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INFLUENCE OF SUBSTITUENT EFFECTS, STERIC HINDRANCE AND INTRAMOLECULAR COORDINATION ON THE EXCHANGE RATES AND EQUILIBRIA IN SUBSTITUTED BENZENESULPHONAMIDES AND THEIR *N*-ARYLMERCURY DERIVATIVES

A.S. PEREGUDOV, D.N. KRAVTSOV and L.A. FEDOROV

Institute of Organo-Element Compounds, Academy of Sciences, Moscow (U.S.S.R)

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Summary

The kinetics of exchange reactions of the metal—metal and metal—proton types and exchange equilibria of the metal—proton type have been studied by PMR for arylmercury derivatives of *N*-methyl-*p*-chlorobenzenesulphonamide, some substituted benzenesulphonanilides and their arylmercury derivatives. The metal—metal exchange has been shown to be accelerated by electron-accepting substituents in the arylmercury group and retarded by electron-donating substituents. The metal—proton exchange is accelerated by electron-withdrawing substituents in the aryl radical on nitrogen and inhibited by electron-releasing substituents, steric hindrance and intramolecular coordination. Both electron-accepting and electron-donating substituents in the arylmercury group can accelerate the metal—proton exchange.

It has been established that purely polar effects of substituents in the aryl group on nitrogen affect the exchange equilibrium of the metal—proton type only slightly, whereas steric hindrance and intramolecular coordination exert a considerable influence upon it. Analysis of the data obtained has demonstrated that with five-membered chelate rings the intramolecular coordinate bond involving the C_6H_5Hg group is stronger than the corresponding internal hydrogen bond, whereas with six-membered chelate rings the contrary is the case.

Introduction

Recently, there has been considerable interest in the NMR studies of exchange reactions involving the O—H, N—H and S—H bonds (exchanges of the proton—proton type) [1—5]. Rather extensive information is available on the exchanges associated with the rupture of the O—MR_n, N—MR_n and S—MR_n bonds (exchange reactions of the metal—metal type) where R_nM is a univalent organometallic group such as RHg, R_3Sn and R_3Pb [6—14], but experimental evidence concerning the exchanges of the metal—proton type is very scarce [15].

Earlier [16—17], we utilized PMR to make a comparative study of exchange processes of the three above types in some NH- and SH-acids and their organometallic derivatives. In the case of NH-acids the previous studies concerned the exchange reactions in substituted *N*-methylbenzenesulphonamides and their *N*-phenylmercury derivatives [16]. The model compounds indicated proved to be very useful in studying the exchanges of the proton—proton and metal—metal types and their dependence upon the nature of solvent and substituents in the phenylsulphonyl moiety.

It seemed useful also to examine the influence of the radical on mercury upon the rates of the metal—metal and metal—proton exchanges, as well as the effect of the aryl group on nitrogen upon the exchange rate of the latter type. The arylmercury derivatives of *N*-methylbenzenesulphonamides could be used to investigate the metal—metal exchange. At the same time, in the case of the metal—proton exchange, substituted benzenesulphono-*o*-toluidides and their *N*-arylmercury derivatives appeared to be more suitable for obtaining the quantitative data necessary to calculate the kinetic and energetic parameters of the corresponding exchange reactions.

Results

The metal—metal exchange reaction (1) was studied employing the model compounds I:

$$\underset{(I)}{4\text{-ClC}_6H_4SO_2N(CH_3)HgAr} + \underset{(I)}{4\text{-ClC}_6H_4SO_2N^{\star}(CH_3)Hg^{\star}Ar} \rightleftharpoons 4\text{-ClC}_6H_4SO_2N(CH_3)Hg^{\star}Ar + 4\text{-ClC}_6H_4SO_2N^{\star}(CH_3)HgAr \quad (1)$$

(a) $Ar = 4\text{-}(CH_3)_2NC_6H_4$; (b) $Ar = 4\text{-}CH_3OC_6H_4$;

(c) $Ar = 2,4,6\text{-}(CH_3)_3C_6H_2$; (d) $Ar = C_6H_5$;

(e) $Ar = 4\text{-ClC}_6H_4$; (f) $Ar = 3,4,5\text{-Cl}_3C_6H_2$.

The kinetics of the metal—proton exchange reaction (2) was examined with the mixtures of the compounds II and III:

$$\underset{(II)}{C_6H_5SO_2NHAr} + \underset{(III)}{C_6H_5SO_2N^{\star}(Ar)HgR} \rightleftharpoons C_6H_5SO_2N(Ar)HgR + C_6H_5SO_2N^{\star}HAr \quad (2)$$

(a) $R = C_6H_5$; $Ar = 2\text{-}CH_3C_6H_4$, $2\text{-}CH_3\text{-}4\text{-BrC}_6H_3$, $2\text{-}CH_3\text{-}4\text{-}NO_2C_6H_3$, $2\text{-}CH_3\text{-}4\text{-}(CH_3)_2NC_6H_3$;

(b) $R = C_6H_5$; $Ar = 2,6\text{-}(CH_3)_2C_6H_3$;

(c) $R = C_6H_5$; $Ar = 4\text{-Br-}2,6\text{-}(CH_3)_2C_6H_2$;

(d) $R = C_6H_5$; $Ar = 2\text{-}CH_3\text{-}4,6\text{-Br}_2C_6H_2$;

(e) $R = C_6H_5$, $4\text{-}CH_3OC_6H_4$, 4-ClC_6H_4, $4\text{-}(CH_3)_2NC_6H_4$; $Ar = 2\text{-}CH_3C_6H_4$.

In order to obtain evidence for exchange processes and evaluate their rates in dependence on concentration, temperature and the nature of substituents in the aryl radicals on nitrogen and mercury, we have used signal shape analysis of the main *N*-methyl group resonance and the corresponding ^{199}Hg satellites for exchange reaction (1) and the signal shape analysis for the peak of the CH_3 group situated *ortho* to the nitrogen atom in the case of the exchange reaction (2).

Apart from the investigation of the exchange rates by the conventional NMR technique based on the dynamic PMR spectrum behaviour, we have also examined the exchange equilibria (3):

$$\underset{(IV)}{C_6H_5SO_2NHAr} + \underset{(V)}{C_6H_5SO_2N(Ar^\star)HgC_6H_5} \rightleftharpoons C_6H_5SO_2N(Ar)HgC_6H_5 + C_6H_5SO_2NHAr^\star \qquad (3)$$

(a) $Ar = C_6H_5$, $4\text{-}(CH_3)_2NC_6H_4$, $4\text{-}CH_3OC_6H_4$, $4\text{-}FC_6H_4$,
$4\text{-}ClC_6H_4$, $4\text{-}IC_6H_4$, $3\text{-}ClC_6H_4$, $3\text{-}FC_6H_4$, $3,5\text{-}Cl_2C_6H_3$,
$2\text{-}FC_6H_4$, $2\text{-}ClC_6H_4$, $2\text{-}BrC_6H_4$, $2\text{-}IC_6H_4$, $2\text{-}CH_3OC_6H_4$,
$2\text{-}CH_3SC_6H_4$, $2\text{-}NO_2C_6H_4$, $2\text{-}CH_3OCOC_6H_4$, $2,5\text{-}[(CH_3)_3C]_2C_2H_3$;
$Ar^\star = 2\text{-}CH_3C_6H_4$;

(b) $Ar = C_6H_5$; $Ar^\star = 2\text{-}CH_3\text{-}4\text{-}BrC_6H_3$, $2\text{-}CH_3\text{-}4\text{-}(CH_3)_2NC_6H_3$;
$2,6\text{-}(CH_3)_2C_6H_3$, $4\text{-}Br\text{-}2,6\text{-}(CH_3)_2C_6H_2$, $2\text{-}CH_3\text{-}4,6\text{-}Br_2C_6H_2$.

Such reactions take place in chloroform solutions of mixtures of the corresponding compounds and are slow on the PMR time scale in this solvent. In order to study these reactions, an indicator *o*-methyl group was introduced into one of the *N*-aryl radicals and the equilibrium constants were determined from the ratio of integral intensities of the methyl group signal for one of the reaction products and one of the starting reactants. The data obtained in this part of the work have provided evidence on the influence of substituent effects, steric hindrance and intramolecular coordination on the exchange equilibria of the metal—proton type in benzenesulphonanilides and their phenylmercury derivatives.

PMR spectra

Metal—metal exchange

As has been noted previously [16], the shape of the *N*-CH_3 group signal in the solution spectra of the *N*-phenylmercury derivatives of *N*-methylbenzenesulphonamides exhibits a temperature dependence characteristic of the three-centre exchange. In the present work, the arylmercury derivatives of *N*-methyl-4-chlorobenzenesulphonamide were chosen as model compounds, in which the exchange of the arylmercury group proceeds at rates suitable for investigation by the high-resolution NMR technique. The parameters of the PMR spectra for these compounds in chloroform and pyridine at various temperatures are listed in Table 1.

