Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

A COMPARATIVE PMR STUDY OF EXCHANGE REACTIONS IN SOME SUBSTITUTED *N*-METHYLBENZENESULPHONAMIDES AND THEIR *N*-PHENYLMERCURY DERIVATIVES

L. A. FEDOROV, A. S. PEREGUDOV and D. N. KRAVTSOV
Institute of Organo-Element Compounds, Academy of Sciences, Moscow (U.S.S.R.)
(Received February 9th, 1972)

SUMMARY

Proton–proton, metal–metal and metal–proton exchange type reactions have been studied for a number of substituted *N*-methylbenzenesulphonamides and their *N*-phenylmercury derivatives through the use of a PMR technique. It has been found that metal–metal type exchange processes proceed more readily than proton–proton processes in some cases. The presence of substituents in the aromatic ring of the benzenesulphonamide moiety has been shown to affect the rate of the metal–metal exchange process to a smaller extent than that of hydrogen exchange. It has been demonstrated that transfer from a chlorobenzene to a pyridine solution accelerates exchange in *N*-methylbenzenesulphonamides but retards exchange in their phenylmercury derivatives, whereas intramolecular coordination inhibits exchanges in both types of compound. The differences in the influence of substituents and solvents upon the rates of the metal–metal and proton–proton exchange processes are discussed in terms of the ease of formation of a transition state in such exchange reactions.

INTRODUCTION

Recent investigations of dynamic processes in organo derivatives of non-transition metals have involved large-scale applications of NMR techniques[1-2]. The use of this method has proved to be most convenient in studying exchange reactions in such compounds, the lifetime of the R_nM–X bond (where R_nM is a univalent organometallic group such as RHg or R_3Sn, and X is a halogen or the moiety of an OH-, NH-, SH- or CH-acid) being consistent with the NMR time-scale. Among various transformations of organometallic compounds the intermolecular exchange reactions:

$$R_nMX_1 + R_mM^*X_2 \rightleftarrows R_nMX_2 + R_mM^*X_1 \qquad (1)$$
$$R_nM = R_mM^*,\ R_nM \neq R_mM^*,\ X_1 = X_2,\ X_1 \neq X_2$$

involving compounds with sufficiently labile M–X bonds have been studied most extensively, especially where $R_nM = R_mM^*$ and $X_1 \neq X_2$.

In general, in the above reactions (exchange of the metal–metal type) the

migration of univalent organometallic groups from one anion-like moiety X_1 to another of the same kind (X_1) or to one of a different kind (X_2) resembles the migration of a proton in hydrogen exchange reactions:

$$HX_1 + H^*X_2 \rightleftarrows H^*X_1 + HX_2 \quad X_1 = X_2,\ X_1 \neq X_2 \qquad (2)$$

in the corresponding XH acids (exchange of the proton–proton type). However, the overall features of reactions (1) and (2) may be entirely different due to the peculiar behaviour of organometallic groups in comparison with that of hydrogen.

Apparently no reports exist in the literature at present of a systematic comparative study of the behaviour of XH acids and their organometallic derivatives in exchange reactions of the type indicated above. Nevertheless such an investigation would appear to be of considerable interest in connection with prototropic and metallotropic tautomeric processes which proceed via an intermolecular mechanism.

In order to compare the migrating abilities of hydrogen and univalent organometallic groups in XH acids and their organometallic derivatives, it is necessary to find suitable model systems which would enable the examination under the same experimental conditions of three different types of exchange reaction, namely: proton–proton exchange in XH acids, metal–metal exchange in their organometallic derivatives and metal–proton exchange in mixtures of the two types of compound. For NH acids, substituted *N*-methylbenzenesulphonamides and their *N*-phenylmercury derivatives appear to provide such model compounds.

Using the PMR technique, we have studied the exchange reactions:

$$YC_6H_4SO_2N(R_1)CH_3 + YC_6H_4SO_2N(R_2)CH_3 \rightleftarrows YC_6H_4SO_2N(R_2)CH_3 + YC_6H_4SO_2N(R_1)CH_3 \qquad (3)$$

(*a*) $R_1 = R_2 = H$; (*b*) $R_1 = R_2 = HgC_6H_5$; (*c*) $R_1 = H$, $R_2 = HgC_6H_5$ $Y = p\text{-}NO_2$, p-Cl, $p\text{-}C_6H_5$, $p\text{-}NH_2$, o-Cl

which occur in solutions of the corresponding compounds. An analysis of the signal shape of the *N*-methyl group resonance has been used to detect the exchange processes and to evaluate their rates.

THE PMR SPECTRA

The parameters of the PMR spectra for the compounds investigated as a function of temperature, concentration and the nature of solvent and substituent in the aromatic ring of the benzenesulphonamide moiety are presented in Table 1.

