Calculations of Steric Effects. Part 3.[1] The Anion-catalysed Substitution of Alkylmercury(II) Bromides by Mercury(II) Bromide in Ethanol

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The steric effect of a neopentyl (Pe) group compared with that of the methyl group has been calculated for both the one-bromide ion and two-bromide ion catalysed reactions of alkylmercury(II) bromides with mercury(II) bromides in ethanol. For the case of one-anion catalysis, calculations were carried out with three model transition states, an open model, an unsymmetrical cyclic model with one bridging bromide ion, and the symmetrical bicyclic model with two bridging bromide ions suggested by Jensen and Rickborn. It is shown that only the Jensen and Rickborn model yields calculated rate ratios k^{Pe}/k^{Me} that are in accord with experiment. Calculations on the two-anion catalysed reactions were carried out on a symmetrical cyclic transition state with one bridging bromide ion, and good agreement between calculated and observed rate ratios was obtained.

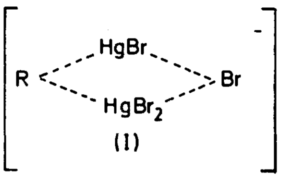
THE substitution of alkylmercury(II) salts by mercury(II) salts, the so-called 'one-alkyl mercury-exchange,' is one of the best documented examples of the simple S_E2 mechanism of electrophilic aliphatic substitution [2-5] [equation (1; R = alkyl)]. The one-alkyl exchange

$$\mathrm{RHgX} + \overset{*}{\mathrm{Hg}}\mathrm{X_2} \longrightarrow \mathrm{R\overset{*}{H}gX} + \mathrm{HgX_2} \qquad (1)$$

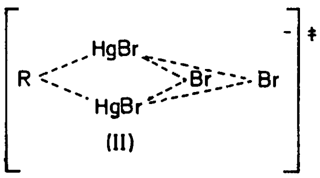
is strongly catalysed by halide ions, and a detailed kinetic study by Ingold and his co-workers [6] showed that two catalytic processes were at work. Both processes proceeded with strict retention of optical activity and configuration, for the case of s-butyl substrates, and were characterised by the incorporation into the transition state of one anion and two anions respectively. Most of the detailed kinetic work on the anion catalysed exchanges was carried out using bromide ion as the catalyst, and we shall confine our discussion to this particular anion.

For the one-anion catalysed reaction, the extra bromide ion can be introduced into the transition state either by $\mathrm{HgBr_3^-}$ or by $\mathrm{RHgBr_2^-}$. Ingold and his co-workers [6] favoured the former alternative, but a recent study by Lucchini and Wells [7] suggests that $\mathrm{RHgBr_2^-}$ is the kinetically significant species and that the actual electrophilic substitution follows equation (2). An unsymmetrical transition state (I) was suggested by Ingold [6,8] but some years later Jensen and Rickborn [3] put forward the idea of a symmetrical transition state (II) with two bridging bromide ions.

$$\mathrm{RHgBr_2^-} + \overset{*}{\mathrm{Hg}}\mathrm{Br_2} \xrightarrow{\mathrm{EtOH}} \mathrm{R\overset{*}{H}gBr} + \mathrm{HgBr_2} + \mathrm{Br^-} \qquad (2)$$



(I)



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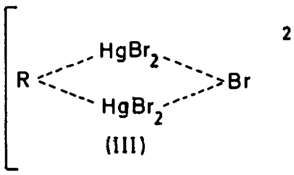

(III)

In the case of two-anion catalysis, Lucchini and Wells [7] tended to favour a mechanism in which both bromide ions were introduced with the alkylmercury(II) bromide [equation (3)] although the process suggested by Ingold [8] [equation (4)] could not be ruled out.

$$\mathrm{RHgBr_3^{2-}} + \overset{*}{\mathrm{Hg}}\mathrm{Br_2} \xrightarrow{\mathrm{EtOH}} \mathrm{R\overset{*}{H}gBr} + \mathrm{HgBr_2} + 2\mathrm{Br^-} \qquad (3)$$

$$\mathrm{RHgBr_2^-} + \overset{*}{\mathrm{Hg}}\mathrm{Br_3^-} \xrightarrow{\mathrm{EtOH}} \mathrm{R\overset{*}{H}gBr} + \mathrm{HgBr_2} + 2\mathrm{Br^-} \qquad (4)$$

The symmetrical transition state (III) was postulated by Ingold [6,8] for the two-anion catalysed reaction; both

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processes (3) and (4) could proceed *via* such a transition state.