A consideration of the line-widths of the main *N*-CH_3 group signal for different compounds at the same temperature, as well as of the temperatures at

TABLE 1

PARAMETERS OF PMR SPECTRA FOR *N*-ARYLMERCURY DERIVATIVES OF *N*-METHYL-*p*-CHLOROBENZENESULPHONAMIDE

ArHg	Solvent	Concentration (*M*)	δ(N—CH$_3$) at 34° (Hz)	Parameters	Temperature (°C)								
					−15	0	15	30	50	60	70	90	110
C$_6$H$_5$Hg	C$_5$H$_5$N	0.15	178.7	*W*[a]	1.4	1.6	2.6	3.5	6.3	5.1	4.4	3.7	2.7
				J[b]	48.9	50.7							
	CHCl$_3$	0.10	166.0	*W*	1.4	1.8	2.0	2.8	5.5				
				J	55.5	57.2	60.2						
4-ClC$_6$H$_4$Hg	C$_5$H$_5$N	0.15	179.6	*W*	1.2	2.6	3.1	4.2	6.1	5.4	4.4	2.4	1.5
				J	50.6								
	CHCl$_3$	0.10	166.2	*W*	1.8	2.5	2.9	4.2	6.9				
				J	63.5	64.1							
4-(CH$_3$)$_2$NC$_6$H$_4$Hg	C$_5$H$_5$N	0.15	180.5	*W*	1.0	1.0	1.0	1.2	2.6	3.5	5.0	3.6	3.0
				J	47.2	48.6	50.2	48.6					
4-CH$_3$OC$_6$H$_4$Hg	C$_5$H$_5$N	0.15	180.1	*W*	1.0	1.0	1.2	1.9	4.5	5.3	5.2	3.0	1.8
				J	48.7	48.9	49.7	51.0					
2,4,6-(CH$_3$)$_3$C$_6$H$_2$Hg	C$_5$H$_5$N	0.15	184.8	*W*	1.0	1.0	1.1	1.6	3.8	4.8	6.0	5.8	5.1
				J	51.0	51.3	51.8	52.0					
3,4,5-Cl$_3$C$_6$H$_2$Hg	C$_5$H$_5$N	0.15	177.1	*W*	3.0	5.7	6.7	3.9	1.2	1.0	1.0	1.0	1.0
				J									

[a] *W* = line-width at the half-height. [b] *J*(^{199}Hg—*N*-CH)

which the ^{199}Hg—N-CH$_3$ spin—spin coupling satellites are still clearly discernible, allows a comparison of the relative ease of the metal—metal exchange for different arylmercury groups. From the data in Table 1 it can be seen that in solutions of Ia - Ic in pyridine the ^{199}Hg satellites are still observable at 30°, whereas for Id the satellites have already disappeared at 15° in this solvent. Accordingly, the main CH$_3$ group signal of the latter compound begins to broaden at lower temperatures than those of the compounds Ia - Ic. From Table 1 it follows as well that introduction of the p-chloro substituent into the arylmercury group (Ie) leads to the disappearance of the ^{199}Hg satellites in pyridine solution already at 0° in contrast to the phenylmercury derivative Id. Upon introduction of three chloro substituents in the positions 3,4 and 5 of the phenylmercury group (Ig), the ^{199}Hg satellites cannot be observed even at —15°.

Thus, electron-donating substituents in the phenylmercury group retard the metal—metal exchange reaction, the influence of the more electron-releasing p-(CH$_3$)$_2$N group being greater than that of the less electron-donating p-CH$_3$O group. The latter conclusion is supported by the values of the line-width for the main CH$_3$ group signal which are 2.6 and 3.5 Hz for Ia at 50° and 60°, and 4.5 and 5.3 Hz at the same temperatures for Ib. At the same time, the decrease in exchange rate with Ic may be associated with both the electron-donating effect of three methyl groups and steric hindrance. On the other hand, such electron-accepting groups as chloro substituents accelerate the exchange reaction discussed. Consequently, depending on the nature of the aryl group on mercury, the rate of the exchange reaction (1) increases in pyridine solution in the order:

$$4\text{-(CH}_3)_2\text{NC}_6\text{H}_4 < 2,4,6\text{-(CH}_3)_3\text{C}_6\text{H}_2 < 4\text{-CH}_3\text{OC}_6\text{H}_4 < \text{C}_6\text{H}_5 <$$

$$4\text{-ClC}_6\text{H}_4 < 3,4,5\text{-Cl}_3\text{C}_6\text{H}_2\,.$$

Analogous results can be obtained by comparing the line-widths of the N-CH$_3$ group signal in compounds I at a fixed temperature.

We also wanted to discover whether the above regularities in the influence of substituents on the rate of the metal—metal exchange still hold in passing from pyridine to a more inert solvent, such as chloroform. Unfortunately, most of the compounds investigated are only sparingly soluble in this solvent, whereas in the case of the sufficiently soluble Ia the signal of the N-CH$_3$ group turned out to be overlapped by the substituent CH$_3$ group resonance. As a result, the relative abilities of the metal—metal exchange in chloroform were compared only for two compounds, Id and Ie. The data of Table 1 show that in the PMR spectrum of Id in chloroform the mercury satellites are clearly seen at 15°, whereas they cannot be observed for Ie at this temperature. Thus, introduction of electron-withdrawing substituents into the arylmercury group accelerates the metal—metal exchange both in pyridine and chloroform solutions.

Kinetics of the metal—proton exchange

In order to obtain information on the influence of various factors upon the rate of the metal—proton exchange, the mixtures of substituted benzenesulphono-o-toluidides (II) and their N-arylmercury derivatives (III) have been studied in a mixture of pyridine and chlorobenzene (2/3 v/v) as solvent. The choice of the solvent was determined by the fact that the arylmercury derivatives are poorly

TABLE 2

PARAMETERS OF PMR SPECTRA FOR 0.15 *M* SOLUTIONS OF EQUIMOLAR MIXTURES OF SUBSTITUTED BENZENESULPHONO-*o*-TOLUIDIDES AND THEIR *N*-ARYLMERCURY DERIVATIVES IN A MIXTURE OF C_5H_5N AND C_6H_5Cl (2/3)

N-Ar	RHg	Coalescence temperature (°C)	Δδ at coalescence temperature (Hz)	t_1 (°C)	r^a at t_1	W^b at t_1	Δδ at t_1 (Hz)	$\tau_A{}^c$ at t_1 (sec)
$2\text{-}CH_3C_6H_4$	C_6H_5Hg	—7	4,6	—15	1,6		4.8	0.35 ± 0.05
$4\text{-}Br\text{-}2\text{-}CH_3C_6H_3$	C_6H_5Hg	—21	7,6	—30	1,9		8.3	0.120 ± 0.005
$2\text{-}CH_3\text{-}4\text{-}(CH_3)_2NC_6H_3$	C_6H_5Hg	10	5,2	0	2.5		7.0	0.32 ± 0.02
$4\text{-}NO_2\text{-}2\text{-}CH_3C_6H_3$	C_6H_5Hg	<—45	8,1	—45		3,7	8,1	<0.015 ± 0.003
$2,6\text{-}(CH_3)_2C_6H_3$	C_6H_5Hg	25	6,1	0	2,7		5,2	0.55 ± 0.07
$4\text{-}Br\text{-}2,6\text{-}(CH_3)_2C_6H_2$	C_6H_5Hg	19	6,0	0	2,6		6.4	0.38 ± 0.03
				31		5,5	6.0	0.050 ± 0.002
$4,6\text{-}Br_2\text{-}2\text{-}CH_3C_6H_2$	C_6H_5Hg	31	6,7	31	coalescence		6.7	0,10 ± 0.01
$2\text{-}CH_3C_6H_4$	$4\text{-}CH_3OC_6H_4Hg$	—23	6,6	—23	coalescence		6.6	0.10 ± 0.01
$2\text{-}CH_3C_6H_4$	$4\text{-}(CH_3)_2NC_6H_4Hg$	—26	3,4	—15		4.6	3.1	0.15 ± 0.03
$2\text{-}CH_3C_6H_4$	$4\text{-}ClC_6H_4Hg$	<—45	5,4	—45		2,4	5.4	<0,01

[a] r = ratio of the maximum height to central minimum. [b] W = line-width at half height. [c] τ_A = mean lifetime of the exchanging species at the given temperature t_1.

soluble in chlorobenzene, whereas in pyridine the rates of exchange (3) are in most cases too high even at low temperatures to be measured by PMR.