1. *Proton–proton exchange*

From Table 1 it may be seen that the *N*-methyl group signal of substituted *N*-methylbenzenesulphonamides in pyridine solution at $-40°$ appears as a doublet due to spin–spin interaction of the methyl protons with the NH proton, the coupling constant J(H–N–C–H) being approximately 5 Hz for all the compounds investigated. At higher temperatures the components of the $N\text{–}CH_3$ doublet progressively broaden and ultimately coalesce to a single line (Fig. 1). The coalescence temperature depends upon the substituent Y and concentration. Thus, for 0.15 *M* solutions the coalescence temperature is $-31°$ for *N*-methyl-*p*-nitrobenzenesulphonamide and $10°$ for the *p*-chloro substituted compound. This doublet persists in the solution spectra of

TABLE 1

PARAMETERS OF PMR SPECTRA AND COALESCENCE TEMPERATURES FOR SUBSTITUTED *N*-METHYLBENZENESULPHONAMIDES

Substituent	*Solvent*	*Concentration (M)*	*Temperature*				*Coalescence temperature (°C)*
			−40°		34°		
			δ(N−CH₃) (Hz)	*J(HNCH) (Hz)*	*δ(N−CH₃) (Hz)*	*J(HNCH) (Hz)*	
p-NO_2	C_5H_5N	0.15	174.8	5.6	168.0	0	−31
	$CHCl_3$	0.15			163.9	5.2	>60
	CH_3NO_2	0.15			160.4	5.2	>100
	CH_3NO_2	1.00	155.3	5.3	161.7	0	−1
p-Cl	C_5H_5N	0.15	169.1	5.2	163.4	0	10
	$CHCl_3$	0.15			159.8	5.3	>60
	CH_3NO_2	0.15			157.2	5.2	>100
	CH_3NO_2	1.00	155.2	5.0	160.2	0	−4
p-C_6H_5	C_5H_5N	0.15			167.2	5.2	>114
	C_5H_5N	0.30			167.4	5.1	54
	$CHCl_3$	0.15			161.5	5.3	>60
	CH_3NO_2	0.40			158.8	5.1	>100
p-NH_2	C_5H_5N	0.15			164.8	5.3	>114
	C_5H_5N	0.30			164.1	5.1	>114
	$CHCl_3$	0.15			157.3	5.4	>60
	CH_3NO_2	1.00			152.1	5.5	>100
o-Cl	C_5H_5N	0.15			163.5	5.3	>114
	C_5H_5N	0.30	167.0	4.9	162.3	0	14
	$CHCl_3$	0.15			155.0	5.2	>60
	CH_3NO_2	1.00			160.4	5.3	>100

compounds with Y = p-C_6H_5, p-NH_2 and o-Cl at the above concentration in pyridine up to 114°. Increasing the concentration of these compounds to twice its original value results in the coalescence of the doublet at 14° for the *o*-chlorosubstituted compound, at 54° for the *p*-phenyl substituted compound and at 114° for the compound in which Y = *p*-NH_2. Only a rather sharp single resonance appears in the spectra of pyridine solutions of *N*-deuterated *N*-methylbenzenesulphonamides.

In 0.15 *M* nitromethane solutions of all the compounds considered, coalescence of the *N*-methyl group signal was not observed at temperatures up to 100°. On increasing the concentration to 1.0 *M*, collapse of the *N*-methyl doublet occurred at −4° for the compound with Y = *p*-Cl and at 1° for the compound with Y = *p*-NO_2. Broadening of the *N*-methyl doublet was not observed over the temperature range 30–100° in the PMR spectra of 1.0 *M* solutions of other *N*-methylbenzenesulphonamides, except for that with Y = *p*-C_6H_5 whose poor solubility prevented the formation of solutions of greater concentration than 0.4 *M*. In chloroform solutions of 0.15 *M* concentration and at temperatures up to 60°, the spectra of all the compounds studied

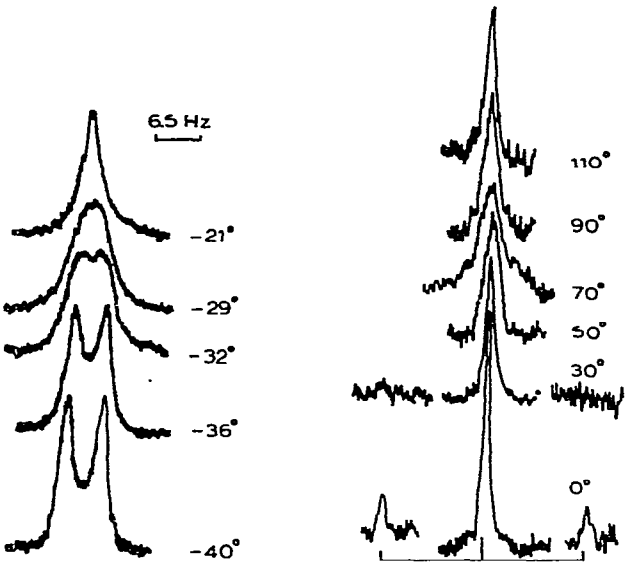


Fig. 1. Temperature dependence of the signal shape for the $N-CH_3$ group in the PMR spectrum of *N*-methyl-*p*-nitrobenzenesulphonamide (0.15 *M* solution in pyridine).

