculations used have been given earlier.[4b]

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Received 4*th November* 1983; *Paper* 3/1965