In the PMR spectra of solutions containing equimolar amounts of the compounds II and III at 0.15 *M* concentration in each of the components only a single resonance of the indicator *ortho*-methyl group is observed at 34° for all the systems investigated between those for the methyl group protons of the individual compounds under similar conditions. On lowering the temperature to —45°, for almost all pairs of compounds II and III, the single resonance splits into two sharp peaks corresponding to the chemical shifts for the methyl protons of the individual compounds under the same conditions. The results obtained provide evidence that the exchange reactions of the metal—proton type take place in the solutions of mixtures of the above compounds, their rates being in most cases measureable on the PMR time scale.

In Table 2 are listed some parameters of the PMR spectra for the solutions containing equimolar quantities of II and III, measured at various temperatures. From the data obtained it follows that the coalescence temperature for the signals of the indicator methyl groups depends substantially on the nature of the aryl radicals on the nitrogen and mercury atoms. However, a comparison of the exchange rates (2) based only on the coalescence temperatures would not be sufficiently correct, since the separation of the methyl group signals in the absence of exchange ($\Delta\delta$) is not the same for different systems. In addition, $\Delta\delta$ is temperature-dependent in some cases.

In this connection, apart from the coalescence temperatures of the CH_3 group peaks and $\Delta\delta$ values at the coalescence temperature, Table 2 lists also the mean lifetimes of the exchanging species (τ_A) at some fixed temperatures t_1. The latter values were chosen in such a way that a comparison of them and τ_A values for different systems could provide a semi-quantitative measure for the influence of the nature of aryl groups on nitrogen and mercury upon the rate of the metal—proton exchange. Thus, for example, in the case of exchange between IIa and IIIa, the τ_A value is 0.35 ± 0.05 sec at —15° for $X = H$, whereas for $X = Br$ it is 0.120 ± 0.005 sec at —30°. Evidently, for the latter system at —15° τ_A will be smaller than 0.120 sec, and, consequently, the exchange rate in this system is greater than in the former system.

Similar considerations for other pairs of compounds IIa and IIIa show that, depending on the nature of substituent in the *p*-position of the aryl group on nitrogen, the exchange rate increases in these systems in the order: $(CH_3)_2N < H < Br < NO_2$. Consequently, it can be concluded that the exchange reaction of the metal—proton type is accelerated by electron-withdrawing substituents and slowed by electron-releasing substituents in the aryl group on nitrogen. As evidenced by comparing the exchange parameters for the mixtures IIa + IIIa ($X =$ H, Br) with the analogous data for the mixtures of the corresponding 6′-substituted compounds (IIb + IIIb, IIc + IIIc), introduction of a second methyl group into the *o*-position of the aryl radical on nitrogen leads to a retardation of the exchange reaction (2). The data of Table 2 reveal also that substitution of the 6′-methyl group by a bromo substituent (IId + IIId) slows the exchange as well.

Further, a consideration of the PMR data for the systems involving different arylmercury groups (IIIe) makes it clear that the character of influence of substituents in the phenylmercury group upon the rate of the metal—proton ex-

TABLE 3

TEMPERATURE-DEPENDENCE OF τ_A FOR 0.126 *M* SOLUTION OF EQUIMOLAR MIXTURE OF 4'-BROMO-2',6'-DIMETHYLBENZENESULHONANILIDE AND ITS PHENYLMERCURY DERIVATIVE IN A MIXTURE OF C_5H_5N AND C_6H_5Cl (2/3)

T (K)	W^a (Hz)	r^b	τ_A (sec)
273		2.3	0.40
278		1.9	0.28
283		1.5	0.20
288		1.3	0.16
293		1.0	0.11
298	6.7		0.068
303	5.7		0.052

[a] W = line-width at the half-height. [b] r = ratio of the maximum height to central minimum.

change is significantly different from their influence on the metal—metal exchange. Thus, it was found that both electron-accepting and electron-donating substituents accelerate the metal—proton exchange in the systems IIe + IIIe, the sequence of increasing exchange rates being represented by: $H < N(CH_3)_2 < OCH_3 < Cl$.

The τ_A values for the system IIc + IIIc assembled in Table 3 were used to obtain an Arrhenius plot (Fig. 1), from which the activation energy of the exchange process was calculated to be 11.3 ± 1.3 kcal/mole. The same system was used to examine the effect of variation of concentration for one of the components at a constant concentration of another upon the lifetimes of the N—H and N—Hg bonds (τ_{N-H} and τ_{N-Hg}), the results obtained being given in Table 4. An analysis of the concentration-dependence of these lifetimes shows that the exchange reaction in the system IIc + IIIc is overall second-order, being first-order in each of the components (0.9 ± 0.2 in 2',6'-dimethyl-4'-bromobenzenesulphonanilide and 1.0 ± 0.2 in its phenylmercury derivative). In Fig. 2 are represented some experimental PMR spectra for different concentrations of the compounds

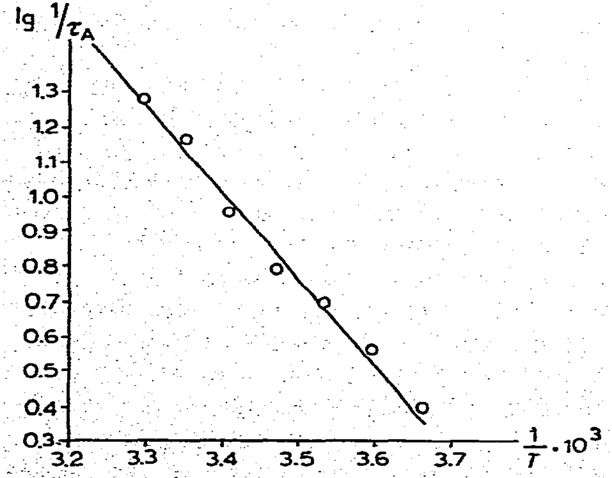


Fig. 1. Plot of log $1/\tau_A$ versus $1/T$ for the exchange of 2',6'-dimethyl-4'-bromobenzenesulphonanilide with its *N*-phenylmercury derivative in a mixture of C_5H_5N and C_6H_5Cl (2/3) for 0.126 *M* concentrations of the reactants.

TABLE 4

CONCENTRATION-DEPENDENCE OF THE MEAN LIFETIMES OF THE N—H AND N—Hg BONDS IN SOLUTIONS OF MIXTURES OF 4'-BROMO-2',6'-DIMETHYLBENZENESULPHONANILIDE (I) WITH ITS *N*-PHENYLMERCURY DERIVATIVE (II) IN A MIXTURE OF C_5H_5N AND C_6H_5Cl (2/3) AT 9°

Concentration of I (*M*)	Concentration of II (*M*)	τ_{N-H} (sec)	τ_{N-Hg} (sec)	k_1 (l/mole·sec)	
				$2/[I]\ \tau_{N-Hg}$	$2/[II]\ \tau_{N-H}$
0.127	0.054	0.520	0.220	71.6	71.2
0.127	0.078	0.320	0.200	78.8	80.2
0.126	0.127	0.210	0.210	75.6	75.0
0.125	0.104	0.260	0.215	74.4	74.0
0.152	0.100	0.250	0.165	79.8	80.0
0.097	0.100	0.240	0.250	82.6	83.4
				$\bar{k}_1 = 78 \pm 4$	

in the system IIc + IIIc along with the corresponding simulated spectra, which were used to calculate the lifetimes.

Exchange equilibria of the metal—proton type

If chloroform is used as solvent instead of the pyridine/chlorobenzene mixture, then the solution PMR spectra of all systems II + III studied at 0.15 *M* concentration in each of the components exhibit even at 60° two sharp peaks of the indicator methyl group, the position of these signals corresponding exactly to the chemical shifts of the methyl resonances for the individual compounds. This fact indicates that the exchange reaction (2) is slow on the PMR time-scale in chloroform.

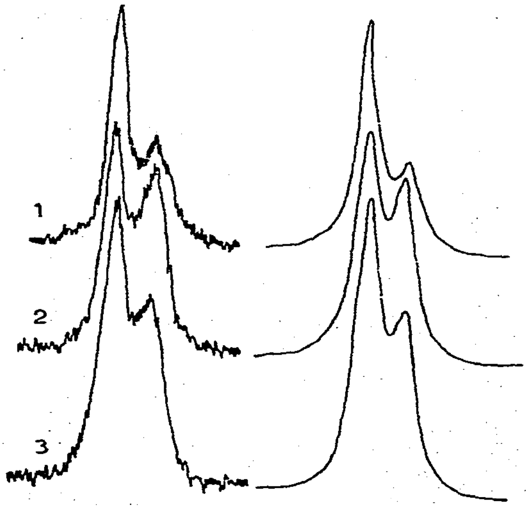


Fig. 2. Experimental and calculated PMR spectra for mixtures of 2',6'-dimethyl-4'-bromobenzenesulphonanilide (A) and its *N*-phenylmercury derivative (B) in C_5H_5N/C_6H_5Cl (2/3) with various concentrations of the components:

1. $C_A = 0.127$ *M*, $C_B = 0.054$ *M*, $\tau_{N-H} = 0.520$ sec, $\tau_{N-Hg} = 0.220$ sec.
2. $C_A = 0.125$ *M*, $C_B = 0.104$ *M*, $\tau_{N-H} = 0.260$ sec, $\tau_{N-Hg} = 0.215$ sec.
3. $C_A = 0.152$ *M*, $C_B = 0.100$ *M*, $\tau_{N-H} = 0.250$ sec, $\tau_{N-Hg} = 0.165$ sec.