Fig. 2. Temperature dependence of the signal shape for the $N-CH_3$ group in the PMR spectrum of a 0.15 *M* solution of *N*-phenylmercury-*N*-methyl-*p*-nitrobenzenesulphonamide in pyridine.

exhibited only two sharp signals attributable to the *N*-methyl group without any detectable broadening.

The spectral changes observed in pyridine and nitromethane solutions on increasing the temperature and concentration of the solute are, evidently, associated with the intermolecular exchange of the NH protons [reaction 3(a)]. At a particular concentration and temperature the increase in the rate of this process leads to coalescence of the components of the *N*-methyl doublet, the mean lifetime of the N–H bond at coalescence being approximately 0.045 s. From the temperature dependence of the *N*-methyl signal shape in *N*-methyl-*p*-nitrobenzenesulphonamide the activation energy of proton exchange in this compound was found to be 11 ± 2 kcal/mol. The constancy of the J(H–N–C–H) values within the limits of the experimental error irrespective of the substituent Y in the corresponding compounds enabled the examination of the variation of the proton exchange reactivity of *N*-methylbenzenesulphonamides with the nature of the substituent Y using coalescence temperatures for the *N*-methyl group doublet as the basis for such a study.

From Table 1 it is evident that in pyridine solution the ease of proton exchange increases in the order: $p\text{-}NH_2 < p\text{-}C_6H_5 < o\text{-}Cl < p\text{-}Cl < p\text{-}NO_2$. In nitromethane the rate of exchange is much greater for compounds with $Y = p\text{-}NO_2$ and *p*-Cl, than for those with $Y = o\text{-}Cl$, $p\text{-}C_6H_5$ and $p\text{-}NH_2$.

2. *Metal–metal exchange*

At 0° the solution spectra of the *N*-phenylmercury derivatives of *N*-methylbenzenesulphonamides in pyridine, chloroform and chlorobenzene show three signals

attributable to the CH_3 protons (Fig. 2): an intense single peak due to molecules with zero-spin mercury isotopes and two satellites of lower intensity stituated symmetrically with respect to the main signal and arising from molecules containing the ^{199}Hg isotope. On raising the temperature, the main peak in the spectra of all phenylmercury derivatives gradually broadens, while the satellites broaden and ultimately disappear, being completely absent at 30°. At a particular temperature, the main signal begins to narrow as the temperature is increased further. The line-widths of the main signal, spin coupling constants $J(^{119}Hg–N–C–H)$ and chemical shifts of the *N*-methyl protons are presented in Table 2.

TABLE 2

PARAMETERS OF PMR SPECTRA FOR PHENYLMERCURY DERIVATIVES OF SUBSTITUTED N-METHYLBENZENESULPHONAMIDES

Substituent	*Solvent*	*Concentration (M)*	*δ(N–CH₃) at 34° (Hz)*	*Temperature*						
				0°		30°	50°	70°	90°	110°
				J(¹⁹⁹Hg–N–C–H) (Hz)	*W[a] (Hz)*	*W (Hz)*				
p-Cl	C_5H_5N	0.15	178.7	50.7	1.6	3.5	6.3	4.4	3.7	2.2
	C_6H_5Cl	0.15	168.4	56.8	2.5	5.1	6.8	5.6	3.6	2.4
	$CHCl_3$	0.15	165.8	55.0	2.4	6.2	7.0	5.0		
p-NO_2	C_5H_5N	0.15	182.2	47.1	1.7	2.5	4.6	6.1	4.0	2.6
o-Cl[b]	C_5H_5N	0.15	178.1	46.5	1.4	1.4	1.5	2.1	3.6	5.3
p-C_6H_5	C_5H_5N	0.15	182.4	49.7	1.8	2.5	4.4	6.4	7.0	4.9
p-NH_2	C_5H_5N	0.15	180.4	52.3	2.2	2.9	6.1	7.5	8.3	4.8
	C_5H_5N	0.30	180.7	51.9	2.4	3.8	7.1	6.3	4.8	3.5

[a] W = line-width at the half-height. [b] The $J(^{199}Hg–N–C–H)$ values for this compound are 48.6, 50.2 and 53.4 Hz at 30°, 50° and 70° respectively.