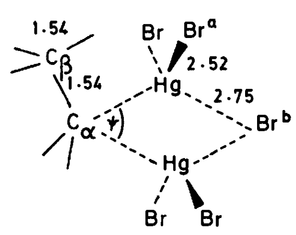
Hughes and Volger[9] reported rate constants for a number of alkylmercury(II) salts in reaction (1) and suggested that the pattern of constitutional effects amongst alkyl groups was steric in origin. They also examined the effect of methyl and neopentyl (Pe) groups on the bromide ion catalysed reactions and showed that the ratio of rate constants k^{Pe}/k^{Me} was 0.33 (uncatalysed reaction), 0.030 (one-anion catalysis), and 0.009 (two-anion catalysis).* We have already been able to calculate the steric effect of alkyl groups on the uncatalysed reaction,[10] and have shown that the pattern of constitutional effects could be accounted for qualitatively and quantitatively in this way. Since Lucchini and Wells[7] have been able to re-examine the anion-catalysed reactions with some success, we felt it of interest to report the results of our calculations of steric effects on these catalysed reactions. We have given in some detail[1,10] our method of calculation of steric effects. The systems in the present work are very close to those we described before,[10] and so we shall not repeat the exposition of the method.

The anion-catalysed reactions present an additional problem, however. In one-anion catalysis, if the extra bromide ion is brought in as $RHgBr_2^-$, then the steric factor k^{Pe}/k^{Me} will include also a contribution from the ratio of the corresponding formation constants, K_f^{Pe}/K_f^{Me}.† It seems to be generally true,[11-13] although

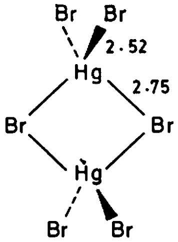
$$RHgBr + Br^- \overset{K_f}{\rightleftharpoons} RHgBr_2^- \qquad (5)$$

an exception is known,[14] that K_f values for equilibria analogous to (5) do not depend very much on the alkyl group R. Indeed for $RHg(SCN)_2^-$ in water or aqueous methanol, K_f is actually slightly larger for the higher alkyl groups than for R = methyl.[11,12] Exactly the same problem exists in the two-anion catalysed reaction if equation (4) is followed, and an extra formation constant arises if equation (3) is correct. All our calculations are based on $RHgBr_2^-$ as the initial state, although with RHgBr as the substrate, almost identical calculated results would have been obtained; we have taken the catalytic ratios as the actual ratios of rate constants.

There seems no controversy over the transition state for two-anion catalysis, and so we set up a model based on (III); details of the geometry are shown in (IV). The Cα-HgBr^{b}Hg atoms define a reaction plane, with the non-bridging bromine atoms symmetrically disposed above and below the plane. The Hg–Br^a bond lengths are the same as those[15] in the complex $Hg_2Br_6^{2-}$ (V) and the non-bridging $Br^a\widehat{Hg}Br^a$ angle is taken as the tetrahedral angle, 109° 28′, since the mercury atoms in (V) are approximately tetrahedrally bonded. We used exactly the same method of calculation as before,[10] the



(IV)



(V)

same van der Waals and covalent radii, and the same non-bonded functions. There are thus two variable parameters, the $Hg\widehat{C}Hg$ angle ψ, and the C · · · Hg partial bond length. We chose various values of these parameters, based mainly on calculations we had already performed[10] for the uncatalysed reaction; details are in Table 1. The nomenclature is that described previously;[1,10] $E^i_{min.}$ and $E^‡_{min.}$ are the energy minima in the neopentyl initial state and transition state (with respect to the methyl group as the standard) in cal mol^{-1}, $F_\beta{}^i$, $F_\alpha{}^‡$, and $F_\beta{}^‡$ are the rotational factors due to restricted rotation of α-methyl and β-methyl groups in the neopentyl initial and transition states, and E and F are the rate factors due to these enthalpic and rotational effects respectively. The required rate factor k^{Pe}/k^{Me} is given by the term FE and is the final column of Table 1. It can be seen that with the non-bridging $Br\widehat{Hg}Br$ angle fixed at 109°, rather a compressed transition state is required. With ψ 76.8° and C · · · Hg 2.15 Å the calculated rate factor of 0.007 is close to that observed (0.009). There is, however, no unique model for the transition state,‡ since had we selected a different value for the $Br^a\widehat{Hg}Br^a$ angle, another set of values of ψ and C · · · Hg would define the transition state. For example, with $Br^a\widehat{Hg}Br^a$ set at 115° we calculate that the required rate factor would be given by ψ *ca.* 84° and C · · · Hg *ca.* 2.29 Å; the latter two values are close to those[1] for the transition state in the uncatalysed reaction (1). We show, however, that the cyclic transition state model (IV), with chemically reasonable

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* The analysis of Lucchini and Wells[7] leads to values of 0.04 (one-anion catalysis) and 0.010 (two-anion catalysis), but the values for the anion catalysed reactions are not very accurate since they are calculated from data[9] at 60 and at 100°.