Initially, for examining such slow exchange reactions in chloroform, the PMR spectrum of a mixture of benzenesulphonanilide IVa ($Ar' = C_6H_5$) and phenylmercury derivative of benzene-*o*-toluidide Va was studied in chloroform solution. It turned out that just after mixing the solutions of the above compounds, i.e. after 1-2 min, the PMR spectrum of the reaction mixture shows along with the methyl group signal of the starting phenylmercury derivative Va, the CH_3 peak of benzenesulphono-*o*-toluidide, evidently formed by the exchange reaction (3). The intensity ratio of these signals does not change with time and the same ratio is observed after mixing the chloroform solutions of benzenesulphono-*o*-toluidide and phenylmercury derivative of benzenesulphonanilide, which indicates the presence of a rapidly established equilibrium.

In Table 5 are given the equilibrium constants for a number of mixtures IV + V in chloroform at 34° for 0.2 *M* concentrations of the starting reactants, which were determined by integration of the corresponding signals. It was shown for the systems with $Ar = C_6H_5$ and $2\text{-}ClC_6H_4$ that a ten-fold decrease in the concentrations of each component scarcely affects the values of equilibrium constants This indicates that the values of equilibrium constants appear not to be influenced by the possible association of benzenesulphonanilides [18]. The use of still smaller concentrations in studying the exchange equilibria was prevented by the limitations in the sensivity of the PMR equipment.

The data in Table 5 throw light on the influence of substituents in differ-

TABLE 5

EQUILIBRIUM CONSTANTS FOR EXCHANGE REACTIONS OF *N*-PHENYLMERCURY DERIVATIVES OF BENZENESULPHONO-*O*-TOLUIDIDES WITH BENZENESULPHONANILIDES IN CHLOROFORM[a]

Reactants: $C_6H_5SO_2N(HgC_6H_5)Ar + C_6H_5NHAr^{\star}$		*K*
Ar	$Ar^{\star}$	
$2\text{-}CH_3C_6H_4$	C_6H_5	1.8
$2\text{-}CH_3C_6H_4$	$4\text{-}CH_3OC_6H_4$	1.7
$2\text{-}CH_3C_6H_4$	$4\text{-}(CH_3)_2NC_6H_4$	1.6
$2\text{-}CH_3C_6H_4$	$4\text{-}FC_6H_4$	2.3
$2\text{-}CH_3C_6H_4$	$4\text{-}ClC_6H_4$	2.5
$2\text{-}CH_3C_6H_4$	$4\text{-}IC_6H_4$	2.6
$2\text{-}CH_3C_6H_4$	$3\text{-}FC_6H_4$	3.1
$2\text{-}CH_3C_6H_4$	$3\text{-}ClC_6H_4$	3.0
$2\text{-}CH_3C_6H_4$	$3,5\text{-}Cl_2C_6H_3$	4.2
$2\text{-}CH_3C_6H_4$	$2,5\text{-}[(CH_3)_3C]_2C_6H_3$	0.062
$2\text{-}CH_3C_6H_4$	$2\text{-}FC_6H_4$	4.3
$2\text{-}CH_3C_6H_4$	$2\text{-}ClC_6H_4$	5.1
$2\text{-}CH_3C_6H_4$	$2\text{-}BrC_6H_4$	9.1
$2\text{-}CH_3C_6H_4$	$2\text{-}IC_6H_4$	17.3
$2\text{-}CH_3C_6H_4$	$2\text{-}CH_3OC_6H_4$	4.4
$2\text{-}CH_3C_6H_4$	$2\text{-}CH_3SC_6H_4$	17.9
$2\text{-}CH_3C_6H_4$	$2\text{-}NO_2C_6H_4$	0.62
$2\text{-}CH_3C_6H_4$	$2\text{-}CH_3OCOC_6H_4$	0.072
$2\text{-}CH_3C_6H_4$	C_6H_5	1.6[b]
$2\text{-}CH_3C_6H_4$	$2\text{-}ClC_6H_4$	4.8[b]
$2,6\text{-}(CH_3)_2C_6H_3$	C_6H_5	2.4
$2\text{-}CH_3\text{-}4\text{-}BrC_6H_3$	C_6H_5	1.7
$2\text{-}CH_3\text{-}4\text{-}(CH_3)_2NC_6H_3$	C_6H_5	1.6
$4\text{-}Br\text{-}2,6\text{-}(CH_3)_2C_6H_2$	C_6H_5	1.7
$2,4\text{-}Br_2\text{-}6\text{-}CH_3C_6H_2$	C_6H_5	0.01

[a] initial concentration of the reactants were 0.2 *M*. [b] For 0.02 *M* initial concentrations of the reactants.

ent positions of the benzenesulphonanilide and benzenesulphono-*o*-toluidide moieties upon the equilibrium (3) in the corresponding systems.

A consideration of the equilibrium constants reveals the following regularities. For the exchange reaction between the phenylmercury derivative of benzenesulphono-*o*-toluidide and benzenesulphonanilide the equilibrium deviates from random and is shifted in favour of the phenylmercury derivative of the latter compound. Introduction of a second methyl group into the 6′-position of V increases the equilibrium constant to a lesser extent than introduction of the first one. A considerably greater effect upon the equilibrium constant is produced by the $(CH_3)_3C$ group in the benzenesulphonanilide moiety. Electron-releasing substituents in the positions 3′ and 4′ of IVa do not materially affect the equilibrium constant, whereas electron-withdrawing substituents increase it slightly, displacing the equilibrium further to the right in favour of the C_6H_5Hg derivative of the more acidic [19] substituted benzenesulphonanilide.

The range of equilibrium constants increases markedly in passing to substituted benzenesulphonanilides, containing in the *o*-position to the nitrogen atom substituents with unshared electron pairs. When these substituents are halogens, methoxy or methylthio groups, the equilibrium is shifted relative to the system involving unsubstituted benzenesulphonanilide further in favour of the C_6H_5Hg derivative of the *o*-substituted compound, the equilibrium constant for the systems IVa + Va increasing in the order:

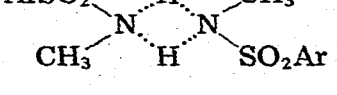
$$F \approx OCH_3 < Cl < Br < I \approx SCH_3$$

The equilibrium deviates from randomness especially strongly in the case of the IVb + Vb system involving 4′,6′-dibromo-2′-methylbenzenesulphonanilide.

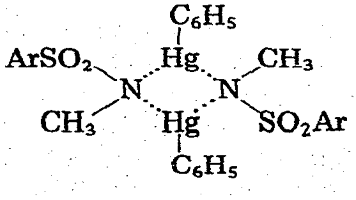
A different picture is observed for the systems including 2′-nitro or carbomethoxy substituted benzenesulphonanilides. With these systems, the equilibrium is displaced in favour of *ortho*-substituted benzenesulphonanilides, the equilibrium constant being the lowest for the latter system.

Discussion

Earlier, in the course of a comparative study of exchange reactions in substituted *N*-methylbenzenesulphonamides and their *N*-phenylmercury derivatives [16], it was suggested, in line with the generally accepted view on the exchange processes connected with the migration of hydrogen [5], or organometallic groups [13, 15], that the exchanges of the proton—proton and metal—metal types proceed by an associative mechanism involving the formation of cyclic transition states VI and VII, respectively:



(VI)

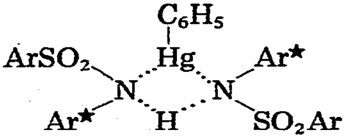


(VII)

In the case of the proton—proton exchange, the formation of VI in the rate-determinging step was supported by the overall second order of the reaction and the comparatively low (11 ± 2 kcal/mole) activation energy. For the exchange reaction of the metal—metal type the dependence of the reaction rate upon the concentration of the phenylmercury derivative has been also found.

The data obtained in the present work are in agreement with the ideas developed previously [16] and throw further light on the mechanism of the exchange processes studied. In particular, the acceleration of the metal—metal exchange both in pyridine and chloroform upon introducing electron-withdrawing substituents into the C_6H_5Hg group and its retardation by electron-releasing substituents in this group provide further support for the associative mechanism of exchange. For the alternative dissociative pathway the contrary should have been the case, because the dissociation of the Hg—N bond is expected to be facilitated by electron-donating substituents in the C_6H_5Hg group and inhibited by electron-accepting ones.