Consideration of the data obtained reveals that the line-width of the *N*-methyl group resonance at a given temperature depends on the nature of the substituent Y. For example, at 110° compounds with Y = *p*-NO_2 and *p*-Cl have approximately equal line-widths (2.6 and 2.2 Hz respectively), whereas at the same temperature the corresponding line-widths for compounds with Y = *p*-C_6H_5 and *p*-NH_2 are 4.9 and 4.8 Hz respectively. The variation of the line-shape for the *N*-methyl protons with temperature also depends on the concentration of the solute. In particular, in the case of the phenylmercury derivative of *N*-methyl-*p*-aminobenzenesulphonamide in pyridine the narrowing of the signal begins at a lower temperature in 0.3 *M* solution than in 0.15 *M* solution. In addition, at those temperatures at which sharpening of the *N*-methyl resonance occurs, the line-width is smaller for 0.3 *M* solutions than for 0.15 *M* solutions.

The temperature variation of the *N*-methyl signal shape is sensitive to the nature of solvent. In 0.15 *M* solutions of the phenylmercury derivative of *N*-methyl-*p*-

chlorobenzenesulphonamide, which was the most soluble of the organomercury derivatives studied, a detectable broadening of the resonance is observable in chloroform and chlorobenzene at lower temperatures than in pyridine. In contrast, in nitromethane over the temperature range $-35°$ to $100°$ the spectrum shows only a single sharp peak attributable to the *N*-methyl group.

The introduction of a substituent *ortho* to the sulphonamide group which is capable of coordinating with the metal atom has a drastic influence on the temperature dependence of the spectrum. For example, in the PMR spectrum of a 0.15 *M* pyridine solution of the phenylmercury derivative of *N*-methyl-*o*-chlorobenzenesulphonamide the main peak of the *N*-methyl group is quite narrow at 50° the ^{199}Hg satellites being observable even at 70°.

The observed temperature variation of the line-shape for the *N*-methyl group indicates that in the organomercury derivatives studied frequent fission of the labile N–Hg bond occurs, such fission being accompanied by the intermolecular exchange of the phenylmercury groups [reaction 3(*b*)]. In order to enable a more detailed investigation of this process, a calculation of the full line-shape for the *N*-methyl resonance was undertaken from the premise that the spin-state populations correspond to the natural abundance of the mercury isotopes. The computer-simulated spectra for $J(^{199}Hg–N–C–H)$ 50 Hz, corresponding to various pre-exchange lifetimes of the N–Hg bond, are presented in Fig. 3.

The variation of the $J(^{199}Hg–N–C–H)$ values with the nature of the substituent Y and of the solvent within the limits characteristic of the compounds investigated (from 46.5 to 56.8 Hz) has no practical effect on the line-width of the computed signal after the disappearance of the ^{199}Hg satellites. This allows the examination of the influence of the substituent, concentration and solvent on the metal–metal exchange rate in the phenylmercury derivatives of *N*-methylbenzenesulphonamides by comparing the line-widths of the main signal in different compounds at a given temperature.

The results of such a comparison reveal that in pyridine, as the nature of the substituent Y is varied, the reaction rate increases in the order: $o\text{-Cl} < p\text{-NH}_2 < p\text{-C}_6H_5 < p\text{-NO}_2 < p\text{-Cl}$. In addition, it may be seen that in pyridine as a solvent, exchange in the phenylmercury derivative of *N*-methyl-*p*-aminobenzenesulphonamide is accelerated by increasing concentration. Finally, the data indicate that with $Y = p\text{-Cl}$, the exchange of the phenylmercury group is very fast in nitromethane ($\tau < 0.002$ s) whereas in chloroform and chlorobenzene it is only slightly faster than in pyridine.

The results obtained also enable the comparison of the migration tendencies of the phenylmercury group and hydrogen in exchange reactions 3(*a*) and 3(*b*) for compounds in which the substituent Y varies. In Table 3 are listed the mean lifetimes τ of the N–H and N–Hg bonds at a given temperature in compounds containing the same substituent Y, the pre-exchange lifetimes τ being estimated by visual comparison of the computed and experimental spectra for 0.15 *M* pyridine solutions. It may be seen that in systems with $Y = p\text{-NO}_2$ and *p*-Cl the rate of hydrogen exchange is greater than that of the phenylmercury group whereas for systems with other substituents the C_6H_5Hg group is more labile than hydrogen.

3. *Proton–metal exchange*

At sufficiently low temperatures the PMR spectra of equimolar mixtures of

TABLE 3

MEAN LIFETIMES OF THE N–H AND N–Hg BONDS IN SUBSTITUTED *N*-METHYLBENZENESULPHONAMIDES AND THEIR PHENYLMERCURY DERIVATIVES AS THEIR 0.15 *M* SOLUTIONS IN PYRIDINE

Substituent	*Temperature* (°C)	τ (s)	
		N–H bond	*N–Hg bond*
p-NO_2	0	0.045 ± 0.003	0.09 ± 0.01
p-Cl	10	0.045 ± 0.003	0.07 ± 0.01
p-C_6H_5	110	> 0.045 ± 0.003	0.004 ± 0.001
p-NH_2	110	> 0.045 ± 0.003	0.004 ± 0.001
o-Cl	110	> 0.045 ± 0.003	0.01 ± 0.002