† This is not so if the bromide ion is introduced as $HgBr_3^-$.

‡ This follows automatically, because we have at least three variables (ψ, C · · · Hg, and $Br^a\widehat{Hg}Br^a$) and only one constant to calculate. If results on the two-anion exchange were known for a series of alkyl groups, we could define the transition state more closely.

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TABLE 1

Calculation of the rate factor $k^{\rm Pe}/k^{\rm Me}$ for the two-anion catalysed exchange, using the transition state model (IV) at 100 °C [a]

$\rm Hg\hat{C}Hg$ ψ (°)	C · · · Hg (Å)	$E^{\rm i}_{\rm min}$	$E^{\ddagger}_{\rm min}$	$E^{\ddagger}_{\rm min} - E^{\rm i}_{\rm min}$	E	$F\beta^{\rm i}$	$F\alpha^{\ddagger}$	$F\beta^{\ddagger}$	F	$(k^{\rm Pe}/k^{\rm Me})$ FE
	2.15	−652	1 309	1 961	0.071	0.634	0.222	0.286	0.100	0.007
76.8	2.25	−652	654	1 306	0.172	0.634	0.265	0.289	0.121	0.021
	2.35	−652	−2 006	−1 354	6.209	0.634	0.319	0.118	0.059	0.366
	2.15	−652	484	1 136	0.216	0.634	0.218	0.293	0.101	0.022
81.0	2.25	−652	−1 273	−621	2.310	0.634	0.258	0.104	0.042	0.098
	2.35	−652	−2 471	−1 819	11.624	0.634	0.307	0.122	0.059	0.686
	2.15	−652	163	815	0.333	0.634	0.213	0.291	0.098	0.033
85.0	2.25	−652	−1 761	−1 109	4.462	0.634	0.251	0.108	0.043	0.192
	2.35	−652	−2 837	−2 185	19.042	0.634	0.297	0.126	0.059	1.123
	2.15	−652	−691	−39	1.054	0.634	0.208	0.290	0.095	0.100
89.0	2.25	−652	−2 159	−1 507	7.631	0.634	0.244	0.111	0.043	0.328
	2.35	−652	−3 137	−2 485	28.537	0.634	0.286	0.130	0.059	1.684
								Observed rate ratio		0.009

[a] Values of $E^{\rm i}_{\rm min}$ and $E^{\ddagger}_{\rm min}$ in cal mol^{-1}.

TABLE 2

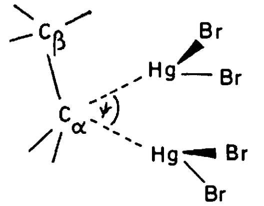
Calculation of the rate ratio $k^{\rm Pe}/k^{\rm Me}$ for the one-anion catalysed exchange, using the transition state model (VIII) at 100 °C [a]

$\rm Br^bH\hat{g}Br^b$ χ (°)	$E^{\rm i}_{\rm min}$	$E_{\rm min}{}^{\ddagger}$	$E^{\ddagger}_{\rm min} - E^{\rm i}_{\rm min}$	E	$F\beta^{\rm i}$	$F\alpha^{\ddagger}$	$F\beta^{\ddagger}$	F	$(k^{\rm Pe}/k^{\rm Me})$ FE
60	−624	−1 287	−663	2.445	0.586	0.378	0.816	0.526	1.286
70	−624	−645	−21	1.029	0.586	0.378	0.742	0.479	0.493
80	−624	−389	235	0.728	0.586	0.378	0.346	0.223	0.162
90	−624	176	800	0.340	0.586	0.378	0.318	0.205	0.070
95	−624	790	1 414	0.149	0.586	0.378	0.310	0.200	0.030
100	−624	1 977	2 601	0.030	0.586	0.378	0.306	0.197	0.006
110	−624	8 279	8 903	0.000	0.586	0.378	0.300	0.194	0.000
							Observed rate ratio		0.030

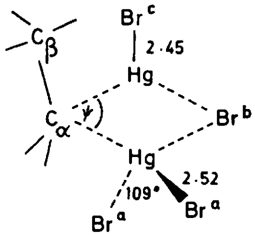
[a] Values of $E^{\rm i}_{\rm min}$ and $E^{\ddagger}_{\rm min}$ in cal mol^{-1}.

geometry, does lead to the correct $k^{\rm Pe}/k^{\rm Me}$ rate ratio for the two-anion catalysed reaction.*

We then turned to the one-anion catalysed reaction (2). First of all, we conclude that an open transition state such as (VI) will not yield the correct rate ratio.