The kinetic data obtained in this work for the exchange reaction of the metal—proton type with the system IIc + IIIc (first order in each of the components and the activation energy of 11.3 ± 1.3 kcal/mole) lead us to suppose that in this case the exchange also proceeds by an associative mechanism through a cyclic four-membered transition state:



The ease of formation should increase with increasing nucleophilic power of the nitrogen atom and coordinating abilities of hydrogen and mercury.

It has been found earlier [16] that due to the competition of the above factors the rate of the metal—proton exchange does not change in parallel with the electronic properties of substituents in the $C_6H_5SO_2$ moiety of *N*-methylbenzenesulphonamide. In contrast, the metal—proton exchange in the system IIa + IIIa is retarded by electron-releasing substituents in the *p*-position of the C_6H_5 group on nitrogen and accelerated by electron-withdrawing ones. This result indicates that with the systems considered the formation of the transition state VIII is to a greater extent facilitated by the enhancement in electrophilic power of the hydrogen and/or metal atoms, than it is inhibited by reduction in nucleophilic power of the nitrogen atom. Similarly, the character of influence of substituents in the C_6H_5Hg group upon the rate of the metal—metal exchange in compounds I affords evidence that the coordinating ability of the metal atom is the dominant factor in this case as well.

At the same time, the acceleration of the metal—proton exchange in the systems IIe + IIIe upon introduction of both electron-donating and electron-accepting substituents into the *p*-position of the phenylmercury group demonstrates that variation of the radical on the metal atom affects both its coordinating ability and the nucleophilic power of the nitrogen atom. Since the electronic interactions through the aryl—mercury bond are mainly of an inductive nature [20-22], it may be expected that the electronic density on the mercury and nitrogen atoms will change with the substituent in the ArHg moiety according to the σ°

values of the substituted phenyl groups. Taking into account that the σ^0 values for the 4-ClC_6H_4 and 4-$(CH_3)_2NC_6H_4$ groups are equal to 0.27 and −0.44 respectively [23] and comparing the τ_A values in Table 2 for the corresponding systems, one is led to the conclusion that a weaker electron-withdrawing substituent in the C_6H_5Hg group accelerates the metal—proton exchange to a greater extent than does a stronger electron-releasing substituent. Finally, it may be suggested that the acceleration of the metal—proton exchange by electron-donating substituents in the ArHg group is associated with the fact that the increase in nucleophilic power of the nitrogen atom strengthens to a greater extent the H . . . N hydrogen bond than the decrease in coordinating ability of mercury weakens the Hg . . . N coordinate bond, thereby facilitating the formation of the transition state VIII.

A further point of interest is the fact that the exchange of the metal—proton type occurs with rates measurable on the PMR time-scale in the mixture of pyridine and chlorobenzene, being markedly slowed in passing to chloroform. As has been shown earlier [16] for the C_6H_5Hg derivative of *N*-methyl-*p*-chlorobenzenesulphonamide, pyridine somewhat retards the metal—metal exchange relative to chloroform. On the other hand, in substituted *N*-methylbenzenesulphonamides the proton—proton exchange is greatly accelerated in pyridine. All these facts suggest that with the metal—proton exchange the formation of the transition state VIII is more strongly facilitated by polarization of the N—H bond due to hydrogen bonding to pyridine than it is inhibited by blocking the vacant mercury orbitals through solvation.

Further, the observed retardation of the metal—proton exchange on introducing a second methyl group in the *o*-position to the $C_6H_5SO_2NH$ moiety (systems IIb + IIIb and IIc + IIIc) apparently arises from steric hindrance to the formation of the transition state. The electronic effect of the second *o*-methyl group seems to be unimportant, since its introduction slows the exchange to a much greater extent than introduction of the *p*-dimethylamino group, the electron-releasing effect of which is greater than that of the *o*-methyl substituent [24]. The observed inhibition of exchange by steric hindrance lends further support for the associative mechanism, because steric interactions should have accelerated the exchange by facilitaing the dissociation of the Hg—N bond, if this dissociation had been the rate-determining step.

Finally, the fact that the metal—proton exchange is slowed to a greater extent on introduction in the 6′-position of a bromo substituent than on introduction of the CH_3 group, appears to be a consequence of intramolecular coordination between the halogen and mercury atoms and, to a lesser degree, of internal hydrogen bonding. This explanation is in agreement with the somewhat smaller Van der Waals radius of bromine compared to that of the CH_3 group [25] and with the overall electron-withdrawing effect of *o*-bromo substituent [24]. According to the results discussed above, the latter factor should have facilitated the exchange, had it been the dominant one.

In turning now to a consideration of influence of various factors upon the equilibrium (3), it should be pointed out that in general this equilibrium must depend on the substituent effects through valence bonds, steric hindrance and the strength of intramolecular coordination or internal hydrogen bonding. The data for the systems involving 3′- and 4′-substituted benzenesulphonanilides IVa show that purely electronic substituent effects influence the equilibrium (3) only slightly. The considerably greater effect of *ortho*-substituents upon the position of this equilibrium and its character provide evidence that the electronic factors are not dominant in this case. Apparently, for the systems involving 2′-substituted compounds steric hindrance and intramolecular coordination are more important. It seems appropriate to consider first the influence of the former factor.

Taking into account the slight effect of electron-donating substituents in the 4′-position of the benezenesulphonanilide moiety upon the equilibrium constant, it can be concluded that the deviation of equilibrium from randomness for the exchange between the C_6H_5Hg derivative of benzenesulphono-*o*-toluidide and benzenesulphonanilide arises from steric interactions. According to the published data [26], in benzenesulphonanilides both with and without substituents in the 2′ and 6′-positions the CNS plane is not coplanar with that of the aromatic ring bonded to the nitrogen atom, the interplanar angle varying from 45° to 80° in the solid state. These results point to the absence of rigidly fixed conformations and to a rather free rotation about the C—N bond, which can arise from the lack of considerable mesomeric interaction between the nitrogen lone electron pair and the aromatic ring. The lack of considerable conjugation of the $C_6H_5SO_2NH$ and $C_6H_5SO_2N(HgC_6H_5)$ groups with the ring is supported by the data on fluorine chemical shifts in 3′- and 4′-fluoro substituted compounds (Table 6). According to these results, the σ_R^0 values for the above groups calculated by the Taft method [27] are equal to —0.18 and —0.19, respectively, being rather small compared to —0.52 for the σ_R^0 value of the $(CH_3)_2N$ group. Thus, it can be expected that deviation from coplanarity between the CNS plane and that of the aromatic ring is not connected with a large loss in resonance energy.

In this connection it appears probable that the influence of steric hindrance is associated with inhibition of rotation around the C—N bond, rather than with the different degrees of twist of the CNS plane from coplanarity with the aromatic ring in benzenesulphonanilides and their phenylmercury derivatives, which would have led to different losses in the energy of resonance between the nitrogen lone pair and the ring. In turn, the effect of hindered rotation can result from either the difference in the ranges of free rotation around the C—N bond for the $C_6H_5SO_2NH$ and $C_6H_5SO_2N(HgC_6H_5)$ groups, or the difference in the potential barriers to rotation around this bond in passing through the eclipsed conformation.

Thus, inspection of molecular models shows that introduction of a methyl group in the 2′-position of the benzenesulphonanilide moiety restricts the range of free rotation for the $C_6H_5SO_2N(HgC_6H_5)$ group to a larger extent than for the $C_6H_5SO_2NH$ group. On the other hand, recent PMR studies [28] have demonstra-

TABLE 6

^{19}F CHEMICAL SHIFTS IN CHLOROFORM RELATIVE TO INTERNAL FLUOROBENZENE (in ppm)

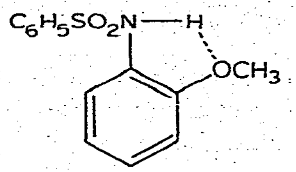
Compound	δ_F
$C_6H_5SO_2NHC_6H_4F$-3	—2.2
$C_6H_5SO_2N(HgC_6H_5)C_6H_4F$-3	—2.0
$C_6H_5SO_2NHC_6H_4F$-4	3.0
$C_6H_5SO_2N(HgC_6H_5)C_6H_4F$-4	3.6

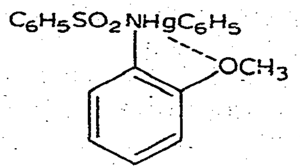
ted the existence of a considerable barrier to rotation around the C—N bond in *N*-benzyl-*p*-toluenesulphono-*o*-toluidide. In this connection, the influence of steric hindrance on the position of equilibrium in our case may be also associated with the fact that the 2′-methyl group increases the barrier to rotation in benzenesulphono-*o*-toluidide to a smaller degree than in its phenylmercury derivative. At the same time, the smaller effect of the second methyl group in the 6′-position on the equilibrium constant is probably due to the fact that this group decreases the range of free rotation of the $C_6H_5SO_2N(HgC_6H_5)$ to a smaller extent than does the first methyl group.