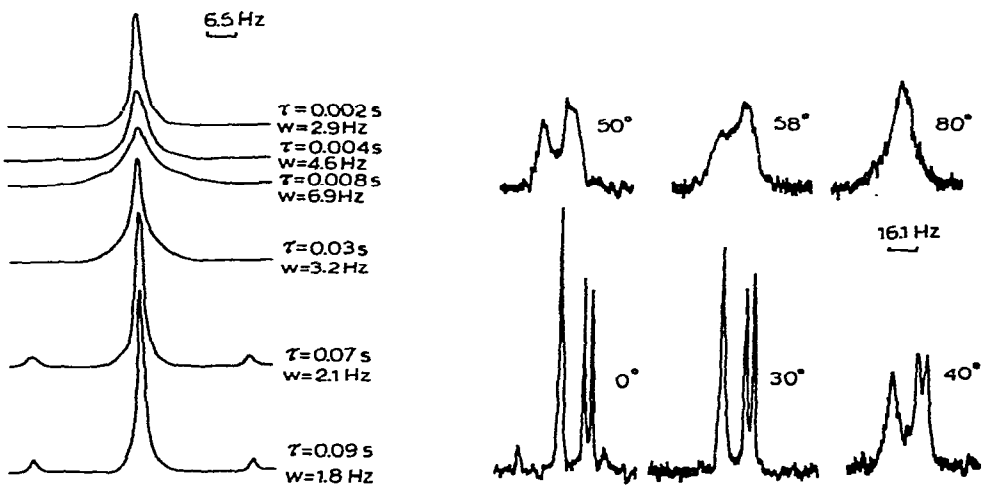


Fig. 3. Computed signal shape for the N–CH_3 group in the presence of three-centre exchange as a function of the mean lifetime of the N–Hg bond.

Fig. 4. Temperature dependence of the PMR spectrum for a mixture of *N*-methyl-*p*-aminobenzenesulphonamide and its phenylmercury derivative (0.15 *M* solution in pyridine).

substituted *N*-methylbenzenesulphonamides and their phenylmercury derivatives in 0.15 *M* pyridine solutions exhibit two sets of signals, namely, the N–CH_3 group doublet of the corresponding sulphonamide and a single peak of the organomercury derivative with the ^{199}Hg satellites. On increasing the temperature gradually the signals of both compounds change shape in approximately the same way as in the spectra of the individual compounds, and at the same time move closer together. On increasing the temperature further, these signals coalesce to form a broadened single peak, the latter showing exchange sharpening at still higher temperatures (Fig. 4).

The influence of the solvent upon the temperature-dependence of the PMR spectrum of the corresponding mixture has been studied for the system in which Y = *p*-Cl. At 0° the spectrum of 0.15 *M* chloroform solution displays (as does that in pyridine) a simple superposition of the signals of the initial reactants. Increasing the tempe-

rature only leads to changes in the shape of the *N*-methyl peak of the phenylmercury derivative, which occur in a similar manner to those which occur in chloroform solutions of the individual phenylmercury derivative of *N*-methyl-*p*-chlorobenzenesulphonamide, giving rise to a broadening of the main signal and the disappearance of the satellites. Other than this change neither broadening of the *N*-methyl doublet of sulphonamide, nor displacement of the reactant signals towards each other was observed. At $-40°$ the spectrum of the mixture in 0.15 *M* nitromethane solution shows three peaks corresponding to the *N*-methyl group: a doublet associated with *N*-methyl-*p*-chlorobenzenesulphonamide and a single peak with no satellites situated 15.2 Hz downfield and corresponding to the phenylmercury derivative. On increasing the temperature these signals move closer together, and at 10° coalesce to a single peak which sharpens at higher temperatures.

The results obtained suggest that in mixtures of the NH acids considered and their phenylmercury derivatives, in addition to proton–proton [3(*a*)] and metal–metal [3(*b*)] exchanges of the type observed in solutions of the individual reactants, an exchange reaction of the proton–metal type also occurs. These processes involve the simultaneous migration of the phenylmercury group and hydrogen between the benzenesulphonamide moieties. The coalescence temperatures of the *N*-methyl group resonance for mixtures with different substituents Y are presented in Table 4

TABLE 4

COALESCENCE TEMPERATURES FOR 0.15 *M* SOLUTIONS OF EQUIMOLAR MIXTURES OF SUBSTITUTED *N*-METHYLBENZENESULPHONAMIDES AND THEIR PHENYLMERCURY DERIVATIVES TOGETHER WITH CHEMICAL SHIFTS OF THE *N*-METHYL GROUP SIGNAL IN SOLUTIONS OF THE INDIVIDUAL COMPOUNDS AT THE COALESCENCE TEMPERATURE