(VI)



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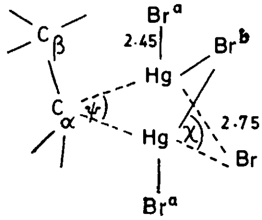

(VIII)

The bromine atoms can rotate about the C · · · Hg axis and avoid any interaction with the neopentyl group; under this circumstance the value of ψ and C · · · Hg would have to be unreasonably small to account for the $k^{\rm Pe}/k^{\rm Me}$ ratio of 0.030. The Ingold [6,8] unsymmetrical model (VII) was next considered. With the fixed dimensions shown, ψ was varied from 76.8 to 89° and the C · · · Hg partial bond length from 2.15 to 2.35 Å. All the combinations of values we tried resulted in $k^{\rm Pe}/k^{\rm Me}$ calculated ratios that were much too large. It was clear that the C_β atom could rotate about the C_α–$\rm Br^b$ (bridge) axis to take up an unsymmetrical position well away from the bromine atom ($\rm Br^a$) above the reaction plane. In this position, steric repulsions between the four bromine atoms and the neopentyl group are extremely small, and cannot account for the extra retardation in the one-anion catalysed reaction. We did not pursue these calculations any further, but concentrated on the symmetrical model proposed by Jensen and Rickborn.[3] The geometry of our model transition state is shown in (VIII). The five atoms C_α, Hg, Hg, $\rm Br^a$, and $\rm Br^a$ all lie in the same plane with the bridging $\rm Br^b$ atoms symmetrically disposed above and below the plane. The Hg–$\rm Br^b$ bonds are each taken as 2.75 Å, and each Hg–$\rm Br^a$ bond as 2.45 Å. To reduce the number of variables, we selected values for ψ (76.8°) and the partial bond C · · · Hg (2.15 Å) that gave a

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* A referee has suggested the possibility of interactions involving solvent molecules bonded to the anionic transition states. We have no means of determining either the extent of such solvation, or the exact geometrical disposition of any bonded solvent molecules. However, since the initial state, $\rm RHgBr_2^-$, also carries a negative charge, we feel that if there are indeed interactions that include solvent molecules in the transition state then these interactions will be compensated to some extent by similar interactions in the initial state.

reasonable rate factor in the one-anion catalysed reaction. This left only the $Br^b\widehat{Hg}Br^b$ angle (χ) as a variable parameter, and in Table 2 we give calculations in which χ is varied from 60 to 110°. A value for χ of 95° yields a rate ratio (0.030) exactly the same as that observed. The calculated rate ratios, however, are very sensitive to the value of χ, and just as in model (IV) there is no unique geometry of (VIII) that leads to the required ratio. It is clear that for a range of values of ψ and the partial bond length $C \cdots Hg$, a value of χ could be found for which the calculated and observed rate ratios are in agreement.

We have shown, however, that the one-anion catalysed one-alkyl mercury exchange reaction probably does not proceed through either an open transition state or an unsymmetrical singly-bridged cyclic transition state, but through the doubly-bridged symmetrical transition state of Jensen and Rickborn. The two-anion catalysed reaction is characterised by a symmetrical singly-bridged transition state. We have not been able to define the transition state models very closely, because of the lack of experimental results. Were rate ratios available for a selection of alkyl groups in the anion-catalysed reactions, we would have been able to specify more exactly the transition state geometry. The various transition state models we have used in our calculations are all ' stiff ' models in that, although rotation of groups is allowed, no account is taken of bond stretching or bond bending. As we have shown before,[1] however, the ' stiff ' models can yield reasonable values for the steric effects provided that the latter, as in the present case, are not too large. The present calculations on the ' stiff ' models (IV) and (VIII) indicate that the steric effect of the neopentyl group in both one- and two-anion catalysis arises from both direct steric interactions (the *E* term) and restricted rotation (the *F* term) in the transition state, with the two terms making almost equal contributions to the overall rate ratios.

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