On the basis of the above considerations, it should be expected that in the case of purely non-bonded interactions between the C_6H_5Hg group and 2′-substituent, the larger the substituent introduced into this position, the more the phenylmercury derivative will be destablized relative to the corresponding benzenesulphonanilide, This assertion receives support from the greater effect of the 2′-$(CH_3)_3C$ group on the equilibrium compared to that of the 2′-CH_3 group. However, for most of the systems studied, the displacement of equilibrium in favour of the C_6H_5Hg derivatives of 2′-substituted benzenesulphonanilides and the inverse relationship of this displacement to the size of the 2′-substituent shows that intramolecular coordination rather than non-bonded interactions is the dominant factor.

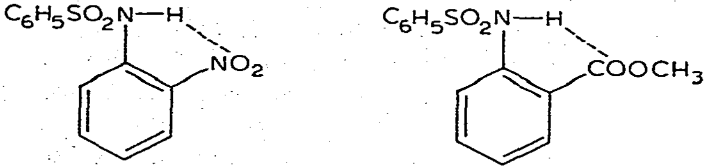
Data on thermodynamic characteristics of the strength of intramolecular hydrogen bonding in *o*-substituted anilines and their derivatives seem to be lacking at present. Nevertheless, the available semi-quantative evidence based on IR and NMR investigations of *o*-substituted anilines, acetanilides and benzenesulphonanilides [29—39] demonstrates the presence in these compounds of intramolecular hydrogen bonding involving halogens, CH_3O, CH_3S, NO_2 and $COOCH_3$ groups. Further, it should be pointed out that, although the electronic substituent effects apparently exert an insignificant influence upon the equilibrium (3), they still should be taken into account in a rigorous analysis of the effect of 2′-substituents on this equilibrium. At the same time, due to the complexity of the general problem of *ortho*-effect [40—41], the correct elimination of the purely electronic effects of 2′-substituents presents some difficulties. At present, the best method seems to be through the use of the data on the ground state electronic effects of *o*-substituents obtained from a PMR study of substituted phenols in DMSO [24]. Finally, it appears appropriate to discuss separately different systems IV + V, in order to elucidate the possibility of separating the role of intramolecular coordination and comparing its strength for the chelate rings involving the C_6H_5Hg group and hydrogen.

The above problems seem to be most readily solved in the case of the system involving the methoxy group. The shift of the equilibrium (3) in favour of the C_6H_5Hg derivative of 2′-methoxybenzenesulphonanilide relative to that of benzenesulphonanilide cannot arise from the electron-donating effect of the CH_3O group, because electron-releasing substituents decrease slightly the equilibrium constant. The purely steric effect of the CH_3O group should have also destabilized the C_6H_5Hg derivative of 2′-methoxybenzenesulphonanilide relative to that of benzenesulphonanilide, since the Van der Waals radius of the oxygen atom is greater than that of hydrogen [25]. There is apparently [39] no intramolecular hydrogen bond in 2′-methoxybenzenesulphonanilide, although a weak hydrogen bond exists in *o*-anisidine [34] and a rather strong one in *o*-methoxyacetanilide [37]. Consideration of the above data shows that the displacement of equilibrium to the right is connected with coordination between the C_6H_5Hg and CH_3O groups and arises from either the absence of intramolecular hydrogen bonding in 2′-methoxybenzenesulphonanilide and the presence of intramolecular coordination in its phenylmercury derivative, or from the greater strength of the Hg · · · O coordinate bond relative to that of the H · · · O hydrogen bond:



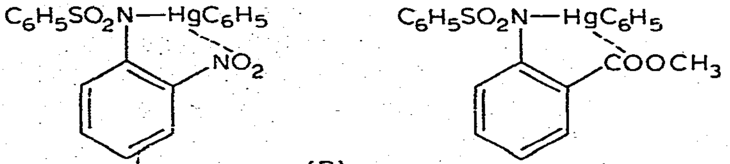


The displacement of equilibrium in favour of the substituted benzenesulphonanilide upon introduction of the NO_2 and especially $COOCH_3$ groups in the 2′-position does not correspond to the expected influence of the strong electron-withdrawing effects of these substituents. On the other hand, purely non-bonded interactions between the C_6H_5Hg group and the above substituents are ruled out on the basis of the results obtained for the C_6H_5Hg derivative of 2′-methoxybenzenesulphonanilide and previous data on the possibility of intramolecular mercury—oxygen coordination [42]. At the same time, it is known that in *o*-substituted-anilines [29, 35],-acetanilides [32, 36] and -benzenesulphonanilides [39] there exist rather strong hydrogen bonds involving the NO_2 and $COOCH_3$ groups. This allows the conclusion to be made that in the case of 2′-nitro- and especially 2′-carbomethoxy-substituted compounds the strength of the chelate rings involving the hydrogen atom (A) turns out to be greater than



(A)

that of the chelate rings involving the C_6H_5Hg group (B).



(B)

Although the influence of halogen substituents and CH_3S group in the 2′-position on the equilibrium constant is similar to that of the CH_3O group, the interpretation of the data in this case is somewhat more difficult, because in contrast to the CH_3O group these substituents exert an overall electron-withdrawing effect from the *o*-position [24]. Nevertheless, a comparison of the influence of electron-accepting substituents in the 2′-, 3′- and 4′-positions of the benzenesulphonanilide moiety upon the equilibrium with their electronic effects [24, 43] shows that intramolecular coordination also plays a decisive role in this case.

Thus, the halogen substituents in the 2′-position differ markedly in their influence on the equilibrium constant, whereas from the 4′-position their effects are small and close for the first and the last members of the series. The equilibrium constant is affected most strongly by the CH_3S group, the electron-withdrawing effect of which from the *o*-position is smaller than that of the *o*-chloro substituent [24]. Introduction of two chloro substituents into the positions 3′ and 5′ gives rise to a smaller displacement of equilibrium than does introduction of most of the substituents in the 2′-position, in spite of the fact that the combined electron-accepting effect of the two chlorines is greater than that of each substituent considered from the 2′-position. These facts provide evidence that the increase in equilibrium constant upon introducing chloro, bromo, iodo and methylthio substituents into the 2′-position arises mainly from the fact that the intramolecular coordinate bond of the C_6H_5Hg group with these substituents turns out to be stronger than the corresponding internal hydrogen bond. The same statement holds for the fluoro substituent, since it exerts a smaller electron-withdrawing effect from the *ortho*-position than does the *meta*-chloro substituent [24, 43], but produces a greater increase in equilibrium constant.

In accordance with the equilibrium constant values, the difference in the strengths of the internal hydrogen bond and intramolecular coordinate bond increases in going from fluorine to iodine and from CH_3O to CH_3S. At the same time, the bulk of the available evidence indicates that the strength of the internal hydrogen bond in *ortho*-substituted anilines and acetanilides apparently increases the same sequence [30,31,34]. This suggests that the strength of the intramolecular coordinate bond in the C_6H_5Hg derivatives of 2′-substituted benzenesulphonanilides also increases in the same order. If this suggestion is correct, then in the case of a five-membered chelate ring the influence of the nature of the donor atom upon the strength of the coordinate bond involving the C_6H_5Hg group is mainly analogous to its influence upon the strength of the mercury—ligand bond in the case of coordination of the CH_3Hg cation to the corresponding anions [44—45].

The above considerations show that with five-membered chelate rings, intramolecular coordinate bonds involving the C_6H_5Hg group turn out to be stronger than the corresponding internal hydrogen bonds, whereas for six-membered chelate rings the contrary is the case. As follows from a comparison of 2′-methoxy substituted compounds on the one hand, and 2′-nitro and 2′-carbomethoxy substituted on the other, the above situation is not connected with the nature of the donor atom. It appears probable that geometric factors are responsible for it. Thus, inspection of molecular models shows that in the case of the compounds with halogens, CH_3O and CH_3S groups in the 2′-position the overlap of the Van der Waals envelopes of the donor and acceptor atoms can be more effective for the C_6H_5Hg group than for the hydrogen atom, the possible non-coplanarity of the CNS plane with the aromatic ring on nitrogen still enhancing this difference. In contrast, for a six-membered chelate ring involving the NO_2 or $COOCH_3$ group there is a possibility of sufficiently effective overlap between the Van der Waals spheres of the hydrogen and oxygen atoms to form a planar ring producing a strong hydrogen bond, whereas in the case of the C_6H_5Hg group the formation of of a planar chelate ring seems to be impossible due to the too-strong overlap of the Van der Waals envelopes of mercury and oxygen, which leads to predominance of repulsion over attraction.

Further, for a six-membered chelate ring the N—H· ·X angle is closer to 180° than for a five-membered chelate ring, thus approaching to a greater extent the preferred geometry of hydrogen bonding [46]. By contrast, for the mercury atom sufficiently effective coordination can take place via the unhybridized *6p*-orbitals, which corresponds to an N—Hg· ·X angle of only 90°. Examples of such coordination are known in the literature [47—48].