Substituent Y	*Solvent*	*Coalescence temperature* (°C)	$\delta(N-CH_3)$ *in* $YC_6H_4SO_2NRCH_3$		$\Delta\delta$ *At coalescence temperature*
			$R=H$	$R=HgC_6H_5$	
p-Cl	C_5H_5N	−5	166.7	182.1	15.4
p-Cl	CH_3NO_2	10	158.0	173.2	15.2
p-NO_2	C_5H_5N	10	169.6	185.0	15.4
p-NH_2	C_5H_5N	58	162.9	177.7	14.8
p-C_6H_5	C_5H_5N	64	166.8	182.3	15.5
o-Cl	C_5H_5N	88	161.4	174.2	15.8

together with the $\Delta\delta$ values representing the separation between the *N*-methyl peaks of the reactants as measured in solutions of the individual compounds at the same concentration at the coalescence temperature. The fact that the $\Delta\delta$ values are virtually independent of the nature of the substituent Y allows the qualitative comparison of the exchange rates for systems with various substituents Y in pyridine solution simply on the basis of the coalescence temperatures. Such a comparison reveals that the relative tendency of proton–metal type exchanges increases in the order: *o*-Cl < *p*-C_5H_5 < *p*-NH_2 < *p*-NO_2 < *p*-Cl.

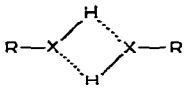
DISCUSSION

Depending on the nature of the migrating species, the exchange reactions [3(*a*)–3(*c*)] studied in the present communication may, in principle, proceed by

different mechanisms. However, in general, only two of these alternative mechanisms appear to be important in the above processes. Firstly, it is possible that the rate-determining step of the exchange reactions involves the formation of ionic intermediates followed by their fast recombination (a monomolecular process). Secondly, it is possible that the reactions proceed through the formation of a four-membered or some other cyclic transition-state (a bimolecular process). It has, however, been shown that the mean lifetimes of the corresponding bonds are concentration-dependent in both proton–proton and metal–metal exchanges. This eliminates a dissociative process from being the rate-determining step of these reactions and suggests that the experimental data are best discussed in terms of a bimolecular mechanism.

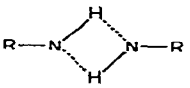
Despite the apparent similarity between cation-like species such as hydrogen and the phenylmercury group in these exchange reactions [3(*a*)–3(*b*)], they behave in an appreciably different manner. These differences may be observed in different solvent effects on the exchange reactivities of *N*-methylbenzenesulphonamides and their phenylmercury derivatives, as well as in different sensitivities of the corresponding reactivities to *p*-substituent effects in the benzene ring.

Hydrogen exchange is quite slow in 0.15 *M* solutions of *N*-methylbenzenesulphonamides, with no significant exchange being observed during the time-scale of measurements, either in chloroform or in strongly polar nitromethane solutions. The exchange is only observable in pyridine where measurements may be made on the PMR time-scale. This behaviour is paralleled by the rather low ability of NH acids to undergo hydrogen exchange in inert solvents and in the pure state in the absence of catalysts[3-4]. According to literature data the predominant mechanism in the hydrogen exchange reactions of XH acids involves the formation of a cyclic transition state[5] of the type:



The most feasible ionic mechanism is of minor importance even in those cases where the exchange reactions occur in solvents of high dielectric constant, which in addition strongly solvate anions due to their hydrogen bonding ability[6]. An analysis of the concentration dependence of the rate of exchange for proton–proton transfer in the systems investigated, which has been undertaken for *N*-methyl-*p*-nitrobenzenesulphonamide, indicates that the reaction is approximately second order. Thus, even if partial dissociation of the compounds studied does take place in pyridine solution this process is not rate-determining.

The ease of formation of a cyclic transition state, which in this particular study may be represented as:



should increase with increasing donor ability of the nitrogen atom, a state of affairs favoured by the presence of electron-donating substituents in the aromatic ring of the benzenesulphonamide moiety. On the other hand, it also should increase with increasing polarity of the N–H bond, which is favoured by electron-withdrawing substi-

tuents. The results obtained clearly show that in the systems studied electron-withdrawing substituents accelerate hydrogen exchange. Thus, it may be concluded that in the case of hydrogen exchange the ease of formation of the transition state is affected more strongly by an increase in electron affinity of the hydrogen atom than by a reduction in the donor ability of the nitrogen.

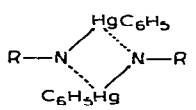
The acceleration of proton–proton exchange on transfer from chloroform to pyridine, and the absence of this effect on going to nitromethane, suggests that the N–H bond is polarized to a greater extent by specific solvation involving hydrogen bond formation than by dipole–dipole interaction with the solvent which is more polar but less capable of forming hydrogen bonds.

In this connection it is worth noting that the formation of a hydrogen bond with pyridine does not apparently appreciably reduce the ability of hydrogen to form a cyclic transition state, while the polarization of the N–H bond considerably increases the donor power of the nitrogen atom which leads to an acceleration of the hydrogen exchange process. The former fact seems to be associated with the absence of sufficiently low-energy vacant orbitals in the electronic structure of hydrogen. As a result partial charge transfer from the unshared electron pair of the pyridine nitrogen into the anti-bonding orbital of the N–H bond[7] produces an approximately equal displacement of electron density along this bond:

$$C_5H_5N:\rightarrow H\rightarrow N\text{–}R$$

without affecting significantly the partial positive charge on the hydrogen atom. Finally, the slower rate of hydrogen exchange in *N*-methyl-*o*-chlorobenzenesulphonamide relative to that in the *p*-substituted analogue suggests that retardation of the exchange reaction occurs through the formation of an internal hydrogen bond. The latter, apparently, prevents the molecule from attaining the conformation necessary for the formation of the transition state.

Although metal–metal type exchanges may also be discussed from the standpoint of a cyclic four-membered transition state:



what is of greater interest in this case is the increased rate of this exchange process in comparison with the proton–proton type exchanges which have sometimes been observed. This is somewhat unexpected from the purely mechanistic standpoint involving ideas regarding the relative migrating abilities of the phenylmercury group and hydrogen. Apparently, the greater coordinating power of the phenylmercury group in comparison with that of hydrogen plays a decisive role in determining the greater ease of formation of the transition state in the former case. Thus the hydrogen atom attached to the aromatic ring, for example, is an inert substituent with respect to specific solvation[8], whereas the arylmercury group has a considerable facility for interacting with coordinating solvents under the same circumstances[9].

It should also be noted that metal–metal exchange is much less sensitive to the influence of substituents in the *p*-position of the benzenesulphonamide moiety than proton–proton exchange. While the range of coalescence temperatures for the

latter exchange in pyridine at 0.15 *M* concentration exceeds 145°, it is not greater than 20° for the former exchange process. This implies that in metal–metal exchange the effect of increasing the electron affinity of the metal atom due to electron-withdrawing substituents, which facilitates the formation of the transition state, is counterbalanced to a considerable extent by both the reduction in the donor ability of the nitrogen and the enhancement of the metal coordination with pyridine molecules.

A considerable difference between hydrogen and metal–metal type exchanges is observed as far as solvent influence is concerned, as in the latter type of process the exchange rate is smallest in pyridine and greatest in nitromethane. The decrease in the exchange rate on passing to pyridine suggests that the formation of the transition state is inhibited to a greater extent by blocking of vacant mercury orbitals with solvent molecules than it is favoured by an enhancement in the electron-donating ability of the nitrogen from polarization of the Hg–N bond. In contrast, nitromethane through its low solvating power increases the donor strength of the nitrogen atom due to polarization of the Hg–N bond without reducing the coordinating ability of the phenylmercury group.

In conclusion, it should be noted that the effect of intramolecular coordination on metal–metal exchange is the same as on proton–proton exchange, introduction of an *ortho*-chloro substituent into the benzenesulphonamide moiety substantially decreasing the exchange rate in both cases. Finally, with proton–metal exchange the fact that the exchange rate is slowest with *o*-chloro substituted compounds and intermediate with *p*-amino substituents is of considerable interest.

Further studies on the exchange reactions between substituted benzenesulphonamides and their organomercury derivatives are in progress and, we hope, will provide more information concerning the influence of electronic effects, steric hindrance and intramolecular coordination upon the proton–metal exchange in the systems indicated.

EXPERIMENTAL

General comments

The PMR spectra of the compounds investigated were measured on a RYA-2305 spectrometer operating at 60 MHz. TMS was used as an internal standard. The measurements of chemical shifts and spin–spin coupling constants were performed by the side-band technique, the experimental error being not greater than ± 0.3 Hz. The temperature was maintained and calibrated with the accuracy of $\pm 1°$.

For two-centre exchanges of the proton–proton type, the equations derived by Gutowsky *et al.*[10] were used to obtain the mean lifetimes τ at coalescence temperatures. For three-centre exchange of the metal–metal type, Bloch equations[11] modified with respect to dynamic processes were employed to calculate the theoretical spectra corresponding to various τ values. A Nairi computer was used for such calculations.

Nitromethane, chlorobenzene and chloroform were purified and dried by conventional procedures. Pyridine was dried over molecular sieves.

Substituted *N*-methylbenzenesulphonamides were prepared by the reaction of substituted benzenesulphone chlorides with an aqueous solution of methylamine. The compounds reported in the literature were identified by their melting points[12–13]. Solutions of *N*-deuterated-*N*-methylbenzenesulphonamides were obtained by adding

a small amount of D_2O to solutions of *N*-methylbenzenesulphonamides in pyridine. It was shown by special experiments that addition of an equivalent amount of H_2O did not produce any changes in the PMR spectra of the above compounds at the same temperature.