Thus, the above considerations demonstrate that for the C_6H_5Hg group geometric factors favour the formation of a five-membered chelate ring to a greater extent than the formation of a six-membered chelate ring, whereas for the hydrogen atom the contrary seems to be the case.

In finishing the discussion of various factors influencing the equilibrium for the metal—proton exchange, it is of interest to note the results obtained for the system involving 4′,6′-dibromo-2′-methylbenzenesulphonanilide and its phenylmercury derivative. Namely, introduction of a bromo substituent into the 6′-position of 4′-bromo-2′methylbenzenesulphonanilide stabilizes the corresponding phenylmercury derivative to a much greater extent than does introduction of this substituent in the 2′-position of benzenesulphonanilide. Evidently, in this case we have to deal with the steric facilitation of chelation [49—50], which strengthens the intramolecular coordination of the C_6H_5Hg group with the bromo substituent to a greater degree than the corresponding internal hydrogen bond. Inspection of molecular models shows that in our case the steric facilitation of chelation results not from the shortening of the Hg . . .Br distance on introduction of the *o*-methyl group, but from inhibition of rotation of the $C_6H_5SO_2N(HgC_6H_5)$ group around the C—N bond, which fixes this group in the conformation favourable for coordination of mercury to bromine.

In conclusion, it may be said that the present investigation has allowed us to establish a number of regularities concerning the influence of substituent effects, steric hindrance and intramolecular coordination upon the rates and equilibria in the exchange reactions of the metal—metal and metal—proton types involving substituted benzenesulphonamides and their arylmercury derivatives. At present, further studies are in progress on exchange equilibria in organo-mercury, -tin and -lead derivatives of substituted thiophenols, to elucidate whether similar relationships apply to exchange reactions involving SH-acids and their organometallic derivatives.

Experimental

General comments

The PMR spectra of the systems studied at various temperatures were measured on a RYA-2305 spectrometer operating at 60 MHz. TMS was used as an internal standard. The experimental error in chemical shifts, line widths and spin—spin coupling constants was not greater than ± 0.3 Hz. The temperature was maintained and calibrated with the accuracy of ± 1°. The exchange equilibria (3) were investigated at 34° using a Hitachi-Perkin-Elmer R-12 spectrometer at 60 MHz. The ^{19}F NMR spectra were recorded at 34° using a Hitachi-Perkin-Elmer R-20 spectrometer operating at 56.4 MHz. The ^{19}F chemical shift measurements were made on solutions of 0.2 *M* concentration. The determination of the ^{19}F chemical shifts by the substitution method has been described elsewhere [51].

The mean lifetimes of the N—H and N—Hg bonds were determined by fitting the experimental PMR spectra to the theoretical curves. The theoretical spectra were calculated by employing the Bloch equations modified with regard to dynamic processes [52] for the case of the two-centre exchange with equal or different populations of the two states. A Nairi computer was used for these calculations. The experimental error in the τ values did not exceed ± 4% in studying their concentration and temperature dependence.

In general, for the exchange reaction:

$$nA + mB \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} pC + qD$$

the mean lifetime τ_A of the exchanging species in the state A between two successive exchanges can be expressed by the following relation [53]:

$$\frac{1}{\tau_A} = \frac{1}{[A]} \frac{d[A]}{dt} = k_{obs}[A]^{n-1}[B]^m$$

where n and m are the orders of the exchange reaction in A and B, respectively. A similar expression can be written for τ_B. Moreover, in our case [54] k_{obs} is equal to $k_1/2$. Hence, knowing the τ_A and τ_B values for some values of [A] and [B], one can calculate n and m. In this work the τ_A and τ_B values were obtained in varying [B] or [A] and keeping, respectively, [A] or [B] constant.

The equilibrium constants for the metal—proton exchange (3) were determined from the relative concentrations of the starting reactants and reaction products at equilibrium, which were calculated from the intensities fo the 2′-methyl-group peaks, corresponding to one of the reactants and one of the products. The ratio of the signal intensities was obtained by integration of the appropriate peaks in the spectrum of the reaction mixture at equilibrium. The error in the equilibrium constants was ± 10%. Chlorobenzene and chloroform were purified and dried by conventional procedure, pyridine was dried over molecular sieves (4 Å).

Substituted benzenesulphonanilides were obtained by the reaction of substituted anilines with benzensulphonyl chloride in pyridine [19]. The compounds reported in the literature were identified by their melting points. The arylmercury derivatives of substituted benzenesulphonanilides and *N*-methyl-*p*-chlorobenzenesulphonamide were prepared by the action of arylmercury hydroxides or acetates upon the corresponding benzenesulphonamides or their sodium salts [55]. 3,4,5-Trichlorophenylmercury derivative of *N*-methyl-*p*-chlorobenzenesulphonamide was obtained from 3,4,5-trichlorophenylmercury bromide via the corresponding nitrate.

Substituted benzenesulphonanilides and their arylmercury derivatives were purified by recrystallization, mainly from ethanol or benzene. For a number of compounds it was shown by special experiments that additional recrystallization of the corresponding benzenesulphono-*o*-toluidide or arylmercury derivative does not affect the parameters of the PMR spectra for the metal—metal or metal—proton exchanges and the character of their variation with temperature. The melting points and analytical data for the compounds not reported in the literature are presented in Table 7. The chemical shifts of the 2′-methyl group protons

TABLE 7

ANALYTICAL DATA AND MELTING POINTS FOR SUBSTITUTED BENZENESULPHONAMIDES AND THEIR *N*-ARYLMERCURY DERIVATIVES

Compound	M.p.^{a} (°C)	Analysis found (calcd.) (%)	
		C	H
4-$ClC_6H_4SO_2N(CH_3)HgC_6H_4OCH_3$-4	168-169	32.43 (32.82)	2.90 (2.75)
4-$ClC_6H_4SO_2N(CH_3)HgC_6H_4N(CH_3)_2$-4	169-172	34.00 (34.29)	3.56 (3.28)
4-$ClC_6H_4SO_2N(CH_3)HgC_6H_4Cl$-4	168-169	29.73 (30.21)	2.10 (2.15)
4-$ClC_6H_4SO_2N(CH_3)HgC_6H_2Cl_3$-3,4,5	205-207	26.39 (26.66)	1.68 (1.55)
4-$ClC_6H_4SO_2N(CH_3)HgC_6H_2(CH_3)_3$-2,4,6	170-172	36.29 (36.64)	3.72 (3.46)
$C_6H_5SO_2NHC_6H_4F$-2	109-110	57.33 (57.36)	4.13 (4.01)
$C_6H_5SO_2N(HgC_6H_5)C_6H_4F$-2	186-188	40.63 (40.95)	2.72 (2.67)
$C_6H_5SO_2NHC_6H_4F$-3	97-98	57.50 (57.36)	4.09 (4.01)
$C_6H_5SO_2N(HgC_6H_5)C_6H_4F$-3	153-155	40.53 (40.95)	2.64 (2.67)
$C_6H_5SO_2N(HgC_6H_5)C_6H_4F$-4	152-153	40.92 (40.95)	2.82 (2.67)
$C_6H_5SO_2N(HgC_6H_5)C_6H_4Cl$-2	140-142	40.09 (39.71)	2.62 (2.59)
$C_6H_5SO_2N(HgC_6H_5)C_6H_4Cl$-3	134-135	39.97 (39.71)	2.62 (2.59)
$C_6H_5SO_2N(HgC_6H_5)C_6H_4Cl$-4	130-131	39.63 (39.71)	2.65 (2.59)
$C_6H_5SO_2N(HgC_6H_5)C_6H_4Br$-2	127-128	36.50 (36.71)	2.47 (2.40)
$C_6H_5SO_2N(HgC_6H_5)C_6H_4I$-2	116-118	34.31 (34.00)	2.44 (2.22)
$C_6H_5SO_2N(HgC_6H_5)C_6H_4I$-4	188-190	33.83 (34.00)	2.35 (2.22)
$C_6H_5SO_2NHC_6H_3Cl_2$-3,5	133-135	47.89 (47.69)	2.82 (3.00)
$C_6H_5SO_2N(HgC_6H_5)C_6H_3Cl_2$-3,5	215-217	37.41 (37.35)	2.38 (2.26)
$C_6H_5SO_2N(HgC_6H_5)C_6H_4OCH_3$-2	171-173	42.38 (42.26)	3.42 (3.17)
$C_6H_5SO_2N(HgC_6H_5)C_6H_4OCH_3$-4	168-169	41.94 (42.26)	3.50 (3.17)
$C_6H_5SO_2N(HgC_6H_5)C_6H_4SCH_3$-2	115-119	41.04 (41.04)	3.14 (3.08)
$C_6H_5SO_2N(HgC_6H_5)C_6H_4N(CH_3)_2$-4	180-181	43.26 (43.29)	3.90 (3.28)
$C_6H_5SO_2N(HgC_6H_5)C_6H_4NO_2$-2	189-191	38.61 (38.95)	2.88 (2.54)
$C_6H_5SO_2N(HgC_6H_5)C_6H_4COOCH_3$-2	119-121	42.80 (42.29)	2.96 (3.02)
$C_6H_5SO_2NHC_6H_3[C(CH_3)_3]_2$-2,5	135-137	69.77 (69.52)	8.00 (7.88)
$C_6H_5SO_2N(HgC_6H_5)C_6H_3[C(CH_3)_3]_2$-2,5	175-177	50.32 (50.19)	4.84 (5.02)
$C_6H_5SO_2N(HgC_6H_5)C_6H_4CH_3$-2	155-156	43.51 (43.55)	3.28 (3.27)
$C_6H_5SO_2N(HgC_6H_4Cl$-4$)C_6H_4CH_3$-2	134-136	40.70 (40.78)	2.98 (2.86)
$C_6H_5SO_2N(HgC_6H_4OCH_3-4)C_6H_4CH_3$-2	179-180	43.13 (43.32)	3.78 (3.43)
$C_6H_5SO_2N[HgC_6H_4N(CH_3)_2-4]C_6H_4CH_3$-2	178-180	44.54 (44.44)	3.85 (3.88)