The phenylmercury derivatives were prepared by treating a methanol solution of *N*-methylbenzenesulphonamide with a solution of phenylmercury hydroxide[14] in the same solvent according to the procedure described previously[15]. The melting points and analytical data for all the compounds not reported in the literature are presented in Table 5. Some typical preparations of substituted *N*-methylbenzenesulphonamides and their *N*-phenylmercury derivatives are given below.

N-methyl-p-chlorobenzenesulphonamide

To a solution of 9.4 g (0.138 mole) of methylamine hydrochloride in 50 ml of water cooled with ice was added 7.7 g (0.138 mole) of KOH. After addition of 9.8 g (0.046 mole) of *p*-chlorobenzenesulphone chloride, the resulting mixture was heated in a stoppered flask on a water bath with occasional shaking for 2 min and cooled. The precipitate formed was filtered, washed with water and dried. Recrystallization from cyclohexane afforded 7.0 g (74%) of colourless crystals with m.p. 59° (lit.[12] 62°).

N-(phenylmercury)-N-methyl-p-chlorobenzenesulphonamide

To a hot solution of 1.03 g (5 mmole) of *N*-methyl-*p*-chlorobenzenesulphonamide in 10 ml of methanol was added a hot solution of 1.47 g (5 mmole) of phenyl-

TABLE 5

ANALYTICAL DATA AND MELTING POINTS FOR SUBSTITUTED *N*-METHYLBENZENESULPHONAMIDES AND THEIR PHENYLMERCURY DERIVATIVES

Compound	*M.p.*[a] (°C)	*Analysis found (calcd.) (%)*	
		C	*H*
p-$NH_2C_6H_4SO_2NHCH_3$	108	45.13 (45.14)	5.44 (5.41)
p-$C_6H_5C_6H_4SO_2NHCH_3$	119–120	63.32 (63.13)	5.06 (5.30)
o-$ClC_6H_4SO_2NHCH_3$	92–93	40.14 (40.88)	3.80 (3.92)
p-$ClC_6H_4SO_2N(CH_3)HgC_6H_5$	143–144	32.43 (32.37)	2.44 (2.51)
p-$NO_2C_6H_4SO_2N(CH_3)HgC_6H_5$	199–201	31.28 (31.68)	2.43 (2.45)
p-$NH_2C_6H_4SO_2N(CH_3)HgC_6H_5$	161–162	33.71 (33.73)	3.11 (3.05)
p-$C_6H_5C_6H_4SO_2N(CH_3)HgC_6H_5$	201–202	43.58 (43.55)	3.33 (3.27)
o-$ClC_6H_4SO_2N(CH_3)HgC_6H_5$	134–135	32.54 (32.37)	2.57 (2.51)

[a] All the phenylmercury derivatives melt with decomposition.

mercury hydroxide[14] in 25 ml of the same solvent. The reaction mixture was evaporated under reduced pressure and the residue recrystallized from toluene yielding 2.0 g (83%) of colourless crystals.

ACKNOWLEDGEMENTS

The authors are greatly indebted to Mrs. V. I. Dostavalova for designing the programme used to compute the theoretical spectra.

REFERENCES

1 K. Moedritzer, *Advan. Organometal. Chem.*, 6 (1968) 173.
2 N. S. Ham and T. Mole, *Progr. Nucl. Magn. Resonance*, 4 (1969) 93.
3 L. P. Belozerskaya, G. S. Denisov and I. F. Tupitsyn, *Theor. Eksp. Khim.*, 6 (1970) 408.
4 A. Saika, *J. Amer. Chem. Soc.*, 82 (1960) 3540.
5 Ya. K. Syrkin, *Dokl. Akad. Nauk SSSR*, 105 (1955) 1018.
6 E. Grunwald, C. F. Jumper and S. Meiboom, *J. Amer. Chem. Soc.*, 85 (1963) 522.
7 S. Bratoz, *Advan. Quant. Chem.*, 3 (1967) 209.
8 P. R. Wells, S. E. Ehrenson and R. W. Taft, *Progr. Phys. Org. Chem.*, 6 (1968) 147.
9 D. N. Kravtsov, B. A. Kvasov, E. I. Fedin, B. A. Faingor and L. S. Golovchenko, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1969) 536.
10 A. Allerhand, H. S. Gutowsky, J. Jonas and R. A. Meiner, *J. Amer. Chem. Soc.*, 88 (1966) 3185.
11 J. A. Pople, W. G. Schneider and H. J. Bernstein, *High-Resolution Nuclear Magnetic Resonance*, McGraw-Hill, New York, 1959.
12 E. L. Eliel and K. W. Nelson, *J. Org. Chem.*, 20 (1955) 1657.
13 L. Demény, *Recl. Trav. Chim. Pays-Bas*, 48 (1929) 1145.
14 G. G. Petukhov, in A. N. Nesmeyanov and P. A. Bobrov (Eds.), *Syntheses of Organic Reagents*, Academy Press, Moscow, 1952, p. 72–73.
15 D. N. Kravtsov and A. N. Nesmeyanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1967) 1741.