(continued)

TABLE 7 (continued)

Compound	M.p.[a] (°C)	Analysis found (calcd.) (%)	
		C	H
$C_6H_5SO_2N(HgC_6H_5)C_6H_3CH_3$-2-Br-4	148-150	38.37 (37.85)	2.61 (2.67)
$C_6H_5SO_2NHC_6H_3N(CH_3)_2$-4-$CH_3$-2	149-150	61.62 (62.04)	6.12 (6.24)
$C_6H_5SO_2N(HgC_6H_5)C_6H_3N(CH_3)_2$-4-$CH_3$-2	183-184	44.64 (44.48)	4.28 (3.91)
$C_6H_5SO_2N(HgC_6H_5)C_6H_3NO_2$-4-$CH_3$-2	202-203	40.11 (40.10)	2.47 (2.83)
$C_6H_5SO_2NHC_6H_2Br_2$-4,6-CH_3-2	141-143	38.30 (38.54)	2.70 (2.74)
$C_6H_5SO_2N(HgC_6H_5)C_6H_2Br_2$-4,6-$CH_3$-2	197-198	33.16 (33.47)	2.11 (2.22)
$C_6H_5SO_2N(HgC_6H_5)C_6H_3(CH_3)_2$-2,6[b]	171-175	45.09 (44.44)	3.98 (3.88)
$C_6H_5SO_2N(HgC_6H_5)C_6H_2(CH_3)_2$-2,6-Br-4	203-204	39.31 (38.94)	2.84 (2.94)

[a] All the arylmercury derivatives melt with decomposition. [b] According to the PMR spectrum, this compound contained a 14% admixture of the parent benzenesulphonanilide, which could not be removed by recrystallization.

for substituted benzenesulphono-*o*-toluidides and their *N*-arylmercury derivatives in chloroform are listed in Table 8. The *N*-phenylmercury derivative of benzenesulphonanilide has been described previously [55]. Some typical preparations of substituted benzenesulphonanilides and their *N*-arylmercury derivatives are given below.

2'-Nitrobenzenesulphonanilide. 6.55 g (37 mmoles) of benzenesulphonyl chloride was added gradually with stirring to a solution of 5.1 g (37 mmoles) of *o*-nitroaniline in 20 ml of pyridine. After completion of the reaction, the reaction

TABLE 8

CHEMICAL SHIFTS OF THE 2'-METHYL GROUP SIGNAL FOR BENZENESULPHONO-*O*-TOLUIDIDES AND THEIR *N*-ARYLMERCURY DERIVATIVES IN CHLOROFORM RELATIVE TO INTERNAL TMS (in Hz)[a]

Compound	$\delta(2'\text{-}CH_3)$
$C_6H_5SO_2NHC_6H_4CH_3$-2	119.7
$C_6H_5SO_2N(HgC_6H_5)C_6H_4CH_3$-2	128.5
$C_6H_5SO_2N(HgC_6H_4OCH_3-4)C_6H_4CH_3$-2	*b*
$C_6H_5SO_2N(HgC_6H_4N(CH_3)_2-4)C_6H_4CH_3$-2	128.4
$C_6H_5SO_2N(HgC_6H_4Cl$-4$)C_6H_4CH_3$-2	128.2
$C_6H_5SO_2NHC_6H_3N(CH_3)_2$-4-$CH_3$-2	115.0
$C_6H_5SO_2N(HgC_6H_5)C_6H_3N(CH_3)_2$-4-$CH_3$-2	124.6
$C_6H_5SO_2NHC_6H_3CH_3$-2-Br-4	118.0
$C_6H_5SO_2N(HgC_6H_5)C_6H_3CH_3$-2-Br-4	125.1
$C_6H_5SO_2NHC_6H_2Br_2$-4,6-CH_3-2	150.0
$C_6H_5SO_2N(HgC_6H_5)C_6H_3Br_2$-4,6-$CH_3$-2	147.0
$C_6H_5SO_2NHC_6H_4NO_2$-4-CH_3-2	*b*
$C_6H_5SO_2N(HgC_6H_5)C_6H_3NO_2$-4-$CH_3$-2	*b*
$C_6H_5SO_2NHC_6H_3(CH_3)_2$-2,6	122.2
$C_6H_5SO_2N(HgC_6H_5)C_6H_3(CH_3)_2$-2,6	128.1
$C_6H_5SO_2NHC_6H_2(CH_3)_2$-2,6-Br-4	119.9
$C_6H_5SO_2N(HgC_6H_5)C_6H_2(CH_3)_2$-2,6-Br-4	124.8

[a] for 0.15 *M* solutions. [b] Solubility problems.

mixture was treated with a solution of 30 ml of concentrated hydrochloric acid in 60 ml of water. The oil which separated solidified on standing. The resulting solid was filtered, washed with water, dried and recrystallized twice from methanol, yielding 3.8 g (37%) of the pure product with m.p. 99 - 101° (lit. [56] 101 - 102°).

N-(Phenylmercury)-2′-nitrobenzenesulphonanilide. A solution of 1.7 g (5 mmoles) of phenylmercury acetate in 100 ml of methanol was added to a solution of 1.34 g (5 mmoles) of 2′-nitrobenzenesulphonanilide and 0.2 g of NaOH in a mixture of 15 ml of methanol and 5 ml of water. After evaporation of the solvent under reduced pressure, the residue was treated with water, the resulting solid filtered, washed with water, dried and recrystallized from ethanol, affording 2.2 g (79%) of pale yellow crystals.

N-(Phenylmercury)-benzenesulphono-o-toluidide. A hot solution of 1.5 g (5 mmoles) of phenylmercury hydroxide in 30 ml of methanol was added to a hot solution of 1.25 g (5 mmoles) of benzenesulphono-*o*-toluidide in 20 ml of the same solvent. After evaporation of the solvent under reduced pressure, the crude product was recrystallized from benzene yielding 2.1 g (80%) of colourless crystals.

3,4,5-Trichlorophenylmercury bromide. To a solution of the Grignard reagent, prepared from 2.6 g (10 mmoles) of 3,4,5-trichlorobromobenzene and 0.24 g of magnesium turnings in 20 ml of dry ether, was added a solution of 3.6 g (10 mmoles) of mercuric bromide in 20 ml of dry THF. The reaction mixture was heated under reflux for 1 h and after cooling to room temperature was decomposed with 50 ml of 5% hydrobromic acid and excess of water. The solid formed was filtered, washed with water, dried and recrystallized from propanol, affording 1.75 g (37%) of colourless crystals with m.p. 223 - 224°. (Found: C, 15.67; H, 0.36. $C_6H_2BrCl_3Hg$ calcd.: C, 15.63; H, 0.40%.)

N-(3,4,5-Trichlorophenylmercury)-N-methyl-p-chlorobenzenesulphonamide. To a solution of 1.1 g (2.4 mmoles) of 3,4,5-trichlorophenylmercury bromide in 150 ml of hot methanol was added a solution of 0.41 g (2.4 mmoles) of silver nitrate in a mixture of 5 ml of water and 15 ml of methanol. The precipitate of AgBr was filtered and the filtrate was added to a solution of 0.49 g (2.4 mmoles) of *N*-methyl-*p*-chlorobenzenesulphonamide and 0.1 g of NaOH in a mixture of 5 ml of water and 20 ml of methanol. The precipitate formed was filtered, washed with water, dried and recrystallized from ethanol, affording 0.90 g (64%) of colourless crystals.

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